# MODELLING PESTICIDES RESIDUES

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# Abstract

This work is a contribution to the development of a specific method to assess the presence of residues in agricultural commodities. The following objectives are formulated: to identify and describe main processes in environment – plant exchanges, to build of a model to assess the residue concentration at harvest in agricultural commodities, to understand the functioning of the modelled system, to characterise pesticides used in field crops and identify optimisation potentials in phytosanitary measures. The frame for the methodological developments corresponds to the procedure for the evaluation of the toxicity provided for the Life Cycle Impact Assessment methodology and for the method Impact 2002+.

In chapter 2, the methodological procedure for the assessment of human toxicity potential is introduced. First the factors of fate and exposure are described, including the notion of harvest fraction, the amount of substance found in harvest per unit of substance emitted initially in the system, the main result of the present study. Then the effect factors and the framework for impact evaluation are introduced.

Chapter 3 describes the principles accounted for the building of the fate model. Wheat crop and a restricted list of substances are chosen for these methodological developments. The model is composed by compartments describing the environment and the plant. Its functioning is based on initial amounts of substance in the source compartments, on transfer rates linking the compartments and on a dynamic evolution as a function of time between the treatment and the harvest. Air, soil and formulation deposit on plant are the primer compartments receiving the treated substance. Each transport is described by a transfer rate accounting for the process and for the equilibrium partitioning between the two exchanging compartments. Degradation of substance and plant growth are additional processes considered. Each compartment is described by a linear differential equation for the variation of mass accumulating and dissipating. Their assembly builds the model solved as a function of time. This exact resolution is complemented by additional tools to better understand the system functioning and to provide further approximations of the results: the system is simplified into subsystems describing the source and the receiving plant compartment and analytically solved using interpretable equations.

Chapter 4 describes and discusses all transport and dissipation processes determining the fate of the substance in the limits of the system. The recent publications concerning the understanding and the modelling of pesticide transfer from formulation deposit on plant through the cuticular membranes give new possibilities to model pesticide fate and to better account for the direct applications on the plant.

In chapter 5, the core model is first applied and its functioning analysed. The low availability and partly unsatisfying quality of data for pesticides description is a main complication for the methodology application: the lack of data for the half-life of the substance in the plant especially leads to a strong extrapolation for this determinant factor. A large difference is observed between early and late applied pesticides with respectively a major release to soil or a release to formulation deposit on plant surface. The initial transport processes quickly distribute the substance in the system. Once each plant compartment has accumulated residues up to a maximum amount, a dissipation phase occurs. The duration of these periods is determinant for the level of residue in harvest. The soil is a determinant source for long term evolutions of the system, for soon applied substances with low degradation rate. The

half-life of substance deposited on plant is equal to a few days, but the transfer is fast from formulation deposit to the inner plant, where degradation is generally much slower. The accumulation of substance from the air is mostly negligible. The sum of the subsystems gives an approximation of the total system, useful for interpretation. The possibility to simplify the subsystem by ignoring the transfer back from receiving to the source compartment underlines the low contribution of these transfers in the functioning of the model. An approximated resolution is based on the determination of the maximum accumulated substance and on the subsequent dissipation process. However, an important loss of precision is observed. This approximation is useful for interpretation and for extrapolations.

In chapter 6, an evaluation of the model is conducted through a sensitivity and uncertainty analysis. The sensitivity analysis consists of evaluating the effect on the output of a change in an input, on the basis of three complementary approaches: the effect of a fixed change in the input of e.g. 0.1%, the effect of a change specific to the uncertainty of the input and the effect of a change in input value from a minimum to a maximum. The uncertainty of an output is evaluated according to the relative contribution of the confidence factors of the inputs. Results show that the half-lives and the time are the most important factors determining the sensitivity of the system and the propagation of uncertainty. The contribution of the half-life to the confidence factor of the harvest fraction reaches between 30% to 98% of the total uncertainty. The confidence factors of results increase exponentially with the time interval between application and harvest. The role of partition coefficients to the behaviour of substances is highly variable, may be determinant or negligible, with increasing or limiting effect on mobility. Sensitivity and uncertainty for parameters describing the agricultural or environmental system are very variable, but sometimes determinant and so confirmed as essential for the system functioning. Consequently, differences in harvest fractions between substances are only significant if they are high. A first comparison of the computed results with measures of residues obtained by an experiment and with references such as tolerance values lead to a pertinent verification of the overall methodology. Finally, the qualitative comparison with other models underlines the specificities and the originality of the present methodology in particular by comparison with environmental multi-media models running in steady state.

In chapter 7, the model is finally applied for an ultimate interpretation. The harvest fractions for more than 100 substances are evaluated. Among all types of substances, low and high levels of residues per treatment are found, representative for the high variability of harvest fractions from 5E-16 for bromoxynil to 7E-03 for tebuconazole sprayed on wheat. The fate process represents the highest source of variation for the toxicity. If the application rate does not explain the high differences in residue level at harvest, the time of application may represent an optimisation potential particularly for late treatments. However, the toxicity needs to account for both fate and effect factors, as only their combination effectively allows to evaluate the toxicity. According to the available list of Human Damage Factors per treatment, problematic substances may be effectively identified and substituted.

In chapter 8 answers to questions brought with the objectives bring a conclusion to the study. The appendices include notably the results of harvest fractions and toxicity per unit substance applied, per treatment and per unit cultivated crop area, for the main substances and field crops. A LCA is also presented on the intensity level of wheat production.

# Résumé

Ce travail contribue au développement d'une méthode pour l'évaluation de la présence de résidus dans les produits agricoles. Les objectifs suivants sont formulés: identifier et décrire les principaux processus d'échanges entre l'environnement et la plante, créer un modèle pour évaluer la concentration en résidus au moment de la récolte, comprendre le fonctionnement du système modélisé, caractériser les pesticides utilisés dans les grandes cultures et identifier les potentiels d'optimisation dans la lutte phytosanitaire. Le cadre de ces développements correspond à la procédure d'évaluation de la toxicité de la méthode de l'Analyse du Cycle de Vie et de la méthode Impact 2002+.

Dans le chapitre 2, la procédure méthodologique pour l'évaluation du potentiel de toxicité humaine est introduite. D'abord, les facteurs de devenir et d'exposition sont décrits, incluant la notion de fraction récoltée, la quantité de substance trouvée dans les récoltes par unité de substance émise initialement dans le système, le principal résultat de cette étude. Ensuite, les facteurs d'effet et le cadre de l'évaluation de l'impact sont introduits.

Le chapitre 3 décrit les principes considérés pour la création du modèle. La culture du blé et une liste réduite de substances sont choisis pour les développements méthodologiques. Le modèle est composé de compartiments décrivant l'environnement et la plante. Son fonctionnement se base sur les quantités initiales de substance dans les compartiments sources, sur les taux de transfert reliant des compartiments et sur une évolution dynamique en fonction du temps entre le traitement et la récolte. L'air, le sol et le dépôt de substance sur la plante sont les compartiments primaires recevant la substance traitée. Chaque transport est décrit par un taux de transfert comprenant le processus et l'équilibre de partition entre les deux compartiments d'échange. La dégradation de la substance et la croissance de la plante sont des processus supplémentaires considérés. Chaque compartiment est décrit par une équation différentielle linéaire pour la variation de masse accumulée et dissipée. Leur assemblage compose le modèle, résolu en fonction du temps. Cette résolution exacte est complétée d'outils additionnels pour mieux comprendre le fonctionnement du système et fournir des approximations supplémentaires des résultats: le système est simplifié en sous-systèmes décrivant la source et le compartiment plante, et est résolu par des équations interprétables.

Le chapitre 4 décrit et discute tous les processus de transport et de dissipation déterminant le devenir de la substance dans les limites du système. Les publications récentes concernant la compréhension et la modélisation du transfert de pesticides depuis les produits déposés sur la plante à travers les membranes cuticulaires donnent de nouvelles possibilités de modéliser le devenir des pesticides et de mieux considérer les applications directes sur la plante.

Dans le chapitre 5, le modèle est d'abord appliqué et son fonctionnement est analysé. La faible disponibilité et la qualité partiellement insatisfaisante des données pour la description des pesticides constitue la principale complication dans l'application du modèle : l'absence de données pour la demi-vie des substances dans la plante conduit en particulier à une extrapolation forte pour ce facteur déterminant. Une différence importante est observée entre les pesticides appliqués précocement ou tardivement, respectivement entre un apport majeur vers le sol ou un apport majeur vers la surface de la plante. Les processus initiaux de transports distribuent rapidement la substance dans le système. Après que chaque compartiment eut accumulé une quantité maximale de résidus, une phase de dissipation survient. La durée de ces périodes est déterminante pour le niveau de résidus. Le sol est une

source déterminante pour des évolutions de longue durée et pour des substances avec une faible dégradation. La demi-vie d'une substance déposée sur la plante est égale à quelques jours, mais le taux de transfert est rapide vers l'intérieur de la plante, où la dégradation est plus lente. Les contributions depuis l'air sont la plupart du temps négligeables. La somme des sous-systèmes donne une approximation du système utile pour l'interprétation. La possibilité de simplifier le système en ignorant le transfert de retour vers la source souligne la faible contribution de ces transferts dans le fonctionnement du modèle. Une résolution approximative est basée sur la détermination de la quantité maximale de substance accumulée et sur sa dissipation subséquente. Toutefois une perte importante de précision peut être observée. Cette approximation est utile pour l'interprétation ou pour certaines extrapolations.

Le chapitre 6 comprend une évaluation du modèle. L'analyse de sensibilité consiste à évaluer l'effet du changement d'un paramètre sur le résultat, selon trois approches: l'effet d'un changement fixe par exemple de 0,1%, l'effet d'un changement spécifique à l'incertitude du paramètre, et l'effet d'un changement considérant les valeurs minimales et maximales du paramètre. L'incertitude du résultat est évaluée sur la base de la contribution relative des facteurs de confiance des paramètres. Les résultats montrent que les demi-vies et le temps sont les facteurs les plus importants déterminant la sensibilité du système et la propagation de l'incertitude. La contribution de la demi-vie au facteur de confiance de la fraction récoltée atteint entre 305 et 98% du total de l'incertitude. Les facteurs de confiance des résultats augmentent de façon exponentielle avec l'intervalle entre le traitement et la récolte. Le rôle des facteurs de partition dans le comportement des substances est très variable, peut être déterminant ou négligeable, avec un effet croissant ou limitant sur la mobilité. La sensibilité et l'incertitude des paramètres décrivant le système environnemental ou agricole sont très variables, parfois déterminants, et ainsi confirmés comme essentiels au fonctionnement du système. Par conséquent, seules de larges différences de fractions récoltées entre substances sont significatives. Une première comparaison des résultats modélisés avec des mesures de résidus obtenues par une expérimentation et avec des références comme les valeurs de tolérance conduisent à une vérification pertinente de la méthodologie. Finalement, la comparaison qualitative avec d'autres modèles souligne la spécificité et l'originalité de la présente méthodologie, en particulier par la comparaison avec des modèles environnementaux multi-media évoluant en état stationnaire.

Dans le chapitre 7, le modèle est finalement appliqué pour une ultime interprétation. L'évaluation porte sur une plus large série de substances. Les fractions récoltées pour plus de 100 substances sont évaluées. Parmi tous les types de substances, des niveaux bas et élevés de résidus par traitement sont trouvés, représentatifs de la variabilité des fractions récoltées, de 5E-16 pour le bromoxynil à 7E-03 pour le tébuconazole utilisés sur le blé. Le processus de devenir représente la source la plus élevée de variation pour l'évaluation de la toxicité. Si la dose de traitement n'explique pas les larges différences de résidus à la récolte, le moment du traitement peut représenter un potentiel d'optimisation, en particulier pour les traitements tardifs. Toutefois, l'évaluation de la toxicité doit prendre en compte les deux facteurs, puisque seule leur combinaison permet effectivement d'évaluer la toxicité. Sur la base de la liste actuellement disponible des facteurs de dommages sur l'humain, les substances problématiques peuvent être identifiées et substituées.

Dans le chapitre 8, les réponses aux défis et questions soulevées avec les objectifs apportent une conclusion à l'étude. Les annexes de l'étude comprennent notamment les résultats des fractions récoltées, des résultats de toxicité par kg appliqué, par traitement, par unité de surface cultivée, pour les principales substances et grandes cultures. Une analyse de cycle de vie est également présentée pour le niveau d'intensité de production du blé.

# 1. Introduction

The use of pesticides in agriculture is subject to steady observation due to the risk for human toxicity and environmental ecotoxicity. The assessment of this agriculturally important input needs adequate methodology. Developments are particularly expected in the evaluation of residue in agricultural commodities because of their toxicological risk. These requirements are also needed for the development of a tool for environmental analysis, the Life Cycle Assessment (LCA) methodology. This work is a contribution to the development of a method to assess the use of pesticides, in particular the presence of residues in agricultural commodities, according to the frame of the Life Cycle Assessment methodology. In this introduction, the problem is exposed by a short review of:

- the conditions for the use of pesticides,
- the LCA methodology in agriculture,
- the existing methods to assess pesticide fate,
- the methodology to assess the toxicity of pesticides.

The objectives of this study are finally described at the end of the introduction.

## 1.1 Use of pesticides

Pesticides were introduced in agriculture for different objectives: to eliminate weeds, to prevent development and damage from pests and diseases, to insure yield level and quality of crop, to control harvest conservation. The use of plant treatment products belongs to ordinary interventions in intensive and integrated cropping systems and participates in the productivity of these cropping systems. However, the use of plant treatment products represents toxicological and ecotoxicological risks inherent in their function to reduce the local activity of living organisms. To achieve this, they need to be propagated in agricultural systems with the ability to remain biologically active for a certain time in different media. A consensus has to be established between the benefit of pesticides use and their presence in food products and the environment. First, legislation frames the use of substances through homologation of plant treatment products. Then agricultural practice enhances these precautions according to the principle that residues are undesirable, even when harmless. For the purpose of homologation, better knowledge and improvements in the use of plant treatment products, different methodologies have been developed specific to the objectives and use.

Specific legislation is established for the use of plant treatment products (e.g. OFAG, 2002). The substances applied are homologated according to a precise use and in so far as no secondary damaging effects appear in humans, animals and the environment. Experts come to a conclusion about the homologation according to data describing the spectrum of action of these substances and their behaviour in the environment. Maximum concentrations are established for food products. This authorization includes the conditions of use and application techniques (concentration), the time of application and the delay of harvest (time elapsed between treatment and harvest). The law prescribes that food products should not contain substances harmful for health. Residues are tolerated below a given level of risk for health and if technically unavoidable. Therefore a maximum concentration of residue is set for each substance and agricultural commodity according to good agricultural practice

provided that the concentration lies under the toxicological limit. The maximum concentration is established by the degradation rate of the substance and the time lapse between treatment and harvest. The toxicological justifiable value corresponds to the acceptable daily intake of the substance for a human (ADI). This threshold is based on the dose of substance with no observed adverse effect (NOAEL) on animals and with a safety factor. In practice, supplemental security is given by the fact that the real residue level and the eventual exposure to human health is largely under the established acceptable daily intake. Consequently the user of plant treatment products applying good agricultural practices is assured to harvest products with a concentration of substance that does not exceed the commercially legal tolerable value.

From the moment when a product is approved, official information available for the use of substances includes the domain of application (type of crop, targeted organism), some technical indications (concentration, technique of use, some indications for restricted annual use), the moment of application and the delay before harvest, the tolerable maximum concentration of substance in and on food products, the toxicological class of the substance, and to general indications for the use and risks of toxic substances. Also, complementary recommendations (efficiency comparison, phytosanitary strategies) are provided by agrochemical firms, research stations for agronomy, plant health services, and extension services. According to the legislative framework, no residue of pesticide is found higher than the tolerable amount under conditions of good agricultural practices. However, neglecting unilateral prohibition of products, even lower concentrations of substance in harvested products may be required for specific environmental initiatives, for particular requests of consumers (e.g. labels) or for a wide-ranging effort to minimise the presence of even harmless residues in food. Admitting the hypothesis that residues are in principle undesirable and that no observable evidence of toxic effect does not mean absence of effect, there is no admitted threshold below which the occurrence of a substance should not be considered. Consequently, the presence of residues in food becomes relevant under the legal maximum tolerable concentration. The evaluation of concentrations below the analytical limits of detection may also be relevant.

However, the presence of residue does not by itself explain the toxicity of a product. It is necessary to also take into account the exposure and the toxicological effect to effectively minimise the risk of toxicity. Advantage should be used from the high variation of plant treatment products and the various phytosanitary strategies. Priority of action should also be established. Quantitative distinction should be put in evidence between products, such as herbicides applied early at the begin of vegetation period and substances applied late to protect the maturing crop, between old products requiring a high dose to be effective and recent substances with high bioactivity at low rate. In many cases, various active substances are available to exert the same function, so that comparison and substitution potentials can be studied according to the presence of residue and their toxicological effect. Methodologies must be further explored to analyse and document the risk of toxicity in the agricultural products.

## 1.2 Life cycle assessment in agriculture

The assessment of toxicity on human health is one of the components included in methods for environmental assessment. Recent developments in Life Cycle Assessment (LCA) methodology have enabled assessment of agricultural systems from an environmental point of view. LCA enables relating the environmental impacts to the main function of a studied

activity. LCA consists of four phases, as described by the International Organisation for Standardisation (ISO14040 and following), and illustrated in Figure 1:

- The goal and scope of an LCA serves to define the purpose and the extent of the study. It includes a description of the system (a system, a process, a product) in terms of a functional unit.
- The inventory analysis performs a quantified inventory of the consumption of resources and of the emissions released to the natural environment. The whole life cycle from cradle to grave is taken into account: the extraction of non-renewable raw energy, the transports, the production phase, the use phase and the final disposal.
- The impact assessment is based on the inventory of emissions and resource consumptions. These impacts are classified in resource depletion, land use, greenhouse effect, photo-oxidant formation, acidification, eutrophication, aquatic ecotoxicity, terrestrial ecotoxicity and human toxicity. Within each impact category, emissions listed by the inventory analysis are multiplied by impact characterisation factors. Characterisation factors express the effect of each emission relatively to a specific environmental problem.
- Interpretation of quantitative data and qualitative information occurs at every stage of the LCA. Normalisation techniques, such as weighting indicators for the different impact categories, or multi-criteria decision making tools are applied during the interpretation phase as complementary tools.

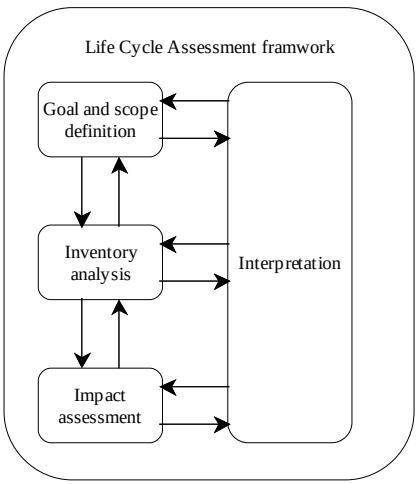



Figure 1. Phases and applications of an LCA (based on ISO14040)

Harmonisation of LCA methodology for the agricultural framework was developed by Audsley et al. (1997) according to a case study: a comparison of British and Swiss wheat

production systems. Variations in production intensities due to crop protection products and also nitrogen fertilisation have been shown with different environmental burdens. Gaillard et al. (1999) showed that low input systems were environmentally better as long as a sufficient yield was obtained.

As introduction to this present study on pesticides an LCA was completed to identify the key parameters of agricultural systems from an environmental point of view and for the role of pesticides (Appendix 1). An environmental assessment of wheat for bread making was performed to optimise agricultural intensity of arable production systems, quality of agricultural products and environmental damages. To assess and compare different intensities of production, adequate functional units were developed to measure main functions of agricultural activity: production and upkeep of farmland. These methodological developments were applied to fertilisation as a factor determining the intensity of production and the quality of the products. The following elements of this study provide a better understanding of the methodology of LCA in agriculture and introduce the development of a methodology to assess the fate of pesticides.

Environmental assessment in agriculture has the particularity that the activity has a multifunctional role and evolves in a complex system close to the environment. Consequently the risk is high that the assessment is biased by reduction of system boundaries, the scenario definition, the choice of the functional unit and the considered impact indicators. The interactions between production inputs and yield are important, with influence on quantity and quality. A method has been specifically developed to take quality into account for Life Cycle Assessment of agriculture crops.

Different cultural techniques are commonly used in European agriculture leading to variations in cultivation intensities, in yield quantities and qualities, and in environmental impacts. High yielding production systems maximising yield with large fertiliser supplies and crop protection interventions are economically advantageous in many European agricultural areas. On the other hand these high intensive systems are usually recognised for exposing the environment to damaging nitrogen, phosphorous and pesticides emissions. However, the "a-priori" thinking that a low intensity crop is environmentally favourable is questioned regarding the reduction in productivity, which could simply lead to pollution shifting to other regions. As cultivation practices generally refer to a complex cropping system, these different factors interact and a combined assessment is therefore necessary.

Environmental problems in arable systems are often reduced to nitrogen and pesticides problems, forgetting the specific high efficiency of these agricultural inputs to the whole production system. However the optimisation of these inputs shows that environmental optimisation of production system cannot be reduced to an optimisation of one input on its own, such as the use pesticide. A larger scale of the system is needed. Other determining agricultural parameters have to be taken into account, such as the interaction between inputs, quality requirements and the multiple function of the agricultural system. The choice of the production intensity also remains linked to the site specific potential, at field level, resulting in a combination of intensive and extensive situations. Best combination between agricultural inputs and land utilisation should therefore be explored together to design best production strategies on an environmental point of view. High intensity level is potentially favourable per ton of product (with constant quality), when demonstrating sufficient yield increase. On the other hand environmental impact per ton of product increases with intensification if agricultural inputs are not satisfactorily combined or more generally if the intensity level exceeds the production potential. In addition, impact per hectare increases with intensification

for all environmental categories except land utilisation, showing that less intensive crops have to be considered for predominantly a land upkeep function. Thus pesticide or fertiliser use cannot be assessed alone, but as a whole with the rest of the system. Further studies about different utilisation strategies of lower production area due to higher productivity should measure the real impact of different intensity levels.

## 1.3 Pesticides assessment

The use of pesticides in agriculture contributes greatly to the intensity level of agricultural systems, to their productivity and to their environmental burdens. Consequently the need for consistent environmental assessment methodologies is particularly required for pesticides on behalf of good reliability and admittance of these methods. Analytical processes usually perform the evaluation of pesticide residue in agricultural commodities. These analyses are often limited to the capacity of sampling and to high concentrations. Complementary or alternative approaches to the analytical ways are necessary to enlarge the possibilities for the evaluation of pesticide occurrence. Ranking methods (Jouany, 1994, Newmann, 1995) are possible approaches to estimate differences between substances. They are based on non-figurative calculations and so do not fit with principles of life cycle analysis which is based on full fate analysis and transparent factual processes. According to this, the modelling of pesticide fate in agricultural production constitutes a challenge to be addressed. Modelling of pesticide is in continuous development in the frame of ecotoxicity assessment. These methods focus on the fate of substances in environmental media (water, soil, air).

Different methods effectively propose to evaluate the fate of pesticide and the risk of occurrence in the environment and in food. Most models including fate processes involved in the transfer of pesticides in the environment are specialised in a specific medium (Newmann, 1995). Detailed processes included in these models complicate the distinction of main variables and their integration in multi-media models. In the frame of LCA methodological developments, we first need to identify the main processes and quantify the determining factors and variations. Consequently, normalised conditions for media and pollutants characteristics are generally adopted.

Different methods already offer an approach for the evaluation of residue in agricultural commodities. These approaches are often shortcuts from the environment to the food chain. Part of actual methods to assess pesticides in LCA can be qualified as partial, because they are based only on applied quantity (Goedkoop, 1995) or on toxicological data (Heijungs, 1992). Other methods (Jolliet and Crettaz, 1997, Huijbregts, 1999, Margni et al., 2001) propose to take into account fate and effect, and so are more adapted to LCA requirements and to overall comparison of different products.

Margni et al. (2002) developed an approach for a full-fate analysis of pollutants through different media and pathways with impact on human health and ecosystems. They calculated that pesticide residues in food caused the highest toxic exposure, higher than consumption of drinking water or inhalation. Due to lack of available information, it was assumed that the pesticide concentrations in food correspond to the 5% of their respective tolerance value. They considered it was a priority to get better estimates of pesticide residues in food. Further study is needed to better quantify the concentration in agricultural products directly exposed to pesticides.

Different environmental models refer to xenobiotics behaviour in vegetation. These models are first intended to assess fate of contaminants in the environment and are generally running in steady state models. They include some vegetation parameters for agricultural soils and can be used to determine pollutants concentration in vegetation as a function of concentrations in the environment. A one-compartment vegetation model, by Trapp and Matthies (1995), combines principal processes between the environment and plant. Hung and Mackay (1997) describe processes of vegetation uptake from soil and air involved in a three compartments system. Severinsen and Jager (1998) developed a vegetation sub-model to complete multi-media models. They show the influence of this added compartment on the environmental fate of xenobiotics on a regional scale. Cousins and Mackay (2001) presented parameters needed to include vegetation compartments in multi-media models and to identify chemical property ranges to measure the opportunity to take vegetation into account in multi-media models.

These multi-media models do not accurately assess chemicals in agricultural systems. Specific dynamic processes occur during the use of plant treatment products from crop sowing to harvest time. However, part of the process relating a chemical's fate between environment and plant is similar in environmental multi-media models and in agricultural systems. Methodological hypothesis need specific improvements for fate assessment of pesticides in agricultural systems.

Once applied, pesticides are distributed between air, soil and plant, depending on crop development at the moment of pesticide application and on active ingredient behaviour. The uptake of pesticide sprayed directly on the plant represents a specific agricultural process, different from particle deposition on plant surfaces and uptake by plant tissue described by previously mentioned multi-media models. Other pathways for pesticide uptake, from the air and from the soil are generally included in environmental models. They represent the other fraction of pollutant sources in agricultural plants. The respective contribution to these different sources can vary greatly, as a function of crop stage at application time, vegetation development and available quantity. Next to uptake processes, pesticides are translocated, diluted and degraded in different physiological organs of the growing plant. All these processes must be included in a dynamic solution so that stage of growth at spray application and time gap between application and harvest are taken into account. Main differences in chemical accumulation must be explored between plant organs according to harvested parts. The choice of determinant transport processes according to LCA and a multi-media development framework are necessary to use key parameters for pesticide characterisation, to avoid unnecessary complexity. These points must be addressed by identifying the main processes responsible for the transfer of substances applied directly on plants and in the near environment and for the dynamic behaviour of substances in plant systems. Answers are given for main conditions, clear of local and specific circumstances.

Finally, beyond the present study, the occurrence of residues in agricultural commodities generates toxicological consequences. To complement the fate behaviour of the emitted pesticide and the resulting presence of residues in the harvest, the exposure to humans and the toxic effect in humans need to be determined to assess the human toxicity in the frame of LCA methodology. The exposure to humans results from the contact with contaminated agricultural commodities or from their consumption through food. The toxic effect results in the damaging action of the substance on human health. Crettaz (2001), Crettaz et al. (2002) and Pennington et al. (2002) developed the methodology for the assessment of human toxicity and published effects factors for a list of 900 substances, including pesticides. The effect factors are eventually expressed in years of life lost per mass taken up.

## 1.4 Objectives

This study aims at developing the assessment of pesticide fate in crops by accounting for the specificities of agricultural conditions. Among the different challenges that have been previously introduced, this study focuses on three main topics and the following questions:

- Process description and modelling phytosanitary measures. How can the fate of pesticides be described, what are the involved processes and in which system ? What is the importance of direct application of a substance on plant compared to release in soil and air for the occurrence of residues, and how can fate processes be modelled ? How does dynamic behaviour affect the final residues in plants depending on the time interval between application and harvest ?
- System understanding. What are the procedure and requirements to simulate the dynamic functioning of the whole system ? What are the most significant relationships describing the functioning of the system ? What are the corresponding pertinent approximations ?
- Assessment of pesticides in agricultural products and practices. What are the residues at harvest for different application times and substances? What are the optimisation factors for pesticide use and the possibility of substance substitutions according to fate, exposure and effect factors of the toxicity ?

According to these questions, the following objectives for the study are formulated:

a) To identify and describe main processes in environment – plant exchanges.

b) To build of a model to assess the residue concentration at harvest in agricultural commodities.

c) To understand the functioning of the system phytosanitary measures - plant - environment.

d) To characterise pesticides used in field cropping systems and identify optimisation potentials in phytosanitary measures.

The frame for the developments of these objectives corresponds to the methodological procedure for the evaluation of the toxicity provided for the Life Cycle Impact Assessment methodology and the method Impact 2002+ (Jolliet et al., 2003). The approach focuses with priority on a way to identify the key processes and to describe them with the most pertinent parameters, avoiding unnecessary complexity in the description of processes and in the functioning of the model. This approach should preserve the possibility to interpret the functioning of the system, to support diagnosis and to propose optimisation potentials, priorities and ways of actions. Figure 2 presents an overview of the frame of the study whose structure is described hereafter.

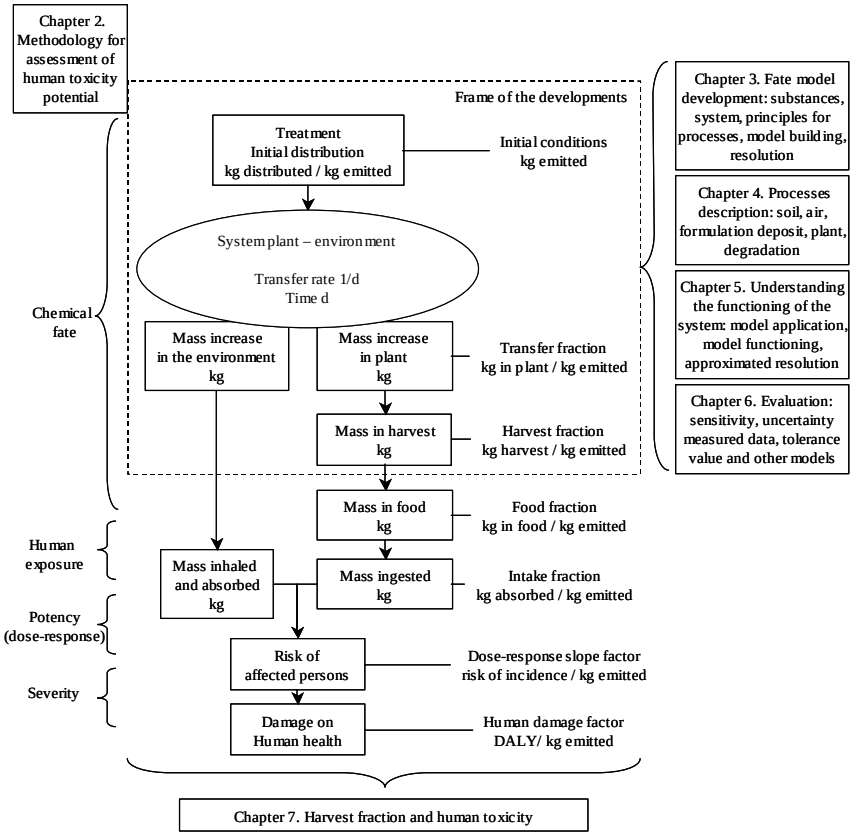



Figure 2. Procedure for the evaluation of human toxicity by plant treatment products, frame and structure of the study.

Chapter 2. Methodology for assessment of human toxicity potential. The full methodological procedure is introduced. First the factors of fate and exposure are described, including the notions of harvest fraction, the main result of the present study, and the food pathways. Then the effect factors and impact evaluation are presented.

Chapter 3. Fate model development. The chapter describes the principles accounted for in the building of the fate model. Ways to characterise the substances are identified. A compartmental structure is defined for the system of phytosanitary measures – plant – environment. The needed factors are identified to describe the initial conditions of the system at the time of substance release. Then the principles for the processes of substance transport and dissipation are established. Finally the building of the model and its resolution are exposed in accordance with the targeted results. Tools are also developed for the understanding and the interpretation of the system functioning.

Chapter 4.Processes descriptions. The chapter describes and discusses all transport and dissipation processes determining the fate of the substance in the limit of the system air, soil, formulation deposit and plant compartments from time of release to harvest.

Chapter 5. Understanding the functioning of the system. The core model is first applied and tested. The parameterisation of the model is clarified and key factors responsible for the transport and dissipation processes are identified. The potency of approximated resolutions and their utility for interpretation are evaluated.

Chapter 6. Evaluation. A sensitivity analysis is performed and key parameters are discussed. Uncertainties complete this analysis and the interpretation of the results. Some particular points of the model building and functioning are discussed according to measured data of residues obtained by an experiment. Computed data are also verified with references such as tolerance values. Finally the status of the model among the different types of existing models is discussed.

Chapter 7. Harvest fraction and human toxicity. The model is finally applied for an ultimate presentation and interpretation. The evaluation is carried out for a range of substances commonly used in field cropping systems with delivery of harvest fraction and intake fraction, combined with the evaluation of the toxicity on humans.

Chapter 8. Conclusions. Answers to the questions introduced in the objectives bring a conclusion to this study.

# 2. Methodology for assessment of human toxicity potential

The awaited core result given by the fate model developed in this study is the quantity of substance found in the harvest. This result expressed as the fraction of the substance applied found in the harvest corresponds to the first step of the methodology for the evaluation of the human toxicity (Figure 2) (Jolliet and Crettaz, 2000, Jolliet et al., 2003). The characterisation factors for the toxicological effects on human health express the toxicological risk and potential impact associated with an emitted substance. According to the methodology presented here the evaluation of the human toxicity is based on two main parameters: the fate and exposure, and the effect. These two determining steps are described with more details hereafter.

## 2.1 Fate and exposure

The fate and exposure is determined by the intake fraction. This parameter is described as the fraction of mass of a chemical released into the environment that is ultimately taken in by the human population as a result of food contamination, inhalation or dermal exposure (Bennett et al., 2002a, 2002b). It is expressed in kg intake per kg emitted. The intake fraction consists of different steps in evaluating the fate of a substance from its emission, through its transport in the environment, to the human exposure by air inhalation, by drinking water and by eating. The dietary step is particularly important as plant treatment products are directly involved in food chain. The development achieved here aims to get more precision in the evaluation of the fate from pesticide release to the residue in harvest. After the harvest, the agricultural commodities are transformed into food directly without denaturising or indirectly through a feed pathway. The feed pathway constitutes a particular point as the transformation of plant material by animals represents an intermediate step to be considered. The final food processing and preparation constitute further steps in the fate of the substance to be taken into account. Finally the intake fraction is derived as a function of the effective uptake of food by human. These steps leading to the intake fraction are described hereafter starting from the residue in plant as a harvest fraction.

### 2.1.1 Harvest fraction

The model developed in this study contributes to evaluating the residue of applied substance in a plant and in harvested commodity. The mass of substance accumulated in a harvested part of the plant contributes to evaluation of the harvest fraction. This key value expresses the efficiency of the substance transport from the source to the harvested plant part, to the receiving plant. The harvest fraction corresponds to the amount of substance found in the harvest per unit of substance emitted initially in the system.

$$hF_i = \frac{M_{i,harvest}}{M_{i,emitted}} \qquad 1$$

with $M_{i,harvest}$ (kg) the mass of substance in the harvest, $M_{i,applied}$ (kg) the mass of substance applied as plant treatment, both giving the harvest fraction $hF_i$ ($kg_{harvest}/kg_{applied}$). The harvest fraction constitutes the core result of the present study. The harvested fraction is then processed to food.

### 2.1.2 Food pathway

After harvest, the agricultural commodity undergoes different steps until it becomes food according to the channel of transformation and trade from the field to the plate. The harvested product may be consumed after a light processing more or less directly (potato, bread), after a high transformation as a refined (sugar) or extracted (oil) product, or after a deep denaturising as a new commodity (milk, ,meat, egg). These very different steps included in the food pathway may lead to an important reduction of residue in food specific to the transformation. In the present study no particular investigation has been undertaken to describe the fate of the residue during the food pathway. However, two main occurring processes are presented as documentation and illustration: the light processing of the harvested agricultural commodity into food, and the feed pathway with the intermediate transformation of the harvested plant material to an animal product (meat, milk, egg).

During the light processing of the harvested agricultural commodity into food, a loss of residual substance in the product may occur due to stocking, washing, peeling, processing. According to Eilrich (1991) in a study on chlorothalonil and taken into account by Margni et al., (2002) for the LCA of pesticides, the processing step leads to 80% loss of residue from field level to processed commodity available for the diet. Consequently the processed fraction corresponds to 20% of the harvest fraction. Due to the lack of other reference in literature, this value is taken by default and is used for all substances and food commodities. The quantity of substance that is effectively exposing humans to toxicity by food ingestion corresponds almost to the food-processing fraction. Additional factors could be complemented for the end preparation of food (cooking). According to the actual status of the present methodology no factor is identified and consequently the intake fraction $iF_i$ ($kg_{ingested}/kg_{applied}$) is identified as:

$$iF_i = f_{fp} \cdot hF_i = \frac{f_{fp} \cdot M_{i,harvest}}{M_{i,emitted}} \qquad 2$$

with $f_p$ ($kg_{processing}/kg_{harvested}$) factor for the processing, with a value of 0.05 for processing from field to food.

The food pathway may include an intermediary transformation when the harvested commodity is used as feed. This pathway corresponds to a biotransfer process according to the denaturising of the plant product into animal products. Biotransfer has been modelled by factors that give a measure of how much of the ingested quantities of a contaminant are transferred to the animal tissue. Margni (2003) has developed the methodological approach for the bioconcentration in human food chain. The proposed methodological framework is based on the relation between the concentration of substance in animal tissue or fluids according to the daily intake of the substance. This approach is based on a steady state relationship between intake and animal products. Travis and Arms (1988) identified typical biotransfer factors, often used as basis for further methodological developments:

$$\log BTF = \log K_{ow} - b \qquad 3$$

with BTF (d/kg) the biotransfer factor, $K_{ow}$ n-octanol – water partition coefficient and b a constant according to the animal product considered, with b=7.6 for beef meat, b=8.1 for milk and b=5.1 for eggs. Margni (2003) has proposed an improved approach by taking into account the specific fat content of meat to evaluate biotransfer factor also for meat of pigs, poultry,

goats and sheep. Maximum threshold for BTF is identified at –0.1. These relations have a similar form to partition coefficient factors previously described for the plant model; however this coefficient describes a steady state condition according to ratio of concentrations between phases (environment and plant).

In accordance with the case study chosen here for methodological developments, the light processing process is considered for the transformation of wheat into bread and so the factor for food processing of 0.05 will be used in the concerned chapters.

## 2.2 Effect factor and impact evaluation

The procedure for the evaluation of human toxicity is described according to two methods: a method by Jolliet and Crettaz (2000), based on the Human reference dose and applied for the evaluation of pesticides by Margni (2003), and a newer method by Crettaz et al. (2002) and Pennington et al. (2002) based on a benchmark dose included in the method IMPACT 2002+ (Jolliet et al., 2003). In this study, the second method is applied as the most actual methodology. Both methods are presented hereafter.

### 2.2.1 Human reference dose

In the comparison of pesticides, Margni (2003) achieved the evaluation of the impact on human health according to the Human Reference Dose (HRD, kg substance / kg body weight / day) of the substance, a common toxicity measure. The human toxicity is described by the overall fraction of the substance that is ingested by all human beings, relative to the yearly HRD, considering a person ingests during one year the HRD of the substance present in food. This ratio is interpreted as the person equivalent that is exposed to the HRD during one year for every kg substance emitted. The human toxicity corresponds to:

$$F_i^f E_i^f = iF_i \frac{1}{\rho_p N \cdot B \cdot HRD_i^f} \qquad 4$$

with $E_i^f$ the effect factor of substance i in food, $F_i^f$ the fate and exposure factor of substance i in food, $iF_i$ the intake fraction of substance i (kg substance intake / kg emitted), $\rho_p$ the population density ($1.1 \times 10^{-5}$ person / $m^2$), N the number of days per year (365.25 days), B the average body weight (70 kg) and $HRD_i^f$ the human reference dose for food ingestion of the substance (kg / kg / day).

The Human reference dose (HRD, kg taken up per kg body weight and day) is used as measure of the toxic effect of the substance. This value is derived from published values, according to the following priority: the acceptable daily intake (ADI, mg taken up per kg body weight and day), the acute reference dose (mg taken up per kg body weight and day), and finally the tolerable daily intake. The effect factor is identified as a function of the HRD as already described:

$$E_i^f = \frac{1}{\rho_p N \cdot B \cdot HRD_i^f} \qquad 5$$

According to the difficulty of understanding the absolute value of toxicity, the relative comparison to a reference substance allows a better interpretation of the final result, expressed as the Human Toxicity Potential of a substance i ($HTP_i$ in kg equivalent lead into the air per kg substance i) and derived as follow:

$$HTP_i = \frac{F_i^f E_i^f}{F_{lead}^a E_{lead}^a} \qquad 6$$

### 2.2.2 Benchmark dose and severity

According to a new approach (Crettaz et al., 2002; Pennington et al., 2002) the Human Damage Factor of a substance i ($HDF_i$), in DALY (Disability Adjusted Life Years) per kg substance emitted corresponds to:

$$HDF_i = iF_i \cdot EF_i = iF_i \cdot \beta \cdot D \qquad 7$$

with $iF_i$ the intake fraction (kg substance intake / kg emitted) and $EF_i$ (DALY / kg intake) the effect factor of the substance i. The effect factor is determined by the human health effect factor ($\beta$i, risk of incidence per kg intake) and the severity (D, in DALY per incidence).

The human health risk factor is based on the concept of health-risk-assessment of benchmark dose (Crettaz et al., 2002; Pennington et al., 2002). It is determined from the dose-response slope factor of the substance, measured by the effect dose inducing a 10% response over background ($ED_{10}$). The preliminary slope factor $\beta_i$ were determined from bioassays on animal data (Toxic Dose 50%, No and Low Observed (Adverse) Effect Level). The human health effect factor ($\beta$i, risk of incidence per kg intake) is equal to

$$\beta_i = \frac{0.1}{ED_{10}} \cdot \frac{1}{B \cdot LT \cdot N} \qquad 8$$

with $ED_{10}$ benchmark dose resulting in 10% effect over background (mg/kg/day), B the average body weight (70 kg), LT the average lifetime of humans (years) N the number of days per year (365.25 days).

The severity (D, in DALY per incidence) accounts for both mortality and morbidity. Default values of 6.7 and 0.67 (years / incidence) are adopted for most carcinogenic and non-carcinogenic effects, respectively.

From the Human Damage Factor, the relative comparison expressed as the $HTP_i$ is derived as follow:

$$HTP_i = HDF_i / HDF_{chloroethylene} \qquad 9$$

with $HDF_{chloroethylene}$ as reference substance for human damaging effects (carcinogen).

# 3. Fate model development

In order to identify the main processes in environment – plant exchanges, and to understand the system of phytosanitary measures – plant – environment. The following challenges are identified: How can the fate of pesticide be described and what are the involved processes and in which system ? What are the procedures and requirements to simulate the dynamic functioning of the whole system ? What are the most significant relationships describing the functioning of the system ? What are the corresponding pertinent approximations ? According to theses questions the following points are developed in this first part of the study.

1) Substances. The substances used as pesticides are shortly introduced.
2) System description. The system includes the crop and the near environment in contact with the plant. Different compartment are involved in the processes. Main ones have to be identified.
3) Initial conditions of the system. The distribution of pesticide in the system at the moment of spraying determines the initial concentrations in the soil, the air and the formulation deposit on plants. The process depends notably on the crop stage. Description of initial conditions gives the amount of substance present in the different compartments.
4) Principles for transport and dissipation processes. The transfer processes regulate the dissemination of the substance between the environment and the plant. Transport and dissipation processes are dynamic and are all expressed in the form of transfer rates. Different types of transfers exist and principles for their description are presented.
5) Building and resolution of the model. The way to build the model and to solve it mathematically is developed. To complement the targeted result, tools for understanding the functioning of the system, for interpretation of the results and for approximations are also developed. A procedure for resolution is finally proposed.

## 3.1 Substances

A treatment product is a formulation composed of an active ingredient and different formulants. Active substances first considered here are pesticides with non-dissociating, neutral and lipophilic characters. The formulants are known adjuvants, diluents, stickers, surfactants, etc. The exact composition of a pesticide formulation is generally not available, except for the concentration of active ingredient. Therefore, the descriptions of the pesticide behaviour are based on the properties of the active substance. However, the formulants may enhance the biological activity or the physiochemical properties of the formulation. Consequently in some precise cases, the processes description will consider the effect of the formulants according to specific development.

The active substances are described by physico-chemical characteristics. Partition coefficients describe the substance behaviour in the environment and distribution between different phases. The molecular weight is a factor of the diffusion process. The half-lives are variable according the media and determinant for the residence time of the substance in the different system compartments. The descriptions of transport processes in the next chapters include the specific data needs and the way they are collected.

The difficulty to get data for substances and the variability of the values constitutes a potential important limit in the quality of the assessment. To get uniformity in the data collection

values are taken in priority from the Agritox database online (INRA, 2003), the Environmental Fate Data Base of the Syracuse Research Corporation online (Syracuse Research Corporation, 2003) and The Pesticide Manual (Tomlin, 1997).

The most commonly applied pesticides in wheat crop are used in the present study to illustrate the model components and to verify and test the model. These substances are herbicides, fungicides, insecticides, and growth regulators, applied specifically at different moment of the crop development. Appendix C. Substances used for the developments and the tests of the model presents the list of these substances, together with their main physico-chemical properties.

## 3.2 System description

Air, soil and formulation deposit are the primer compartments receiving the sprayed substance and sources for accumulation in plant. Different plant compartments are participating in the processes according to the sources of pesticide from the environment and to internal transport processes (Figure 3). Pesticides in the soil are taken up through fine roots. Also growing in the soil, storage organs, like thick roots (sugar beets) or tubers (potato) are in contact with fine roots and aerial plant parts. Above soil plant parts, basically stems and leaves are in contact with the air and with deposit of pesticides resulting from spraying. Fruit plant parts are in equilibrium with the stem or with the leaf according to the exposure of this organ to the applied substance. In case of direct application on fruit, it is considered as leaf-like; in case the fruit is protected, equilibrium with the stem is chosen. Trapp et al. (1994) and Trapp (1995) proposed comparable organisation of plant model, including four vegetative compartments: root, stem, leaves and roots.

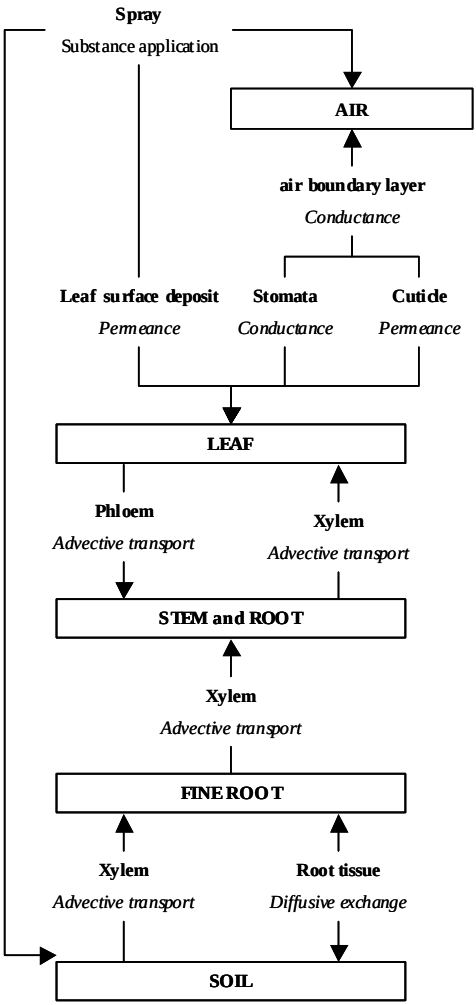



Figure 3. Environmental and crop system: compartments and transfer processes

The environmental compartments and their characteristic parameters are considered to remain constant, whereas plant compartments evolve during plant growth. The dynamic development of the plant is taken into account by its growth with an influence on diverse transport and dissipation processes.

A simple representation of plant development is chosen in order to describe the system at the beginning of vegetation, at pesticide application and at harvest. Data needed to that purpose are the masses and volumes at the beginning of the growing period and for the end of vegetation, considered as harvest time. The type of growth may follow different types of evolution. Exponential growth is chosen per default, which involves considering a short period from end of growth till harvest. The way to take into account the effect of growth is described in the chapters related to the description of the transfer and dissipation processes.

## 3.3 Initial conditions of the system

The initial conditions of the system describe the distribution of the substance at the moment of application and identify the system parameters before the dynamic evolution. The target of the sprayed product is the bare soil before plant emergence and the crop canopy later; the substance entering the canopy is partly intercepted by the plant and the rest reaches the soil. The substance that does not reach the target is considered as losses. One part of the losses is the substance that remains in the air; the other is disseminated outside the field. According to this description, the substance is distributed between the plant surface, the soil, the air and outside of the field. These different fractions of substance distribution are described hereafter, first identifying the fraction to the air and the fraction outside of the field, and then the quantity that reaches the canopy with subsequent distribution between plant and soil.

### 3.3.1 Fraction to the air and fraction outside of the field

Losses consider the fraction of sprayed product that does not directly reach the crop canopy. They consist of gas-phase pesticide and in small droplets or particles that remain in the air and are likely to be transferred outside of the field.

Large variations of losses are reported, typically ranging from a few percent of applied dose up to 30% and more (Van den Berg et al., 1999). Losses during application are mainly influenced by spraying technique, product formulation and meteorological conditions. Active ingredient properties have limiting importance at the moment of application. The spraying technique (sprayer, nozzle) has an important influence on the size of the droplets and on their trajectory to the target. Product formulation aims at modifying the viscosity of the applied mixture to reduce losses. Meteorological conditions also have an influence on the route of spray (drift) and on the stability of droplets (evaporation): wind speed, temperature, air humidity. Small droplets are lost as spray drift and may be transported to a long-range, as they are evaporated more easily. Larger ones better attain the targeted area, but the distribution on plant is less precise and may conduct to leaching from the plant surface to the soil.

Drift model are designed to account for all meteorological and agricultural practice conditions, showing the above mentioned relatively large variations in the fraction of the dosage that misses the target surface (van den Berg et al., 1999). These variations are reduced if good agricultural practices are considered. In that case, standard processes can be described and indicative data used for the model development according to good agricultural practices, to normalised technical application methods and to typical meteorological conditions. These initial transfers to the air could be described by a factor of spray efficiency at the moment of application.

A fraction of losses to the air is likely to be transported outside of the field. Part of it is finally deposited after drift. Complex drift models are available with consideration of meteorological

and technical conditions. Indicative data have been modelled according to crop type and to distance from field margin (Ganzelmeier et al., 1995). Drift for field crops reaches 4% of applied rate at a distance of 1 meter from field margin. Total loss from the field reaches around 5% with final ground deposit on soil or eventually on water surface. The soil deposited part creates residues on other crops. Assumed to have an equal effect, this fraction is not considered as a loss and so follows the same fate as the amount of substance that reaches the canopy.

Finally, data about distribution of substance to the air at application, as gas-phase pesticide or as particles is only available as a first order of magnitude. A default a fraction of 0.1 of applied dose is considered as lost in the air for some models (RIVM, VROM, VWS, in Linders, 2000). This loss in the air is available for direct accumulation in plants, for long-range transports to other agricultural surfaces or for dissemination out of agricultural systems. These fractions may be identified as a function of land occupation. In the present study, the total applied dose is considered to remain available in the air for accumulation in agricultural plants.

### 3.3.2 Plant interception and soil deposition

The evaluation of the amount of substance that reaches the canopy at application needs to be accounted for in the growth stage of the vegetation. According to Glydenkearne et al. (1999), large variations in ground deposition could be related to the canopy density, so that it appears that most the important parameter to characterise the interception of spray by the plant is given by the Leaf Area Index (LAI). With a simple model for field crops, they express the product distribution between soil and canopy according to the plant growth and the amount applied to the canopy ($M_t$ , $kg/m^2_{soil}$):

$$M_s = M_t \cdot \exp(-k_{LAI} LAI) \qquad 10$$

where the amount of pesticide reaching the soil $M_s$ ($kg/m^2$ soil) depends on the Leaf Area Index LAI ($m^2_{leaves}/m^2_{soil}$), which is the surface of vegetation per unit soil surface, and on a pesticide capture coefficient $k_{LAI}$ (-), taking into account the plant architecture and its interception capacity. This exponential model was proposed to be used in pesticide risk assessment. Although it was developed for soil deposition, the relationship has been chosen also here to evaluate the plant interception and the surface deposition. The difference between the amount of substance entering the canopy and the quantity that reaches the soil is considered to be deposited on plant surface. According to Figure 4, application time strongly affects the distribution of products between soil and canopy: the amount of treated substance entering the canopy that reaches the soil varies from 100%, for an application before crop emergence, to less than 10% when the crop is fully developed. This is mainly due to the variation in LAI which varies for a cereal from 0 before emergence to about 4 $m^2$ leaf surface /$m^2$ soil at full plant development.

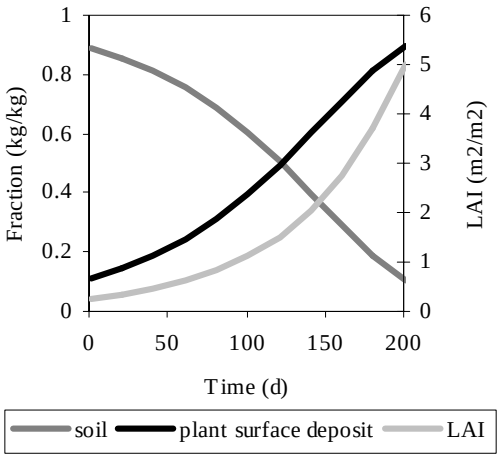



Figure 4. LAI development and fraction of substance distributed between soil and plant surface formulation deposit as a function of time and crop development.

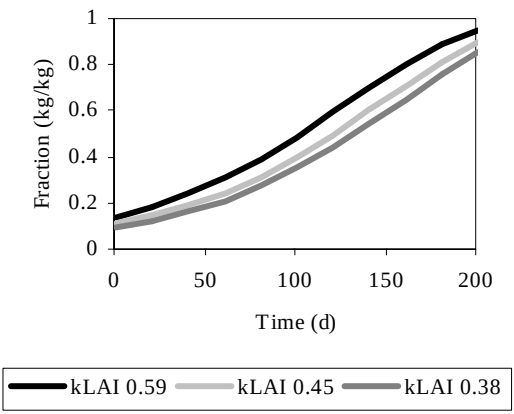



Figure 5. Fraction of leaf surface formulation deposit as a function of time for different capture coefficients $k_{LAI}$.

Under good agricultural practices, this capture coefficient is less variable than LAI (Figure 5). The capture coefficient depends on the plant architecture and on the turbulence in the canopy; the value for a cereal is 0.45 approximately. Turbulence in the canopy depends on the

composition of the applied product (surfactant) and on the technique of spraying (droplet size and velocity). Gyldenkaerne et al. (1999) showed an increase in the capture coefficient by about 0.05 due to surfactant only. The value for a cereal is typically 0.45, going from 0.382 (barley without surfactant) to 0.589 (tall wheat plants with surfactant). Consideration of different spray techniques did not yield more clear understanding of deposition.

Differences in distribution can also be observed within the canopy according to the plant architecture and the leaves disposition. The outer leaves and the top of the canopy are more exposed according to spray techniques and conditions. The detailed study of such distribution would go beyond needed precision first expected by the model development, as we are mainly interested in average residues in the crop. Finally the thin layer of product accumulated just after spraying represents the major source of substance accumulation by plant for late applications on grown crops. Standardised values for the interception fraction have also been proposed for different crops and growth phase by Linders et al. (2000); data for cereals are given in Table 1.

Table 1. Proposal for crop and growth phase-specific interception fractions ($F_{int}$) for crops. According to Linders (2000) and to capture coefficient ($k_{LAI}$). BBCH: code of plant stage.

| Crop | Growth phase | BBCH | $F_{int}$ Linders | $F_{int\ kLAI}$ |
|---|---|---|---|---|
| Bare soil – pre-emergence | - | - | 0 | 0 |
| Cereals I | Leaf development | 10-19 | 0.25 | 0.1-0.25 |
| Cereals II | Tillering | 20-29 | 0.5 | 0.2-0.4 |
| Cereals III | Stem elongation | 30-39 | 0.7 | 0.35-0.6 |
| Cereals IV | Booting/senescence | 40-99 | 0.9 | 0.5-0.90 |

Comparison of the interception fractions provided by Linders et al. (2000) or obtained by dynamic simulations according to the LAI and $k_{LAI}$ (0.45 and 0.59) shows differences (Table 1). Data by Linders tend higher and apparently correspond to the latest growth stage of the range considered. Part of this difference comes from the exponential growth in the LAI, that gives probable underestimation for intermediate crop growth stage (tillering and stem elongation) and more weight to the last growth phases. However, the use of a dynamic simulation allows a finer analysis according to the effective different moments of spraying. This method is chosen for the model development.

## 3.4 Principles for transport and dissipation processes

The initial conditions having been defined, transport and dissipation processes regulate the dissemination of the substance between the environment and the plant. These processes are dynamic as a function of the time between the release of substance, corresponding to the application of the plant treatment product, and the harvest of the agricultural commodity. The transport and dissipation processes between all compartments of the system have to be expressed in form of transfer rates in accordance to the methodology used for the resolution of the model. The detailed way of resolution is described in Chapter 3.5 Building and resolution of the model.

Transfer rates are derived from an algorithm describing transport and dissipation processes. Each transfer rate accounts for the type of transfer process and for the equilibrium partition resulting from the concentrations ratio between the two exchanging phases under thermodynamic equilibrium. Effect of the plant growth has also to be accounted for. After an

explanation for the notion of equilibrium partitioning, basic mathematical expressions for the different types of transfer rates, for the dissipation rates, and for the way to account for the plant growth are described hereafter.

### 3.4.1 Equilibrium partitioning

Equilibrium partitioning is the expression of the substance distribution between two neighbouring, non-mixable phases. It corresponds to the ratio of the concentrations in these two phases, when the system is in thermodynamic equilibrium:

$$K_{mn} = C_m / C_n \qquad 11$$

where K is dimensionless and C the concentration in media m and n. This property is specific to each substance. Several transfer processes directly or indirectly depend on this property, so that the equilibrium partitioning between exchanging media are important parameters for the substance behaviour description.

The basic partition coefficients largely used in environmental modelling and available in databases are the air-water partition coefficient $K_{aw}$, base on Henry's law constant [*Pa* $m^3$ $mol^{-1}$], and the n-octanol - water partition coefficient $K_{ow}$ and the organic carbon - water partition coefficient $K_{oc}$. The positioning of substances as a function of $K_{aw}$ and $K_{ow}$ shows their affinity between air, water and n-octanol (lipid, hydrophobic media, etc.) phases. Figure 6 illustrates this positioning for a range of pesticides (169) used in field crops. The variability of the properties is put in evidence.

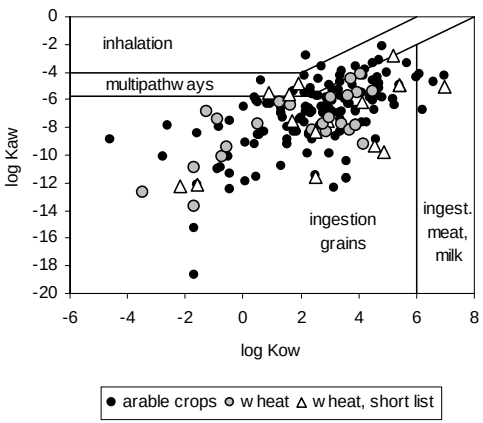



Figure 6. Distribution of the partition coefficients log $K_{aw}$ and log $K_{ow}$ for a range of substances used in field crops. Exposure classification of the substances: inhalation, multipathways, ingestion by grains, ingestion by meat or milk according to Bennett et al. (2002b) and Margni (2003). A short list of substances used in wheat is selected for specific methodological developments.

Bennett et al. (2002b) and Margni (2003) studied a set of 308 organic chemicals with a wide range of physicochemical properties according to which log $K_{ow}$ ranged from –3 to 8 and log $K_{aw}$ from –14 to 2. The substances were classified for the exposure as a function of $K_{ow}$ and $K_{aw}$ parameters. The proposed classification indicated that air pathway was dominant for substances with log Kaw over -4, that the ingestion pathway was dominant for substances with log Kaw lower than –6 or log Koa higher than 8, and that the other substances were multipathways substances. The classification is illustrated in Figure 6 for the substances used in field crops. According to this classification, pesticides cover a restricted range and the present set of substances is mainly concerned by ingestion pathways, with some multipathways chemicals. This confirms the need for modelling the fate of residues in plant.

Only the substances applied in wheat are used for methodological development in the present study. Their use first concerns the general description and illustration of transport processes. According to Figure 6 these substances show a good reproduction of pesticides variability. A specific short list of substances used in wheat is also identified to be used as case study for the core model developments; these substances have be chosen to cover all types of phytosanitary interventions (herbicides, growth regulators, fungicides and insecticides), all periods of application during growing season, and to represent a wide range of physico-chemical properties. These substances are described with more details in Chapter 5.1.2 Test substances.

### 3.4.2 Transfer rate by advection

Two types of transfer occur: transport within the system and losses outside the system. Both of these can take place by advection or diffusion. Transport by advection constitutes the simplest expression of substance transport from a compartment to another. It is calculated as the advective flux from a compartment to another multiplied by the concentration of the substance in the source compartment

$$N^{i}_{mn,adv} = Q_{mn} C^{i}_{m} = Q_{mn} \frac{M^{i}_{m}}{V_m} = M^{i}_{m} k_{mn} \qquad 12$$

With $N^{i}_{mn,adv}$ (kg/d) the advective transport of substance i from compartment m to n, $Q_{mn}$ ($m^3$/d) the flux of media (e.g. water) between the two compartments, $C^{i}$ (kg/$m^3$) the concentration of substance i in source compartment m, $M^{i}_{m}$ (kg) the mass of chemical in the source compartment m with volume $V_m$ ($m^3$), and $k_{mn,adv}$ (1/d) the transfer rate by advection from compartment m to n. The transfer rate is then equal to

$$k_{mn,adv} = Q_{mn} / V_m \qquad 13$$

This advective transport is typical for the transport of substance by transpiration stream from the soil to the plant as well as for the transport in the plant by the xylem and the phloem streams.

### 3.4.3 Transfer rate by diffusion

Transport by diffusion describes exchanges due to different concentrations of substances between two adjacent compartments. The transport process works in both direction and the concentration gradient between compartments determines the net direction of the flux.

$$N^{i}_{mn,dif} = D^{i} A_{mn} \frac{C^{i}_{m} - C^{i}_{n}}{L} = (C^{i}_{m} - C^{i}_{n}) V_{m} k^{i}_{mn,dif} \qquad 14$$

with $N^{i}_{mn,dif}$ (kg/d) the diffusive transport of substance i from compartment m to n, $D^{i}$ ($m^2$/d) the diffusion coefficient in water or in gas of the substance i, $A_{mn}$ ($m^2$) the surface of exchange between compartments m and n, $C^{i}_{m}$ (kg/$m^3$) the concentration of substance i in the compartment m and $C^{i}_{n}$ (kg/$m^3$) in the compartment n, L (m) the diffusion length, $V_m$ ($m^3$) the volume of compartment m and $k^{i}_{mn,dif}$ (1/d) the transfer rate by diffusion from compartment m to n. The transfer rate is then equal to:

$$k^{i}_{mn,dif} = D^{i} A_{mn} \Big/ (L V_{m}) \qquad 15$$

In the case of missing value of diffusion coefficient, it is extrapolated from a reference substance corrected on the basis of the molecular weight of the reference substance $MW^{ref}$ (g/mol) and the diffusing substance i $MW^{i}$ (g/mol) (Schwarzenbach et al., 1993). The diffusion coefficient of the substance i $D^{i}$ ($m^2$/d) is then:

$$D^{i} = D^{ref} \sqrt{MW^{ref} \Big/ MW^{i}} \qquad 16$$

Based on diffusion principles, conductance in air and permeance in water are also used to describe transport processes. This way of process description is helpful if the diffusion length of the limiting barrier is not identified. Transport according to conductance is then:

$$N^{i}_{mn,con} = G^{i} A_{mn} (C^{i}_{m} - C^{i}_{n}) = (C^{i}_{m} - C^{i}_{n}) V_{m} k^{i}_{mn,con} \qquad 17$$

With $N^{i}_{mn,con}$ (kg/d) the transport by conductance of substance i from compartment m to n, $G^{i}$ the conductance (m/d). Transfer rate according to conductance $k^{i}_{mn,con}$ (1/d) is:

$$T^{i}_{mn,con} = G^{i} A_{mn} \Big/ V_{m} \qquad 18$$

where $T^{i}_{mn,con}$ (1/d) is transfer rate by conductance. Similar relations for transport and transfer rate by permeance are given for $P^{i}$ (m/d).

According to the phases in which the substance concentration is considered and between which the transports occur, partition coefficients are needed in the transfer rate expressions. This will be stated in each detailed process description.

### 3.4.4 Degradation rate

Transformation of the substance by degradation is an important source of losses.

$$N^{i}_{m,\deg} = -M^{i}_{m} T^{i}_{m,\deg} \qquad 19$$

with $N^{i}_{m,deg}$ (kg/d) the transformation by degradation of substance i in compartment m, $k^{i}_{m,deg}$ (1/d) the degradation rate of the substance i in the compartment m. The degradation rate depends on the half-life of the substance i in the medium m $t^{i}_{1/2,m}$ (d):

$$k^{i}_{m,\deg} = \ln(2) / t^{i}_{1/2,\deg} \qquad 20$$

### 3.4.5 Plant growth rate

As plant organs are growing, by volume and areas, concentrations and transfer rates evolve. Environmental compartments are considered to remain constant.

Growth is determined as a function of the plant development. Growth rate is calculated here as an exponential development, setting aside other form of growth (Chapter 3.2). Volume of a plant compartment at moment t of growth phase $V_t$ ($m^3$) is described as

$$V_t = V_0 \cdot e^{k_g (t - t_0)} \qquad 21$$

with $V_0$ ($m^3$) the initial plant volume, $k_g$ (1/d) growth rate, $t_0$ and t (d) the time duration. Growth rate is then equal to:

$$k_g = \ln(V_t / V_0) / (t_t - t_0) \qquad 22$$

Similar growth rate determination is considered for other plant parameters (areas). The need and the way to consider the growth rate in the different transport processes will be specified for each case.

## 3.5 Building and resolution of the model

Environmental multi-media models consider mostly steady state conditions. The transport processes are in equilibrium, the receiving plants are equal to sources. Emissions are considered as disperse disseminations. Processes describing the fate of substances determine the distribution over the different environmental compartments. Time has no dynamic influence. First evaluations of pesticides according to the processes described above were achieved in steady state conditions, according to common resolution of multi-media models. For the different transport processes, the transfer efficiency was assessed according to the fraction of substance accumulated in each compartment per unit emitted constant source (Charles et al., 2001). Results gave mainly a first appreciation of pesticides behaviour, especially for the range of variation between substances. Differences of $10^7$ were observed

between substances according to their capacity to enter the plant and be accumulated. However absolute results were not comparable to practise conditions as the time of application and the time till harvest were not taken into account. Resolution for dynamic conditions was then developed in accordance to the specificities of the study. The primary developments helped to interpret the functioning of the system and gave indications for the modelling developments (Charles et al., 2001, 2002, 2003, 2004; Weiss, 2001). The building and resolution of the dynamic model is further developed according to these first results.

The system including the environment and the plant can be described and solved by different approaches. Different representations of the system have been developed and explored. The resolution of the full plant - environment system is useful for precise results. However, single processes are difficult to isolate, particularly to identify the efficiency of the transfers from the environmental compartments to plant organs. The environment is systematically the source of substance and the plant the receiver. Three different sources (soil, air, formulation deposit) are highlighted and their specific contributions to the accumulation in the plant are of interest. Consequently the total system can also be divided in three subsystems, with source compartment in the environment and a receiving plant compartment as plant organ. The full system and the subsystems are described in Figure 7.

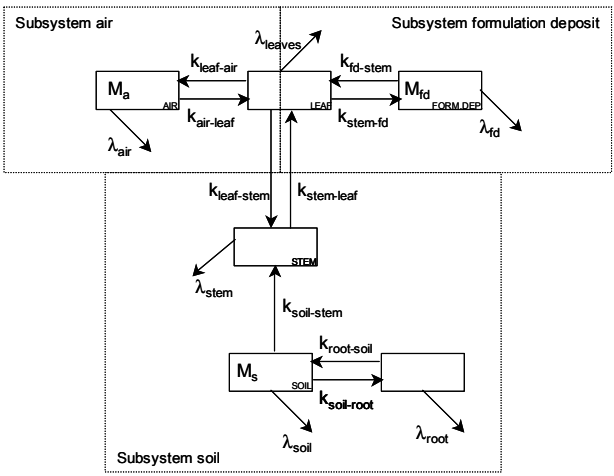



Figure 7. System description with three subsystems, initial masses in the environment, transfer and elimination rates.

Based on a simplified description of the system, new approaches and resolutions are developed. Simplified approaches consider only exchanges at the level of two compartments with or without symmetric exchanges. The resolution of these systems concerns dynamic processes. However, steady state resolution is generally practiced in environmental multi-media models. Similarities and differences between both resolutions can be identified. Finally

all these approaches are discussed and compared according to the results obtained with substances used in wheat.

To study each approach, the developments enclose the following elements. The system and the processes are described mathematically in detail. The scope, the limits and the key parameters for the resolution are identified. The functioning of the system is interpreted. Finally an approximation of the system is developed. On this basis, the building and resolution of the model includes the following chapters:

1) *Full model.* A first resolution with the total plant-environment system is developed to give a full mathematical resolution of the mass evolution in the system.
2) *Two compartments with bi-directional transfer*. A system of two compartments with bi-directional transfer between the source of substance (air, soil or formulation deposit) and the proximate plant organ as the receiving plant compartment is developed as a simplified approach. The source and the receiving plant compartments have mutual transfers, meaning that the source compartment receives back a portion of the emitted substance. All other transfer processes with other compartments are considered as negligible and not taken into account in the resolution.
3) *Cascade of two compartments*. The preceding approach is reduced to a system in cascade without any transfer back of substance from the receiving plant compartment to the source compartment.
4) *Two compartments in steady state*. The dynamic resolution is the rule for the functioning of the model. However, similarities exist with steady state resolution used in multi-media models; these elements are identified.
5) *Procedure*. The developed approaches are compared and a procedure is proposed for the resolution of the system and the running of the model.

### 3.5.1 Full model

The full model includes all compartments and processes of the plant environment system. The identified transfer rates correspond to the processes primarily identified as relevant. Some transports have already been neglected according to the description of the process in literature. Further evaluation of the relevance of each process will be possible according to the study of the functioning of the system and the results. The Figure 7 illustrates the system and its complexity when taken as a whole. This system represents the full environment-plant model. The mathematical resolution to determine the evolution of the system, that is the variation of the mass accumulating and dissipating in the different compartments of the system, is a developed hereafter according to the linear differential equations for the variation of mass in each compartment, their expression as a matrix and the general solution method.

The variations of mass in the n compartments $dm_n(t)/dt$ of the system are equal to

$$
\begin{aligned}
dm_1(t)/dt &= -k_1 m_1(t) + k_{21} m_2(t) + k_{31} m_3(t) + ... + k_{n1} m_n(t) \\
dm_2(t)/dt &= k_{12} m_1(t) - k_2 m_2(t) + k_{32} m_3(t) + ... + k_{n2} m_n(t) \\
dm_3(t)/dt &= +k_{13} m_1(t) + k_{23} m_2(t) - k_3 m_3(t) + ... + k_{n3} m_n(t) \\
dm_n(t)/dt &= k_{1n} m_1(t) + k_{2n} m_2(t) + k_{3n} m_3(t) + ... - k_n m_n(t)
\end{aligned}
\qquad (23)
$$

with $k_{mn}$ the transfer rates from compartment m to n, - $k_m$ the total removal rate from the compartment m and $m_n(t)$ the mass in the n compartments as a function of time. The transfer and removal rates correspond to the inverse of the residence times, having unit 1/day. The removal rate includes the sum of the degradation rate and of the total transfers from the considered compartment to the others.

The differential equations are resumed in a matrix form as:

$$\frac{d\vec{M}}{dt} = \vec{AM} = \begin{pmatrix} -k_1 & k_{12} & \dots & k_{1n} \\ k_{21} & -k_2 & \dots & k_{2n} \\ \dots & \dots & \dots & \dots \\ k_{n1} & \dots & \dots & -k_{nn} \end{pmatrix} \begin{pmatrix} m_1 \\ m_2 \\ \dots \\ m_n \end{pmatrix} (t) \qquad 24$$

The matrix coefficients are the transfer rates between compartments of the system. The negative removal rates from the n compartments ($-k_n$) are ordered as diagonal elements. The general solution of the linear differential equation system is (Braun 1983, Jacquez 1972, in Trapp and Matthies 1998):

$$m(t) = C_1\vec{V_1}\exp(\mu_1 t) + C_2\vec{V_2}\exp(\mu_2 t) + \dots + C_n\vec{V_n}\exp(\mu_n t) \qquad 25$$

with, in accordance to matrix $\vec{A}$, $C_n$ the constants calculated from the initial conditions (t=0), $\vec{V_n}$ the eigenvectors, $\mu_n$ the eigenvalues and t the time.

The mass evolution of the substance in the system is resolved dynamically as a function of time. The matrix calculations are performed using mathematical routines in computer programs, in the present study by Poptools (Hood, 2002) a macro running under Microsoft Excel.

According to the studied system environment – plant, the matrix includes six compartments with identified transfer rates.

Table 2. Matrix of the transfer rates between the compartments of the system environment – plant.

| | Air | Soil | Form.deposit | Root | Stem | Leaf |
|---|---|---|---|---|---|---|
| Air | $-k_{air}$ | | | | | $k_{leaves\text{-}air}$ |
| Soil | | $-k_{soil}$ | | $k_{root\text{-}soil}$ | | |
| Form.deposit | | | $-k_{form.dep.}$ | | | $k_{leaves\text{-}form.res.}$ |
| Root | | $k_{soil\text{-}root}$ | | $-k_{root}$ | | |
| Stem | | $k_{soil\text{-}stem}$ | | | $-k_{stem}$ | $k_{leaves\text{-}stem}$ |
| Leaf | $k_{air\text{-}leaf}$ | | $k_{form.res.\text{-}leaf}$ | | $k_{stem\text{-}leaf}$ | $-k_{leaf}$ |

Results of the full model consist of the final mass in each compartment, as a function of the initial masses, the transfer rates and the time. The need to perform the whole calculation in one step limits the possibility to mathematically interpret the functioning of the system. Ways for interpretation are developed in the next chapters.

### 3.5.2 Two compartments with bi-directional transfer

Exchanges between the environment and the plant can be simplified as a system with two compartments with reciprocal exchanges. A compartment plays the role of source (compartment 1), the second compartment is the receiving plant (compartment 2). The transfers between the two compartments depend on the initial mass in the source compartment ($m_0$), the exchange rate from source to the receiving plant ($k_{12}$) and the transfer back from the receiving plant to source ($k_{21}$). The fate also depends on the elimination rates, by degradation or by transport outside of the system, in each compartment ($\lambda_1$ and $\lambda_2$). There is no initial mass in the plant compartment. Figure 8 describes the system.

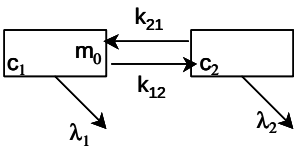



Figure 8. System description with two compartments, source ($c_1$) and receiving plant ($c_2$), initial mass ($m_0$), transfer ($k_{12}$ and $k_{21}$) and elimination ($\lambda_1$ and $\lambda_2$ ) rates.

The mathematical resolution aims at describing the evolution of mass in the system as a function of time. Variation of mass in source compartment is:

$$dm_1(t)/dt = k_{21}m_2(t) - \lambda_1 m_1(t) - k_{12}m_1(t) \qquad 26$$

The variation of mass in the receiving plant compartment is given by:

$$dm_2(t)/dt = k_{12}m_1(t) - \lambda_2 m_2(t) - k_{21}m_2(t) \qquad 27$$

The system can be given as :

$$\frac{d\vec{M}}{dt} = \overline{\overline{A}}\vec{M} = \begin{pmatrix} -k_1 & k_{21} \\ k_{12} & -k_2 \end{pmatrix}\begin{pmatrix} m_1 \\ m_2 \end{pmatrix}(t) \qquad 28$$

with dissipation rates, as the sum of the elimination and transfer rates for exchanges between compartments:

$$k_1 = \lambda_1 + k_{12} \text{ and } k_2 = \lambda_2 + k_{21} \qquad 29$$

Variation of mass as a function of time has the following solution expressed by the eigenvalues ($\mu_1$ and $\mu_2$), the eigenvectors ($\vec{v_1}$ and $\vec{v_2}$ ) and two constants ($C_1$ and $C_2$):

$$M(t) = C_1\vec{V_1}\exp(\mu_1 t) + C_2\vec{V_2}\exp(\mu_2 t) \quad (30)$$

Eigenvectors are determined so that the second components of the vectors are equal to 1 and ordered so that eigenvalues are then defined so that $\mu_1 < \mu_2$. Associated to $\mu_1$ respectively $\mu_2$, eigenvectors $\vec{V_1}$ and $\vec{V_2}$ are equal to :

$$\vec{V_1} = \begin{pmatrix} V_{11} \\ V_{12} \end{pmatrix} = \begin{pmatrix} \dfrac{-k_1 + k_2 - \sqrt{(k_1 - k_2)^2 + 4k_{12}k_{21}}}{2k_{12}} \\ 1 \end{pmatrix} = \begin{pmatrix} \dfrac{\mu_1 + k_2}{k_{12}} \\ 1 \end{pmatrix}$$
$$\vec{V_2} = \begin{pmatrix} V_{21} \\ V_{22} \end{pmatrix} = \begin{pmatrix} \dfrac{-k_1 + k_2 + \sqrt{(k_1 - k_2)^2 + 4k_{12}k_{21}}}{2k_{12}} \\ 1 \end{pmatrix} = \begin{pmatrix} \dfrac{\mu_2 + k_2}{k_{12}} \\ 1 \end{pmatrix} \quad (31)$$

Eigenvalues according to matrix $\vec{A}$ are equal to:

$$\mu_1 = \frac{1}{2}(-k_1 - k_2 - \sqrt{(k_1 - k_2)^2 + 4k_{12}k_{21}})$$
$$\mu_2 = \frac{1}{2}(-k_1 - k_2 + \sqrt{(k_1 - k_2)^2 + 4k_{12}k_{21}})\} \quad (32)$$

$C_1$ and $C_2$ are determined at time t = 0 according to equation 30, with initial mass located in source compartment only.

$$m_2(0) = C_1V_{12} + C_2V_{22} = C_1 + C_2 = 0 \quad (33)$$

$$m_1(0) = C_1V_{11} - C_1V_{21} = C_1\frac{-\sqrt{(k_1 - k_2)^2 + 4k_{12}k_{21}}}{k_{12}} = m_0 \quad (34)$$

$$C_1 = -C_2 = -\frac{m_0k_{12}}{\sqrt{(k_1 - k_2)^2 + 4k_{12}k_{21}}} = -\frac{m_0k_{12}}{\mu_2 - \mu_1} \quad (35)$$

The evolution of the mass as a function of time is derived for the two compartments according to the identified eigenvalues, eigenvectors and constants. The mass as a function of time in source compartment is obtained from equation 30, and is equal to:

$$m_1(t) = C_1(V_{11}\exp(\mu_1 t) - V_{21}\exp(\mu_2 t)) \quad (36)$$

$$m_1(t) = -\frac{m_0}{2(\mu_2 - \mu_1)}$$
$$((-k_1 + k_2 - \mu_2 + \mu_1)\exp(\frac{t}{2}(-k_1 - k_2 - \mu_2 + \mu_1)) \quad (37)$$
$$-(-k_1 + k_2 + \mu_2 - \mu_1)\exp(\frac{t}{2}(-k_1 - k_2 + \mu_2 - \mu_1)))$$

The mass as a function of time in the receiving plant compartment is:

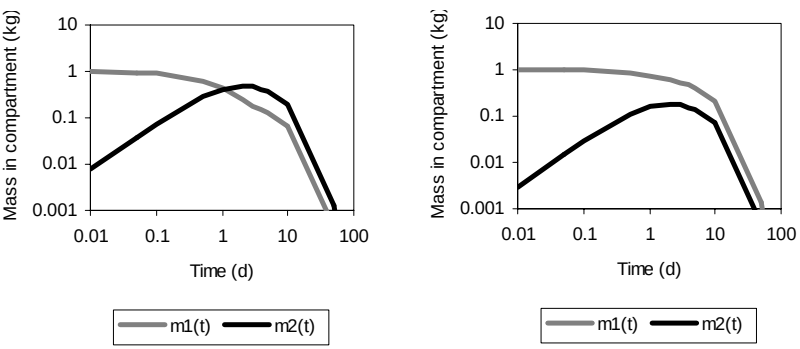
$$m_2(t) = C_1(V_{12}\exp(\mu_1 t) - V_{22}\exp(\mu_2 t)) = -\frac{m_0 k_{12}}{\mu_2 - \mu_1}(\exp(\mu_1 t) - \exp(\mu_2 t))$$
$$= -\frac{m_0 k_{12}}{\mu_2 - \mu_1}(\exp(\frac{t}{2}(-k_1 - k_2 - \mu_2 + \mu_1)) - \exp(\frac{t}{2}(-k_1 - k_2 + \mu_2 - \mu_1))) \quad (38)$$

The following equality has been used in the preceding equations.

$$\mu_2 - \mu_1 = \sqrt{(k_1 - k_2)^2 + 4k_{12}k_{21}})\} \quad (39)$$

### *3.5.2.1 Functioning of the system*

Figure 9 illustrates typical evolutions of the mass of substance in the two compartments. This evolution includes different steps. The system starts with a mass initially located in the source compartment only. The substance is then transferred to the receiving plant compartment up to a maximum point. Finally the mass decreases in both compartments. The relative evolution of the mass in the compartments evolves according to the difference between $k_1$ and $k_2$. In case $k_1 > k_2$ the mass in the receiving plant compartment exceeds the one in the source compartment. In the other case, the source compartment maintains a higher mass throughout




time.

A. $k_1>k_2$ B. $k_1<k_2$

Figure 9. Evolution of mass as a function of time for two compartments with bi-directional transfer, source compartment $m_1(t)$ and receiving plant $m_2(t)$. A. $k_1>k_2$ with $m_0=1$, $k_{12}=0.8$ 1/d, $k_1=1$ 1/d, $k_{21}=0.3$ 1/d, $k_2=0.4$ 1/d. B. $k_1<k_2$ with $m_0=1$, $k_{12}=0.3$ 1/d, $k_1=0.4$ 1/d, $k_{21}=0.8$ 1/d, $k_2=1$ 1/d (hypothetical substances).

A better knowledge of the functioning of the system is necessary to identify key parameters for interpretation and ways to simplify processes. The expressions of the basis equations are complex. No relevant reformulation of these expressions was identified. Single factors or groups of factors are not easily interpretable. Nevertheless some explanations for the curves evolution can be given as a function of the elimination and transfer rates. In particular the following points are explored:

- the simplification of some processes,
- the description of the point of maximum mass in the receiving plant compartment,
- the description of the ratio between the masses of both compartments.

#### *3.5.2.2 Simplification of processes*

The mass evolution in each compartment results from different processes. For each compartment the single processes are simplified to help the interpretation.

The net evolution of mass in the receiving plant compartment relies on the mass transferred from the source compartment, on the elimination out of the system and on the transfer back to the source compartment. The net process corresponds to

$$m_2(t) = \int_0^t \frac{dm_{2,source}(s)}{ds} ds - \int_0^t \frac{dm_{2,transferback}(s)}{ds} ds - \int_0^t \frac{dm_{2,elimination}(s)}{ds} ds \qquad 40$$

Where source, loss, transfer back and elimination are the cumulated mass in the compartment from time 0 to time t. These three processes are the following:

The source process, given by the cumulated transfer of mass from compartment 1 to 2, is equal to:

$$\int_0^t \frac{dm_{2,source}(s)}{ds} ds = \int_0^t k_{12} m_1(s) ds = C_1 k_{12} \left(\frac{V_{21}}{\mu_2}(1-\exp(\mu_2 t)) - \frac{V_{11}}{\mu_1}(1-\exp(\mu_1 t))\right) \qquad 41$$

The cumulated transfer back of mass from the receiving plant compartment to the source compartment is equal to:

$$\int_0^t \frac{dm_{2,transferback}(s)}{ds} ds = \int_0^t k_{21} m_2(s) ds = C_1 k_{21} \left(\frac{1}{\mu_2}(1-\exp(\mu_2 t)) - \frac{1}{\mu_1}(1-\exp(\mu_1 t))\right) \qquad 42$$

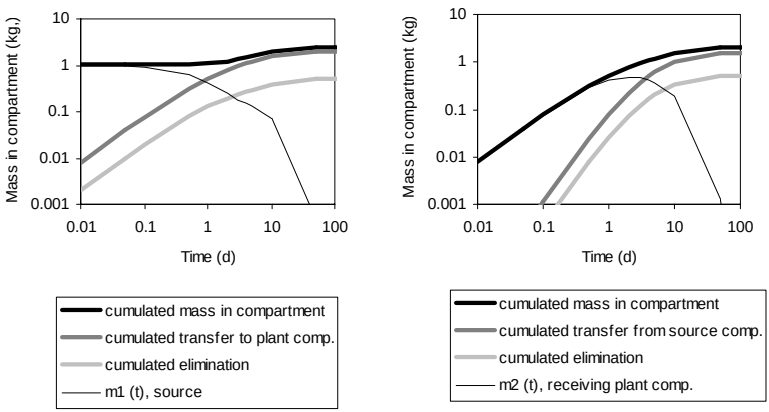
The cumulated elimination of mass in the receiving plant compartment is equal to:

$$\int_0^t \frac{dm_{2,elimination}(s)}{ds} ds = \int_0^t \lambda_2 m_2(s) ds = C_1 \lambda_2 \left(\frac{1}{\mu_2}(1 - \exp(\mu_2 t)) - \frac{1}{\mu_1}(1 - \exp(\mu_1 t))\right) \quad 43$$

Similarly, the cumulated elimination of mass in the source compartment is equal to:

$$\int_0^t \frac{dm_{1,elimination}(s)}{ds} ds = \int_0^t \lambda_1 m_1(s) ds = C_1 \lambda_1 \left(\frac{V_{21}}{\mu_2}(1 - \exp(\mu_2 t)) - \frac{V_{11}}{\mu_1}(1 - \exp(\mu_1 t))\right) \quad 44$$

The evolution of these processes is illustrated in Figure 10.




A. B.

Figure 10. Evolution in time of a two compartments system with bi-directional transfer. Cumulated mass in compartment, cumulated transfer to compartment, cumulated elimination from compartment and mass evolution as a function of time. A. Compartment 1 acting as source B. Compartment 2 acting as the receiving plant compartment. With $m_0$=1, $k_{12}$=0.8 1/d, $k_1$=1 1/d, $k_{21}$=0.3 1/d, $k_2$=0.4 1/d (hypothetical substance).

According to the expression $(1 - \exp(\mu t))$, the eigenvalues relative to the increase in time describe the rapidity of the evolution of the total system towards total elimination of the substance. In each compartment, the similar progress of the curves after maximum accumulation has been reached in the receiving plant compartment, give a first indication of the respective contribution of each process to the evolution of the system. The limits of the integrated equations correspond to the total mass transported by the process at the "end" of the system evolution. Main routes of transport are then easily identified hereafter.

The total mass transferred from source to the receiving plant compartment is equal to:

$$\lim_{t \to \infty} \int_0^t k_{12} m_1(s) ds = C_1 k_{12} \left(\frac{V_{21}}{\mu_2} - \frac{V_{11}}{\mu_1}\right) = \frac{k_{12} k_2 m_0}{k_1 k_2 - k_{12} k_{21}} \quad 45$$

The total mass transferred back from the receiving plant to source compartment is equal to:

$$\lim_{t \to \infty} \int_0^t k_{21} m_2(s) ds = C_1 k_{21} \left(\frac{1}{\mu_2} - \frac{1}{\mu_1}\right) = \frac{k_{21} k_{12} m_0}{k_1 k_2 - k_{12} k_{21}} \quad 46$$

The total mass eliminated from the source compartment, by degradation or by transfer out of the system, is equal to:

$$\lim_{t \to \infty} \int_0^t \lambda_1 m_1(s) ds = C_1 \lambda_1 \left(\frac{V_{21}}{\mu_2} - \frac{V_{11}}{\mu_1}\right) = \frac{\lambda_1 k_2 m_0}{k_1 k_2 - k_{12} k_{21}} \quad 47$$

The total mass eliminated from the receiving plant compartment is equal to:

$$\lim_{t \to \infty} \int_0^t \lambda_2 m_2(s) ds = C_1 k \lambda_2 \left(\frac{1}{\mu_2} - \frac{1}{\mu_1}\right) = \frac{\lambda_2 k_{12} m_0}{k_1 k_2 - k_{12} k_{21}} \quad 48$$

The determinant of the matrix appears systematically in these integrations as the denominator. It could be used to assess the capacity level of accumulation between different substances or systems.

With time, total mass is eliminated in both compartments. The sum of this eliminated mass corresponds logically to the initial mass

$$\lim_{t \to \infty} \int_0^t \lambda_1 m_1(s) ds + \lim_{t \to \infty} \int_0^t \lambda_2 m_2(s) ds = m_0 \quad 49$$

The transfer back from the receiving plant compartment to source compartment contributes to a cyclic process due the exchanges between the compartments. The importance of this cycle can be demonstrated by the total mass transferred through the compartment expressed relatively to the initial mass at the beginning of the system.

$$\lim_{t \to \infty} \int_0^t k_1 m_1(s) ds / m_0 = C_1 k_1 \left(\frac{V_{21}}{\mu_2} - \frac{V_{11}}{\mu_1}\right) / m_0 = \frac{k_1 k_2}{k_1 k_2 - k_{12} k_{21}} = 1 + Ff \quad 50$$

This relation corresponds to the feedback factor (1+Ff) described for the steady state resolution of multi-media models (Margni et al., 2003). It shows that the resolution of dynamic models tends to be similar to the resolution of steady state models as time tends to infinite. In the case of steady state resolution the feedback factor is often considered as negligible in comparison to generally high variation between substance behaviour. However the analysis of this factor helps better understand the transport and dissipation of substances in multi-media systems. The possibility to ignore this feedback process in dynamic models enables one to study the effect of a transfer back. This approach will be developed in the chapter describing a system with two compartments in cascade.

The use of the feedback factor to express the limits of the integrated equations corresponding to the total mass transported by the processes allows new formulations easily interpretable by the following model equation:

The total mass transferred from a compartment is equal to:

$$\lim_{t \to \infty} \int_0^t transfer\_process(s)ds = \frac{k_{mn}}{k_m}(1+Ff)m_0 \quad 51$$

with $k_{mn}$ the transfer rate describing the process from compartment m to n, $k_m$ the total removal rate from the compartment m, (1+Ff) feedback factor and $m_0$ the initial mass.

The total mass transferred from source to the receiving plant compartment is equal to:

$$\lim_{t \to \infty} \int_0^t k_{12}m_1(s)ds = \frac{k_{12}}{k_1}(1+Ff)m_0 \quad 52$$

The total mass transferred back from the receiving plant to source compartment is equal to:

$$\lim_{t \to \infty} \int_0^t k_{21}m_2(s)ds = \frac{k_{21}}{k_2}\frac{k_{12}}{k_1}(1+Ff)m_0 \quad 53$$

The total mass eliminated from the source compartment is equal to:

$$\lim_{t \to \infty} \int_0^t \lambda_1 m_1(s)ds = \frac{\lambda_1}{k_1}(1+Ff)m_0 \quad 54$$

The total mass eliminated from the receiving plant compartment is equal to:

$$\lim_{t \to \infty} \int_0^t \lambda_2 m_2(s)ds = \frac{\lambda_2}{k_2}\frac{k_{12}}{k_1}(1+Ff)m_0 \quad 55$$

#### *3.5.2.3 Maximum mass*

The typical evolution of mass as a function of elapsed time shows a maximum point in the receiving plant compartment. Schematically the mass accumulates in the receiving plant compartment as long as this transfer process is superior to the dissipation due to the transfer back and to the elimination. Beyond this point the relative importance of these processes are reversed and the mass decreases in the compartment. The point of maximum mass can be expressed as a point with equilibrium between the transfer from the source (compartment 1) the receiving plant compartment (compartment 2) and the total loss in plant compartment $dm_2(t)/dt=0$ (equation 27). Consequently the description of the maximum point offers the possibility to help the diagnosis of substance behaviour. The time necessary to reach the maximum in the receiving plant compartment and the corresponding quantity of mass are identified according to the derivation of equation 38. The time $t_{max}$ with maximum mass in the receiving plant compartment is:

$$t_{max} = \frac{\ln(\mu_1/\mu_2)}{\mu_2 - \mu_1} \quad 56$$

According to time $t_{max}$, the maximum mass in the receiving plant compartment is equal to

$$m_{2\max} = \frac{m_0 k_{12}}{\mu_2 - \mu_1}\left(\left(\frac{\mu_1}{\mu_2}\right)^{\mu_1/(\mu_2-\mu_1)} - \left(\frac{\mu_1}{\mu_2}\right)^{\mu_2/(\mu_2-\mu_1)}\right) \quad 57$$

### *3.5.2.4 Ratio between masses*

The masses in the receiving plant compartment and in the source compartment show a similar evolution particularly after the maximum point. Looking at the ratio between these masses shall help the description of the evolution of the system. The ratio as a function of time is equal to

$$\frac{m_2(t)}{m_1(t)} = \frac{k_{12}(\exp(\mu_1 t) - \exp(\mu_2 t))}{(\mu_1 + k_2)\exp(\mu_1 t) - (\mu_2 + k_2)\exp(\mu_2 t)} \quad 58$$

Two points of this relation are of interest: the point of maximum mass in the receiving plant compartment as a significant point of the system evolution and the limit of system evolution as the time tends to the infinite.

At $t_{max}$ the ratio of masses between the two compartments is equal to a simple relation between the transfer rate from source to the receiving plant compartment ($k_{12}$) and the elimination rate in the receiving plant compartment ($k_2$):

$$\frac{m_2(t_{\max})}{m_1(t_{\max})} = \frac{k_{12}}{k_2} \quad 59$$

This simple expression underlines the particular situation at this maximum point. At $t_{max}$, the mass in the receiving plant compartment is precisely equal to the mass in the source compartment times the ratio between the transfer rate acting as source ($k_{12}$) and the transfer rate acting as dissipation ($k_2 = k_{21} + \lambda_2$).

Beyond $t_{max}$, the ratio of mass between the compartments tends to a defined limit equal to the eigenvector $V_{21}$ (for the first component equal to 1).

$$\lim_{(t \to \infty)} \frac{m_2(t)}{m_1(t)} = \frac{k_{12}}{\mu_2 + k_2} = 1/V_{21} \quad 60$$

Figure 11 illustrates the evolution of the ratio $m_2(t)/m_1(t)$ as a function of time, as different elements characterising this ratio. The ratio varies with time from a value less than 1 to a superior value, which clearly underlines the transfer of mass from one source compartment to the receiving plant compartment. When the time tends to infinite, the ratio tends to a limit identified as the inverse of the ($1/V_{21}$). This tendency is observable rapidly after the time when maximum mass in the receiving compartment ($t_{max}$) has been reached, as the ratio is equal to the ratio $k_{12}/k_2$.

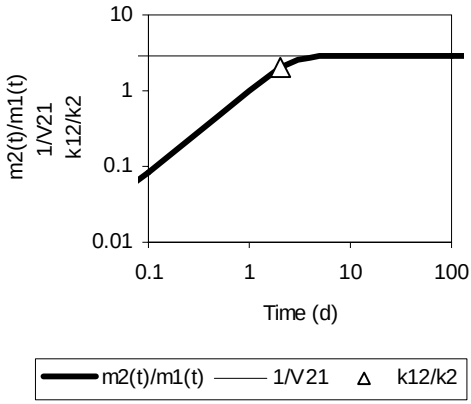



Figure 11. Evolution of the ratio $m_2(t)/m_1(t)$ as a function of time, limit of the ratio equal to $1/V_{2,1}$ as the time tends to infinite, and point identified as equal to $k_{12}/k_2$ at $t_{max}$ when mass in receiving plant compartment reaches the maximum point. With $m_0$=1, $k_{12}$=0.8 1/d, $k_1$=1 1/d, $k_{21}$=0.3 1/d, $k_2$=0.4 1/d (hypothetical substance).

The evolution of mass in the source compartment includes two possibilities to extrapolate the mass in the receiving plant compartment: at the maximum point and according to the limit of their ratio at time tends to infinite.

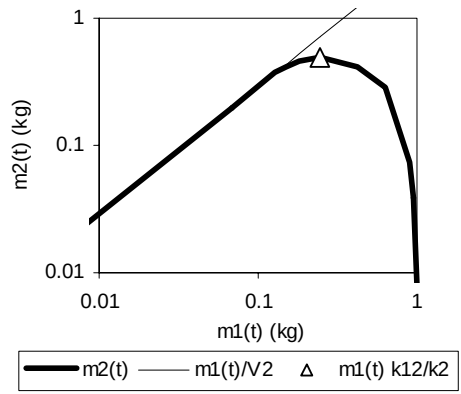



Figure 12. Evolution of the mass in the receiving plant compartment $m_2(t)$ as a function of evolution of the mass in the source compartment $m_1(t)$, with the limit $(m_1(t)/V_{2,1})$ when the time tends to infinite, and at maximum mass in the receiving plant compartment ($m_{2max}=m_1(t)$ $k_{12}/k_2$). With $m_0$=1, $k_{12}$=0.8 1/d, $k_1$=1 1/d, $k_{21}$=0.3 1/d, $k_2$=0.4 1/d (hypothetical substance).

### *3.5.2.5 Approximation*

According to the preceding descriptions of the processes involved in the system evolution, distinction may be proposed between main parameters and secondary, or even negligible, ones in order to select elements useful for simplifying the system approach and the results of calculation by approximation.

The evolution of the mass in the receiving plant compartment $m_2(t)$ before and after the maximum point depends on the relative contribution of the two terms of the equation including the eigenvalues (equation 38). The mass in the compartment depends directly on the difference between these two terms. Per definition, the first eigenvalue was determined to be the greater $\mu_1 < \mu_2$ (equation 32). Consequently, the term formed by first eigenvalue $\mu_1$ decreases first with increase of time and is almost insignificant relatively to the other term passed the maximum point. Simultaneously the term formed by second eigenvalue $\mu_2$ becomes approximately equal to the exact solution, particularly after the maximum point has been reached. This can be used as a potential of simplification of the equation beyond the maximum point.

$$m_2(t) = C_1(\exp(\mu_1 t) - \exp(\mu_2 t)) \approx -C_1 \exp(\mu_2 t) \qquad 61$$

The evolution of mass in the receiving plant compartment therefore follows two stages: first the accumulation until the maximum, then the elimination of this accumulated mass. An approximation of the system would tend to consider only the elimination evolution after the system has reached the maximum, in particular if the time to attain the maximum is short compared to the time considered for the system evolution. The description of the point of maximum mass in the receiving plant compartment can be used for simplification of the curves evolution. From this point onward, the elimination of accumulated mass can be considered as a simplification potential.

$$m_2(t) \approx m_{2\max} \exp(\mu_2 (t - t_{\max})) \qquad 62$$

In the case the evolution of the mass in the source compartment is easily interpreted, the limit of the ratio between the masses (equation 60) may be used. The following approximation is possible:

$$m_2(t) \approx m_1(t) / V_{21} \qquad 63$$

Finally appropriate simplifications are possible in the formulation of the equations according to the individual values of the transfer rates characterising the studied systems, by neglecting minor factors. One of these possibilities is studied in the next chapter describing the resolution of a system in cascade, in the case no transfer back occurs (advective transport) or in the case a transfer back is indubitably negligible.

### *3.5.2.6 Synthesis*

A synthesis of the different equation is proposed in the Table 3.

Table 3. Main equations describing a system of two compartments with symmetric of exchanges.

| | |
|---|---|
| Eigenvectors | $\overrightarrow{V_1} = \begin{pmatrix} \frac{\mu_1 + k_2}{k_{12}} \\ 1 \end{pmatrix}$ |
| | $\overrightarrow{V_2} = \begin{pmatrix} \frac{\mu_2 + k_2}{k_{12}} \\ 1 \end{pmatrix}$ |
| Eigenvalues | $\mu_1 = \frac{1}{2}(-k_1 - k_2 - \sqrt{(k_1 - k_2)^2 + 4k_{12}k_{21}})$ |
| | $\mu_2 = \frac{1}{2}(-k_1 - k_2 + \sqrt{(k_1 - k_2)^2 + 4k_{12}k_{21}})$ |
| Constant | $C_1 = -C_2 = -\frac{m_0 k_{12}}{\mu_2 - \mu_1}$ |
| Mass in source compartment | $m_1(t) = C_1(V_{1,1}\exp(\mu_1 t) - V_{2,1}\exp(\mu_2 t))$ |
| Mass in the receiving plant compartment | $m_2(t) = C_1(\exp(\mu_1 t) - \exp(\mu_2 t))$ |
| Feedback factor | $1 + Ff = \frac{k_1 k_2}{k_1 k_2 - k_{12}k_{21}}$ |
| Time to reach the maximum mass in the receiving plant compartment | $t_{max} = \frac{\ln(\mu_1 / \mu_2)}{\mu_2 - \mu_1}$ |
| Maximum mass in the receiving plant compartment | $m_{2\,max} = C_1((\frac{\mu_1}{\mu_2})^{\mu_1/(\mu_2 - \mu_1)} - (\frac{\mu_1}{\mu_2})^{\mu_2/(\mu_2 - \mu_1)})$ |
| Ratio between masses at $t_{max}$ | $\frac{m_2(t_{max})}{m_1(t_{max})} = \frac{k_{12}}{k_2}$ |
| Limit of ratio between masses | $\lim_{(t \to \infty)} \frac{m_2(t)}{m_1(t)} = 1/V_{2,1}$ |
| Approximation when $t>t_{max}$ | $m_2(t) \approx -C_1 \exp(\mu_2(t))$ |
| | $m_2(t) \approx m_{2\,max} \exp(\mu_2(t - t_{max}))$ |
| | $m_2(t) \approx m_1(t)/V_{21}$ |

### 3.5.3 Cascade of two compartments

The approach of a system in cascade considers two compartments with transport processes from one compartment to the other but without transfer back. This especially concerns exchanges between environment and plant for which the transport occur by an advective flux, opposite to diffusive processes where the transport depends on gradient of concentration and equilibrium processes. A system of cascade is also of interest for conditions where the feedback fraction is identified as negligible in a system with bi-directional transfer. The description of the system in cascade (Figure 13) is developed here.

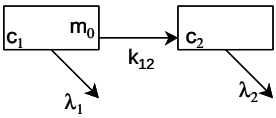



Figure 13. System description with two compartments, initial mass, transfer and elimination rates.

The mathematical solution is based on the same approach developed for the system with bi-directional transfer. The different relations for the cascade system are reformulated by simplification according to the absence of transfer back $k_{21}$.

Variation of mass in source compartment as a function of time is:

$$dm_1(t)/dt = -\lambda_1 m_1(t) - k_{12} m_1(t) = -k_1 m_1(t) \qquad 64$$

Where $\lambda_1$ (1/d) is the degradation rate from compartment 1, $k_{12}$ (1/d) the transfer rate from compartment 1 (source) to compartment 2 (the receiving plant compartment), and $k_1$ (1/d) the dissipation rate from the compartment 1.

The variation of mass in compartment 2 is given by:

$$dm_2(t)/dt = k_{12} m_1(t) - k_2 m_2(t) \qquad 65$$

Where $k_2$ (1/d) is the dissipation rate out of the compartment, as a degradation process or a transfer to a third compartment.

The matrix of the system is given as :

$$\frac{d\vec{M}}{dt} = \vec{AM} = \begin{pmatrix} -k_1 & 0 \\ k_{12} & -k_2 \end{pmatrix} \begin{pmatrix} m_1 \\ m_2 \end{pmatrix}(t) \qquad 66$$

with

$$k_1 = \lambda_1 + k_{12} \text{ and } k_2 = \lambda_2 \qquad 67$$

The eigenvalues, the eigenvectors and the constants are determined in accordance with the developments presented for the resolution with bi-directional transfer (Chapter 3.5.2).

Eigenvalues, eigenvectors and constants are equal to:

$$\mu_1 = -k_1$$
$$\mu_2 = -k_2 \qquad 68$$

$$\overrightarrow{V_1} = \begin{pmatrix} V_{11} \\ V_{12} \end{pmatrix} = \begin{pmatrix} \frac{k_2 - k_1}{k_{12}} \\ 1 \end{pmatrix} \qquad \overrightarrow{V_2} = \begin{pmatrix} V_{21} \\ V_{22} \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad 69$$

$$C_1 = -C_2 = -\frac{m_0 k_{12}}{k_1 - k_2} \qquad 70$$

The variation of masses is derived according to these new expressions. The mass as a function of time in source compartment is equal to

$$m_1(t) = m_0 \exp(-k_1 t) \qquad 71$$

For the receiving plant compartment, the mass is equal to:

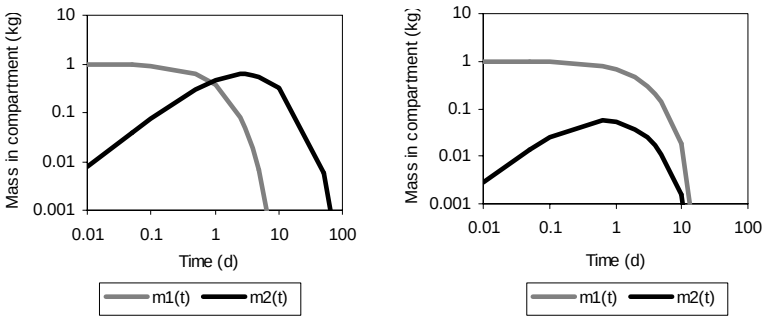
$$m_2(t) = \frac{m_0 k_{12}}{k_2 - k_1}(\exp(-k_1 t) - \exp(-k_2 t)) \qquad 72$$

for the case $k_1$=$k_2$, the solution is:

$$m_2(t) = m_0 k_{12} t \exp(-k_1 t) \qquad 73$$

#### *3.5.3.1 Functioning of the system*

Figure 14 illustrates typical evolutions of substance mass in each compartment. The system in cascade shows similar evolution of the mass in the compartments compared to the preceding system with bi-directional transfer.




A. $k_1>k_2$ B. $k_1<k_2$

Figure 14. Evolution of mass as a function of time for two compartments in cascade, source compartment $m_1(t)$ and the receiving plant $m_2(t)$. A. $k_1>k_2$ with $m_0=1$, $k_{12}=0.8$ 1/d, $k_1=1$ 1/d, $k_{21}=0$ 1/d, $k_2=0.1$ 1/d. B. $k_1<k_2$ with $m_0=1$, $k_{12}=0.3$ 1/d, $k_1=0.4$ 1/d, $k_{21}=0$ 1/d, $k_2=4$ 1/d (hypothetical substances).

The systems with bi-directional transfer and in cascade highlight differences in the functioning between the conditions where $k_1>k_2$ and where $k_1<k_2$. In the system in cascade the asymmetric system of transfers due to the absence of transfer back has particular consequences on the fact that $k_1$ and $k_2$ are relatively lower or higher. This difference discerns both system in their interpretation, and so that specific developments are useful for the system in cascade and are given hereafter. Based on previous developments for the bi-directional transfers, different points of interpretation about the functioning of the system in cascade are described in the next chapters:

- the simplification of some processes,
- the description of the point of maximum mass in the receiving plant compartment,
- the description of the ratio between the masses of both compartments,
- the ways to simplify the system to understand its functioning and to result in approximations to the resolution,
- and finally the synthesis of the main points developed for the system of cascade with two compartments.

#### *3.5.3.2 Simplification of processes*

The analysis of the simplified system indicates similar evolutions of the single processes, except the absence of the transfer back from the receiving plant compartment to the initial source of substance. The processes of the receiving plant compartment are reduced to a transfer of substance from the source compartment and to a single dissipation process, which is easily interpretable. Due to the simplification of the system, the expressions of the equations are more comprehensible, which helps the interpretation of the system evolution.

Specific developments are consequently of interest in order to identify perspectives of better understanding and additional simplification offered in the resolution of the cascade.

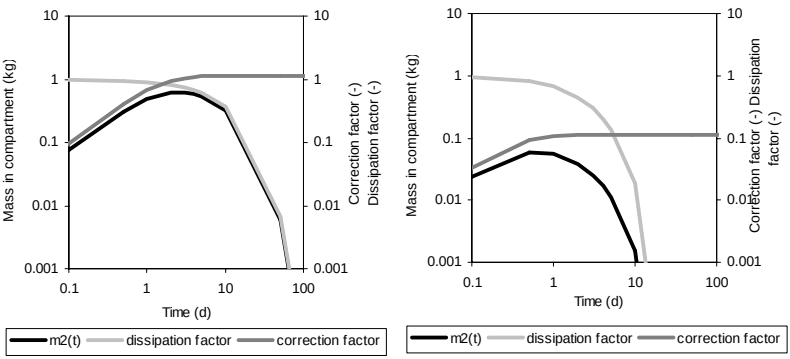
Reformulation of equation 72 in an interpretable expression provides the following solutions including three different components: a transferred fraction, a dissipation factor and a correction factor:

$$m_2(t) = \underbrace{m_0 \frac{k_{12}}{k_1}}_{transf.fract.} \underbrace{\exp(-k_2 t)}_{dissip.fact.} \underbrace{\left[\frac{k_1}{k_1 - k_2}(1 - \exp(-t(k_1 - k_2)))\right]}_{correct.fact.} \quad 74$$

which is also equal to

$$m_2(t) = \underbrace{m_0 \frac{k_{12}}{k_1}}_{transf.fract.} \underbrace{\exp(-k_1 t)}_{dissip.fact.} \underbrace{\left[\frac{k_1}{k_2 - k_1}(1 - \exp(-t(k_2 - k_1)))\right]}_{correct.fact.} \quad 75$$

Transfer fraction is given by the initial ($m_0$) mass multiplied by the ratio of transfer rate from source to the receiving plant compartment ($k_{12}$) to the total dissipation rate of source compartment ($k_1$). The dissipation factor is given by the time and in one solution by the transfer rate out of the receiving plant compartment ($k_2$) and in the other solution by the transfer rate out of the source compartment ($k_1$). The correction factor is also time dependent and includes the dissipation rates of both compartments. Figure 15 illustrates the variation of the two components varying as a function of time (dissipation factor and correction factor) and the general solution $m_2(t)$.




A) B)

Figure 15. Evolution of the mass in the receiving plant compartment as a function of time $m_2(t)$, and of the dissipation and correction factors, both determining $m_2(t)$ by multiplication with the transferred fraction. For two conditions A) $k_1 > k_2$ $m_2(t)$ according to equation 74 with $m_0$=1, $k_{12}$=0.8 1/d, $k_1$=1 1/d, $k_{21}$=0 1/d, $k_2$=0.1 1/d, and B) $k_1 < k_2$ $m_2(t)$ according to equation 75 with $m_0$=1, $k_{12}$=0.3 1/d, $k_1$=0.4 1/d, $k_{21}$=0 1/d, $k_2$=4 1/d (hypothetical substances).

These reformulations are helpful to interpret the processes evolution. Applying equations 74 for the case $k_1>k_2$ and equation 75 for the case $k_1<k_2$, the limit of the correction factor as time tends to infinite has an identified limit. This limit is equal to

$$\lim_{(t \to \infty)} cf(t) = \left| \frac{k_1}{k_1 - k_2} \right| \qquad 76$$

This identified limit may be used for the approximation of the system evolution after a long time. Evolution of mass in the receiving plant compartment is approximated in the long term according to the difference between $k_1$ and $k_2$:

$$\text{for } k_1>k_2 \quad m_2(t) \approx \underbrace{m_0 \frac{k_{12}}{k_1}}_{transf.fract.} \underbrace{\exp(-k_2 t)}_{dissip.fact.} \underbrace{\left[ \frac{k_1}{k_1 - k_2} \right]}_{correct.fact.} = m_0 \frac{k_{12}}{k_1 - k_2} \exp(-k_2 t) \qquad 77$$

and

$$\text{for } k_1<k_2 \quad m_2(t) \approx \underbrace{m_0 \frac{k_{12}}{k_1}}_{transf.fract.} \underbrace{\exp(-k_1 t)}_{dissip.fact.} \underbrace{\left[ \frac{k_1}{k_2 - k_1} \right]}_{correct.fact.} = m_0 \frac{k_{12}}{k_2 - k_1} \exp(-k_1 t) \qquad 78$$

These approximations give a good overview of the system evolution according the dissipation and correction factors, as the respective importance of the different transfer and dissipation rates. After a certain time, the correction factor is proximate to a constant value corresponding to its limit. The contribution of the dissipation factor and more precisely of the determining dissipation rate is then identified according to the difference between $k_1$ and $k_2$. In the case $k_1>k_2$ the dissipation of substance in the receiving compartment is controlled by the dissipation rate ($k_2$) of the receiving plant compartment. In the case $k_1<k_2$ the evolution of substance in the system is controlled by the dissipation rate of the source compartment ($k_1$). However the pertinence of these approximations depends on the required time for the correction factor to approach the identified limit. In all cases, this time corresponds at least to the moment with maximum accumulation in the plant compartment. This point is more precisely described in the next chapter.

#### *3.5.3.3 Maximum mass*

The point of maximum mass is a particular moment in the system evolution as described before. The time to reach the maximum $t_{max}$ is equal to

$$t_{max} = \frac{\ln(k_2 / k_1)}{k_2 - k_1} \qquad 79$$

with in the case $k_1=k_2$:

$$t_{\max} = \frac{1}{k_1} \qquad 80$$

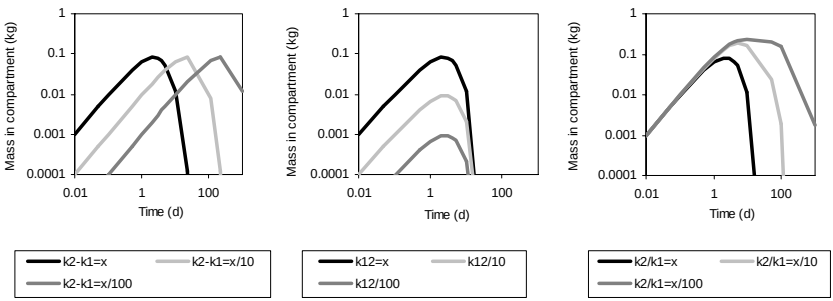
The time to reach the maximum mass depends on the natural logarithm of the ratio between $k_1$ and $k_2$ and on the difference between both dissipation rates. At this precise point $t_{max}$ the correction factor of equation 74 is equal to 1. Consequently, the point of maximum mass can be described as the transfer fraction times the dissipation factor $k_2$ with $t=t_{max}$.

$$m_{2\max} = m_0 \frac{k_{12}}{k_1} \exp(-k_2 t_{\max}) \qquad 81$$

It can also be observed that at $t_{max}$ the correction factor has a derivative equal to dissipation rate of the receiving plant compartment:

$$\frac{d}{dt} cf(t_{\max}) = k_2 \qquad 82$$

Sensitivity study for the evolution of mass in the receiving plant compartment as a function of the three factors $k_1$, $k_2$ and $k_{12}$ shows clear influences of these factors on the point and level with maximum mass. With constant ratio $k_2/k_1$ the evolution of $t_{max}$ increases as a function of the difference between dissipation rates ($k_2$-$k_1$), but the level of mass is not influenced. The transfer rate from source to the receiving plant ($k_{12}$) determines the level of maximum mass. Finally the ratio between dissipation rates ($k_2/k_1$) has an influence on both $t_{max}$ and on $m_{2max}$: decrease in the ratio speed up the time to reach the maximum point and reduces the level of maximum mass accumulated. This process is reached by an increase in the degradation rate in the source compartment or by an increase in the transfer rate to the receiving plant compartment. These different contributions of the factors $k_1$, $k_2$ and $k_{12}$ are illustrated by Figure 16.




A) B) C)

Figure 16. Mass in the receiving plant compartment as a function of time $m_2(t)$, with different variation factors. A) Variation of the difference between dissipation rates ($k_2$-$k_1$) by a factor 10 and 100. B) Variation of the transfer rate from the source to the receiving plant ($k_{12}$) by a factor 10 and 100.C) Variation of the ratio between dissipation rates ($k_2/k_1$) by a factor 10 and 100.

### *3.5.3.4 Ratio between masses*

Interesting relations of the ratio between the masses in both compartments has been pointed out in the system with bi-directional transfer. Looking at this ratio in a system in cascade leads to the following equation:

$$\frac{m_2(t)}{m_1(t)} = \frac{k_{12}(1-\exp[t(k_1-k_2)])}{k_2-k_1} \qquad 83$$

The evolution of this ratio differs as a function of time and of the difference between $k_1$ and $k_2$. Two moments of this evolution are of interest: at the time with maximum mass in the receiving compartment and in the infinite.

At $t_{max}$ the ratio of masses of the two compartments is equal to a simple relation between the transfer rate from source to the receiving plant ($k_{12}$) and the dissipation in the receiving plant compartment ($k_2$):

$$\frac{m_2(t_{max})}{m_1(t_{max})} = \frac{k_{12}}{k_2} \qquad 84$$

This relation may be used to also determine the maximum mass in the receiving plant compartment according to the source compartment.

$$m_2(t_{max}) = \frac{k_{12}}{k_2} m_1(t_{max}) = \frac{m_0 k_{12}}{k_2} \exp(-k_1 t_{max}) \qquad 85$$

According to this relation and to equation 81, the following equality is also determined at $t_{max}$.

$$k_1 \exp(-k_1 t_{max}) = k_2 \exp(-k_2 t_{max}) \qquad 86$$

In the system with bi-directional transfer the long-term evolution of the ratio tends to defined limits. In the system in cascade, differences appear according to the difference between the dissipation rates. The ratio between masses tends to a constant value with the increase of time when $k_1<k_2$, whereas there is no identified limit in the case $k_1>k_2$:

$$k_1<k_2 \quad \lim_{(t \to \infty)} \frac{m_2(t)}{m_1(t)} = \frac{k_{12}}{k_2-k_1} = \frac{1}{V_{11}} \qquad 87$$

$$k_1> k_2 \quad \lim_{(t \to \infty)} \frac{m_2(t)}{m_1(t)} = +\infty \qquad 88$$

The identified limit in the case $k_1<k_2$ has to be put in relation with the fact that the process of accumulation in the receiving plant compartment is controlled on the long term by the dissipation rate of the source compartment. This element was described in the Chapter 3.5.3.2 Simplification of processes. It can also be observed that the slope of the integrated ratio between masses is identified as equal to

$$\frac{dm_2}{dm_1} = \frac{k_{12}}{k_2 - k_1}\left[1 - \frac{k_2}{k_1}\exp^{t(k_1 - k_2)}\right] \quad 89$$

with a limit of the slope that corresponds to

$$k_1<k_2 \quad \lim_{(t \to \infty)} \frac{dm_2}{dm_1} = \frac{k_{12}}{k_2 - k_1} \quad 90$$

$$k_1>k_2 \quad \lim_{(t \to \infty)} \frac{dm_2}{dm_1} = +\infty \quad 91$$

It appears that the limit of the ratio $m_2(t)/m_1(t)$ and of the slope $dm_2/dm_1$ in the condition $k_2>k_1$ corresponds to the first component of first eigenvector of the matrix $V_{11}$ (according to the conditions established for the determination of the eigenvalues and eigenvectors in the system in cascade). In the same way as for the system with bi-directional transfer, the evolution of the ratio of masses and the limit for $k_1<k_2$ are illustrated by Figure 17.

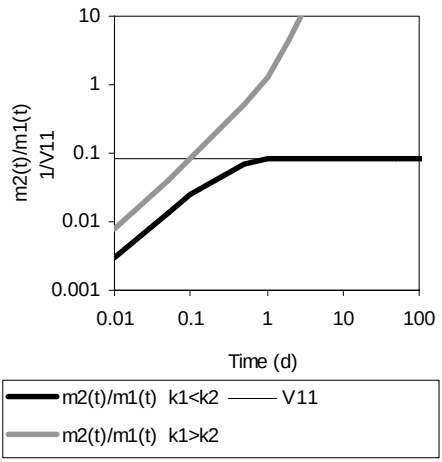



Figure 17. Evolution of the ratio $m_2(t)/m_1(t)$ as a function of time, limit of the ratio equal to $1/V_{11}$ as the time tends to infinite. With in case $k_1>k_2$: $m_0$=1, $k_{12}$=0.8 1/d, $k_1$=1 1/d, $k_{21}$=0 1/d, $k_2$=0.1 1/d., in case $k_1<k_2$ with $m_0$=1, $k_{12}$=0.3 1/d, $k_1$=0.4 1/d, $k_{21}$=0 1/d, $k_2$=4 1/d (hypothetical substances).

### *3.5.3.5 Approximation*

According to the system with bi-directional transfer and to the development brought in this chapter describing the system in cascade, different approximations in the resolution are possible. The simplification of the expression in long-term evolution has been demonstrated as possible in accordance with the simplification of the processes (Chapter 3.5.3.2) as follow:

$$\text{for } k_1>k_2 \quad m_2(t) \approx m_0 \frac{k_{12}}{k_1 - k_2} \exp(-k_2 t) \qquad 92$$

and

$$\text{for } k_1<k_2 \quad m_2(t) \approx m_0 \frac{k_{12}}{k_2 - k_1} \exp(-k_1 t) \qquad 93$$

These equations are potentially used for $t > t_{max}$.

The simplification of the process description by considering the maximum mass and its following dissipation constitutes a second possibility of approximation, already described in the system with bi-directional transfer. Adaptation of this method for the system in cascade is easier to interpret as the former one. It provides the following equation, considering the difference between the dissipation rates:

$$\text{for } k_1>k_2 \quad m_2(t) \approx m_{2\max} \exp(-k_2 (t - t_{\max})) \qquad 94$$

and

$$\text{for } k_1<k_2 \quad m_2(t) \approx m_{2\max} \exp(-k_1 (t - t_{\max})) \qquad 95$$

Finally by using the long-term relation between $m_1(t)$ and $m_2(t)$ in the case $k_1<k_2$ an approximation of $m_1(t)$ is available for $t>t_{max}$.

$$\text{for } k_1<k_2 \quad m_2(t) \approx m_1(t)/V_{11} = \frac{m_0 k_{12}}{k_2 - k_1} \exp(-k_1 t) \qquad 96$$

This approximation is obtained in accordance to equation 93.

### *3.5.3.6 Synthesis*

The equations describing the cascade system are listed in Table 4.

Table 4. Main equations describing a system with cascade of two compartments.

| | |
|---|---|
| Eigenvectors and eigenvalue | $\mu_1 = -k_1$<br>$\mu_2 = -k_2$<br>$\overrightarrow{V_1} = \begin{pmatrix} \frac{k_2 - k_1}{k_{12}} \\ 1 \end{pmatrix}$<br>$\overrightarrow{V_2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ |
| Constants | $C_1 = -C_2 = -\frac{m_0 k_{12}}{k_1 - k_2}$ |
| Mass in source compartment | $m_1(t) = m_0 \exp(-k_1 t)$ |
| Mass in the receiving plant compartment | $m_2(t) = \frac{m_0 k_{12}}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right]$ |
| Feedback factor | None |
| Time to reach the maximum mass in the receiving plant compartment | $t_{max} = \frac{\ln(k_2 / k_1)}{k_2 - k_1}$ |
| Maximum mass in the receiving plant compartment | $m_{2\,max} = m_0 \frac{k_{12}}{k_1} \exp(-k_2 t_{max})$ |
| Ratio between masses at $t_{max}$ | $\frac{m_2(t_{max})}{m_1(t_{max})} = \frac{k_{12}}{k_2}$ |
| Limit of ratio between masses | $k_1>k_2 \quad \lim_{(t \to \infty)} \frac{m_2(t)}{m_1(t)} = +\infty$<br>$k_1<k_2 \quad \lim_{(t \to \infty)} \frac{m_2(t)}{m_1(t)} = 1/V_{11}$ |
| Approximation | for $k_1>k_2$ $m_2(t) \approx m_0 \frac{k_{12}}{k_1 - k_2} \exp(-k_2 t)$<br>for $k_1<k_2$ $m_2(t) \approx m_0 \frac{k_{12}}{k_2 - k_1} \exp(-k_1 t)$<br>for $k_1>k_2$ $m_2(t) \approx m_{2\,max} \exp(-k_2 (t - t_{max}))$<br>or $k_1<k_2$ $m_2(t) \approx m_{2\,max} \exp(-k_1 (t - t_{max}))$ |

### 3.5.4 Two compartments in steady state

The functioning of a dynamic system shows very similar conditions to steady state conditions at some very precise points in the evolution of the mass in the compartments: point of maximum mass, and for the ratio between masses in long term evolution. Consequently the functioning of the steady state system represents some interest for the interpretation of dynamic resolution.

Steady state conditions are usually used in multi-media environmental modelling. Equilibrium of exchanges between compartments depends on a source of mass entering the system. The transfer rates and the elimination rate are the same between compartments as for the dynamic model ($k_{12}$, $k_{21}$, $\lambda_1$ and $\lambda_2$). The system is described by Figure 8.

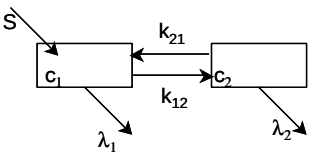



Figure 18. System with two compartments, source, transfer and elimination rates.

The mathematical resolution aims at describing the conditions of equilibrium in the system and the mass in each compartment. The variation of mass in compartment receiving the source as a function of time is:

$$dm_1(t)/dt = -\lambda_1 m_1(t) - k_{12} m_1(t) + k_{21} m_1(t) + S \qquad 97$$

The variation of mass in the receiving plant compartment is given by:

$$dm_2(t)/dt = k_{12} m_1(t) - \lambda_2 m_2(t) - k_{21} m_2(t) = k_{12} m_1(t) - k_2 m_2(t) = 0 \qquad 98$$

Under steady state conditions, for dM/dt=0, the conditions of equilibrium between both compartments gives the following equalities in the source compartment:

$$S + k_{21} m_2 = \lambda_1 m_1 + k_{12} m_1 \qquad 99$$

and in the receiving plant compartment

$$k_{12} m_1 = \lambda_2 m_2 + k_{21} m_2 \qquad 100$$

Mass in each compartment is then

$$m_1 = \frac{S\ k_2}{k_1 k_2 - k_{12} k_{21}} \qquad 101$$

$$m_2 = \frac{S\ k_{12}}{k_1 k_2 - k_{12} k_{21}} = \frac{m_1 k_{12}}{k_2} \qquad 102$$

According to Margni et al. (2003), the feedback factor gives the fraction of the emission that comes back to the medium of release after transfer to the other media. It is equal to

$$F_f = 1 - \frac{k_1 k_2}{k_1 k_2 - k_{12} k_{21}} \qquad 103$$

Integrating the feedback factor in the equation of mass in source compartment $m_1$ gives following resolution:

$$m_1 = \frac{S\ k_2}{k_1 k_2 - k_{12} k_{21}} = \frac{S}{k_1} \frac{k_1 k_2}{k_1 k_2 - k_{12} k_{21}} = \frac{S}{k_1}(1 + F_f) \qquad 104$$

At the point of maximum mass, the relation between the masses is the same for the dynamic solution and for the steady state solution. Consequently the maximum point of the dynamic approach is effectively a point of equilibrium or a point of rupture in the system evolution.

$$\frac{m_{1\max}}{m_{2\max}} = \frac{m_1}{m_2} = \frac{k_2}{k_{12}} \qquad 105$$

The study of other relations between the functioning of the steady state and the dynamic solution does not provide any tool likely to improve the interpretation of the systems or to get an approximation for dynamic conditions from a solution in steady state. In particular the studies focused on the relation between the initial mass in dynamic resolution and the source in steady state: is it possible to identify a source so that the resolution in steady state approaches the dynamic solution? No useful footbridge between both approaches could be put in evidence. The resolution of each system needs specific methodology.

### 3.5.5 Procedure for resolution

Different approaches for the resolution of the system have been developed. The possibility is given to get a precise solution of the total system. The interpretation of these results is then complex. The simplification of the system into subsystems according to the different source of the substance is a way in simplification in order to identify the key factors. In this simplified context, two approaches are possible according to the importance of the bi-directional transfer between the compartments. According to the feedback, the resolution needs an approach taking into account the bi-directional processes or is shorten into a system in cascade of compartments. Table 5 lists the procedure and characteristics of the developed approaches.

Table 5. Procedure of different resolutions

| Approach | Full system | Simplified system according to the source | |
|---|---|---|---|
| | | with bi-directional transfer | in cascade |
| Criteria for use | Exact solution | Interpretation of the system and the processes<br>Simplified resolution | |
| Resolution | Exact resolution of full system | Exact resolution of the subsystems<br>Approximation by simplified processes or equations; potentially simplification into a cascade system | Exact resolution of the subsystems<br>Approximation by simplified processes or equations |
| Methodological significant steps<br>Elements of results | Resolution in one step: matrix of transfer rates, initial mass, time | Calculation of keys for interpretation: maximum point (time and mass), feedback factor<br>Simplified steps for approximated results | Calculation of keys for interpretation: maximum point (time and mass), long term evolution according to conditions ($k1>k2$ and $k1<k2$)<br>Simplified steps for approximated results |

# 4. Processes descriptions

Main processes in environment – plant exchanges have to be identified and described to build of the system phytosanitary measures – plant – environment. Particularly, the original methodological developments concern the specific processes related to agricultural vegetation and to pesticides dissemination in plants. The following questions were addressed in the introduction regarding the involved processes: How can the fate of pesticide be described and what are the involved processes and in which system ? What is the importance of direct application of substance compared to release in soil and air for the occurrence of residues and how can fate processes be modelled ? New sources and models from literature are systematically identified to complement processes often already described in environmental multimedia models in order to build a reliable model for the system phytosanitary measures – plant – environment. This especially concern the transfer from formulation deposit into the plant.

The different processes needed in the building of the environment – plant system model are described hereafter in accordance to the three sources of substance, soil, air, and formulation deposit, to secondary processes between the different media and compartments, and to degradation processes.

1) *Transfers from soil*. The transfer from the soil to the plant includes two main processes, the advective transport with assimilation and the diffusion processes between the soil and the root tissues.
2) *Transfers from air*. The exchange between air and plant are mainly regulated by stomatal and cuticular pathways.
3) *Transfer from formulation deposit on plant*. The transfer from plant surface deposits to the plant is a specific process in relation to the use of pesticides.
4) *Transfer between plant compartments*. Distribution of substance within the plant depends on the mobility of the substance in the assimilation and transpiration stream; it is the expression of the systemic behaviour of the substance.
5) *Secondary transfers*. Different types of exchanges occur between air and soil; these processes are secondary compared to the processes with the plant, but may redistribute the substance after the spray. Sources of dissipation occur including the losses outside the agricultural system and the transports to the “far” environment.
6) *Degradation*. Degradation is a priori an important factor determining the residence time of the substance in the system. High variations differentiate the compartments.

All along these methodological developments, the wheat crop and the substances used in it are chosen as the case study for the description of the functioning of the system.

## 4.1 Transfers from soil

The identification of determinant transfers from soil to the plant needs first to describe the root system. In the system description (Chapter 3.2), distinction has been made between fine roots as absorbing organs and thick roots or tubers as storage organs growing in the soil. Fine roots constitute the interface between soil and plant for the transport of substance from the soil solution into the plant. Thick storage roots are considered as intermediate organs between

fine roots and aerial plant parts. Finally, tubers are stem-like organs in contact with the soil by the xylem, but mainly with aerial vegetation by the phloem. These distinctions about the root system are accounted for in the following descriptions of substance transfers from the soil.

The transport of substance from soil to the plant considers two processes: advective uptake with transpiration and diffusion. Advective uptake is due to the transpiration stream in the xylem from the soil solution, through the roots into the aerial plant parts. Transport by diffusion occurs from air- and water-filled pores into the fine roots. Both transport processes depends on the substance distribution and availability in the soil. The relative contribution of each process varies according to substances properties and to the quantity of water taken up by the transpiration. Chiou et al. (2001) evaluated the extent of approach to partition equilibrium for different published data in order to develop a partition coefficient for the plant uptake according to various plant components (water, carbohydrates and lipids). They could show that the distance to equilibrium depends on the transport rate of contaminants in soil water into the plant and on the volume of soil water required for the plant contaminant level to reach equilibrium with the external soil-water phase. Uptake of insoluble substance by plants could not be explained only by the volume of water transpiration so that other mechanisms were considered to be involved like diffusion into the plant. Highly water-soluble contaminants showed a higher quasi-equilibrium factor and were expected to approach equilibrium with soil water more efficiently. The role of reservoir by lipids in plant was identified for highly water-insoluble contaminants and the uptake of substances with high $K_{ow}$ was related to the lipid fraction. Detailed models were also proposed for neutral and dissociating organic compounds. Difficulty to approach equilibrium between root and surrounding solution was underlined for polar compounds, but also for lipophilic compounds (Trapp, 2000).

According to these different elements, advection and diffusion are complementary transport pathways from soil to plant. Processes and equations needed for the description of these transports are described in the next chapters.

### 4.1.1 Substance distribution in soil

Due to the processes involved (mainly in water), the availability of a substance in soil water solution must be identified. The equilibrium state of the substance in the soil is given by the partition coefficient between bulk soil and soil water, equal to the ratio of substance concentrations in water solution and in bulk soil. This coefficient describes the availability of the substance in the different soil phases. It considers the different fractions composing the bulk soil, the matrix, the solution and the gas fractions and the equilibrium between the different phases (Trapp, 1995). The partition coefficient between bulk soil and soil water $K_{sw}$ (-) is equal to

$$K_{sw} = C^{i}_{sb} / C^{i}_{sw} = s_{volw} + K_{aw}(s_{por} - s_{volw}) + K_{d}\rho_{sb} / \rho_{w} \qquad 106$$

with $s_{volw}$ (%) the volumetric water fraction, $K_{aw}$ (-) the equilibrium partition coefficient between air and water, $s_{por}$ (%) the porosity, the partition coefficient between soil matrix and soil water Kd (kg/kg), $\rho_{sb}$, (kg/m$^3$) the density of dry soil, and $\rho_w$, (kg/m$^3$) the density of water. The described difference between the porosity and the volumetric water fraction gives effectively the volumetric gas fraction. This partition coefficient is obtained from the organic

content of soil (OC, kg/kg) and the partition coefficient between the organic carbon and water $K_{oc}$.

$$K_d = OC \cdot K_{oc} \qquad 107$$

The substance available for transport depends on the fractions present in the gas, the organic carbon and the water compartments of the soil. The partition coefficient between bulk soil and water depends essentially on the organic carbon fraction, and to some extent on the volumetric water fraction, whereas the air contribution is negligible. Volumetric soil water is constant, whereas the partitioning between soil organic carbon and water is varying as a function of the partition coefficient between organic carbon and water $K_{oc}$ of the substance. Organic carbon content in the soil also influences the availability of a substance for transport processes into the plant. Increasing soil binding capacity diminishes the availability to plant translocation. Hsu et al. (1990) illustrated the effect of soil binding capacity on the concentration in the transpiration stream with an increase of organic matter in the soil.

### 4.1.2 Advective uptake

Plant transpiration activity controls the advective flux of substances from soil. The availability of substance in the soil for transport in the xylem constitutes the other factor determining substance uptake from the soil into the plant. Both elements are presented hereafter in order to identify the needed transfer rates. Original references from literature concern mainly transport from soil to the stem, from which transport from soil to the root are then derived.

The advective transport of a substance from the soil to the roots and to the aerial plant parts depends on the flux in the xylem. Water transport in the xylem stream depends on plant biomass and growth stage. Geisler (1988) established a transpiration coefficient for different crops according to the relation between the quantity of water transpired and the dry biomass produced (Table 6). This relation allows one to determine the advective stream in the xylem as a function of crop development during the growing period.

Table 6. Transpiration coefficient of field crops (Geisler, 1988).

| Crop | Transpiration coefficient (l $H_2O$/kg dry matter) |
|---|---|
| millet | 200-300 |
| mais, beet | 300-400 |
| barley, rye | 400-500 |
| potatoes, sunflower, wheat | 500-600 |
| rape, grain legumes, oat | 600-700 |
| Soybean | >700 |

The transpiration stream in the xylem determines the uptake of substance by the plant. During the growing period, the transpiration stream shows a variation as a function of plant development and biomass accumulation. As the system here considers mainly the active growing period of the crop, an approximation with a constant stream is preferred in a first step for the model development. The mean stream in the xylem for the period between treatment and harvest is considered.

The availability of a substance in soil water was already described by the partition coefficient between bulk soil and soil water (equation 106). Additionally the availability of the substance for uptake by plant and advective transport in the xylem is needed. This partition coefficient is given by the so-called Transpiration Stream Concentration Factor TSCF (-), that represents the ratio between the concentration in the xylem, measured in the stem, and the concentration in the soil water. The determination of this factor is based on experimental measures regarding the transpiration stream (Briggs et al., 1982, Hsu et al., 1990, Burken and Schnoor, 1999). Different plants and laboratory techniques were studied to determine the TSCF and similar relationships were obtained where TSCF is expressed as a function of $K_{ow}$. Relation by Briggs et al. (1982) for barley was

$$TSCF = \frac{C^i_{xy}}{C^i_{sw}} = 0.784 \cdot \exp[-(\log K_{ow} - 1.78)^2 / 2.44] \qquad 108$$

With $C^i_{xy}$ (kg/m$^3$) the concentration of substance i in the xylem, $C^i_{sw}$ (kg/m$^3$) the concentration of a substance i in soil water, TSCF (-) the Transpiration Stream Concentration Factor, $K_{ow}$ the partition coefficient between n-octanol and water (-).

Hsu et al. (1990) for soybean equation (equation 109), and Burken and Schnoor (1999) for hybrid poplar trees (equation 110) obtained the following relationships.

$$TSCF = 0.7 \cdot \exp[-(\log K_{ow} - 3.07)^2 / 2.78] \qquad 109$$

$$TSCF = 0.756 \cdot \exp[-(\log K_{ow} - 2.50)^2 / 2.58] \qquad 110$$

Differences in plant species, plant size and experimental conditions explain the differences between the equations. Maximum uptake is obtained for compounds that can cross hydrophobic membranes, but are not retained by lipid-like tissues (Bromilow et al., 1995). The comparison of the three relationships underlines the variability of $K_{ow}$ and the similarity of the equations (Figure 19). Hsu et al. (1990) considered the divergence with the equation by Briggs as small, according to the differences in experimental frame. The equation by Briggs has been chosen here for TSCF determination as it was obtained for barley a cereal like wheat. The relation by Briggs et al. (1982) was determined for pesticides that have a log $K_{ow}$ in the range of -0.5 and 4.5. Most systemic pesticides are included in this range. High uncertainty concerns the behaviour of substances out of this range. On the one side hydrophobic membranes constitute a barrier for hydrophilic substances. The more lipophilic compounds cross the endodermis much less efficiently than water, scarcely moving to the stem at all (Bromilow et al., 1995). Schwartz (2000) uses a constant TSCF for lower (log $K_{ow}$ < -0.5) and upper (log $K_{ow}$ > 4.5) coefficients. This assumption is admitted at this step of the model development. Consequently the variability of TSCF is limited to a range of log $K_{ow}$ between –0.5 and 4.5 with a resulting partition coefficient respectively by 0.02 and 0.09 with an optimum of transfer coefficient by 0.78. The choice to consider a constant TSCF for the range out of the limits of experimentation has a larger influence on substances with a low $K_{ow}$ than on substances with a high $K_{ow}$ (Figure 19). This also means that a minimum availability of partitioning to the transpiration stream is admitted. The consequence of this assumption will be more precisely assessed in the sensitivity study.

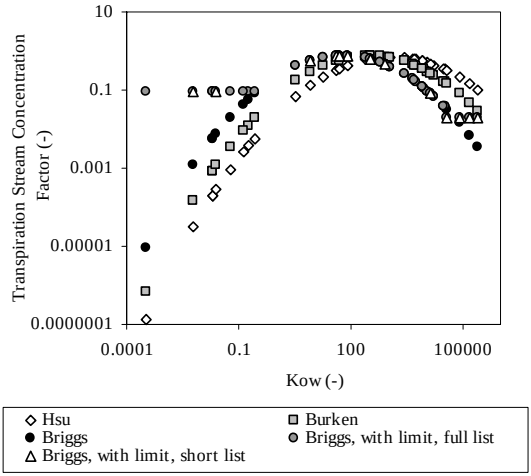



Figure 19. Transpiration Stream Concentration Factor according to different studies: Briggs et al. (1982), Hsu et al. (1990), Burken and Schnoor (1999) and chosen relation by Briggs with constant limit out of experimental value, for full list of substances used in wheat and for short list.

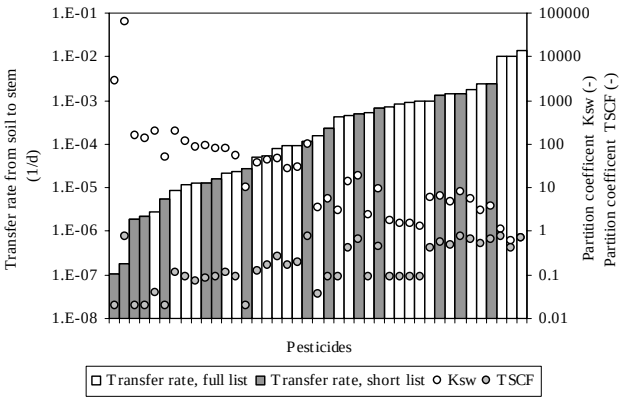
A substance in the soil volume $V_s$ ($m^3$) is taken as the source for substance uptake. The volume of soil compartment is considered as constant in the system. It depends on the depth considered for the soil processes. Soil tillage is generally practiced between some centimetres up to 30 cm generally considered as the arable depth, where the main part of the root compartment is growing. However the substance is first accumulated in the surface layer (1 cm), before its further distribution in the soil horizons. Models for pesticide fate in soil use different layers to separate the different processes of loss (runoff) (Leonard et a., 1995). In the present approach, the soil is considered as a single layer of 30 cm depth available for the different processes.

The rate of substance uptake from the soil by the plant is determined in accordance with the elements described above. The description of this transport that is the closest to the literature sources corresponds to the uptake from the soil through the xylem up to the aerial plant. It is an advective transport and so it is based on equation 13. The transfer rate of a substance from bulk soil to stem $k_{sst}$ (1/d) is equal to

$$k_{sst} = Q_{xy} TSCF \Big/ (K_{sw} V_s) \qquad 111$$

with $Q_{xy}$ ($m^3$/d) the transpiration stream, TSCF (-) the Transpiration Stream Concentration Factor, $K_{sw}$ (-) the partition coefficient between bulk soil and soil water, and $V_s$ ($m^3$) the volume of soil.

Figure 20 illustrates the transfer rate from soil to stem for the set of substances used in wheat. Substances are grouped between a transfer rate of $10^{-4}$ and $10^{-2}$ 1/d, for a xylem flux rate of $10^{-2}$ 1/d. The variability of the flux in the xylem is low during the growing period so that this parameter is considered as constant. Variability of the transfer rate by advective uptake increases with the affinity of the substance to the soil water ($1/K_{sw}$) and with the Transpiration Stream Concentration Factor (TSCF). The effect of these two parameters is multiplied which explains the high variability of the transfer rates from soil to the stem with an order of




magnitude of 4 between substances.

Figure 20. Transfer rate from soil to stem (1/d) and partition coefficients $K_{sw}$ and TSCF of the substances for the full list of substances used in wheat and for the short list.

$K_{sw}$ itself strongly depends on Koc whereas variations of TSCF on $K_{ow}$ are relatively limited. Therefore the soil to stem transfer rate mostly varies with $K_{oc}$.

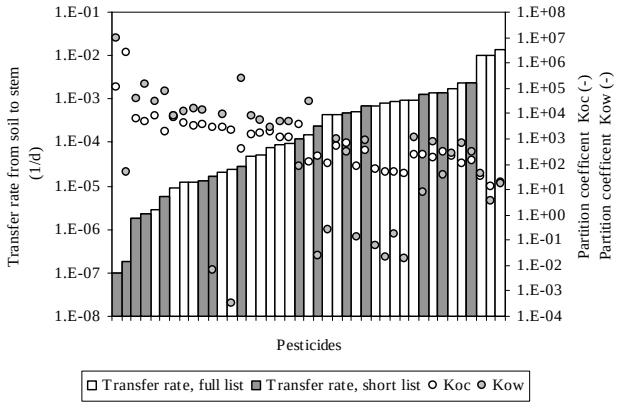



Figure 21. Transfer rate from soil to stem (1/d) and partition coefficients $K_{oc}$ and $K_{ow}$ of the substances for the full list of substances used in wheat and for the short list.

The advective transport from soil to plant has first been described assuming the relation between soil and xylem concentrations given by the Transpiration Stream Concentration Factor. This factor does not give any detailed indication for the transport of substance to the fine root, which are particularly influenced by the exchanges with soil. Methodological developments for the transport model from soil to fine roots were proposed by Trapp et al. (1995), based on already described factors. The concentration ratio between xylem sap and soil solution, the TSCF, corresponds to the fraction of substance that enters the xylem (passing the symplast of the endodermis). Consequently, the fraction of the chemical that enters the plant with the transpiration stream but is reflected back by the endodermis, is considered to remain in the roots. According to this assumption, the transfer rate from the soil to the roots $k_{sr}$ (1/d) is

$$k_{sr} = Q_{xy}(1 - TSCF) \Big/ (K_{sw} V_s) \qquad 112$$

with (1- TSCF) the reflected fraction.

The processes described above have been developed for the fine roots with nutrition (and anchoring) function. However some plants also have a thick root, like sugar beets, another field crop. Generally thick roots have a storage function, are not directly absorbing soil solution and play a role of interface between fine roots and aerial plant parts. A complementary model was developed for the transport of substance from the soil to thick vegetable roots, like carrots (Trapp, 2002). In this model, the total uptake of water with the transpiration stream was considered as the source of substance for the thick root core, assuming at the same time a loss of substance with the transpiration stream upward in the plant and an equilibrium between the concentration of substance in xylem sap and in the root core. According to these assumptions, the transfer rate from the soil water to the root core $k_{swrc}$ (1/d) corresponds to :

$$k_{swrc} = Q_{xy} \Big/ (K_{sw} V_s) \qquad 113$$

and the subsequent transfer rate from the root core to the stem $k_{rcst}$ (1/d)) is equal to :

$$k_{rcst} = Q_{xy} \Big/ (V_{rc} \cdot K_{rcw}) \qquad 114$$

This advective transport for thick roots appeared to be important for slowly diffusing lipophilic compounds and concerns thick vegetable roots like carrots after peeling (Trapp, 2002). For the transport process in the peel of thick roots, an equilibrium approach by diffusion gave better prediction (transfer by diffusion see next chapter).

Conclusively, the building of an adapted model to describe the advective uptake of substance from the soil depends on the architecture and functioning of plant, but also on the necessity to account effectively for the different plant organs in the model building.

### 4.1.3 Diffusive exchange

The diffusive processes concern the equilibrium state between bulk soil and the plant tissue at the root level. Campbell (1985) and Trapp (1995) developed the evaluation of passive uptake into root tissue, based on diffusive processes between air and water in the soil and the plant water. Both sources are used in the description of the transfer rate according to equation 15. Transfer rate from soil to root includes both the diffusion coefficient for water, for transport from water filled pores, and the diffusion coefficients for gas. The relation is implemented with the partition coefficient from air to water for the transfer from air filled pores. The diffusion coefficients are corrected according to the tortuosity given by the soil structure (Trapp, 1995). The surface of exchange between soil and root is based on a middle root diameter and on the root mass evaluated according to plant species (Könneke, 1967). The diffusion length is a middle value for the crossing pathway between soil and root. Root surface follows plant growth dynamic (equation 21) and a mean value is taken for the considered growing period.

According to this description, the following transfer rate from soil to root $k_{sr}$ (1/d) is obtained

$$k_{sr} = (D_{ws} t_{tw} + D_{as} K_{aw} t_{ta}) A_{sr} / (L_{sr} K_{sw} V_s) \qquad 115$$

with $D_{ws}$ ($m^2$/d) the diffusion coefficient for water, $D_{as}$ ($m^2$/d) the diffusion coefficients for gas, $t_{ta}$ (-) and $t_{tw}$ (-) the tortuosity of the soil structure, $K_{aw}$ (-) the partition coefficient air to water, $A_{sr}$ ($m^2$) the surface of exchange between soil and root, $L_{sr}$ (m) diffusion length, $K_{sw}$ (-) the partition coefficient between bulk soil and soil water, and $V_s$ ($m^3$) the volume of soil.

Processes in water dominate transfer rates from soil to the root, although transport by diffusion is faster in air (Figure 22). This is due to the low affinity of the considered substances to the air fraction compared to the water fraction in the soil (low $K_{aw}$). The only exception is given by pendimethalin with the highest transfer rate from air filled pores due to a high $K_{aw}$.

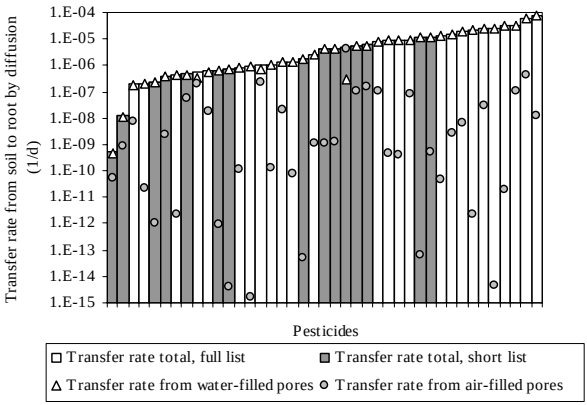



Figure 22. Transfer rates (1/d) from air- and water-filled pores and total transfer rate from soil to root by diffusion, for the full list of substances used in wheat and the short list.

As transport is based on a diffusion process between concentrations in soil solution and root water, reverse transport is based on the same assumptions.

$$k_{rs} = (D_{ws}\, t_{tw} + D_{as}\, K_{aw}\, t_{ta}) A_{sr} / (L_{sr}\, K_{rw}\, V_r) \qquad 116$$

A partition coefficient for equilibrium between root tissue and water $K_{rw}$ (-) is needed for the description of this transfer process. Specific partition coefficients have been developed for transport processes including plant compartments and tissues. Briggs (1982) showed that the equilibrium between concentrations in root and in external solution is based on the partitioning of substances to lipophilic root solids. A partition coefficient was first identified for root (Briggs et al., 1982; Briggs et al., 1983; Trapp and Pussemier, 1991) and developed more generally for all plant tissue (Trapp, 1995). Partitioning with plant tissue is characterized by the lipophilic behaviour of the substance and by the composition of the plant tissue.

$$K_{pw} = (P_w + P_l \cdot K_{ow}^{\,b})\, \rho_p \,/\, \rho_w \qquad 117$$

The partition coefficient between plant tissue and water $K_{pw}$ (-) depends on plant water content $P_w$ (kg/kg) and lipid $P_l$ (kg/kg) content, on $K_{ow}$ with a correction exponent b (-) accounting for the difference between plant lipid (crop specific) and n-octanol, and on the ratio between density of plant tissue $\rho_p$ (kg/l) and of water $\rho_w$ (kg/l). The following variability was considered from log $K_{ow}$ -2.2 to 5.4 (substances used in wheat), water tissue content from 75% (stem) to 95% (root), b-correction exponent of 0.75 for bean roots and stems, of 0.77 for barley roots, of 0.95 for barley shoots and of 0.97 for citrus cuticles (Trapp, 1995), density of tissue between 0.75 and 0.95 kg/l. Consequently partition coefficients vary mainly as a function of the substance specific $K_{ow}$. Plant composition and type of organ play an important role for substances with high lipophilic behaviour (Figure 23).

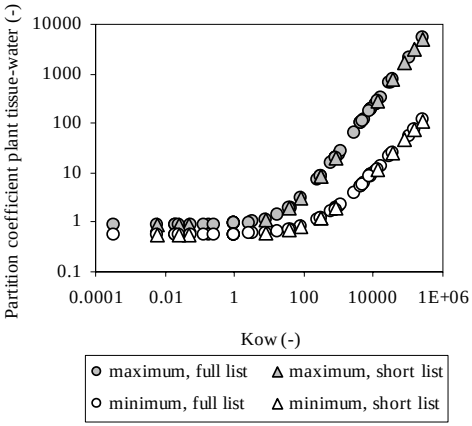



Figure 23. Partition coefficient between plant tissue and water as a function of $K_{ow}$. Minimum and maximum values as a function of variations of plant tissue composition (equation 117), for the full list of substances used in wheat and the short list.

### 4.1.4 Total soil

The comparison of the two processes responsible for the transport from soil to plant shows that substances show a similar ability to transport whatever the transport process, advective uptake or diffusion. In fact, both processes depend mainly on the availability of the substance in soil water and on the partition coefficient bulk soil to water ($K_{sw}$). However, the advective uptake from the soil is systematically faster than the diffusive transport (Figure 24). The variation of the transfer rates between substances reaches 3 to 4 orders of magnitude.

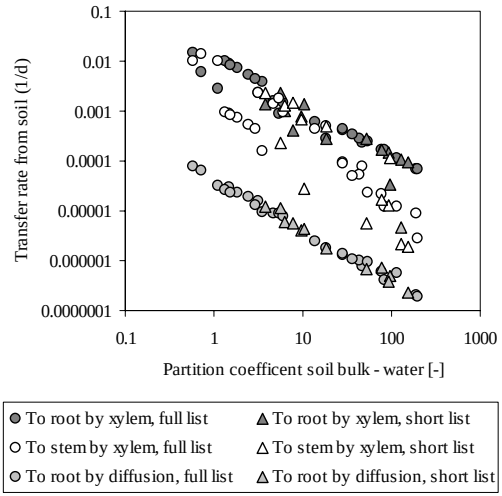



Figure 24. Transfer rates from soil to plant as a function of the partition coefficient bulk soil to water: advective transport in the xylem to root and to stem and diffusive transport (root), full list of substances used in wheat and short list.

The main process for accumulation in plant is therefore given by the advective transport in the xylem from the soil to the stem.

## 4.2 Transfers from air

Relations between air and plant have been extensively described by methods for assessment of atmospheric pollutants. To understand and identify main processes in the air and leaf exchanges, the different pathways at the leaf surface and leaf interior are described hereafter. Two pathways from air to plant leaf are generally identified: through cuticle and trough stomata, after a first barrier created by the air boundary layer at the leaf surface. However, cuticle and stomata represent determinant barriers between environment and plant, more limiting than further barriers in the leaf interior. The conductance of cuticle and stomata is positioned in series with the air boundary layer, so that the total conductance from air to leaf is equal to

$$G_l = \frac{1}{\frac{1}{G_b} + \frac{1}{G_c + G_s}} \qquad 118$$

where $G_l$, $G_b$, $G_c$ and $G_s$ (m/d) are respectively the leaf, the boundary, the cuticle and the stomata conductances. We will now examine how to calculate each conductance and then derive the total air to plant transfer rate.

### 4.2.1 Boundary layer

The first barrier for the air to plant exchanges is given by the air boundary layer at the leaf surface. This diffusion process was described by Riederer (1995) and is given here as conductance:

$$G_b = D_b^{air} \Big/ L_b \qquad 119$$

where $G_b$ (m/d) is the conductance of the boundary layer between leaf surface and the atmosphere, $D_b$ ($m^2$/d) the diffusion coefficient of the substance in the air and $L_b$ (m) the thickness of the layer. The diffusion coefficient is calculated according to equation 16. This first barrier is positioned in series with each process of the transport from the air into the plant through cuticle and stomata. Its variability depends on molecular weight and according to the substances, though pesticides generally show a low variability.

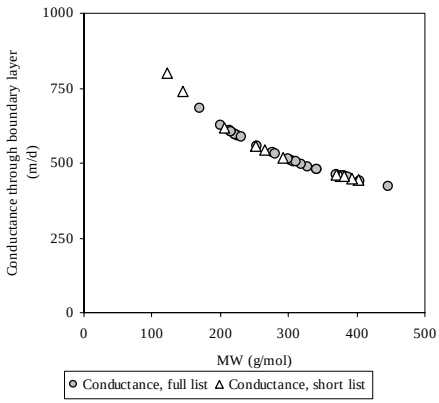



Figure 25. Conductance through boundary layer as a function of the molecular weight of the substance; full list of substances used in wheat and short list.

### 4.2.2 Cuticle

Transport across the plant cuticle has been described according to the permeability of the plant cuticle to a solute or to a vapour-based gradient (Kerler and Schönherr, 1988b; Riederer, 1995; Trapp, 1995; Riederer and Schreiber, 2001). The permeance depends on the mobility of the substance and the solubility according to the cuticle. The cuticular membrane separates an outer vapour phase and the aqueous leaf interior. Kerler and Schönherr (1988b) established a relationship for permeation of lipophilic chemicals across the plant cuticle separating two aqueous phases, as

$$\log P_c = -11.2 + 0.704 \log K_{ow} \qquad 120$$

Where $P_c$ (m/s) is the cuticular permeance determined as a function of the n-octanol-water partition coefficient $K_{ow}$ of the substance. This relation established for a given plant species (*Citrus* cuticle) is mostly used in models for transport from the air to the plant (Riederer, 1995).

Permeance data of other cuticle types may also be used, as the variation can be wide. For example the central 50% of collected data of permeance for water from different plants showed a variation factor of 8, from $2.2 \times 10^{-6}$ to $1.8 \times 10^{-5}$ m $s^{-1}$ (Riederer and Schreiber, 2001).

Different pathways have been identified across the cuticle: through cuticular wax by lipophilic solutes or through pores filled with water by water-soluble organic compounds and by inorganic ions (Riederer and Schreiber, 2001). The size of the molecule and its charge determine the respective importance of each pathway, the overall permeability appearing to be dominated by the transfer through the lipophilic pathway.

Since transport occurs from the air, permeation, determined for aqueous phases, is transformed to air conductance for the cuticle according to

$$G_c = P_c 86400 \big/ K_{aw} \qquad 121$$

where Gc (m/d) is the conductance through cuticle, Pc (m/s) the permeance of cuticle (with correction from second to day, 86400 s/d) and $K_{aw}$ the partition coefficient air to water. According to equations 120 and 121, the conductance through cuticle mostly depends on the ratio $K_{ow}/K_{aw}=K_{oa}$, that is the n-octanol-air partition coefficient. Figure 26 confirms this relationship, the highest conductance being given generally to lipophilic substances.

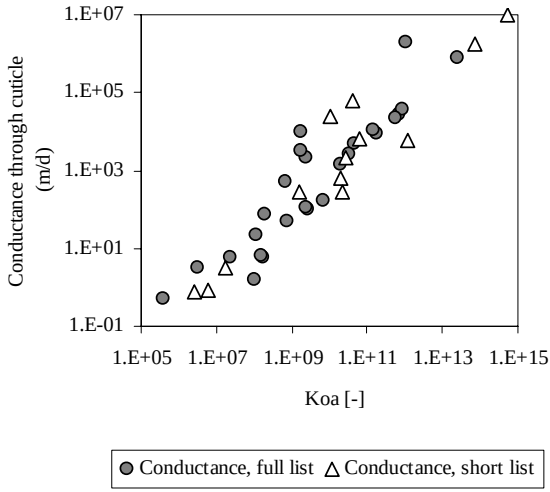



Figure 26. Conductance through cuticle (m/d) as a function of the partition coefficient $K_{oa}$ of the substances; full list of substances used in wheat and short list.

More recent developments for the cuticular transport have been proposed for pesticides deposited on leaf surface (Schönherr and Baur, 1994, 1996) and could be used to identify the transfer rate from the air. These new developments are presented below for transfers from deposit layer into the leaf.

### 4.2.3 Stomata

Air exchange with the leaf occurs through stomata pores, opened during photosynthetic active periods of plant development. Stomata transfer depends on the diffusion coefficient of the substance in the air and on stomatal pore characteristics (Nobel, 1991; Riederer, 1995). Stomatal conductance was identified as

$$G_s = D_a \cdot na_s \cdot \alpha_s \Big/ (x_s + y_s) \qquad 122$$

where $G_s$ is the stomatal conductance (m/d), $D_a$ ($m^2$/d) the diffusion coefficient of the substance in the air, $na_s$ (m2/m2) the portion of leaf surface area in form of pores, $a_s$ (-) the portion of opened stomata, $x_s$ (m) and $y_s$ (m) the stomata depth and the pore radius. Transport through stomata depends on the same diffusion coefficient as transport through a boundary layer (Figure 27). The conductance through stomata is lower than the boundary layer conductance due to the lower surface of exchange (stomata cover only a portion of leaf surface) although the diffusion length is thinner ($1x10^{-5}$ m for stomata, $1x10^{-3}$ m for boundary layer).

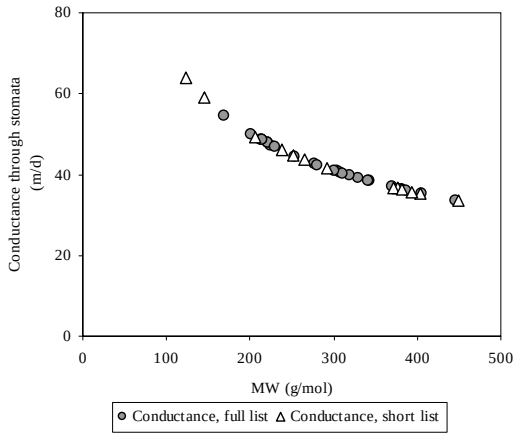



Figure 27. Conductance through stomata as a function of the molecular weight of the substance; full list of substances used in wheat and short list.

### 4.2.4 Mesophyll

The resistance from air in the atmosphere through the cuticle and the stomata are higher than the resistances of further tissues in the plant (Schönherr and Riederer, 1989). Consequently these barriers are identified as the limiting factors for transport into the leaf. But if needed, some developments have been proposed to take into account an inner mesophyll resistance (U.S. EPA, 1999). These processes are not considered here according to the targeted level of detail and to the frame of this model. The complexity of the leaf composition and organisation would need detailed descriptions to effectively measure the nature and the location of substance accumulation in the leaf tissue.

### 4.2.5 Total air

The conductance boundary layer $G_b$, cuticle $G_c$ and stomata $G_s$ (m/d) determine the conductance of leaf $G_l$ which is used here to describe the transfer rate through the leaf according to equation 18:

$$k_{al} = G_l A_l / V_a \qquad 123$$

where $k_{al}$ (1/d) is the transfer rate from air to leaf, $G_l$ (m/d) the leaf conductance, $A_l$ ($m^2$) the surface of exchange between leaf and air, and $V_a$ ($m^3$) the volume of air.

The process is reversible, so that the transfer rate from leaf to air through the cuticle can be described as:

$$k_{la} = G_l A_l K_{aw} / V_l K_{lw} \qquad 124$$

where $k_{la}$ (1/d) is the transfer rate from leaf to air, $G_l$ (m/d) the conductance of leaf, $A_l$ ($m^2$) the surface of exchange, $K_{aw}$ (-) and $K_{lw}$ (-) the partition coefficient between air and water, respectively leaf and water, and $V_l$ ($m^3$) the leaf volume. $K_{lw}$ is derived as a function of plant tissue to water partition coefficient (equation 117). The surface of exchange is equal to the Leaf Area Index LAI ($m^2$ leaf/$m^2$ soil)

Several methods are reported to calculate the partition coefficient between plant tissue and air. If current estimation methods agree well with each other, it is difficult to make a single founded choice, because of the insufficient understanding of the equilibrium processes between plant and environment (McLachlan, 2000). Consequently elementary partition coefficients $K_{ow}$ and $K_{aw}$ are used to approximate more complex relationships like the non-linear approach in equation 117.

The comparison of the different pathways shows the limiting processes from the air to the leaf (Figure 28). Lowest transfer rates to leaf are controlled by stomatal conductance and concern substances with a low transfer rate through cuticle. A low $K_{oa}$ characterises theses substances, but also a low molecular weight. Highest transfer rates into the leaf are controlled by the boundary layer. Substances with a low molecular weight show a higher diffusion coefficient and so a better conductance through this layer. Substances controlled by the transfer rate through cuticle, which is lower than the transfer through the boundary layer but higher than the stomatal pathway, give an intermediate situation. This intermediate situation concerns only a few substances, as the transfer rate through cuticle and boundary layer are very close with a low variability. Globally the transfer rate from air to leaf varies between 0.05 and 1.12 1/d. The total transfer rate from the air to the plant can generally be characterised as a function of the molecular weight and of the $K_{oa}$ that determine the stomatal conductance. Lowest transfers rates are given by low $K_{oa}$ and high molecular weight (Figure 29).

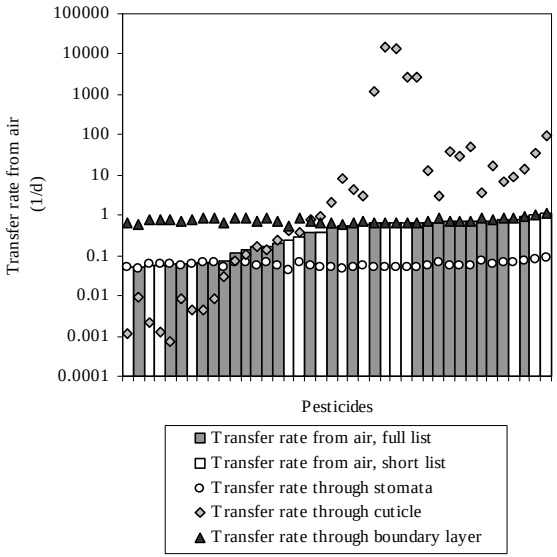



Figure 28. Transfer rate through cuticle, stomata and boundary layer and total transfer rate from the air to the plant; full list of substances used in wheat and short list.

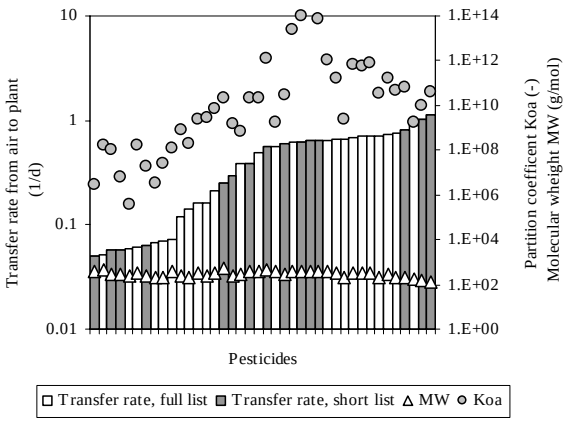



Figure 29. Transfer rate from the air to the plant, molecular weight and n-octanol-air partition coefficient of the substances; full list of substances used in wheat and short list.

## 4.3 Transfer from formulation deposit on plant surface

An important portion of pesticide applied in agriculture directly reaches the plant surface. The description of the transfer processes from deposit on plant surface is a major challenge for the model development. Newest research results and models are evaluated here for their implementation in the model. These developments constitute a specific contribution for the modelling of pesticides residues, which makes the model distinct to environmental multimedia models.

Different steps of foliar uptake can be considered. Different successive phases are identified. During an initial phase the penetration of substance in the plant is low, the solute partially evaporates. During the second period, this evaporation leads to an increase of substance concentration in the deposit on plant surface and to a larger uptake of substance. The third phase shows finally a decrease of uptake (Knoche et al., 2000). More precisely, different processes are considered in the transport: the formulation deposit and the leaf surface sorption, diffusion into the surface cuticular waxes, diffusion into the cuticular membrane, diffusion into the inner plant across the cell walls and accumulation in the symplast (Kirkwood, 1999)

In this study the formulation deposit corresponds to the fraction of pesticide remaining on the plant when almost all water has evaporated just after spraying (second and third phases). The relative importance of each phase greatly depends on the composition of the solute and residue. The fraction of active ingredients taken up just after spraying, while evaporation of water and solvent takes place, is generally limited, so that the main uptake occurs from the plant surface deposit. The presence of additives in the crop protection products modifies the mobility of active ingredients in the cuticle and the partitioning of the solute, before and after droplets evaporation. Rate of uptake may change with the evaporation of the solute.

The transport through the cuticle has been previously described for the exchanges between air and plant by a permeation process (equations 120 and 121). This methodology could be a priori used to assess the penetration of formulation deposit into the plant. The process was describing the cuticle permeability, but did not account for the specificities of the cuticle and for the presence of solute with specific properties. Since the limiting skin of the cuticle is considered as a determinant factor, new developments were carried out to characterize the transport processes according to the cuticular membrane properties. A new method to determine the mobility of solutes was proposed based on the properties of the limiting skin and on the solute size (Schönherr and Baur, 1994; Schönherr and Baur, 1996, Buchholz et al., 1998, Schönherr et al., 1999). According to these new elements, a specific cuticular penetration is derived for the penetration of substance deposited on plant as formulation deposit:

$$G_{fd} = k^{*} \cdot L_{ls} \cdot K_{wxfd} \qquad 125$$

where $G_{fd}$ (m/d) the permeation through cuticle is determined by $k^{*}$ (1/d) the solute mobility in the limiting skin, $L_{ls}$ (m) the path length of the limiting skin and $K_{wxfd}$ (-), the partition coefficient between cuticular wax and formulation deposit. These factors are presented hereafter in order to identify the transfer rate from formulation deposit to the inner plant.

### 4.3.1 Mobility rate

New developments (Schönherr and Baur, 1994; Schönherr and Baur, 1996, Buchholz et al., 1998, Schönherr et al., 1999) have shown that the cuticular skin, composed of cutin and wax, is the limiting factor for the transport through the cuticle, and that the sorption compartment of the cuticular membrane shows a lower resistance. The mobility of the pesticide in the cuticular membrane of a given plant species depends on the selectivity of the limiting skin and on the molar volume of the substance penetrating. This mobility rate is equal to

$$k^* = k^{*0} \cdot e^{-2.3\beta' \cdot V_x} \qquad 126$$

where $k^*$ (1/d) the mobility rate in the limiting skin of a substance depends on $k^{*0}$ (1/d) the mobility rate of a hypothetical compound having zero molar volume, $\beta'$ (mol/mL) the size selectivity of the cuticular membrane, $V_x$ the molar volume of the substance (mol/mL). This relation accounts simultaneously for plant and substance factors.

Different plants have been tested, showing that the size selectivity of the membrane does not differ much between species (Bucholz et al., 1998; Baur et al., 1999). Among different species and plant organs the size relativities ranged from 0.007 to 0.012 mol/mL. Size selectivity decreases with increasing temperature. An average value of this parameter of $\beta'$ = 0.0095 mol/mL is proposed for a temperature range between 15 and 35 °C. The solute mobility for a substance with zero molar volume $k^{*0}$ represents the other plant specific factor responsible for differences in permeability ranging from log $k^{*0}$ -2.33 to -5.27 1/s (Bucholz et al., 1998). The value of log $k^{*0}$ –4.0 1/s is chosen for the model development.

The molar volume is the only substance characteristic that influences the mobility in the cuticular skin. This parameter is available only from specific studies in literature. The characteristic atomic volumes are used to calculate missing values according to the methodology described by Abraham et al. (1987).

According to the variation of the molar volume of the studied substances, the mobility rate varies by a factor $10^4$. The solute mobility adds a factor $10^3$ to the variations of the mobility rate (Figure 30).

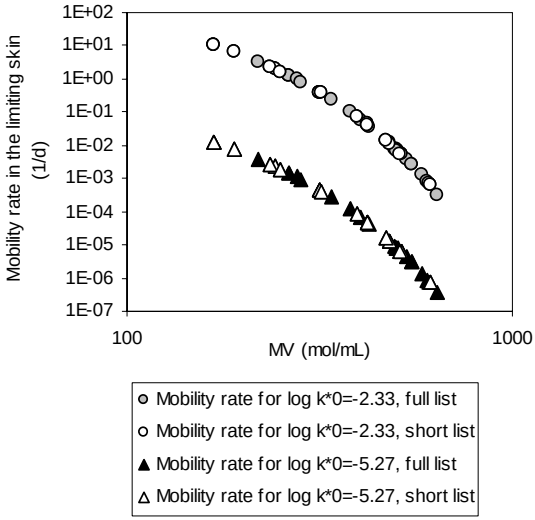



Figure 30. Mobility rate in the limiting skin as a function of the molar volume of substances for 2 different levels of solute mobility; full list of substances used in wheat and short list.

### 4.3.2 Diffusion path length

The permeation through the cuticle depends on the mobility of the substance and on the diffusion path length of the cuticle. The diffusion path could not be described according to the thickness of cuticular membrane or to the amount of wax covering the cuticular limiting skin (Schönherr et al., 1999). It is determined by tortuosity of the cuticle, that is the ratio between the path length in the cuticular membrane and in the polymer matrix membrane (Baur et al., 1999; Riederer and Schreiber, 2001). The polymer matrix membrane corresponds to extracted cuticles consisting of cutin and polysaccharides, after extraction of waxes. Indeed, highly ordered wax regions explain partly low mobility in the cuticular membrane. The tortuosity depends on the openings for diffusion left by the disposition of the lamellae composing the cuticle proper. It expresses a difference of mobility (tortuous diffusion), without affecting the selectivity. Variations of tortuosity between 28 and 759 (-) were estimated. The path length can be characterised as a function of the number of lamellae composing the cuticle (2 to 20), to the tortuosity of each lamella (10 to 100) and the thickness of the lamella, considering the thickness of the cuticle is constant (1 µm) (Baur et al., 1999).

### 4.3.3 Partition coefficient formulation deposit to cuticle

The limiting skin has been identified as the limiting barrier describing the mobility of the substance through the cuticle and the path length described according to the tortuosity of the membrane. The last factor needed to determine the transport process of formulation deposit to the plant is given by the partition coefficient needed to account for the different phases considered in the transport: the leaf surface sorption, diffusion into waxes, diffusion into the

cuticular membrane, diffusion across the cell walls. The penetration of substance is at its maximum when the formulation deposit is a saturated solution and as long as the formulation volume remains sufficient. Consequently the uptake of substance causes a decrease in concentration at the cuticular surface and a decrease in the penetration rate with time. This can be prevented if the volume of deposit decreases at the same time as the penetration of substance, namely by adjuvants in the formulation composition (Schönherr et al., 1994). Although almost all water has evaporated just after spraying, the formulation deposit remains liquid due to the formulants and to some water retained in it. It is drawn between the cuticular surface wax crystallites by capillary action (Schönherr et al., 1999).

Most models consider the partition coefficient of the substance between the cuticular wax and the formulation deposit ($K_{wxfd}$) as the determining driving force for penetration into leaves. The partition coefficient between the polymer matrix of (extracted) cuticle and water ($K_{cw}$) is easily accessible as it is very proximate to the $K_{ow}$ of the substance and used in models (Schönherr and Baur, 1994; Baur et al., 1997; Knoche et al., 2000). The driving force through the cuticle is given more precisely by the partition coefficient between the formulation deposit and the cuticular wax. Effectively the limiting barrier is given by the cuticular skin, composed notably of wax. Besides, observations show a smaller sorptive capacity of the cuticular wax; the wax water partition coefficient is smaller by a factor 10 than the $K_{ow}$ (Schönherr et al., 1999). However, different solutions are interacting in the equilibrium distribution between the formulation deposit and the leaf. The inner surface of the cuticle and the water of the epidermal cells are easily approximated using $K_{ow}$. However the equilibrium between formulation deposit and the wax is more difficult to determine due to the varying physical state of the formulation deposit and leaf surface. A value of the partition coefficient between wax and n-octanol ($K_{wxo}$) equal to 0.1 is assumed as a reasonable value (Schönherr and Baur., 1994). A better description of the specific influence of the formulation deposit is necessary before determining the appropriate partition coefficient $K_{wxfr}$.

Different publications provide detailed descriptions about the effects of adjuvants on foliar uptake, notably accounting for the effects on partition coefficients between cuticle and surface deposit, as on the mobility in cuticle (Schönherr and Baur, 1996; Baur et al., 1997; Baur et al., 1999; Knoche and Bukovac, 1999; Baur, 1997). Presence of adjuvants modified the partition coefficient $K_{cw}$ up to 6 orders of magnitude according to the specificities of the adjuvants (Baur et al., 1997). The significance of the molecular size for mobility is notably decreased by the presence of adjuvants, so that large compounds show an increased mobility (Baur et al., 1999). The mobility rate is also modified according to the volume and concentration of surfactant (evolving to saturation with time), to the droplet (or deposit) at leaf interface area, to the capacity of adjuvant to penetrate into the wax and cuticle, and to the interaction with the cutin and the wax (fluidity). The effects of adjuvants also concern the evaporation of sprayed droplets on plant surface and the time for substance penetration (Baur, 1997). Interactions of adjuvants with especially temperature and to some extent with humidity are also documented. However, according to the variability and the complexity of the effects of adjuvants, no general easy relation between lipophilic behaviour of solutes ($K_{ow}$) and rate of uptake should be expected.

In summary the adjuvants contribute to increase the efficacy of penetration, and to limit the risk of substance losses due to external (climatic) factors, by simplifying and insuring biological activity. In this study, the composition of the solute formulation needs first to have a constant effect on the uptake rate between active ingredients studied. Consequently a scenario with no adjuvant is accounted for, in order to focus on the strict comparison between active ingredients. The consequences of this choice may be a lower fraction of substance

considered as taken up by the plant for some substance, but also a higher variability between active substances. This risk of underestimation is partly limited by the fact that no climatic factors, notably counterbalanced by adjuvants, interact in the processes.

In conclusion, best approximation of the partition coefficient of the substance between the cuticular wax and the formulation deposit ($K_{wxfd}$) is based on the partition coefficient between cuticle and formulation deposit ($K_{cfd}$) simplified to the partition coefficient between cuticle and water ($K_{cw}$) and equal to $K_{ow}$. However limits have been presented here, notably for the physical state of the formulation deposit, and its potential varying lipophilic character due to the presence of adjuvants.

### 4.3.4 Total formulation deposit

According to the permeance and identified and described here, the transfer rate is determined as:

$$k_{fdl} = G_{fd} A_c / V_{fd} \qquad 127$$

where $k_{fdl}$ (1/d) is the transfer rate from formulation deposit to leaf through cuticle, $G_{fd}$ (m/d) the permeance of cuticle for surface deposit, $A_c$ ($m^2$) the surface of exchange between residue and leaf, and $V_{fd}$ ($m^3$) the volume of surface deposit. However, the transfer rate may be directly determined from the mobility rate determining the permeance, so that difficult identified parameters, like diffusion path length are not necessary. The transfer rate is than equal to:

$$k_{fdl} = k^* \cdot K_{cfd} \qquad 128$$

Figure 31 illustrates the transfer rate of substances as a function of the parameters specific to the substance, the molar volume and the partition coefficient between cuticle and deposit of crop protection product. Highest transfer rates are obtained for substances with a low molar volume, a high mobility rate, and a high affinity to the cuticle. The partition coefficient plays the most important role with a variation of 8 orders of magnitude between extreme values.

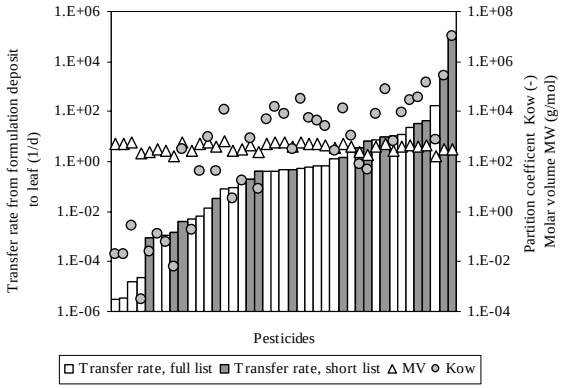



Figure 31. Transfer rate from formulation deposit to leaf (1/d), molar volume (mol/mL) and partition coefficient between cuticle and deposit of crop protection product $K_{cfd}$ (-) given as Kow (-); full list of substances used in wheat and short list.

According to the rapidity of the transfer and the probable uptake into leaf cells or translocation into the plant, the reverse transfer due to equilibrium between the compartments can be neglected. Part of a reverse transport is assumed by the cuticular transport from the leaf to the air according to equation 124. However the transfer from leaf to surface deposit as an equilibrium process between surface deposit and leaf could be described as following:

$$k_{lfd} = G_{fd} A_c / (V_l K_{lc}) \qquad 129$$

where $k_{lfd}$ (1/d) is the transfer rate from leaf to surface deposit through cuticle, $G_{fd}$ (m/d) the permeance of cuticle for surface deposit, $A_c$ ($m^2$) the surface of exchange between residue and leaf, $K_{wc}$ the partition coefficient between leaf in cuticle (given as $1/K_{ow}$) and $V_l$ ($m^3$) the volume of leaf.

## 4.4 Transfer between plant compartments

Transport between plant compartments have been determined by the flux in plant (xylem, phloem) and by the partition coefficient between sources and the receiving plant compartments. This approach considers two fluxes in the plant, schematically an acropetal flux in the xylem and basipetal flux in phloem. The importance of each flux is interdependent and varies according to instant plant activity and development, to the single plant organ considered and to the type of substance transported, to the source and the receiving plant. Two distinct main streams can be identified: flux from soil to aerial part in the xylem and flux from air and spray exposed leaves to storage organs (fruit, stem, thick roots) with the phloem. As long as roots are not considered as storage organs, substance transport by phloem into the fine roots is considered as insignificant (Trapp, 1995).

The xylem stream was described formerly for transport from soil. The phloem stream is derived from xylem, as it is more difficult to evaluate. It has been assumed to be 5% of xylem flow (Paterson et al., 1994). Transport rates between plant organs are considered as constant

during plant growth, as the flux and the respective volume of each compartment evolves at the same development rate. The partition coefficient between plant tissues and xylem corresponds to the coefficient plant tissue and water (equation 117). The same relation is used for phloem. According to these assumptions, the transfer rate from the stem to the leaf $k_{stl}$ (1/d) is

$$k_{stl} = Q_{xy} \Big/ (K_{stxy} V_{st}) \qquad 130$$

with $Q_{xy}$ ($m^3$/d) the transpiration stream in the xylem, $K_{stxy}$ (-) the partition coefficient between stem and xylem stream, and $V_{st}$ ($m^3$) the volume of stem. The transfer rate from the leaf to the stem $k_{lst}$ (1/d) is

$$k_{lst} = Q_{ph} \Big/ (K_{lph} V_l) \qquad 131$$

with $Q_{ph}$ ($m^3$/d) the phloem stream, $K_{lph}$ (-) the partition coefficient between leaf and phloem stream, and $V_l$ ($m^3$) the volume of stem.

Complex models have been built to understand the distribution and efficacy of substances in the plant according to the phloem mobility (Kleier, 1988; Hsu and Kleier, 1996). A differentiated relationship has also been developed for the phloem mobility to stem and fruit that takes into account the acidity of the substances relatively to the basic phloem sap. These models are based on an empirical relationship between the permeability of the sieve-tube membrane and the properties of the substance, the n-octanol-water partition coefficient $K_{ow}$. They take also into account the plant specie, the localisation within the plant and the growth stage. These models show a high complexity, which is too specific for the present model development.

## 4.5 Secondary transfers

Specific transport processes occur between each environmental compartment included in - or out of the limit of the system plant – environment. These processes are considered a priori of secondary importance, as the plant is the core of the system. However they could represent a concurrent transport to the flux from the environment to the plant and diminish potentially the importance of the net transfers to the plant. These secondary processes are notably in form of exchanges between the soil, the air and the formulation deposit on plant.

Part of these processes concern initial processes occurring at the moment of spraying. Consequently they contribute principally to the initial distribution of the plant treatment product in the system. Description of these processes and the way to consider them were developed in Chapter 3.3 Initial conditions of the system. Consequently, their contributions are not considered to be relevant as dynamic transport processes.

These secondary exchanges are also part of cyclic transports in the system on a longer term. According to resolutions of multi-media models (Margni et al., 2003), the feedback is often considered as negligible. Consequently, the need to consider them is more motivated by their potential concurrent effect than by the need to consider the complexity in the functioning of the model. To this point, the processes between soil and air are probably not relevant for the interpretation of the functioning of the system because the initial conditions have considered the very first initial redistribution processes between air, soil and deposit on plant.

Finally some processes contribute to transfers of substance out of the system. Considering the system boundaries, transfers out of the considered limits are considered as losses. Only processes that represent substantial transfer out of the system should be considered. Dissipation sources are particularly important for the dynamic evolution of the system as they are combined with time according to different types of substance and phytosanitary measure. Transfers to environmental compartments out of the system are considered as losses, as this amount of substance is subtracted from the direct exposition of agricultural commodities. Processes of losses are described below.

A description of secondary processes is given hereafter and main references to their description are brought in case detailed analysis should be necessary and integration in the model pertinent.

### 4.5.1 Volatilisation

The volatilisation concerns mainly the formulation deposit on soil or on plant, or the substance distributed in the soil gaseous phase. The droplets during the drying phase and subsidiary the dry deposit should be differentiated. A dynamic process of the drying droplets occurs in the first hours of the evolution of the system. This process depends mainly on the flux of wind and the partition coefficient between plant surface deposit and air (Leonard et al., 1987). Different approaches for volatility rates are proposed in literature (listed in Trapp and Matthies, 1998). In the present model the losses from droplets are considered in the description of the initial conditions of the system (Chapter 3.3) and no dynamic process for volatilisation from the wet deposit is retained for the dynamic resolution.

Volatilisation processes from the dry deposit and from the soil contribute to the dynamic evolution of the system. Volatilisation from the soil can be estimated on the basis of diffusion with two film resistances according to the described approach for the diffusion through stomata between the plant and the air (Chapter 4.2). The specificity concerns the partitioning of the substance between the bulk soil and gas phase, which is derived according to the partition coefficient between bulk soil and soil water (Chapter 4.1.1). The same approach may be proposed for the dry residue, considering a diffusion process through the dry deposit. However diffusion in such media is very slow and can be neglected.

### 4.5.2 Deposition

Initial conditions of the system consider a direct transfer of substance to the air. Part of this amount may be deposited within the agricultural system as wet and dry deposition. These descriptions are directly taken from the Impact 2002+ model (Jolliet et al., 2003) and also Trapp and Matthies, (1998). The main parameters are the velocities of transfers and the partitioning between the air (gas) and the particles. The wet deposition transfer rate $k_{dw}$ (1/d) corresponds to:

$$k_{dw} = G_r f_a w_a A_s /(K_{ap} V_a) \qquad 132$$

where $G_f$ the rainfall velocity (m/d), $f_a$ the aerosol phase fraction ($m^3$ / $m^3$ air), $w_a$ the aerosol washout ratio (($kg/m^3$ rain) relative to the air ($kg/m^3$ air), the area of soil intercepting ($m^2$), $K_{ap}$ the partitioning between air and particles (-) and $V_a$ the volume of air($m^3$). The partition coefficient is equal to

$$K_{ap} = f_a + (1 - f_a)/(K_{oa}\rho_p f_p) \quad 133$$

with $K_{oa}$ the partition coefficient n-octanol to air, $\rho_p$ the density of particles (kg/m$^3$) and $f_p$ the fraction of particles (-).

The dry deposition transfer rate $k_{dw}$ (1/d) corresponds to:

$$k_{dd} = G_{dd} f_a A_s/(K_{ap} V_a) \quad 134$$

with $G_{dd}$ the dry deposition velocity (m/d).

### 4.5.3 Surface deposit dislodgement by rainfall

The substance deposited on the leaf surface is potentially dislodged by hard rain (Leonard et al., 1987 and 1995; Willis, 1987). The transfer rate of this process depends mainly on the quantity of rate of rainfall and its occurrence after spraying. The intensity of rain is less significant. These losses contribute to the accumulation of substance in the soil.

In a rather simplified approach for this model, the transfer rate due to residue dislodgement from plant surface to soil by rainfall considers the number of days with a precipitation quantity higher than 10 mm per day, considered as necessary to produce a dislodgement process, the fraction of residue exposed is determined according to a coefficient (foliar extraction coefficient for substance wash off per centimetre of rainfall) and to the partition coefficient between n-octanol and water of the substance. The process is discontinuous according to climatic conditions. According to the good agricultural practices, it is considered as not occurring in the first hours after the application and is neglected in the present model.

### 4.5.4 Losses from soil

A part of the substance in soil is lost by runoff. This loss out of the system evolves in concurrency in time to the uptake by the plant and is therefore interesting. Losses out of the system from the soil compartment are mainly due to run-off. These descriptions are directly taken from Impact 2002+ (Jolliet et al., 2003). Losses are calculated as a function of the availability of substance in the considered phases: water and solids. Transfer from soil to water, as run-off is the main process. It depends on the partition coefficient of bulk soil to soil water. The transfer by run-off is obtained as a function of a rainfall and a run off fraction (Jolliet et al., 2003b). The transfer rate by run-off in water ($k_{swro}$) is equal to:

$$k_{swro} = R_w A_s / (V_s K_{sw}) \quad 135$$

where $R_w$ (m/d) is the transfer by run-off in water phase, As (m$^2$) the surface of soil, Vs the volume of soil, $K_{sw}$ (-) the partition coefficient bulk soil to water (equation 106).

A similar approach is possible for the run-off of solids. The partition coefficient bulk soil to soil matrix is derived from the $K_{sw}$. The transfer rate by run-off with solids ($k_{smro}$) is equal to:

$$k_{smro} = R_m A_s / (V_s K_{sm}) \quad 136$$

Both transfers show low rates in first simulations and could be negligible according to the other processes. The contributions of these processes are mainly determinant for substances with a low degradation rate.

### 4.5.5 Losses from the air

Losses from the air have already been discussed for the description of the initial conditions at application time. These initial losses are represented by a factor of spray efficiency. Subsequently a portion of substance assigned to the air may be transported long range or deposited after a short distance out of the limits of the considered system. In this study, long-range transports are considered as negligible losses for the dynamic evolution of the system. Consequently the potential amount submitted to such transports processes are considered to remain in the agricultural system as a source for accumulation in plant. However, the long-range transport could concern normalisation approaches to regional scale.

## 4.6 Degradation

The degradation of the substance in the different media represents the main source of substance losses. In each compartmental phase a distinct degradation value should be available. The difficulty to get data includes two problems: the availability of data for the different substances and media and the choice of a value.

Availability of values is linked to precise experimental designs and no indicative values may be extrapolated for general situations. Half-life values allow describing the substances but quantification is a sensitive problem. Half-life values for main environmental media are available in literature, so that a choice between values is possible. Conservative or median values are chosen according to the aim of the study. In the present study and in the case of sufficient choices, median values have been used as best approximation.

### 4.6.1 Degradation in environmental compartments

The half-life in air is calculated as a function of the degradation by OH radicals and the deposition. The photochemical reactivity of the substance is given by the rate constant for its reaction with the hydroxyl (OH) radical. These values are available as atmospheric rate constant ($cm^3$ / molecule-sec) from the Environmental Fate Data Base of the Syracuse Research Corporation online http://esc.syrres.com/interkow/physdemo.htm (Syracuse Research Corporation, 2003). An average radicals concentration in the air is used to determine the degradation rate of the substance in the air.

The persistence in soil consists of diverse types of data: laboratory values and field data, each data given under different types of soil (texture, pH, organic matter, localisation), temperature and applied dose of substance. Several data are available according to the different databases. The best choice is possible taking into account the descriptions given for the conditions of data acquisition (arable soils, no particular conditions). For the present study, median values have been chosen between large choices of data (when available). Data were collected in priority from the Agritox database online (INRA, 2003), the Environmental Fate Data Base of

the Syracuse Research Corporation online (Syracuse Research Corporation, 2003) and The Pesticide Manual (Tomlin, 1997).

Data for degradation in water and in sediment are not used in the present study and are generally less available.

### 4.6.2 Degradation in plants

The persistence in plants does not belong to the available values in databases. Sources for metabolism of specific studied substance are available in literature. Pharmaceutical industry produces such data for the purpose of substance registration, but these values remain confidential during and after the official procedure. Maximum concentrations of residue are indirect values for the maximum persistence of the substance in plant. Maximum concentrations are established as a function of the degradation rate of the substance and of the time lapse between the treatment and the harvest. However these data do not give a pertinent indication for substances with high degradation rate or used a long time before harvest. For theses cases, the residue level is generally lower than the limit of analytical detection. Because of good agricultural practices, the real residue level is mostly largely under the established limit.

Different limitation rates are identified for the metabolism of pesticides in plants. Komossa et al. (1995) differentiated between two extreme situations: rate limitation of metabolism by surface structures of the plant (cuticle) and by plant internal metabolic enzymes. The first rate limitation is influenced by the partition coefficient between n-octanol and water. The enzymatic pathway dominates the intracellular metabolism. Actually, no model is available to evaluate the degradation in plant. Pesticide loss processes in the soil are completely different from the degradation in plants. Sunlight and enzymes are major pathways for pesticide degradation in the plant and are more efficient than sources of dissipation in soil (bacteria, sorption).

In order to achieve in the present study a screening of a large number of substances, a value for degradation in the plant has to be extrapolated. The following assumption is made: pesticide degradation is more efficient in the plant than in soil so that values for half-life in soil represent upper limits for plants and half of this value is considered per default. Besides, substance degradation in the air is generally faster compared to soil, except for some substances where stability in the air is particularly high. Consequently the degradation in the air (when faster than in soil) could be considered as the lowest threshold for plant degradation; however the risk of underestimation is high according to the very low values of degradation in the air. An alternative solution is the inventory of data obtained from literature or from collaboration with the pharmaceutical industry.

### 4.6.3 Degradation on foliage

Considering the fraction of pesticide intercepted by the canopy and “stabilised” consequently to first losses, the residue left on plant surface is submitted to different processes with subsequent losses: adsorption, uptake, alteration, volatilisation, removal by water. These secondary processes have been described above and are not taken into account in the model. Values for field half-life of a few days (2-10 days for most substances) were calculated from references in literature (Willis at al., 1987). These value includes different types of shortcomings: no measure of effective quantity intercepted, imprecision of time boundaries

from moment of application, no information about the main sources of dissipation and the fate of the removed substance (substance, weather, plant, environment, degradation). According to this, values of a few days for foliar half-life may be overestimated. Weather conditions and formulants are particularly decisive for the progress of these processes including complex processes. Consequently existing database should be used with known limits (Willis et al., 1987) or determinant processes may be modelled as a default.

Various routes that affect the persistence of substance on foliage in the model could be included in the model development. However in order to get a transparent functioning of the model and according to the apparent low efficiency of feedback routes to the core of environmental models (Margni et al., 2003, see also different points in Chapter 3.5), the expression of the dissipation process(es) from surface deposit should be as concise as possible. The numerous data by Willis et al., 1987 show that a low variation between substances is observed, (mostly between 1 and 10 days half-life) and that the variation for a substance reaches the same order of magnitude. Besides these values are generally higher than values obtained for the half-life in the air. Consequently a constant half-life of 5 days for all substances is considered as a medium value for all conditions and substances.

# 5. Understanding the functioning of the system

The inspection of the underlying theory of the model has been developed in Chapter 2 Methodology for assessment of human toxicity potential and in Chapter 3 Fate model development, and then main single parameters composing the model have been described in Chapter 4 Processes descriptions. Starting from this basis, the model is applied and the functioning of the system is analysed, as prerequisites of the model evaluation. The chapter treats the following three parts:

1) *Model application*. The model is applied and parameterisation of the model is explicitly clarified according to a case study of phytosanitary measures in wheat. Description is given from the start of its parameterisation to the end results.
2) *Functioning of the system*. Starting from the evaluation of the different phytosanitary measures, the functioning of the system is interpreted. Key factors, mechanisms responsible for the transport and dissipation processes are identify and discussed. Different ways for interpreting the results are applied to define the scope of the method and the accuracy of the model running.
3) *Approximated resolution*. The potency of approximated resolutions to characterise and differentiate the substances, as their utility for interpretation or approximation of the harvest fraction are interpreted.

## 5.1 Model application

The model is applied and interpreted from initial parameterisation of the model to interpretation of the harvest fraction and the presentation of the results. The aim is to look at the full functioning system, including the results and ways of interpretation of the core model. Whereas variables and transfer rates were previously individually described, the analysis and interpretation here focuses on the final results. Different assumptions set up the frame and the scope of the model; they have to be explicitly clarified all along the procedure. The description of the parameters needed to run the model and to perform the calculation of the harvest fraction is also needed. In order to understand the functioning of the system, the case study of a wheat crop is chosen, in order to base interpretation on practical considerations. To facilitate the interpretation of the core model, only a selected choice of substances is considered in the chapter. Application will be generalised to a large number of substances in the last section once the model has been validated. The model application follows four steps developed in the next chapters:

1) Short system description
2) Test substances
3) Initial conditions
4) Harvest fraction

### 5.1.1 Short system description

Phytosanitary interventions are evaluated in the wheat crop. According to Chapter 3.2 System description, the harvested organs of the wheat plant are the grains that are considered to be in equilibrium with the stem and so included as a fraction of this compartment. The plant system

includes the root, the leaf and the stem organs. The considered pesticides are applied at different moments of crop development. Only transfer rates in direct relation to the plant are taken into account; no direct time dynamic exchanges are considered between source compartments in this module, except initial considerations for the distribution of substance between the compartments. Losses from the soil as runoff are taken into account. The model is run according to the full and simplified resolutions.

The main parameters with influence on the behaviour of the substances are constant in the present application of the model, due to the single crop evaluated and to the constant conditions of the environmental compartments. Particularly low variation is awaited from parameters determining equilibrium partition coefficients. According to the actual state in the development of environmental compartments, requirements are also lower for parameters describing environmental conditions of the system. Consequently a limited set of parameters is tested by the present screening of substances. A pertinent choice of test substances is especially needed in accordance with factors related to different crop development stages, with the lapse between substance application and harvest time, and with the variation of the physico-chemical characters of substance.

### 5.1.2 Test substances

A set of test substances chosen among pesticides frequently applied in wheat and showing a wide range of physico-chemical properties is used to better understand the model and the system. The need for reliable data characterising these substances is essential to perform the evaluation. A basic requirement concerns the availability of the essential parameters, principally Henry's constant, $K_{ow}$, degradation in soil and air, molecular weight and volume. The value of theses parameters need to be checked by comparing different databases, in order to identify singular data and draw attention to eventual probable distinct environmental behaviour. The models that describe transport processes are generally based and validated on substances with most conventional behaviour, so that extreme values, especially for environmental partitioning, have to be considered with precaution. The value of half-life in plants is generally not available and requires to be extrapolated, creating additional need to check reliability in the interpretation of the results. The compounds that have a polar behaviour or that dissociate have to be removed from analysis of the present model; specific developments to the models should be added for such substances. The contribution of formulants and adjuvants in the plant treatment products is not taken into account in the evaluation of the fate of the substances. This limit must not be neglected in the interpretation of the results. The degradation products are not considered in the evaluation of fate and toxicity, meaning that a substance is considered as removed as soon as a transformation occurs (polarity, ionisation, degradation). Improvements according to specific transformation cases could be considered by adding a rate of transformation of the substance into a modified substance or into degradation metabolites. The selection of test substances to evaluate the system is the following: 4 herbicides (diflufenican, ioxynil, isoproturon, pendimethaline), 3 growth regulators (chlormequat, ethephon, trinexapac-ethy), 4 insecticides (deltamethrine, lambda-cyhalothrine, teflubenzuron, pirimicarb) and 4 fungicides (azoxystrobin, chlorothalonil, cyproconazole). Characteristics for these substances are presented in Table 7 and in Figure 32. These data are a synthesis of data collected in different database: Agritox database online (INRA, 2003), Environmental Fate Data Base of the Syracuse Research Corporation online SRC (Syracuse Research Corporation, 2003) and The Pesticide Manual (Tomlin, 1997). A preliminary interpretation of the behaviour of these substances can be

carried out, in order to analysis the pertinence of values and to foresee the general environmental behaviour of these substances.

Table 7. Description of phytosanitary substances used in wheat: name, CAS, half-life in air (t1/2 air, based on the degradation by OH radicals and deposition), half-life in soil, molecular weight (MW), and molecular volume (MV, computed values). Syntheses of data collected from different database (Agritox, SRC and Tomlin).

| | | CAS | t1/2 air | t1/2 soil | MW | molecular volume |
|---|---|---|---|---|---|---|
| | | | days | days | g/mol | cm3/mol |
| herbicides | Diflufenican | 83164-33-4 | 5 | 156 | 394 | 257 |
| | Ioxynil | 1689-83-4 | 74 | 10 | 371 | 145 |
| | Isoproturon | 34123-59-6 | 2 | 20 | 206 | 178 |
| | Pendimethalin | 40487-42-1 | <1 | 67 | 281 | 215 |
| growth regulators | Chlormequat chloride | 999-81-5 | 2 | 15 | 123 | 114 |
| | Ethephon | 16672-87-0 | 13 | 14 | 145 | 83 |
| | Trinexapac-ethyl | 95266-40-3 | <1 | 1 | 252 | 193 |
| insecticides | Deltamethrine | 52918-63-5 | <1 | 21 | 505 | 321 |
| | Pirimicarb | 23103-98-2 | <1 | 121 | 238 | 189 |
| | Lambda-cyhalothrin | 91465-08-6 | 1 | 22 | 450 | 318 |
| | Teflubenzuron | 83121-18-0 | 5 | 34 | 381 | 222 |
| fungicides | Azoxystrobin | 131860-33-8 | 3 | 10 | 403 | 305 |
| | Chlorothalonil | 1897-45-6 | 584 | 35 | 266 | 152 |
| | Cyproconazole | 113096-99-4 | 1 | 27 | 292 | 229 |
| | Prochloraz | 67747-09-5 | <1 | 22 | 377 | 260 |

The half-life of these substances shows shorter persistence of substances in the air and longer one in the soil (Table 7). Special values are particularly observed for high half-life in the air (deposition included) for ioxynil and chlorothalonil, but also high values in soil for diflufenican and pirimicarb, as well as short persistence for trinexapac-ethyl in soil. This asks for particular care in the interpretation of the results of these substances and the factor half-life will be attentively analysed in the sensitivity studies. The molecular weight and molecular volume tends to be lower for the growth regulator and appear to characterise this type of substance linked to their diffusion capacity.

Figure 32 presents the repartition of substances in term of $K_{ow}$ and $K_{aw}$. In particular a low transfer capacity from the soil to the plant is characteristic for substance with a log $K_{ow}$ under –0.5 (chlormequat and ethephon) or above >4.5 (deltamethrine, diflufenican, teflubenzuron). The capacity of transport to the harvest organ (stem) from the air to the leaf is also partly limited for a substance with high $K_{ow}$. The high $K_{oc}$ of deltamethrine (log $K_{oc}$ 6.4) could limit the availability of this substance for the transport from the soil; the other substances have a log Koc between 1.9 and 3.8. The $K_{aw}$ has a low influence on the accumulation in the stem, but could explain some particular low accumulation from the air. Among the studied substance not one shows a particular affinity for the air. Compared to the analysis carried out by Bennet et al., (2002b) and Margni (2003), these commonly used pesticides cover a restricted range of properties, usually involving a high transfer in grain.

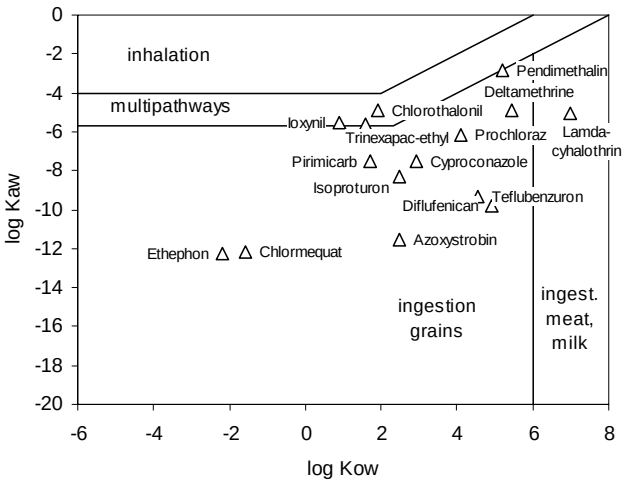



Figure 32. Repartition of substances as a function of the partition coefficient between n-octanol and to the partition coefficient between water and air. Exposure classification of the substances: inhalation, multipathways, ingestion by grains, ingestion by meat or milk according to Bennett et al. (2002b) and Margni (2003). Set of substances used in wheat.

### 5.1.3 Initial conditions

The distribution of the substance varies between the compartments operating as sources (air, soil and plant surface deposit) according to different types of phytosanitary interventions, as they occur at different moments of the crop development. These initial conditions are important as they determine the compartment where the substance is mostly localised and the time for the system evolution. The quantity of substance intercepted by the plant surface is more than doubled from the moment of herbicide application (20% intercepted for herbicide applied after crop emergence) to the moment of fungicide application (50% intercepted for fungicide applied on shoots) (Figure 33). On the contrary, the fraction of fungicide reaching the soil is much lower (40%) compared to the fraction of herbicide (70%). On the other side the time for the system evolution is approximately half for a fungicide compared to an herbicide. These different time delays vary greatly also amongst each type of phytosanitary measure, so that the cases studied here cannot be considered as representative for each type of pesticide application. For example more contrasted values would be obtained for herbicides applied before crop emergence, when almost all substance reaches the soil with a little fraction lost in the air, or for late applied fungicide on ears.

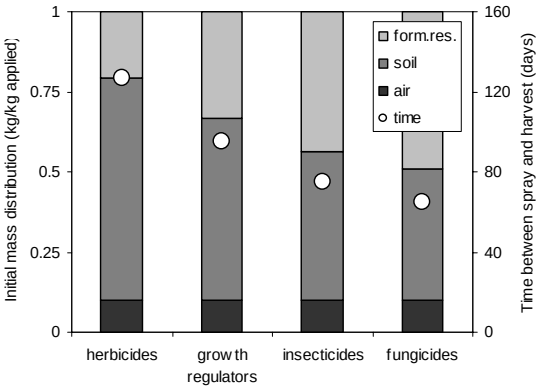



Figure 33. Initial distribution of substance between air, soil and plant surface deposit, and time between typical spray application and harvest According to different types of phytosanitary interventions.

### 5.1.4 Harvest fraction

The principal results given by the model are the harvest fraction, that is the quantity of substance found in the harvest per unit of substance initially emitted in the system. This assessment step characterises the level of transfer from the source to harvest. To run the model transfer rates between compartments of the system are determined for each substance. Indicative transfer rates are given for 2 substances in Table 8, which represents the matrix including the linear differential equations for each compartment of the system (Chapter 3.5.1 Full model). The matrix coefficients are the transfer rates between compartments of the system. The negative removal rates from the compartments are ordered as diagonal elements. The removal rate includes the total transfers from the considered compartment to others, and the degradation rate.

Table 8. Matrix of transfer rates (1/day) between compartments air, soil, plant surface deposit, root, stem and leaf; 2 substances used in wheat: herbicide ioxynil, fungicide cyproconazole.

| ioxynil | air | soil | form.dep. | root | stem | leaf |
|---|---|---|---|---|---|---|
| dMa/dt | -1.1E-01 | - | - | - | - | 4.5E-01 |
| dMs/dt | - | -8.1E-02 | - | 2.6E+00 | - | - |
| dMfd/dt | - | - | -2.6E-01 | - | - | - |
| dMr/dt | - | 1.0E-02 | - | -2.7E+00 | - | - |
| dMst/dt | - | 9.0E-04 | - | - | -1.3E+00 | 2.2E-01 |
| dMl/dt | 9.6E-02 | - | 1.2E-01 | - | 1.1E+00 | -8.1E-01 |

| cyproconazole | air | soil | form.res. | root | stem | leaf |
|---|---|---|---|---|---|---|
| dMa/dt | -2.0E+00 | - | - | - | - | 3.6E-03 |
| dMs/dt | - | -3.4E-02 | - | 9.8E-01 | - | - |
| dMfd/dt | - | - | -1.2E+00 | - | - | - |
| dMr/dt | - | 7.9E-03 | - | -1.0E+00 | - | - |
| dMst/dt | - | 4.3E-04 | - | - | -1.2E-01 | 1.3E-02 |

| | | | | | | |
|---|---|---|---|---|---|---|
| dMl/dt | 1.4E+00 | - | 1.0E+00 | - | 6.7E-02 | -6.9E-02 |

In accordance to both substances, transfer rates tend to be highest from the sources of air and formulation, and for degradation (difference between the sum of transfers rates and dissipation rate). The highest dissipation rates are observed from the air and from the surface deposit to the leaf. Transport from the soil is much slower. The exchanges between the leaf and the stem vary as a function of the substance. The transfer rates, the initial masses and the results for the total set of substances are give in Appendix D.1 Transfer rates between compartments and Appendix D.2 Initial conditions and results of the model. Numerical results presented in the next chapters are taken from these tables.

Figure 34 compares the evolution of grain fraction, leading to the harvest fraction (Table 9), for herbicide, growth regulator, insecticide and fungicide. Large differences in grain fraction evolution and in final harvest fraction are observed between the substances, even between substances with a similar function. Exposure classification given by Figure 32 does not show high contrasts between the substances, although differences are put in evidence. Consequently the values of half-life (Table 7) and the time between application and harvest (Figure 33) become determining factors to identify differences between substances. The initial dose or initial accumulation phase is not so determinant for the harvest fraction due to the subsequent dissipation processes.

The application of herbicides is early in the growing period, but their persistence in the soil allows a continuous transfer to the plant and a final harvest fraction as high as for substances applied later. Some of these substances have effectively a much higher half-life in soil, than for air and for plant surface deposit. The high persistence in soil eventually requires more detailed processes for the fate of substances in this compartment. This particularly concerns the evolution of the diflufenican with a very low transfer rate to the plant and a long persistence in the soil (half-life 156 days).

The three growth regulators show among the lowest harvest fractions due to their low persistence and to a lower mobility in the plant, indicated by a low $K_{ow}$. The similar evolution of ethephon and chlormequat is in accordance with their exposure classification. The rapid dissipation of trinexapac-ethyl is explained by low half-life values in air and soil. The resulting harvest fraction is among the lowest. The relative behaviours of the four insecticides are the same so that the initial mass applied becomes an important factor. The variation between the fungicide shows that within a short period high differences between substances may occur. Azoxystrobin, with a half-life of 10 days in soil, is clearly faster removed compared to chlorothalonil and cyproconazole with 35 and 27 days respectively.

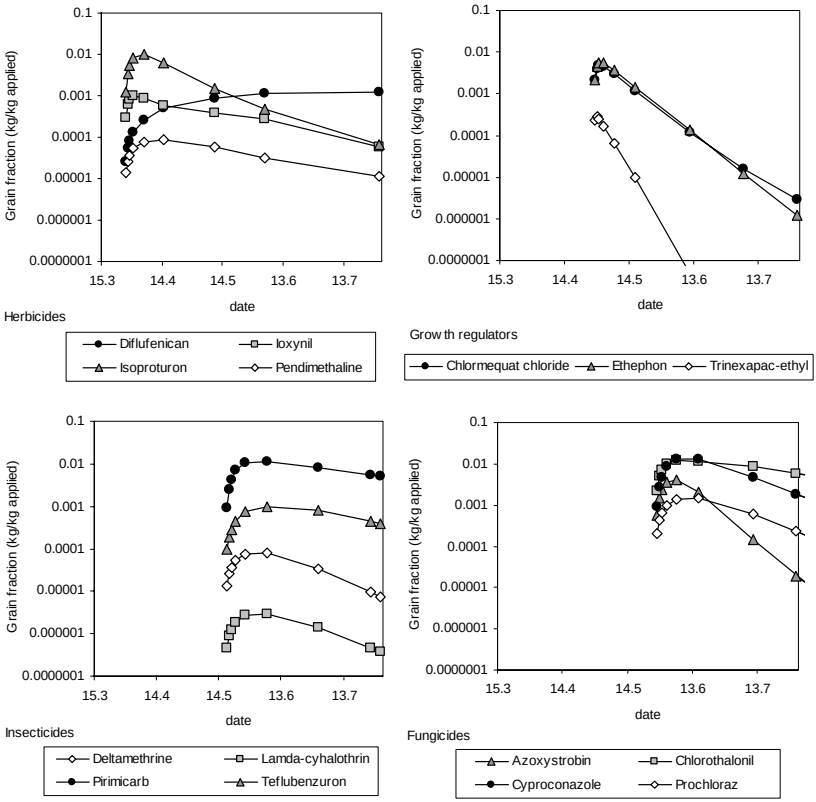



Figure 34. Evolution of grain fraction leading to the harvest fraction from time of substance application to the time of harvest for different substances grouped according to the types of plant treatment: A. herbicide, B. growth regulator, C. insecticide and D. fungicide.

Table 9. Mass sprayed (kg/ha) and harvest fraction (kg in grain / kg applied) for a set of substances used in wheat.

| Substances | Mass sprayed kg applied / ha | Harvest fraction kg in grain / kg applied |
|---|---|---|
| Diflufenican | 0.075 | 1.3E-03 |
| Ioxynil | 0.355 | 5.9E-05 |
| Isoproturon | 1.500 | 6.6E-05 |
| Pendimethaline | 1.600 | 1.1E-05 |
| Chlormequat | 1.150 | 2.9E-06 |
| Ethephon | 0.720 | 1.2E-06 |
| Trinexapac-ethyl | 0.150 | 2.8E-15 |
| Deltamethrine | 0.008 | 7.4E-06 |
| Lamda-cyhalothrin | 0.008 | 3.6E-07 |
| Pirimicarb | 0.075 | 5.2E-03 |
| Teflubenzuron | 0.060 | 3.9E-04 |
| Azoxystrobin | 0.250 | 1.9E-05 |
| Chlorothalonil | 1.500 | 5.9E-03 |
| Cyproconazole | 0.080 | 1.8E-03 |
| Prochloraz | 0.450 | 2.4E-04 |

This short overview of the evolution of the system and the calculation of the harvest fraction introduce the next chapter describing the functioning of the system.

## 5.2 Functioning of the system

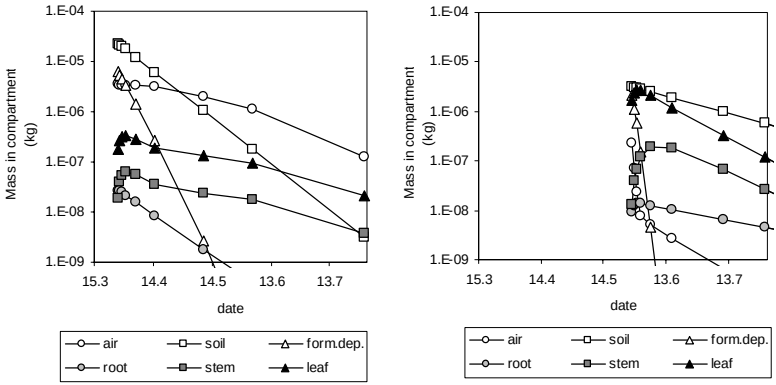
There is a need to identify the parameters useful for interpretation of the behaviour of the substances and of the results. Following chapters deal with the description of the functioning of the system.

1) *Evolution of the compartments*. The transports of mass in the different compartments make the system evolving from the time of substance release to the harvest time. Analysis of this evolution helps to highlight main transport processes. The evaluation of mass transport as a function of sources (air, formulation deposit, soil) is needed to evaluate the key processes. The importance of the variability among substances belongs also to the analysis.
2) *Maximum accumulated mass*. Point with maximum accumulated mass in the plant is a key data to interpret the results and also the functioning of the system.

### 5.2.1 Evolution of the compartments

The evolution of the system is illustrated in Figure 35 for two substances, showing the evolution of mass in the different compartments from the time of application to the time of harvest. This delay varies according to the different types of substances. The initial mass in the system also differs from one substance to the other. The time to reach the maximum accumulated mass in the plant compartments is short; the system is generally "stabilised" after a few days, before the mass in the system decreases, according to an exponential decay. The accumulation and dissipation in the plant varies with the considered plant compartments. Stem and leaf evolve similarly due to bi-directional exchanges between both compartments,

whereas root is more in relation with the soil. Formulation deposit of cyproconazole decreases extremely rapidly due to quick transfer to the leaf. At harvest the accumulated mass is highly depending on the (dissipation) degradation rate in each compartment and on the exchanges in the system.




A. Ioxynil B. Cyproconazole

Figure 35. Evolution mass in the compartments of the system (air, soil, formulation deposit, root, stem and leaf) from spray time to harvest (kg in compartment per $1m^2$ crop). A. Herbicide ioxynil ($3.6\ 10^{-5}$ kg applied $/m^2$) B. Fungicide cyproconazole ($8\ 10^{-6}$ kg applied $/m^2$)

The evolution of the system may also be evaluated for each single source to interpret their single (potential) contribution to the functioning of the model. Figure 36 presents the harvest fraction for the different substances according to the full system and to each single source: soil, air, surface deposit. The results of harvest fraction of the full system are the endpoint of the evolution according to Figure 34 previously discussed. The harvest fraction for each single source expresses the mobility of a substance starting from a designated single source ending in the harvested compartment, passing through the full system.

There is no systematic difference in the transfer behaviour between sources, but some elements may be interpreted here. In tendency the soil is a less important source, but that the inverse also occurs. Typically the low harvest fraction for soil of deltamethrine is explained by a very low transfer rate from the soil to the stem ($10^{-9}$ 1/day) , due to a low availability in the soil solution (high $K_{oc}$) and a limited transfer in the xylem. The low harvest fraction of trinexapac-ethyl is explained by the low half-life values. For this substance, formulation deposit is the main source for accumulation in harvest with a harvest fraction of $10^{-14}$ kg/kg highly contrasting with the results for soil $10^{-32}$ kg/kg and those for air $10^{-36}$ kg/kg. These differences are explained by the combination between the transfer rate from source to plant and the degradation rate in source. The high transfer rate from deposit to leaf (0.1 1/day) is combined with a rather low removal rate (0.1 1/day), comparatively with corresponding values for soil with 0.001 and 0.7 1/day respectively and for air with 0.1 and 4 respectively. A similar analysis explains the results of ethephon with a relatively high persistence in the air, a relatively high transfer rate from the air to the plant and finally a low transfer back to the air,

comparatively to the other sources. However, the absence of systematic trend in the efficiency between sources confirms the need to consider each source as potentially determinant.

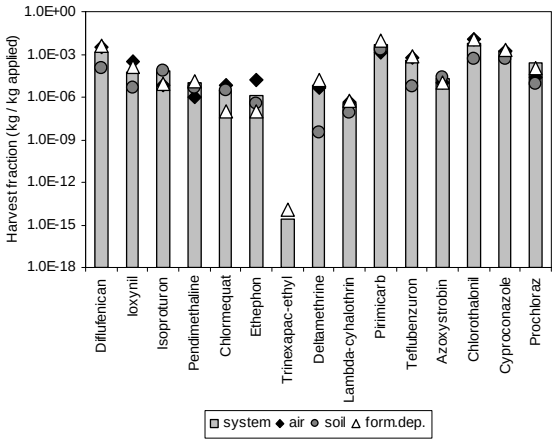



Figure 36. Harvest fraction for substance applied as single source in air, soil and surface deposit compared with substance applied in the full system. Harvest fraction expressed as kg substance in harvest / kg substance applied in the single medium, respectively in the system .

### 5.2.2 Maximum accumulated mass

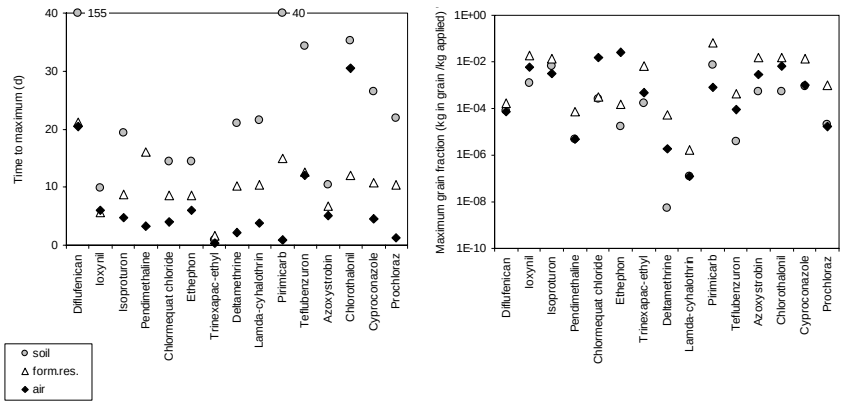
The evolution of the system is characterised by a point with maximum accumulated mass in the plant, which is specific to each substance. In order to interpret the functioning of the system, the following key values are associated with this point (Chapter 3.5.5 Procedure): the maximum point and the level of maximum mass. These parameters are analysed hereafter.

The time delay to reach the maximum point is rather short, within a few days (Figure 37). The source compartments show differences to reach this point. According to equation 79 for a system in cascade, the main parameters are the dissipation rates in both compartments. The higher the difference between the dissipation rates is, the sooner the maximum accumulation is reached. Additionally high persistence enlarges the time to reach the maximum point. These principles explain clearly the contrast between the rapidity to reach the maximum for a source in the air (dissipation rate of substances mostly between 0.1 and 3 1/day, half-life around 1 day) and the longer interval for a source in the soil (dissipation rate of substances mostly between 0.01 and 0.1 1/day, half-life higher than 10 day). Diflufenican and pirimicarb have a high half-life in soil, with 156 and 121 days respectively, and consequently maximum accumulated mass is reached after a long delay. Similarly the low half-life values for trinexapac-ethyl explain the rapidity to reach a maximum level.

According to equation 81, the level of maximum accumulated mass in a system in cascade depends on the following factors: the level of accumulated mass is increased proportionally by a high transfer rate from the source to the plant or by a low dissipation rate in source compartment, and exponentially by a short time to reach the maximum point and by low

dissipation rate in the plant compartment. The distribution of substances between the different compartments at application time constitutes also a preliminary factor determining the level of accumulation as a function of sources. The maximum accumulated mass in plant is represented in Figure 37 for the set of test substances, expressed here as grain fraction, leading finally to harvest fraction. Compared to the other sources, the surface deposit mostly leads to the highest maximum grain fraction. It is partly due to the high fraction of sprayed mass intercepted by the plant, particularly for late applied substances like insecticides and fungicides. It is also explained by the high transfer rates observed generally for this transport process. For the same reason, grain fractions from the air may also be relatively high (chlormequat, ethephon) and grain fractions from soil tend to be lower than from formulation deposit. The low level of harvest fractions for deltamethrine and for lambda-cyhalothrine is explained by the low mobility of these substances in the plant system, from the leaf to the stem, but also in the xylem from the soil to the stem.

Most grain fractions do not exceed 1 hundredth of the applied mass. The level of harvest fraction shows that a large part of the substance already dissipates, while the initial mass is transported through the system. This loss of substance is mainly explained by the high of degradation in the air and in the surface deposit. No relations could be put in evidence between the maximum grain fraction presented here and the final harvest fraction. It appears that the results of this intermediate level are not sufficient to be representative of the specific contribution of each source to the final state at harvest. This may be interpreted by the fact that the system evolution before and after maximum point depends on other key processes. The initial evolution of the system, from release of substance to maximum point, can be described as a full distribution of substance in the system, shared between transport and dissipation processes. The period after the maximum point is largely dependent on dissipation processes of accumulated mass in the different compartments, with low redistribution of substances within the system.




A. Time B. Grain fraction

Figure 37. Maximum point for a set of substances used in wheat. A Time (d) to reach the maximum mass accumulated in harvested part of the plant according to the sources of substance. B Maximum grain fraction (kg substance in grain per kg substance applied in the system) leading to harvest fraction, as a function of the source of substance.

## 5.3 Approximated resolution

The approximation resolution is based on the simplification of the full system integrating further simplifications as developed in Chapter 3.5.2 Two compartments with bi-directional transfer and Chapter 3.5.3 Cascade of two compartments. (Chapter 3.5.5 Procedure). These procedures and the different mathematical developments are tested here according to the methodological significant steps described in Table 5. Following points are studied:

1) *Comparison between full resolution and subsystems approach*. The pertinence of the resolution according to three subsystems is analysed by comparison with the full system.
2) *Comparison between bi-directional transfer and cascade systems.* The need to consider the transfer back from the plant compartment is evaluated by comparison of cascade and bi-directional systems.
3) *Comparison between simplified equations* . Approximated resolutions of subsystems are compared.
4) *Approximation of harvest fraction*. The harvest fraction is determined using the different methods for system and resolution simplification and compared to the exact resolution of the full system.

These different ways of simplification are useful for the interpretation of the system and the processes. The comparisons between approaches and resolutions are first achieved to test the mathematical functioning of the model; substances used in figures are not identified and correspond to the long list of pesticides used in wheat. The last steps of this chapter, describing the harvest fraction, use the short set of identified substances in figures.

### 5.3.1 Comparison between full resolution and subsystems approach

The full system was described in Figure 7 and the resolution for it was developed according to the general solution (equation 25). The simplification of the full system in subsystems considers three sub units composed of two compartments: the three sources of substances (air, deposit on leaf surface and soil) and each corresponding receiving plant compartment (nearest plant compartment). Only transport processes between both source and the receiving plant compartments are considered, and also the degradation. Dissipation routes out of the subsystem, transfers from other subsystems, are not considered. The transfers from the sources to the plant consider the effective route to the appropriate plant organ relevant for the evaluation of substance accumulation. In the case of wheat, the ears and grains are considered to be in equilibrium with the stem so that all transports are considered to the stem. The subsystem soil considers just a transfer from soil to plant stem and so is solved in cascade. The compartment fines roots is here not considered, as it is mainly an equilibrium state with the soil and as it does not represent a compartment relevant for sink in the full system. Both other subsystems have bi-directional transfers and offer different ways of resolution: with bi-directional transfer or in cascade as a further simplification according to the importance of the feedback. The three subsystems are described in Figure 38.

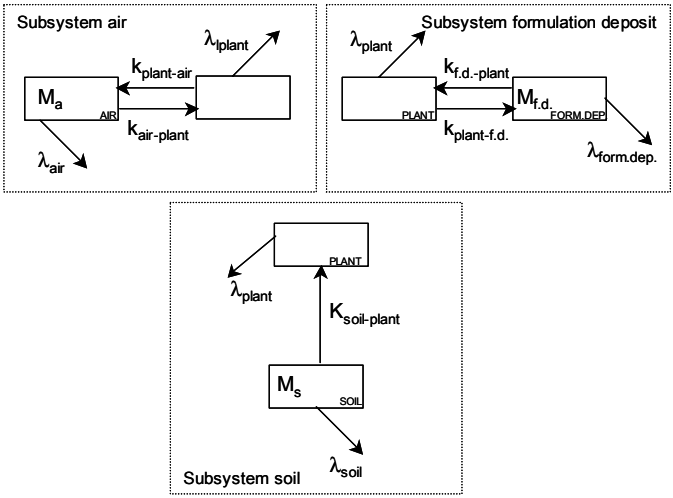



Figure 38. Subsystems description, initial masses in the environment, transfer and elimination rates.

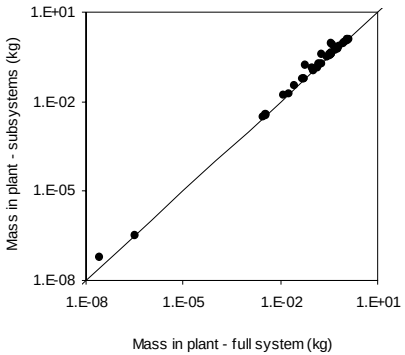
The sum of masses accumulated in the plant in each subsystem should be approximately equal to the mass accumulated in the plant according to the full system.

$$m_{tot\_plant} = m_{air-plant} + m_{form.dep.-plant} + m_{soil-plant} \qquad 137$$

The evaluation concerns 1 kg substance available in each source compartment. The system configuration (crop development) at application time is specific to each substance and consequently gives a large range of different cases useful for the test. In order to evaluate the accuracy of the system subdivision and the approximations, the system is running for a short period, which is more critical than for a long time. The interval corresponds to 21 days for all substances (also herbicides), which is a frequent legal minimum delay between spray time and harvest.

The comparison between full resolution and subsystem approximation gives a good concordance for the tested substances (Figure 39). No deviant point is observed and precision appears the same for low and high transfer conditions. Other tested time ranges for the system evolution give similar observations. The possibility to solve the system according to the partial resolutions is especially interesting for the interpretation of the functioning of the system and relative importance of the processes. The subsystem approach gives a slight overestimation of the accumulated mass due to the simplification. The absence of root, as a sink compartment is a part of the explanation, especially when the difference between degradation in soil and in plant is high. The absence of transfers through the plant to high dissipating compartments also plays a probable role. It shows also that the processes in and between the source compartment and the nearest receiving plant compartment mainly determine the fate. It also indicates that no important transfer (back) occurs out of the

receiving plant compartment (the plant) to other compartment (the environment). A simplification of the receiving plant compartments shall also be identified. It concerns especially the number and the type of compartments according to the harvested plant part.




These points are developed in the related chapter.

Figure 39. Comparison of accumulated mass in plant according to the resolution of the full multi-media system and according to the resolution of three subsystems of two compartments.

### 5.3.2 Comparison between bi-directional transfer and cascade systems

Ana additional way of simplification and interpretation proposes to transform a system of two compartments with bi-directional transfer into a system in cascade. Two subsystems show bi-directional transfer: the air and the plant surface deposit. The comparison of results for both resolutions gives a good concordance (Figure 40). The feedback factor is a measure of the differences observed, as it indicates the level of cyclic exchanges between both compartments with bi-directional transfer. It is generally very low for almost all substances in both subsystems so that the simplification of the system is pertinent.

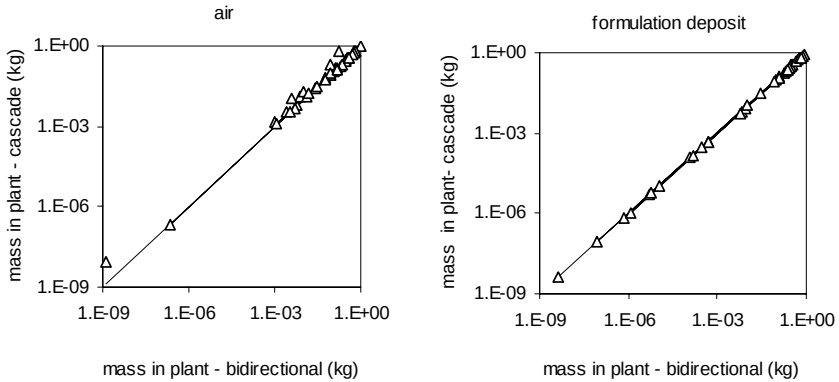



Figure 40. Comparison of accumulated mass in plant according to the resolution of a system with bi-directional transfer and according the resolution of a system in cascade. For the subsystems air and formulation deposit.

### 5.3.3 Comparison between simplified equations

The third way to improve the interpretation and the resolution procedure concerns the simplification in the expressions of the equations or in the process description of the subsystems approach: simplification of the equations and by the dissipation of the maximum reached mass (Chapter 3.5.2 Two compartments with bi-directional transfer in Table 3 and Chapter 3.5.3 Cascade of two compartments in Table 4). Figure 41 illustrates these possibilities considering bi-directional transfer for the subsystem “formulation deposit”. The approximation according to the long-term relation between both compartments shows outliers. These substances are characterised by a long time to reach the maximum mass and a very low accumulated maximum mass. Logically, better approximation is given for a longer delay for the system evolution (here 21 days). The transfer rate from the source to the receiving plant is very low for theses substances. This way of approximations is generally better for the subsystem air, for which no occurrence of low transfer rates from source to the receiving plant compartment is observed. According to the risks of deviation, this approximation way should only be used for very long term resolutions.

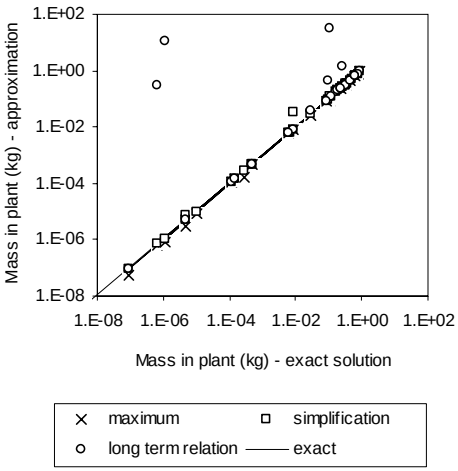



Figure 41. Comparison of exact solution and approximation solutions: dissipation of maximum reached mass, simplification of equation, long-term relation between both compartments. Accumulation in the plant from the surface deposit, with bi-directional transfer.

The approximations for cascade conditions are submitted to conditions and precautions : the relation between dissipations rates (transfer and degradation) determines the validity to consider the long-term relation between the compartments. Good approximation is possible for systems that have a dissipation rate higher in the receiving plant compartment than in the source. Concerning this case study, the three subsystems have dissipation rates higher in the source compartment. Consequently conditions for this approach are not satisfied.

The potential of good approximation for systems in cascade depends also on the difference between the dissipations rates. When values are very similar, the approximations are unreliable, especially the simplification of the equation, but also the process simplification (dissipation from maximum). The transfers from the soil to the plant illustrate these conditions for the dissipation rates that are almost the same (Figure 42). This situation occurs when degradation rates are identical in both compartments and higher than the transfer from source to the receiving plant. For cases when the differences are high between dissipation rates the approximation tools are more reliable for the surface deposit and for the subsystem air. According to this good concordance and to the fact that in this case the contribution from the soil is not dominant, the aggregation of the three subsystems solved in cascade constitutes a good approximation of the resolution of the full multi-media system. A similar good relation is obtained as illustrated in Figure 39.

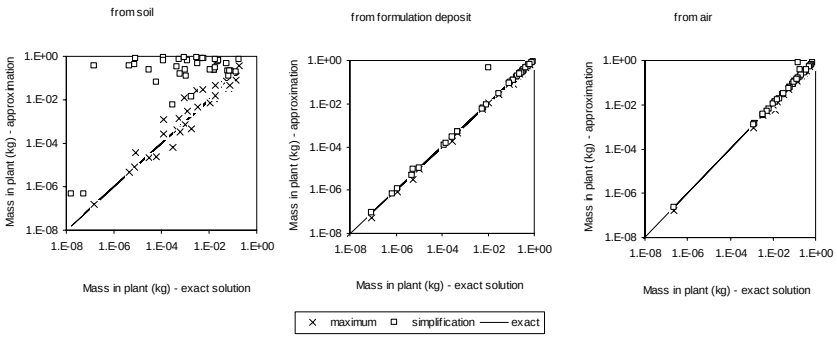



Figure 42. Comparison of exact solution and approximation solutions: dissipation of maximum reached mass and simplification of equation. Accumulation in the plant from the soil, from the formulation deposit and from the air for a system in cascade.

### 5.3.4 Approximation of harvest fraction

In accordance to the methods presented above for system and resolution simplification, approximations of harvest fraction are presented here: The exact mathematical solution of the full system is compared to simplified system solved exactly and with the simplified system solved as a function of the maximum point.

The results of the approximations are presented in the Figure 43. These approximations are rather conforming relatively to the exact solution of the full model and the ranking of the substances is respected. Deviating results of some substances corresponds to particular behaviours already put in evidence by the evaluation of the functioning of the system, explaining the risk of approximation for single particular cases: trinexapac-ethyl with low half-life (not show in figure), pirimicarb and diflufenican with late maximum point, deltamethrine with low mobility from soil to plant.

Beyond the possibility to interpret the functioning of the system, the intention of these approximations aims at complementing the exact results given by the model with key values useful for additional extrapolations. This would allow performing complementary evaluation without any need to compute systematically the full model and resolution. The results can be effectively complemented with the description of the maximum point and the dissipation rate of the harvested plant compartment.

In Chapter 5.2 Functioning of the system, interpretation of the single (potential) contribution of each single source to the functioning of the system was evaluated to study the transport through the different pathways (Figure 36). No systematic distinction could be made between sources, although in tendency soil has appeared as less efficient. Concluding evaluation of sources is presented here according to the effective amount of substance distributed in the system to each source. Figure 44 gives the results, which are contrasting according to the time of application. Early applied substances show a major contribution from the compartment in which the substance has the highest persistence: ioxynil from the air, isoproturon from the soil. The late applied substances show a generally important contribution from the surface deposit. This is due to the efficiency of this transport pathway, but also to the high

interception of substance by the plant at a late time of spray. Pirimicarb combines late application and low degradation rate in soil and in plant, which contributes to a high harvest fraction.

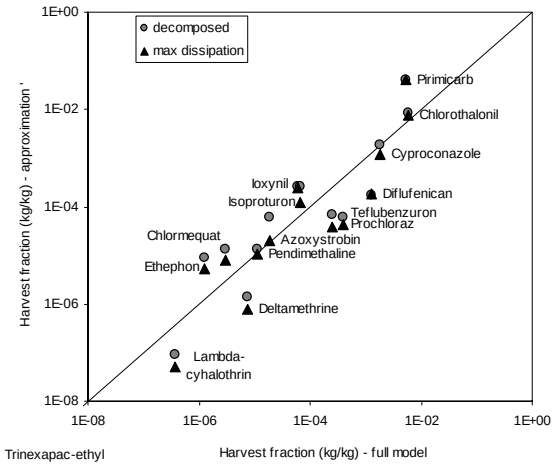



Figure 43. Harvest fraction according to the full model compared to approximation by a simplified system resolution and by a dissipation of maximum point.

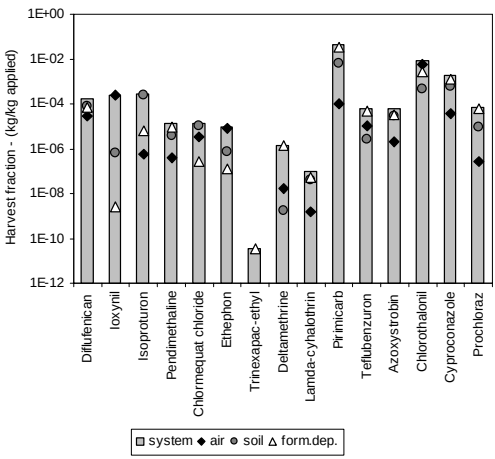



Figure 44. Harvest fraction according to the single subsystems air, soil and plant surface deposit, and for the total system. Harvest fraction expressed as kg substance in harvest / kg substance applied in the system.

# 6. Evaluation

"Reliance on model is essential, but the beauty (or deception) of models is that their output can be so impressive even if there is almost no validation beneath. This is particularly troubling when models are used by persons who do not understand their limitations". This citation (Glaze in Schwartz, 2000) illustrates the challenge of model validation. Schwartz (2000) studied the quality assurance of exposure models and comes to precise demonstrations and protocols for the validation of models. Without entering the (existing) scientific and philosophic debate of validation, main points are introduced here to verify the methodological approach chosen and developed in this study. Consequently, the present chapter is mainly developed in the form of an evaluation, including one single part of effective validation.

The evaluation should bring a picture of the functioning of the individual processes and the full model to have a clear understanding of the behaviour of substances. The processes selected to be involved in the model (Chapter 2) have been developed in the frame of very focused studies and mostly solved according to experimental and analytical approaches. All these processes have been simultaneously experimentally validated. According to these methodological frameworks, a same approach could a priori be expected for the evaluation of the full model developed in this study. If the analytical approach is based on a real case study from which the reality may be derived, the model approach tends to the same objective, with another perspective and in a complementary approach. The purpose of a model approach tends precisely to exceed the real analytical limits in the determination of pesticide fate and to represent cases where analytical steps do not bring satisfactory answers. Conditions of evaluation by models are determined to cover a broad range of a general situation, opposite to strictly local and temporal determined case studies. The meaning of validation in the present study is to compare the accuracy of the computed data given by the total system versus experimental measures. The detailed processes and system functioning, described by the mathematical model, cannot be proved as true in their most complex forma, and so cannot be validated under the classical meaning of the term. The validation of the model by experimentation of single processes is consequently not pertinent in this case. It would need a distinct specific validation process, effectively already done in literature accounted for in the choice of the pertinent processes needed for the building of the model.

According to Schwartz (2000), the core of validation, or evaluation, includes inspection of the underlying theory, sensitivity analysis, scenario analysis and comparison with observed data, uncertainty analysis, comparison with alternative models, and evaluation of the used data.

1) *Sensitivity analysis*. A sensitivity analysis is performed for the single transfer rates and for the total model, in order to identify the key parameters affecting the results.
2) *Uncertainty analysis*. In a continuation to the sensitivity analysis, the uncertainty of the main parameters and of the most uncertain one is necessary to test the precision of the results.
3) *Comparison with measured data of residues* in wheat. A validation comparing point-by-point analytical and computed data is limited according to the different elements introduced before. However some particular points of the model building and functioning are discussed according to an experiment carried out in the frame of this study.

4) *Concentration at harvest*. The way to control the results is necessary in order to verify their scope and their pertinence. In particular the concentration in harvest can be compared to reference values, such as tolerance values.
5) *Qualitative comparison* with other models. The comparison with alternative models shall help the identification of improvement brought by the model: through the comparison, it is possible to identify further potential new developments of the model. The status of the model among the different types of existing model is also to be clarified.

## 6.1 Sensitivity analysis

The aim of the present sensitivity analysis is to test the functioning of the model and identify the key parameters and processes. The high variation between the substances makes each one distinct in regard to the functioning of the system. Consequently the limiting parameters depend on the substance. The analysis aims at identifying the parameters of the model that contributes to the highest variations in the result, and at indicating the variability in the sensitivity.

1) *Methodology for the sensitivity analysis*. As introduction, the methodology for the sensitivity analysis is presented.
2) *Sensitivity analysis.* In a first analysis, the sensitivity analysis is performed for each transfer rate building the model.
3) *Sensitivity analysis* of full model. In a final step, the analysis is performed for the full resolution.
4) *Discussion.* According to these different points of analysis, main inputs are identified and their contributions to the variability of the system are discussed. In particular, the analysis aims at highlighting which are the most important factors among those describing the environmental and plant system, those characterizing the substances, and those determining the dynamic evolution of the system.

### 6.1.1 Methodology for the sensitivity analysis

The sensitivity analysis consists of evaluating the effect on the output of a change in an input. The present analysis is performed on the basis of three complementary approaches: the effect of a fixed change in the input, the effect of a change specific to the uncertainty of the input, and the effect of a change in input value from its minimum to its maximum across all substances. The short list of substances applied in wheat is used for the analysis.

In accordance with the classical methodology, the effect on the output due to a change in an input is measured by the sensitivity and expressed by the following equation:

$$S = (\Delta output / output) / (\Delta input / input) \qquad 138$$

with S the sensitivity, $\Delta input$ the change in the input and $\Delta output$ the resulting effect on the output. This method is applied for the first and second steps of the analysis described hereafter.

In the first step, a fixed change in the input by 0.1% is applied. The results of the tested substances are summarized by the median on all substances of sensitivity values and the

corresponding minimum and maximum. The evaluation is carried out for the main transfer rates (source to plant transports) and for the full model, as a function of main parameters.

The evaluated processes and the full model are not built with strictly linearly multiplicative parameters and high variations in sensitivity are expected between substances. This approach evaluates the linearity level of the sensitivity within the substances. Only the multiplicative parameters within a linear relation have a sensitivity of 1 or –1 and do not show any variation between substances. This analysis focuses strictly on the relative variation of the model as a function of a change in a parameter. This first part of the sensitivity analysis is carried out as preliminary step for the uncertainty analysis described and performed subsequently (Chapter 6.2 Uncertainty analysis) according to a method applied to multi-media models (MacLeod, 2002, Morgan and Henrion, 1990).

In the second step of the sensitivity analysis, the change of input is based on a factor identified specifically to each parameter, the confidence factor. This factor is related to the standard deviation of the parameter and describes its potential variations. The confidence factor is applied in this step of the sensitivity analysis in order to take into account the level of variation around the parameter, opposite of the constant relative change in the input applied before. The confidence factor is presented in detail in the Chapter 6.2 Uncertainty analysis, and the specific values for the parameters are given in Table 18 of that chapter. Sensitivity is calculated similarly to the preceding step (equation 138). Additionally the minimum and maximum outputs obtained of a change of input based on the confidence factor are given in relative value to the primary output. This later result, given for the full model only, is used as a first evaluation of uncertainties.

The parameters of the model do not vary all according to the same scale. The third sensitivity analysis tests the range of variation to be expected due to the potential absolute variation of each parameter. The variation of the parameters describing the substances and the system (plant, soil, etc.) was partly analysed in the description of the single processes. This new analysis aims at identifying the maximum output variation according to the minimum value or the maximum value present within parameters, on all substances. These values are easily obtained for the parameters describing the substances. The variations of parameters describing the system are less simple to identify systematically. Some parameters evolve according to the crop development, from which minimum and maximum values are obtained. Other parameters are constant in accordance to the present case study. For these parameters, without any variation, a minimum and maximum value is calculated by using the confidence factor as a multiplying and dividing factor, to obtain the minimum and maximum values respectively. The evaluation is applied for each substance by replacing the original input value by the maximum and the minimum on all substances and by identifying the maximum effect on the outputs. The transfer rates and the full model are evaluated. The outputs obtained from minimum and maximum values of the parameter are expressed in relative value to the original output. The maximum relative difference in output represents the range of outputs potentially covered at each parameter level.

The results of the three steps of analysis are presented and interpreted commonly in the next chapters.

### 6.1.2 Sensitivity analysis of transfer rates

The sensitivity analysis gives very similar results by applying a fixed factor (0.1%) or a varying factor (confidence factor). This similarity underlines within the considered range defined by the confidence factor that non-linear relations do not lead to significantly different results from linear approximation. On the other side, the interpretation is adequate if possibility is given to put in evidence the levels of sensitivity and the differences in sensitivity between substances. Consequently interpretation is made principally on the sensitivity given by the constant factor, which results will be used in the uncertainty analysis, and on the maximum difference in relative output. Detailed results of analysis are given in Appendix E (E.1 Sensitivity analysis: change in input by 0.1% and E.2 Sensitivity analysis: maximum relative output).

The sensitivity analysis of each transfer rate in chapter 6.1.2 is a very detailed analysis; this iterative evaluation helps mainly to understand of the relative role and significance of each parameter. More attention should be given to the sensitivity analysis of the full model presented subsequently in chapter 6.1.3, as it the basis for the discussion of the sensitivity analysis and as it initiates the uncertainty analysis.

#### *6.1.2.1 Transfers between air and plant*

Table 10 presents the results of the sensitivity analysis for the transfer rate between air and leaf ($k_{al}$). This transfer rate is proportional (with a S value of 1) to the leaf area index (LAI) and the rate of conductance ($G_{al}$), and inversely proportional (with a S value of -1) to the volume of air ($V_a$). The growth of leaf area index ($T_{lai}$) shows a high sensitivity, but with a low variation between substances. On the contrary, the fraction of area with stomata ($A_s$) shows a lower sensitivity, but with an important variation between substances, with a minimum sensitivity by 1E-10 and a highest by 9.1E-01. This variation of sensitivity depends on the dominating transfer process: the sensitivity is high for substances with high stomatal transfer and low for substances with high cuticular transfer. This variation underlines the necessity to consider both transfer processes. The plant and air parameters produce a maximum relative difference in output of some about tent percents.

The partition coefficients, as characteristics for the substances behaviour, show a very large range between maximum and minimum sensitivity results. A high maximum relative difference in the transfer rates is observed between substances, as expected. The partition coefficients of a part of the tested substances generate a low sensitivity, mainly in the cases with the boundary layer as limiting factor.

The sensitivity values of transport parameters show a higher variation between substances for the cuticular permeation than for the diffusion processes (stomata layer $l_s$ and boundary layer $l_b$). Permeation depends on the partition coefficient between n-octanol and water ($K_{ow}$), with a very high variability between substances, whereas the diffusion is related to the molecular weight (MW), less variable. The length of diffusion of the boundary layer ($l_b$) concerns all substances and the variation is low. The sensitivity to the diffusion length through stomata ($l_s$) is more variable, as the process may be dominated by the cuticular pathway.

The effects of parameters in relation to the plant dynamic development (time duration $t_d$, leaf area index LAI and growth of leaf area index $T_{lai}$) is sufficiently high to consider these factors

as determinant, as indicated by their sensitivity and the difference of outputs between minimum and maximum input.

Table 10. Sensitivity analysis of transfer rate from air to leaf ($k_{al}$), as a function of main parameters of the model. Median, minimum and maximum sensitivity for a change in input by 0.1%, median sensitivity for a change in input by factor equal to the confidence factor and by a factor equal to the inverse of the confidence factor, maximum relative difference in output due to a change in input (%). Results of the short list of substances used in wheat.

| | Change in input by 0.1% | | | Change in input by factor CF | Change in input by factor 1/CF | Maximum relative difference |
|---|---|---|---|---|---|---|
| $k_{al}$ | median | minimum | maximum | | | |
| Plant and air | | | | | | |
| LAI | 1 | | | | | 119 |
| $V_a$ | -1 | | | | | 150 |
| $T_{lai}$ | 3.0E+00 | 2.9E+00 | 3.0E+00 | 3.4E+00 | 2.6E+00 | 135 |
| $A_s$ | 1.2E-02 | 1.4E-10 | 9.1E-01 | 1.2E-02 | 1.2E-02 | 109 |
| Partition coefficient | | | | | | |
| $K_{aw}$ | -7.5E-02 | -5.7E-01 | -4.1E-05 | -4.5E-02 | -1.2E-01 | 1324 |
| $K_{ow}$ | 5.3E-02 | 2.9E-05 | 4.0E-01 | 3.3E-02 | 8.1E-01 | 968 |
| Transport | | | | | | |
| $G_{al}$ | 1 | | | | | 2275 |
| $P_c$ | 7.5E-02 | 4.1E-05 | 5.7E-01 | 4.7E-02 | 1.2E-01 | 968 |
| $D_a$ | 9.3E-01 | 4.3E-01 | 1.0E+00 | 8.8E-01 | -1.5E+00 | 300 |
| MW | -4.6E-01 | -5.0E-01 | -2.1E-01 | -4.3E-01 | -5.0E-01 | 181 |
| $l_s$ | -1.2E-02 | -9.0E-01 | -1.4E-10 | 8.1E-03 | -1.8E-02 | 144 |
| $l_b$ | -7.1E-01 | -1.0E+00 | -7.6E-02 | -5.2E-01 | -9.4E-01 | 150 |
| Time | | | | | | |
| $t_d$ | 1.2E+00 | 8.7E-01 | 2.0E+00 | 1.3E+00 | 1.2E+00 | 251 |

#### *6.1.2.2 Transfers between soil and plant*

The advective uptake with the xylem sap to root and to stem (Table 11) depends directly on the active flux ($Q_{xy}$), on the Transpiration Stream Concentration Factor (TSCF) and on the partitioning of the substance between bulk soil and soil water ($K_{bw}$). This latter factor explains a large part of the differences in outputs between substances. It is determined by parameters with a high sensitivity: the partitioning between organic carbon and water ($K_{oc}$), the density of soil ($r_{sm}$) and the organic content of soil (OC).

The TSCF, derived from the partition coefficient between n-octanol and water ($K_{ow}$), is the other important partitioning parameter. A minimum TSCF was admitted for $K_{ow}$ upper and lower than a limited range in the model development. The minimum threshold for TSCF reduces effectively the differences between substances. The maximum relative difference is 3.9 E+03 % in case of threshold and 6.6E+04 % in absence of limit, based on the set of tested substances. As this higher difference is given by lower transfer rates for some substances, the consequence of this assumption may result in an overestimation of the transfer for some substances. This assumption will be further analysed in the evaluation of the full model and in the discussion of this chapter.

The flux of sap ($Q_{xy}$) is a determinant factor for the transport process. Consequently the biomass quantity and so the plant growth rate ($T_g$) are sources of high sensitivity and high effect on output. The parameters linked to the transfer of substance from air in the soil to the

plant (partition coefficient between air and water $K_{aw}$, soil porosity $s_{por}$) show a low sensitivity and low effect on the output and so are not determinant.

Table 11. Sensitivity analysis of transfer rate from soil to stem ($k_{sst}$), as a function of main parameters of the model. Median, minimum and maximum sensitivity for a change in input by 0.1%, median sensitivity for a change in input by factor equal to the confidence factor and by a factor equal to the inverse of the confidence factor, maximum relative difference in output due to a change in input (%). Results of the short list of substances used in wheat.

| | Change in input by 0.1% | | | Change in input by factor CF | Change in input by factor 1/CF | Maximum relative difference |
|---|---|---|---|---|---|---|
| $k_{sst}$ | median | minimum | maximum | | | |
| Plant and soil | | | | | | |
| $V_{sb}$ | -1 | | | | | 150 |
| $T_g$ | 2.2E+00 | 2.2E+00 | 2.2E+00 | 2.4E+00 | 2.0E+00 | 125 |
| $r_{sm}$ | -9.8E-01 | -1.0E+00 | -9.2E-01 | -6.6E-01 | -1.5E+00 | 150 |
| $s_{por}$ | -1.2E-09 | -2.5E-07 | 0 | -1.2E-09 | -1.2E-09 | 100 |
| $s_{volw}$ | -1.4E-02 | -8.4E-02 | -3.1E-06 | -1.4E-02 | -1.4E-02 | 101 |
| OC | -9.8E-01 | -1.0E+00 | -9.2E-01 | -6.6E-01 | -1.5E+00 | 150 |
| Partition coefficient | | | | | | |
| TSCF | 1 | | | | | 3910* |
| $K_{bw}$ | -1 | | | | | 2.7E+06 |
| $K_{aw}$ | -7.1E-10 | -1.5E-07 | 0 | -7.1E-10 | -7.1E-10 | 100 |
| $K_{ow}$ | 0.0E-00 | -8.3E-01 | 3.2E-01 | -1.5E-02 | -1.5E-02 | 450 |
| $K_{oc}$ | -9.8E-01 | -1.0E+00 | -9.2E-01 | -4.0E-01 | -2.4E+00 | 2.7E+06 |
| Transport | | | | | | |
| $Q_{xy}$ | 1 | | | | | 106 |
| Time | | | | | | |
| $t_d$ | 8.7E-01 | 6.1E-01 | 1.4E-00 | 9.2E-01 | 8.2E-01 | 191 |

*6.6E+04 in case TSCF non limited

Diffusive transport between soil water and root ($D_{woO2}$) represents the more relevant transport process according to the sensitivity results of related parameters (Table 12). The transport in the xylem ($Q_{xy}$) show lower sensitivity results and low range of difference between outputs. The transfer rate from soil to root by diffusion depends directly on the plant parameters (surface root $A_r$, diffusion length $l_{ro}$), on the soil volume ($V_{sb}$), on the partitioning between bulk soil and soil water ($K_{bw}$), and on the diffusion coefficient determined for soil to plant. The latter parameter is composed of two diffusion coefficients, from water filled pores ($D_w$) and from air filled pores ($D_a$). The process from water-filled pores causes the main source of sensitivity as already described in the processes description. The transport by diffusion from air in the soil (logically) shows lower sensitivity results and lower relative change in outputs between substances. Similarly to the transfer from soil to stem, the effect of soil parameters results mainly from the presence of water fraction in the bulk soil. Variations in the porosity of the soil ($s_{por}$) and in the fraction of water filled pores ($s_{volw}$) cause an important variation in the transfer rates. The processes in relation to air vary greatly according to the type of substance, but induce minor sensitivity of the process compared to diffusion in water. Time ($t_d$) and plant growth rate ($T_g$) also show an important contribution to the sensitivity of this transfer rate.

Table 12. Sensitivity analysis of transfer rate from soil to root ($k_{sr}$), as a function of main parameters of the model. Median, minimum and maximum sensitivity for a change in input by 0.1%, median sensitivity for a change in input by factor equal to the confidence factor and by a factor equal to the inverse of the confidence factor, maximum relative difference in output due to a change in input (%). Results of the short list of substances used in wheat.

| | Change in input by 0.1% | | | Change in input by factor CF | Change in input by factor 1/CF | Maximum relative difference |
|---|---|---|---|---|---|---|
| $k_{sr}$ | median | minimum | maximum | median | median | |
| Plant | | | | | | |
| $V_{sb}$ | -1 | | | | | 150 |
| $T_g$ | 2.2E+00 | 2.2E+00 | 2.2E+00 | 2.4E+00 | 2.0E+00 | 125 |
| $A_r$ | 9.3E-01 | 8.7E-01 | 9.7E-01 | 9.3E-01 | 9.3E-01 | 119 |
| $l_{ro}$ | -9.3E-01 | -9.7E-01 | -8.7E-01 | -6.2E-01 | -1.4E+00 | 149 |
| $r_{sm}$ | -9.8E-01 | -1.0E+00 | -9.2E-01 | -6.6E-01 | -1.5E+00 | 150 |
| $s_{por}$ | -1.8E+00 | -1.9E+00 | -1.9E-01 | -1.5E+00 | -2.0E+00 | 120 |
| $s_{volw}$ | 2.9E+00 | 1.4E+00 | 3.2E+00 | 3.3E+00 | 2.6E+00 | 136 |
| OC | -9.8E-01 | -1.0E+00 | -9.2E-01 | -6.6E-01 | -1.5E+00 | 150 |
| Partition coefficient | | | | | | |
| $K_{bw}$ | -1 | | | | | 2.7E+06 |
| $K_{aw}$ | 9.4E-04 | 2.0E-08 | 2.9E-01 | 9.7E-04 | 9.7E-04 | 146 |
| $K_{ow}$ | 0.0E+00 | -2.7E-02 | 2.3E-02 | 1.3E-03 | 6.2E-03 | 109 |
| $K_{oc}$ | -9.8E-01 | -1.0E+00 | -9.2E-01 | -4.0E-01 | -2.4E+00 | 2.6E+06 |
| TSCF | -3.2E-02 | -9.1E-02 | -2.1E-03 | -3.2E-02 | -3.2E-02 | 109 |
| Transport | | | | | | |
| $Q_{xy}$ | 7.1E-02 | 2.5E-02 | 1.3E-01 | 7.1E-02 | 7.1E-02 | 101 |
| $D_w$ | 9.0E-01 | 6.0E-01 | 9.7E-01 | 9.0E-01 | 9.0E-01 | 295 |
| $D_a$ | 9.7E-04 | 2.0E-08 | 2.9E+01 | 9.7E-04 | 9.7E-04 | 157 |
| MW | -4.6E-01 | -4.9E-01 | -4.4E-01 | -4.3E-01 | -5.0E-01 | 192 |
| Time | | | | | | |
| $t_d$ | 8.7E-01 | 6.1E-01 | 1.4E+00 | 9.2E-01 | 8.2E-01 | 191 |

### *6.1.2.3 Transfers between formulation deposit and leaf*

The transfer from formulation deposit ($k_{fdl}$) is highly dependent on the partition coefficient between cuticle and formulation deposit given by the partition coefficient between n-octanol and water ($K_{ow}$), with a high sensitivity and a large difference between outputs (Table 13). The transport process is also submitted to high sensitivity due to the molecular volume (MV) and the size selectivity of the cuticular membrane ($\beta$). Namely these parameters intervene as exponential factors in the equation. Low variation is observed in the sensitivity between substances, which underlines the rather linear contribution for the parameters involved in this process.

Table 13. Sensitivity analysis of transfer rate from surface deposit to leaf ($k_{fdl}$), as a function of main parameters of the model. Median, minimum and maximum sensitivity for a change in input by 0.1%, median sensitivity for a change in input by factor equal to the confidence factor and by a factor equal to the inverse of the confidence factor, maximum relative difference in output due to a change in input (%). Results of the short list of substances used in wheat.

| | Change in input by 0.1% | | | Change in input by factor CF | Change in input by factor 1/CF | Maximum relative difference |
|---|---|---|---|---|---|---|
| kfdl | median | minimum | maximum | | | |
| Plant and formulation deposit | | | | | | |
| LAI | 1 | | | | | 119 |
| Vfd | -1 | | | | | 235 |
| Tlai | 1.7E+00 | 1.6E+00 | 2.2E+00 | 1.9E+00 | 1.5E+00 | 124 |
| Partition coefficient | | | | | | |
| Kow | 1 | | | | | 4.3E+09 |
| Transport | | | | | | |
| k*0 | 1 | | | | | 300 |
| MV | -4.6E+00 | -7.0E+00 | -1.8E+00 | -3.7E+00 | -5.7E+00 | 1.9E+04 |
| β’ | -4.6E+00 | -7.0E+00 | -1.8E+00 | -3.7E+00 | -5.7E+00 | 190 |
| Time | | | | | | |
| td | 1.2E-00 | -8.7E-01 | 2.0E+00 | 4.3E+00 | 1.2E+00 | 251 |

### *6.1.2.4 Transfers between plant compartments*

As the transfer processes between leaf and stem respectively between stem and leaf depend on analogous parameters, the results of the sensitivity analysis are the same (Table 14). The transfer rates between plant compartments depend highly on the partition coefficient between plant tissue and water (xylem $K_{stxy}$ and phloem). The highest sources of sensitivity and variability range in outputs come from the partition coefficient between n-octanol and water ($K_{ow}$), and variations between substances may be high. The composition of the tissue plays also a role due to the following parameters: correction for difference between lipid and n-octanol ($b_{st}$), water content ($w_{st}$) and lipid content ($l_{st}$).

Table 14. Sensitivity analysis of transfer rate from stem to leaf ($k_{stl}$) and of transfer rate from leaf to stem ($k_{lst}$), as a function of main parameters of the model. Median, minimum and maximum sensitivity for a change in input by 0.1%, median sensitivity for a change in input by factor equal to the confidence factor and by a factor equal to the inverse of the confidence factor, maximum relative difference in output due to a change in input (%). Results of the short list of substances used in wheat.

| | Change in input by 0.1% | | | Change in input by factor CF | Change in input by factor 1/CF | Maximum relative difference |
|---|---|---|---|---|---|---|
| $k_{stl}$ $k_{stl}$ | median | minimum | maximum | | | |
| Plant | | | | | | |
| $V_{st}$ | -1 | | | | | 120 |
| $b_{st}$ | -5.3E+00 | -1.2E+01 | 2.7E-03 | -4.2E+00 | -6.5E+00 | 294 |
| $w_{st}$ | -4.1E+00 | -5.0E+00 | -4.0E+00 | -4.1E+00 | -4.1E+00 | 150 |
| $l_{st}$ | -8.9E-01 | -1.0E+00 | -2.0E-04 | -8.2E-01 | -9.7E-01 | 110 |
| Partition coefficient | | | | | | |
| $K_{stxy}$ | -1 | | | | | 3.6E+05 |
| $K_{ow}$ | -8.5E-01 | -9.5E-01 | -1.9E-04 | -3.7E-01 | -1.8E-+00 | 3.6E+05 |
| Transport | | | | | | |
| $Q_{xy}$ | 1 | | | | | 106 |

### 6.1.3 Sensitivity analysis of full model

The aim of analysing the total model is to evaluate the complex exchanges between the three source compartments and the main plant compartment, the stem. The sensitivity is first evaluated as a function of the transfer rates (Table 15) and then as a function of the main parameters (Table 16). This analysis is complemented by the evaluation of a change of input based on the confidence factor and accounting for the level of variation around the parameter (Table 17). The results of these three tables are all together analysed here, as the results tend to similar interpretations and do not need any detailed separate analysis.

The substances are first distributed within the system in very rapid processes, so that main evolution of processes is determined by removal processes. The mass in the stem is consequently highly sensitive to all removal processes ($k_{stot}$, $k_{atot}$, $k_{fdtot}$, $k_{rtot}$, $k_{sttot}$, $k_{ltot}$). A high sensitivity is also observed for the degradation in plant ($k_{pdeg}$) and for the time between spray and harvest ($t_d$). The transport processes from the different sources of substance to the plant ($k_{al}$, $k_{fdl}$, $k_{sst}$) and the degradation in the sources ($k_{adeg}$, $k_{sdeg}$, $k_{fddeg}$) show similar values of sensitivity. The exchanges between leaf and stem are important factors of variation between substances for the accumulation in the stem, with a rather high sensitivity.

The maximum relative difference in outputs is the highest for the transfer from air to the leaf ($k_{al}$ and $k_{la}$), with a high sensitivity for some substances. This underlines the high potency of relevant exchanges between air and plant for a part of substances, but also the negligible transfer to be expected from this source for other substances. The transfer back from plant to air ($k_{la}$) has also a high maximum relative difference in outputs, but lower than the difference due to the transfer from air to leaf ($k_{al}$). Both sensitivity results have to be interpreted in parallel, as the exchange between both compartments is a diffusive process, depending on concentrations equilibrium.

Transfer rates with the root ($k_{rs}$, $k_{rtot}$, $k_{sr}$) show a high variation of sensitivity between substances and the maximum difference between outputs is among the lowest values, indicating the possibility of ignoring this plant compartment, in the case of grain crops.

Table 15. Sensitivity analysis of mass accumulated in the stem, as a function of main transfer rates of the model. Median, minimum and maximum sensitivity for a change in input by 0.1%, maximum relative difference in output due to a change in input (%). Results of the short list of substances used in wheat.

| | Change in input by 0.1% | | | Maximum relative difference |
|---|---|---|---|---|
| Stem | median | minimum | maximum | |
| Soil | | | | |
| $k_{sst}$ | 5.7E-02 | 2.3E-04 | 9.5E-01 | 2.0E+04 |
| $k_{sr}$ | 1.0E-02 | 3.8E-09 | 3.1E+00 | 2.5E+02 |
| $k_{sdeg}$ | -5.0E-02 | -3.5E+00 | -3.8E-04 | 3.6E+07 |
| $k_{stot}$ | -8.2E-02 | -6.9E+00 | -3.8E-04 | 1.7E+08 |
| Air | | | | |
| $k_{al}$ | 2.1E-01 | 3.8E-02 | 8.7E+00 | 1.8E+41 |
| $k_{adeg}$ | -7.0E-02 | -4.0E+00 | -6.7E-03 | 5.8E+03 |
| $k_{atot}$ | -2.1E-01 | -1.6E+01 | -3.9E-02 | 6.0E+04 |
| Formulation deposit | | | | |
| $k_{fdl}$ | 7.3E-01 | 1.7E-02 | 9.4E-01 | 7.7E+05 |
| $k_{fddeg}$ | -3.5E-02 | -6.6E-01 | -9.2E-04 | 3.5E+02 |
| $k_{fdtot}$ | -7.9E-01 | -1.0E+00 | -4.0E-02 | 5.5E+04 |
| Root | | | | |
| $k_{rs}$ | 1.0E-02 | 3.8E-09 | 3.1E+00 | 1.2E+04 |
| $k_{rtot}$ | -1.0E-02 | -3.1E+00 | -3.8E-09 | 2.9E+12 |
| Stem | | | | |
| $k_{stl}$ | 3.3E-01 | 1.7E-05 | 1.6E+01 | 3.8E+06 |
| $k_{sttot}$ | -2.3E+00 | -1.8E+01 | -6.4E-01 | 2.2E+21 |
| Leaf | | | | |
| $k_{lst}$ | 1.1E+00 | 9.4E-01 | 1.7E+01 | 1.8E+07 |
| $k_{la}$ | 3.2E-02 | 8.0E-06 | 8.2E+00 | 7.4E+15 |
| $k_{ltot}$ | -3.0E+00 | -2.3E+01 | -9.2E-01 | 3.3E+18 |
| Plant | | | | |
| $k_{pdeg}$ | -3.0E+00 | -8.0E+00 | -7.3E-01 | 2.6E+08 |
| Time | | | | |
| $t_d$ | -3.6E+00 | -2.6E+01 | 1.5E-02 | 5.8E+04 |

The sensitivity of the model due to substance parameters is characterized by a high variation (Table 16 and Table 17). The maximum relative differences in output produced by half-life in soil ($t_{0.5s}$) illustrate high variations between substances. This variation is logically also observed for half-life in plant ($k_{0.5p}$), extrapolated from half-life in soil. The median sensitivities of the partition coefficients are similar to the median values of the half-life parameters. Their sensitivity may even be positive or negative according to the substance. The variability between substances is particularly high for the partition coefficient between organic carbon and water ($K_{oc}$). The growth rate ($T_g$) of plant parameters appears as an important factor particularly combined with the time between spray and harvest ($t_d$).

The maximum relative difference of mass accumulated in the stem for the Transpiration Stream Concentration Factor (TSCF) is equal to 618% in case of minimum threshold, but is equal to 1948% without any limit, that is about a factor of 3 lower. Without any threshold, the lower TSCF corresponds to a lower transfer rate from soil to stem and consequently a lower accumulation in the stem. Consequently the difference between substances is enhanced. The pertinence of this threshold is discussed in the next chapter.

Table 16. Sensitivity analysis of mass accumulated in the stem, as a function of main parameters of the model. Median, minimum and maximum sensitivity for a change in input by 0.1%, maximum relative difference in output due to a change in input (%). Results of the short list of substances used in wheat.

| | Change in input by 0.1% | | | Maximum relative difference |
|---|---|---|---|---|
| Stem | median | minimum | maximum | |
| Plant | | | | |
| $T_g$ | 2.9E-01 | -3.9E+00 | 2.0E+00 | 1.4E+02 |
| LAI | 2.9E-02 | -6.9E+00 | 1.1E-01 | 1.6E+02 |
| $T_{lai}$ | 4.5E-01 | -2.0E+01 | 1.2E+00 | 5.2E+02 |
| $A_s$ | 5.1E-07 | -5.9E+00 | 3.4E-02 | 1.7E+02 |
| $l_s$ | -5.1E-07 | -3.4E-02 | 5.9E+00 | 8.4E+02 |
| $l_b$ | -5.9E-03 | -9.7E-02 | 5.5E-01 | 1.3E+02 |
| $V_{st}$ | 6.5E-01 | 1.1E-02 | 9.7E-01 | 1.2E+02 |
| $b_{st}$ | -7.5E-01 | -1.1E+01 | 1.5E+00 | 2.5E+02 |
| $w_{st}$ | -1.1E+00 | -1.1E+01 | 3.6E+00 | 2.4E+02 |
| $l_{st}$ | -1.8E-01 | -1.1E+00 | 4.1E-01 | 1.1E+02 |
| $A_r$ | 8.5E-06 | -1.7E-04 | 1.8E-03 | 1.0E+02 |
| $l_{ro}$ | -8.5E-06 | -1.8E-03 | 1.7E-04 | 1.0E+02 |
| Air | | | | |
| $V_a$ | -5.3E-02 | -1.6E-01 | 8.7E+00 | 1.8E+03 |
| Soil | | | | |
| $V_{sb}$ | -5.5E-02 | -7.1E-01 | -2.2E-04 | 1.3E+02 |
| $r_{sm}$ | -5.4E-02 | -6.9E-01 | -2.2E-04 | 1.3E+02 |
| $s_{por}$ | -1.3E-05 | -3.6E-03 | 2.3E-04 | 1.0E+02 |
| $s_{volw}$ | -3.9E-04 | -4.4E-02 | -1.3E-08 | 1.0E+02 |
| OC | -5.4E-02 | -6.9E-01 | -2.2E-04 | 1.3E+02 |
| Formulation deposit | | | | |
| $V_{fd}$ | -1.7E-02 | -3.3E-01 | 4.6E-02 | 1.2E+02 |
| $\beta$' | -4.7E-02 | -1.4E+00 | 2.0E-01 | 1.1E+02 |
| substances | | | | |
| $K_{aw}$ | -5.0E-03 | -3.8E-01 | 2.2E+00 | 8.7E+03 |
| $K_{ow}$ | -7.3E-02 | -1.4E+00 | 4.6E-01 | 3.5E+02 |
| $K_{oc}$ | -5.4E-02 | -6.9E-01 | -2.2E-04 | 4.7E+02 |
| TSCF | 5.6E-02 | 2.3E-04 | 7.4E-01 | 6.2E+02 |
| $K_{bw}$ | -5.5E-02 | -7.1E-01 | -2.2E-04 | 4.7E+02 |
| $K_{stxy}$ | 6.5E-01 | 1.1E-02 | 9.7E-01 | 1.2E+03 |
| MW | -8.0E-03 | -4.9E-02 | 3.2E+00 | 7.3E+02 |
| MV | -4.7E-02 | -1.4E+00 | 2.0E-01 | 1.5E+02 |
| $t_{0.5s}$ | 5.0E-02 | 3.8E-04 | 3.5E+00 | 3.6E+07 |
| $t_{0.5a}$ | 7.0E-02 | 6.7E-03 | 4.1E+00 | 5.8E+03 |
| $t_{0.5fd}$ | 3.5E-02 | 9.2E-04 | 6.6E-01 | 3.5E+02 |
| $t_{0.5p}$ | 3.0E+00 | 7.3E-01 | 8.1E+01 | 2.6E+08 |
| Transport | | | | |

| | Change in input by 0.1% | | | Maximum relative difference |
|---|---|---|---|---|
| Stem | median | minimum | maximum | |
| $G_{al}$ | 2.2E-02 | -6.9E+00 | 9.8E-02 | 4.6E+02 |
| $P_c$ | 6.9E-05 | -4.3E-01 | 1.9E-02 | 1.4E+02 |
| $D_a$ | 1.6E-02 | -6.4E+00 | 9.7E-02 | 1.1E+04 |
| $D_w$ | 8.0E-06 | -1.2E-04 | 1.8E-03 | 1.0E+02 |
| $k_{*0}$ | 1.7E-02 | -4.6E-02 | 3.3E-01 | 1.3E+02 |
| $Q_{xy}$ | 3.9E-01 | 8.6E-02 | 9.9E-01 | 1.1E+02 |
| $Q_{ph}$ | 8.4E-01 | 4.2E-01 | 1.0E+00 | 1.1E+02 |
| $t_d$ | -3.6E+00 | -2.6E+01 | 1.5E-02 | 5.8E+04 |

Table 17. Sensitivity analysis of mass accumulated in the stem, as a function of main parameters of the model. Minimum and maximum outputs obtained by a change of input based on the confidence factor given in relative value to the primary output. Results of the short list of substances used in wheat.

| | Output by a change input by confidence factor in relative value to primary output (%) | |
|---|---|---|
| Stem | minimum | maximum |
| Plant | | |
| $T_g$ | 6.9E+01 | 1.4E+02 |
| LAI | 5.0E+01 | 1.9E+02 |
| $T_{lai}$ | 1.1E+01 | 5.2E+02 |
| $A_s$ | 5.6E+01 | 1.7E+02 |
| $l_s$ | 7.2E+00 | 8.4E+02 |
| $l_b$ | 8.3E+01 | 1.3E+02 |
| $V_{st}$ | 9.1E+01 | 1.1E+02 |
| $b_{st}$ | 3.3E+01 | 2.5E+02 |
| $w_{st}$ | 3.0E+01 | 2.4E+02 |
| $l_{st}$ | 9.0E+01 | 1.1E+02 |
| $A_r$ | 1.0E+02 | 1.0E+02 |
| $l_{ro}$ | 1.0E+02 | 1.0E+02 |
| Air | | |
| $V_a$ | 1.3E+00 | 1.8E+03 |
| Soil | | |
| $V_{sb}$ | 7.6E+01 | 1.3E+02 |
| $r_{sm}$ | 7.6E+01 | 1.3E+02 |
| $s_{por}$ | 1.0E+02 | 1.0E+02 |
| $s_{volw}$ | 1.0E+02 | 1.0E+02 |
| OC | 7.6E+01 | 1.3E+02 |
| Formulation deposit | | |
| $V_{fd}$ | 8.6E+01 | 1.1E+02 |
| $\beta$' | 8.6E+01 | 1.1E+02 |
| substances | | |
| $K_{aw}$ | 1.2E+01 | 9.0E+02 |
| $K_{ow}$ | 2.1E+01 | 2.6E+02 |
| $K_{oc}$ | 5.5E+01 | 1.9E+02 |
| TSCF | 5.0E+01 | 2.1E+02 |
| $K_{bw}$ | 5.3E+01 | 2.0E+02 |
| $K_{stxy}$ | 4.1E+01 | 2.3E+02 |
| MW | 7.3E+01 | 1.4E+02 |
| MV | 8.6E+01 | 1.1E+02 |

| | Output by a change input by confidence factor in relative value to primary output (%) | |
|---|---|---|
| Stem | minimum | maximum |
| $t_{0.5s}$ | 6.3E+00 | 1.2E+03 |
| $t_{0.5a}$ | 4.5E-02 | 1.5E+03 |
| $t_{0.5fd}$ | 6.0E+01 | 3.5E+02 |
| $t_{0.5p}$ | 1.0E-02 | 3.6E+04 |
| Transport | | |
| $G_{al}$ | 1.8E-02 | 1.5E+04 |
| $P_c$ | 4.3E+01 | 1.4E+02 |
| $D_a$ | 2.3E-02 | 1.1E+04 |
| $D_w$ | 1.0E+02 | 1.0E+02 |
| $k_{*0}$ | 6.4E+01 | 1.3E+02 |
| $Q_{xy}$ | 3.4E+01 | 2.9E+02 |
| $Q_{ph}$ | 3.3E+01 | 3.0E+02 |
| $t_d$ | 5.6E+00 | 9.0E+02 |

### 6.1.4 Discussion

The sensitivity analysis highlights different points about the significance of plant and environmental parameters, the variability between substances, and the potential contribution of each transfer rate in the functioning of the system. An overview summarizes here the main elements put in evidence.

The need for a threshold in the case of high varying parameters was developed for the Transpiration Stream Concentration Factor. This query could also be raised for other partition coefficients. The plant parameters relating the composition of tissues are important sources of sensitivity. The aqueous and lipid fraction of plant tissue and the correction factor between plant lipid and n-octanol interact directly as determinant factors in the processes of transport and represent an important source of variability between substances. In the same order of influence, the soil parameters (partition coefficient between carbon and water, organic carbon content) play a similar role. The high variation between substances underlines the different mobility capacities in the system as a function of the partition coefficients. This variability is directly dependent from the very high variability of the basic partition coefficients between media (air, water, n-octanol, organic carbon). A possible limit of the variability range has been studied for the Transpiration Stream Concentration Factor. This threshold effectively results in a lower variability between substances. Besides the potential overestimation of substance accumulation in plant reaches a significant level. In other cases, an underestimation would also have been possible. Due to the importance of the partition coefficients in the model function, a threshold should be based on arguments systematically applicable for this parameter or from case to case as scientifically demonstrated. In accordance to these elements, the threshold for TSCF is not maintained in the final model.

No detailed processes have been described and developed for the functioning of environmental compartments, so that relatively few determining processes and parameters are involved. The transfer processes directed toward the plant, in particular the stem compartment, logically show the highest sensitivity. Additionally the variability of the parameters determining theses processes generates among the highest differences between outputs. In opposite, the transfers back from plant to environmental compartments (from leaf to air and from root to soil) are submitted to less variation between substances. This confirms

the low efficiency of feedback pathways previously discussed and that a cascade model without feedback could provide a good approximation (Chapter 3.5.3. Cascade of two compartments).

Since the substances have been initially transported and distributed within the system, main contribution to the system evolution is due to time and removal processes. Consequently these processes in the different compartments are source of high sensitivity and of differences between substances, as they decrease the accumulation capacity in the stem. As the root compartment represents only a two-sided exchange with the soil and since it is not a harvested plant part, it may not be considered for a wheat crop. Degradation half-life combined with time between application and harvest becomes the most important source of sensitivity among all parameters. The sensitivity results of degradation rate in plant highlight the need for precise values or best approximations for the determination of this parameter.

Next to removal processes, the sensitivity to elapsed time between application and harvest is also explained by the influence on plant parameters, especially through growth. The capacity of substance accumulation increases with the growth of leaf area. Increasing water transport in the xylem from soil to stem is also depending on the plant development. The sensitivity to elapsed time underlines the importance of the dynamic evolution of the system and of a dynamic resolution of the model.

Finally two additional external considerations have to be kept in mind in the analysis of the sensitivity of present system. A priori the influences of the climatic and local conditions can have a significant influence on sensitivity of substance behaviour. Additionally, the formulants of the plant treatment product aim at diminishing the variation between substances and consequently the sensitivity due to other parameters like climatic ones. These parameters are specifically not studied here and could be addressed when considering the whole multi-media model.

## 6.2 Uncertainty analysis

The uncertainty analysis aims at identifying the main sources of uncertainty among all parameters. The chosen methodology shall help the interpretation of the model by linking sensitivity to the uncertainty analysis. Since the uncertainty analysis is a continuation to the sensitivity analysis, main determining parameters for the functioning of the model have been already identified. The uncertainty analysis shall identify which of the limiting parameters contribute to the uncertainty of the transfer rates in the model, and to that of the final results. The model uncertainty due to a given input parameter is dependent on the model sensitivity to this parameter and on the uncertainty range of this parameter. Consequently, the analysis focuses on the determination of the specific uncertainty of the main input parameters, and then on their contribution to the uncertainty of transfer rates and of the harvest fraction.

The uncertainty is reliant on the high variation identified by the sensitivity analysis of the main parameters. It also depends on the deviation of the initial factors needed to characterise the parameters. A screening analysis is first performed on the transfer rates and on their contributions to the full model uncertainty. A complementary detailed analysis based on single substances is then performed in more details. The uncertainty analysis presented here includes the following parts:

1) Method for the uncertainty analysis

2) Uncertainty analysis of transfer rates
3) Uncertainty analysis of single substances
4) Discussion

### 6.2.1 Method for the uncertainty analysis

The uncertainty analysis is performed according to a method used by MacLeod (2002) and well described by Morgan and Henrion (1990), as an alternative to the Monte Carlo analysis that is often adopted in environmental modelling. The method is described as an approximate technique based on a Taylor series expansion of the function that relates input variables to outputs. Good correlations were obtained by MacLeod with Monte Carlo analysis. It first characterises the uncertainty of the input parameters and then determines the related output uncertainty.

#### *6.2.1.1 Uncertainty of input parameters*

Environmental models generally compute results from multiplicative factors. According to this, uncertainties are evaluated considering that the variance shows a lognormal distribution. Confidence factors are used as expressions of variance. A confidence factor implies that 95% of all values lie in the considered distribution range around the median:

$$probability\left\{\frac{\mu}{Cf} < X > Cf \cdot \mu\right\} = 0.95 \qquad 139$$

with μ as median and Cf as confidence factor. The determination of the confidence factor is a sensitive point. According to the above definition, the confidence factor is related to the standard deviation. This parameter can be determined from the geometric standard deviation, which is often available in literature for log normal distribution. It can also be estimated from minimal information characterising the parameter (Strom et al., 2000). The confidence factor (Cf) is equal to

$$Cf = e^{2\sigma} = GSD^2 \qquad 140$$

with σ the standard deviation and GSD the geometric standard deviation.

In the present study, the confidence factors of the input parameters are determined according to lists of assumed input confidence factors proposed as defaults for chemical, environmental and kinetics input parameters (MacLeod, 2002). Alternatively, standard deviations are determined according to different literature sources for the availability and the uncertainty of parameters in environmental modelling (Huijbregts et al., 2000; Schwartz 2000). These different sources were used to determine the confidence factors for input parameters needed for the present uncertainty analysis. As differences in the evaluation of the uncertainty can be observed between authors, the retained confidence factors are listed in Table 18 for the main inputs. Input parameters are supposed to follow a log normal distribution, which is realistic for chemical, environmental and kinetics input parameters, but not established for several descriptive environmental and plant parameters.

Table 18. Confidence factors for the substance parameters, plant and environmental inputs and transport data.

| Inputs | Confidence factor |
|---|---|
| Substance | |
| Partition coefficient air water | 2.5 |
| Partition coefficient n-octanol water | 2.5 |
| Partition coefficient organic carbon water | 2.5 |
| Molecular weight | 1 |
| Molecular volume | 1.1 |
| Half-life soil, plant, surface deposit, water and air | 3 |
| Plant | |
| Mass, volume, surface, density | 1.1 |
| Composition | 1.1 |
| Correction factor for plant lipid | 1.1 |
| Soil, air, surface deposit | |
| Volume, density | 1.5 |
| Porosity, fraction of water, air | 1.1 |
| organic carbon in soil | 1.5 |
| Transport | |
| Conductance, permeance, diffusion, flux | 3 |
| Diffusion length | 1.5 |
| Size selectivity | 1.1 |

#### *6.2.1.2 Output uncertainty*

The uncertainty of an output is evaluated according to the relative contribution of the confidence factors of the inputs according to the following equation (MacLeod, 2002):

$$Cf_0 = \exp[S_{I1}^2(\ln Cf_{I1})^2 + S_{I2}^2(\ln Cf_{I2})^2 + ...S_{In}^2(\ln Cf_{I1})^2]^{1/2} \quad 141$$

with $S_{In}$ the sensitivity to input n, as defined by equation 138, and $Cf_{In}$ the confidence factor of input n. The explicit way of uncertainty propagation and the possibility to identify the main uncertainty sources helps the interpretation of the processes and the model. Similarly to the performed sensitivity analysis, the uncertainty is carried out for the transfer rates and for the full model resolution.

In a first step, median results of the sensitivity analysis performed previously (Chapter 6.1.2 Sensitivity analysis) are used to give a rough overview of confidence factors to be expected for transfer rates and for the full model. Finally, single substances are analysed in detail for the determinant sources of uncertainty.

### 6.2.2 Uncertainty analysis of transfer rates

The results of uncertainty analysis for transfer rates are given in Table 19, with the list of determining inputs in term of contribution to uncertainty (>5% contribution to transfer rate

uncertainty). These results are indicative for the list of studied substances and based on median sensitivity values. High variation in the sensitivity analysis has been formerly demonstrated. This underlines the requirement to practice finer analysis at the substance level for more precise purposes.

Analysed parameters may be grouped as a function of the way they contribute to uncertainty. Partition coefficients and transport parameters are characterized by high confidence factors. Parameters describing the compartments (volume of the air $V_a$ and the soil $V_{sb}$, density of the soil $r_{sm}$) show high sensitivity levels. Some very specific inputs combine high values of sensitivity and of confidence factor, and are consequently identified as high sources of uncertainty for the transfer rate: size selectivity for transfer into leaf from formulation deposit ($\beta'_{fd}$), molecular volume (MV), correction factor for plant lipid ($b_{st}$). Plant parameters have a generally low contribution to uncertainty, except the xylem ($Q_{xy}$) and phloem ($Q_{ph}$) fluxes with high confidence factors and sensitivity levels.

Table 19. Confidence factors for the transfer rates and main inputs contributing (>5%) to the uncertainty.

| Transfer rate | Confidence factor | Determinant inputs |
|---|---|---|
| $k_{al}$ | 2.8 | $V_a$, $D_a$ |
| $k_{la}$ | 4.2 | $b_{st}$, $K_{aw}$, D |
| $k_{sdr}$ | 5.4 | A, l, V, r, OC, K, D |
| $k_{sxr}$ | 5.0 | $V_{sb}$, $r_{sm}$, OC, $K_{oc}$, $Q_{xy}$ |
| $k_{sst}$ | 5.1 | $V_{sb}$, $r_{sm}$, OC, $K_{oc}$, $Q_{xy}$ |
| $k_{rs}$ | 3.5 | $A_r$, $b_r$, $l_{ro}$, $K_{ow}$, $D_w$ |
| $k_{fdl}$ | 6.9 | $K_{ow}$, MV, $\beta'_{fd}$, $k_{*0}$ |
| $k_{lfd}$ | 7.1 | $K_{ow}$, $k_{*0}$, $\beta'_{fd}$, MV |
| $k_{stl}$ | 4.1 | $b_{st}$, $K_{ow}$, $Q_{xy}$ |
| $k_{lst}$ | 4.2 | $b_{st}$, $K_{ow}$, $Q_{ph}$ |
| $k_{deg}$ | 3.0 | $t_{0.5}$ |

### 6.2.3 Uncertainty analysis of the full model

A screening analysis of the full model based on transfer rates only helps to put in evidence main sources responsible for the uncertainty of the model. Results of confidence factors for mass accumulated in the stem are presented in Table 20, with the list of determinant inputs. Dissipation processes dominate the sensitivity of the full model. Additionally, half-life parameters have high confidence factors. Uncertainty level of the results is consequently highly depending on the degradation processes. The degradation rate for soil, also used as data source for the evaluation of the degradation in plant, is the dominating source of uncertainty. Distinction is made with and without the contribution of half-life, to get a more detailed analysis. The average overall confidence factor is 83 for accumulation in the stem. Neglecting the contribution of degradation rates, the confidence factor is much lower with a median value of 5.6. A detailed analysis is given hereafter with the analysis of single substances.

Table 20. Confidence factors for mass in the stem and mass in leaf and main inputs contributing (>5%) to the uncertainty propagation.

| Mass | Confidence factor | Determinant inputs |
|---|---|---|
| all transfer rates in the stem | 83 | $k_{pdeg}$, $k_{sdeg}$, $k_{lst}$, $k_{stl}$ |

| | | |
|---|---|---|
| transport processes without degradation rates in the stem | 5.6 | $k_{lst}$, $k_{stl}$ |

### 6.2.4 Uncertainty analysis of single substances

Sensitivity analysis and uncertainty analysis have been carried out for each single substance of the short list. The results condensed here in the uncertainty analysis itemize the preceding analysis with 13 precise cases. All detailed results of the sensitivity and uncertainty analysis are given in Appendix F. The results of the uncertainty analysis are summarised in Table 21. Each confidence factor (CF) is supplemented with a partial confidence factor* (CF*), determined by excluding the contribution of half-life factors to the uncertainty. This second value shall help the interpretation of the substances mobility by setting aside the dominating effect of degradation processes on the uncertainty results. CF levels lower than 10 open good perspectives to highlight effective differences between substances. Substances with a factor of uncertainty over 100 probably need better characterisation. For these substances, the partial CF* gives additional information on the origin of the uncertainty of the substance mobility. The difference between the total confidence factor and partial confidence factor* gives an overview on the importance of the uncertainty due to degradation processes.

On the basis of the set of substances studied here, the dominating contribution of half-life to the uncertainty is effectively confirmed. An interesting level of precision is obtained for the transfer processes (except trinexapac-ethyl, with a low harvest fraction and high CF and CF*). Highly limiting and uncertain inputs explain the particularly high levels of the partial confidence factor for some substances.

Table 21. Harvest fraction and confidence factors for a set of substances used in wheat. Two levels of uncertainty: total confidence factor CF, partial confidence factor CF* excluding uncertainty due to half-life inputs.

| | Harvest fraction | CF | CF* |
|---|---|---|---|
| Diflufenican | 2.3E-03 | 9 | 6 |
| Ioxynil | 1.1E-04 | 35 | 5 |
| Isoproturon | 1.2E-04 | 87 | 3 |
| Chlormequat | 4.7E-06 | 170 | 4 |
| Ethephon | 2.0E-06 | 8097 | 3 |
| Trinexapac-ethyl | 4.1E-10 | 70771 | 11649 |
| Deltamethrine | 1.3E-05 | 341 | 8 |
| Pirimicarb | 9.1E-03 | 6 | 4 |
| Teflubenzuron | 7.0E-04 | 46 | 7 |
| Azoxystrobin | 3.3E-05 | 142 | 3 |
| Chlorothalonil | 1.1E-02 | 7 | 3 |
| Cyproconazole | 3.2E-03 | 31 | 3 |
| Prochloraz | 4.2E-04 | 110 | 5 |
| Tebuconazole | 1.2E-02 | 7 | 3 |

The high contribution of half-life to the uncertainty may be understood by looking at the dynamic evolution in the confidence factor. The duration of the dynamic evolution of the system explains partly the high level of uncertainty due to these parameters. Figure 45 illustrates the propagation of the uncertainty for a substance (azoxystrobin). The uncertainty increases with time, according to the increasing importance of the degradation pathways on a long term. The time has limited effect on the uncertainty of the transport processes within the system which remain stable (in this case between 3 and 6). Only the precise analysis of the combination between sensitivity of transport and of degradation processes may give a satisfying interpretation to uncertainty propagation of each studied case.

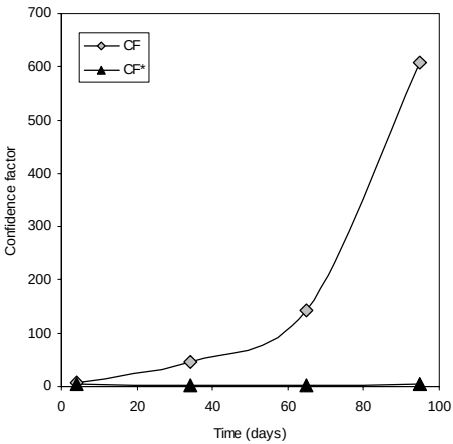



Figure 45. Evolution of the confidence factor (CF) and the partial confidence factor (CF*, without half-life contribution) of harvest fraction as a function of the time of the system. Case study of azoxystrobin.

Figure 46 illustrates the evolution and the confidence interval of grain fraction for azoxystrobin on the base of Figure 34, evolution of grain fraction from time of substance application to the harvest, and Figure 45, evolution of the confidence factor with the time. The uncertainty grows logically with the system evolution. Consequently, the result of harvest fraction is situated in an interval between $10^{-2}$ and $10^{-7}$ kg substance in harvest per kg applied. The way to interpret the high uncertainty level is discussed in the next chapter.

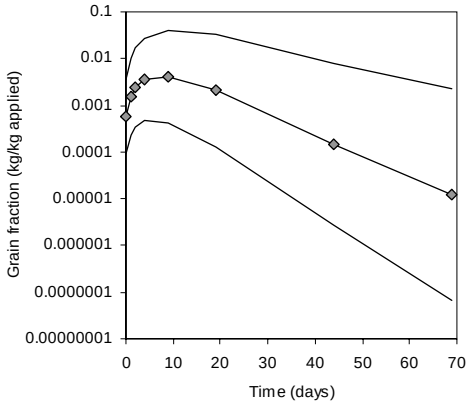
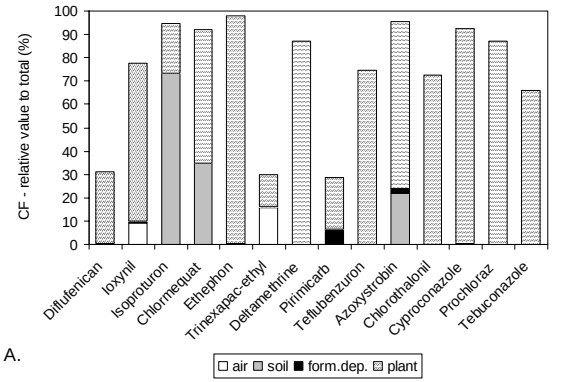



Figure 46. Evolution grain fraction and of the confidence interval as a function of the time of the system from substance application to the harvest. Case study of azoxystrobin.

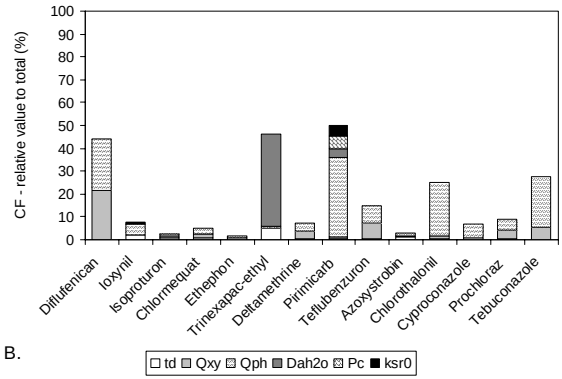
The contribution of the half-life to the confidence factor of the harvest fraction reaches between 30% and 98% of the total uncertainty (Figure 47). As the confidence factor for the single data of half-life are considered as identical, the importance of the uncertainty analysis corresponds to those of the sensitivity analysis. The half-life in plant is the main contribution to sensitivity and the uncertainty for the set of substances analysed. However, some substances are limited by degradation in environmental compartments, particularly degradation in soil.

Uncertainty due to transport inputs (conductance, permeance, diffusion, fluxes, and time duration) underlines the importance of transports within the plant, mainly xylem, but also phloem flux. The importance of plant internal fluxes indicates the necessity of precision in the identification of plant biomass (from which the transpiration and the phloem fluxes are identified) at the different stages growing crop. A better description of the xylem and phloem fluxes is also a potential improvement of the model, including the advective mobility of substance within these fluxes. According to the set of substances presented here, all routes may be limiting for a substance and contribute to the uncertainty of the model. This confirms the necessity to include all processes formerly identified.

The contribution of the partition coefficient at less than 2-3% is low compared to the transport factors (up to 40%). These factors have a specific confidence factor that is relatively high, but their sensitivity is not so high as it could be a priori expected. The time dynamic evolution of the model explains the low contribution of the equilibrium partition coefficients to the confidence factors. In a resolution at steady state, a higher importance of these factors would be observed.




A.

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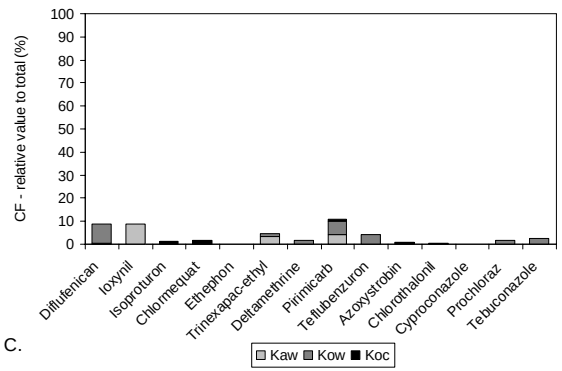
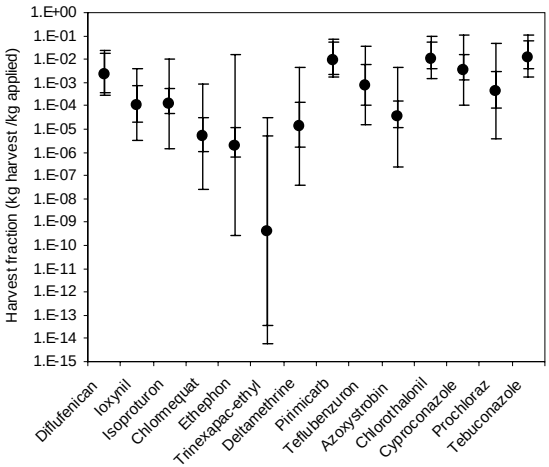



C.

Figure 47. Confidence factors of harvest fraction for the main parameters in relative value to the total. Results of the short list of substances used in wheat. A. Half-life values. B. Transport parameters. C. Partition coefficients.

Finally the combination of the harvest fraction value and the corresponding uncertainty gives the precision of the results and enables discussion about how differences between substances are significant (Figure 48). Many apparent differences within the set of tested substances are not significant due to the high uncertainty level. Later applications have the highest harvest fraction (chlorothalonil, prochloraz, tebuconazole), though differences are often significant only according to the partial confidence factor. The long residence time of the substances in soil mainly explains the high values for the herbicides. However, precise tendencies may be put in evidence according to the partial confidence factors. Growth regulators show low values, although a high uncertainty. The tendencies indicate possibilities of substitutions within types of substances, according to the fate of substance. However, complement analysis




of the toxicity is still needed to take final decision on substitutions.

Figure 48. Harvest fraction and confidence factors for a set of substances used in wheat. Two levels of uncertainty: total confidence factor CF, partial confidence factor CF* excluding uncertainty due to half-life inputs.

### 6.2.5 Discussion

The uncertainty analysis underlines the following elements: the main role played by the half-life of the substance and its propagation due to the duration of the system, the relative acceptable uncertainty level of the transfer processes, the need of more precise data characterizing the substances, and the benefits and limitations of the adopted methodology. These elements are discussed hereafter.

The confidence factors of the final results are high compared to the uncertainty of single transfer rates used for the resolution of the system. The main source of uncertainty comes from the half-life and due to the elapsed time between application and harvest. The analysis has shown that the propagation of uncertainty is due to the system evolution, especially in relation to the exponential increase in confidence factor with time. The high level of

uncertainty due to the high sensitivity level of degradation processes and uncertainty of half-life is therefore no more surprising. Improvement in the availability of reliable half-life is only more imperative.

The distinction can be made between uncertainty due to degradation of substance and uncertainty due to exchanges between compartments. For this purpose a partial confidence factor* has been identified. The processes in the compartments nearest to the targeted compartment logically show high sensitivity and are sources of uncertainty. This confirms the possibility to simplify the system resolution to the main exchanges directly linked to the receiving plant compartment and the need for good understanding and description of these specific processes. Transport processes from soil to plant, and within the plant, are lasting processes and determinant for many substances. Single parameters for the transfers from the air or from the formulation deposit are highlighted by some substances. Finally all pathways of transport from the environment to the plant appear to be determinant for specific substances in relation to high variability in the substance characteristics. The interpretation of uncertainty should use both the confidence factor and the partial confidence factor in accordance with the influence of dynamic evolution of the system.

Among the input parameters, mainly data for the characterization of substances show a large confidence factor. Once uncertainty due to half-lives is excluded, the environmental partition coefficients may be important parameters with a high variability between substances. Related to this, the parameters determining the composition of a compartment (plant tissue composition) and consequently the partitioning behaviour in it are also important. The molecular weight and molecular volume (even if extrapolated) may have a significant contribution to the uncertainty. Source parameters for transport mechanisms (diffusion coefficient, mobility) are characterized by a high uncertainty, and their sensitivity effect is relatively variable between the substances. These parameters may be determinant for the uncertainty level of some substances results.

Depending on the model complexity, the uncertainty analysis is time-consuming to enable a pertinent conclusion. The methodology presented here has the advantage to explicitly show the key points. It allows a good understanding of the source of uncertainty, as a function of parameters sensitivity and data precision. However, part of the assumed confidence factors need to be controlled and additional specific ones are needed. The effective availability of these data is often deficient, or the search for it is time-consuming. However, the simple application of the method, using some shortcomings, gives a pertinent possibility to provide a rapid overview on the results uncertainty.

## 6.3 Comparison with measured data of residues in wheat

Experimental validation of the final aggregated plant model is limited due to the complexity of the system, to simplifications in expressions of processes undertaken for wide-ranging conditions (local conditions, weather) and to the difficulty to isolate specific points issues in the model construction. However, the validation by experimentation procedure may be interesting to test the accuracy and the order of magnitude of the calculated harvest fractions, and to identify limits and applicability of the model. According to Schwartz (2000), the comparison of measured field data and computed results mostly shows a low accuracy (higher than a factor 10). Models often have to be applied with adjustments to limit high errors in predictions. In the present study, an experiment was conducted on residues in wheat grains.

Measured data of residue evolution have been used to assess the two main phases of the fate: the initial concentrations in plant and the dissipation process into the plant.

Distribution of the substance is the result of a process; it is not a process itself, but an important factor. It determines the initial conditions as a starting point for the evolution of the system. Specific methodologies have been discussed to describe this process in Chapter 3.3 - Initial conditions of the system. Especially the effects of climatic spraying conditions were underlined according to the losses (drift) of substance. The model is considered to function for normalised conditions without climatic variations and under good agricultural practices. However, the possible high loss due to drift can be an important source of variations. Considering this potential source of high variation, one objective of the experimentation focuses on ensuring a consistent and uniform spraying for all substances.

An important parameter is missing in the characterisation of the substances: the substance degradation in plant. As this data is not available, an indicative value is calculated from experimental data to be compared with data available for other media (soil, water and air) and discussed according to the extrapolation made from half-life in soil and used for the functioning of the model.

Finally, the experimental part is needed to provide an overview of the overall accuracy of the results given by the model, also providing experience in the analytical evaluation of residues.

This experimental step was carried out by measuring the evolution of residue in a trial with wheat crop. Experimental work was conducted to measure pesticide residues in wheat, Analytical developments and measures were carried out by the laboratory of Cecotox, EPF-Lausanne, F. De Alencastro and D. Grandjean. Two studies by Chatelain (1999) and by Cao (2001) detail these experimentations. The main experimental results are presented hereafter. Measures of initial concentrations and residues in harvest are compared with the values calculated by the model. Determined values of half-life in plant are compared with data from literature. Weiss (2001) made a first comparison between the measures and the computed concentrations.

### 6.3.1 Material and method

Data were collected to identify the interception of treatment product by plant and the evolution of residue till the harvest. Six active substances were applied on wheat as a late treatment, one month before harvest: four fungicides (Chlorothalonil, Cyproconazole, Prochloraz, Tebuconazole) and two insecticides (Deltamethrine, Pirimicarb). Measures of residue in plant were made regularly from the day of treatment till the harvest. Data of initial concentrations and residue evolution were then compared with calculated value obtained by the model. Main characteristics of the substances for running the model are given in  and Table 22 and Table 24.

Table 22. Substance, mass sprayed ($M_s$), molecular weight (MW), molecular volume (MV), air/water partition coefficient (log $K_{aw}$), n-octanol/water partition coefficient (log $K_{ow}$), organic carbon/water partition coefficient (log $K_{oc}$).

| Substance | $M_s$ (g/m2) | MW g/mol | MV mL/mol | log $K_{aw}$ - | log $K_{ow}$ - | log $K_{oc}$ - |
|---|---|---|---|---|---|---|
| Chlorothalonil | 0.15 | 266 | 152 | -4.9 | 1.9 | 2.9 |
| Cyproconazole | 0.008 | 292 | 229 | -7.5 | 2.9 | 2.6 |
| Prochloraz | 0.03 | 377 | 260 | -6.2 | 4.1 | 3.4 |
| Tebuconazole | 0.025 | 308 | 248 | -8.2 | 3.7 | 3.0 |
| Deltamethrine | 0.00075 | 505 | 321 | -4.9 | 5.4 | 6.4 |
| Pirimicarb | 0.0075 | 238 | 189 | -7.5 | -1.3 | 2.6 |

Treatment products were diluted in water for an application rate of 300 l/ha. The substances were applied separately on six isolated experimental plots ($10m^2$) with a manual field sprayer, in a field of the experimental domain of Changins-Nyon. The application was carried out in the morning by favourable climatic conditions. The wheat crop was cultivated in accordance with good agricultural practices.

The first wheat sample was taken in the late afternoon of the same day of application. In order to avoid a contaminated sample caused by the drift from the other plots during application, all the samples were taken from the middle of the plot. Three samples of wheat ears were harvested for each plot and were kept in deep freeze at $-30^oC$. Additional samples were harvested to determine the fresh and dry plant biomass. Samples of ears were collected on the $1^{st}$, $7^{th}$, $24^{th}$ and $30^{th}$ (harvest) day for residue analysis. During the entire test, analyses were performed on complete unwashed ears.

The samples were crushed into powder with a solvent medium, so that the solvents penetrated well into plant cells. Most of the investigated pesticides are quite polar, so that a solvent sufficiently miscible in water such as methanol was used for the extraction from plant materials. A method based on liquid to liquid partitioning was used for the clean up process. Evaporating to dryness was performed before injecting at gas chromatograph.

All the pesticides were applied at quite high concentration level and the first samples were analyzed short after application, to avoid measuring very low concentrations of pesticides. The final extracts were diluted in isooctane up to 20 or 30 ml, and 20 times more for chlorothalonil. More advanced analysis was required for samples collected at the harvest time, especially for cyproconazole and tebuconazole, that are difficult to detect at low concentration. Most of the matrices could be analyzed using GC-ECD. This method was applied successfully with chlorothalonil, prochloraz and deltamethrine which contain a reasonable amount of halogens and also aromatic groups. This was also possible for tebuconazole and cyproconazole despite the high detection limits. For this reason a standard was injected before and after each sample. Exceptionally, pirimicarb was determined by GC-PFPD (Pulse flame photometric detector).

All standards materials with certified purity > 98% were supplied by Dr. Ehrenstorfer GmbH. Stock solutions were prepared by dissolving the pesticides in acetone to obtain concentrations of about 1mg/ml and further dilutions were made with isooctane. Solvents (methanol, dichloromethane, isooctane, n-hexane) were all super purity solvent (ROMIL). Anhydrous reagent grade sodium sulphate (Merck) was heated at $400^oC$ for 3h and cooled in a dessicator.

Sodium chloride PA reagent grade was supplied by Merck. Filters with 150mm diameter (S & S Folded Filter) were used with a filter holder SPARTAN 13, 0.2 µm (Schleicher & Schuell)

Approximately 40g amount of wheat sample was milled using a Buchi Mixer B – 400. Twenty five grams of sample homogenized with a KA Ultra-Turrax T25 were weight in a 150ml centrifuged tube and extracted three times for 3min with 100 ml methanol each time using an Ultra-Turrax. The crude extract was centrifuged at 4000rpm by a SORVALL, Superspeed centrifuge, SS-3 Automatic and filtered through a folder filter into a 1000ml reparatory funnel. 200 ml double distilled water, 50 ml saturated sodium chloride and 75 ml dichloromethane were added and shaken vigorously for 1 min. The organic layer (lower) was filtered through a glass fibber filter previously washed with 15 ml $CH_2Cl_2$ and containing a bed of anhydrous sodium sulphate. The previous step was repeated 2 times with 50ml dichloromethane. The whole dichloromethane layer then was concentrated to dryness in a vacuum rotary evaporator, Buchi Rotavapor model, with a bath water at 30°C. The residue was dissolved in 20 - 30ml isooctane. No further clean up was used. This extract was filtered over a 0.2 µm filter, and the filtrate was collected in a 2ml-auto sampler vial.

The GC-ECD system was a Model 6890 by Hewlett-Packard equipped with a $^{63}$Ni ECD, with a column 60m x 0.25mm x 0.25 µm DB-5, with a volume of injection of 1 µl. The GC-NPD system was a Varian Star 3400 CX gas chromatograph equipped with an P-FPD, with a column 25m x 0.2mm x 0.33 µm DB-5 and a filter 400nm with an injection in splitless mode and a volume of injection 1 µl. The GC data output and processing system was a Varian Star Chromatography Workstation, Version 5.3.

For recovery experiments, the grain samples were spiked at 2 fortification levels. Quantification was based on a standard prepared in a grain matrix to obtain a realistic determination. After shaking carefully, these samples were allowed to stand for 2 hours at room condition before extractions. The proposed method provided a good recovery for all the used compounds.

### 6.3.2 Initial concentrations

The calculated initial concentration of the compounds in the aerial plant part are well correlated with measured value, but lead to a systematic overestimation of a factor 2 to 5 compared to the results of measures. Variations due to losses during trial management, manipulations of harvested material, conditioning and analytical part are potentially high. Redistribution of substance between plant and environment in the first hours can also be potentially high. Consequently effective intercepted substance by the plant is difficult to assess precisely, and can be somewhat hidden by redistribution and degradation processes.

No specific experimental design was developed to assess these uncertainties. However, some sources of variations can be estimated. According to identical substances present in two treatments in the trial (chlorothalonil and cyproconazole), variation coefficients of 11 and 16% are calculated for the results of the initial concentrations. The recovery of substances during the analytical part showed a variation coefficient of less than 5% up to more than 30% according to repeated measures. However these variations for the trial and the measures do not explain the total differences between measures and calculated data. The differences, with a factor from 2 to 5, indicated a systematic loss of substance for the initial distributed mass on the plant. An initial loss of 20% of sprayed amount was considered in the model, corresponding to 10% loss by drift and to 10% initial volatilization based on good agricultural

practices. However more than 50-60% of dosage can be lost during application depending upon technique, formulation and environmental conditions (Van den Berg et al., 1999). Considering the results of measures, the losses are probably closer to 60% in this experimental study. Different reasons can be mentioned according to experimental conditions but also to the model construction. A part of these losses was probably due to the short distance drift in an experimental design with narrow plots, and eventually to local experimental climatic conditions (air pressure). The collect of samples 6 hours after application is a sufficient delay for a partial redistribution of substance in the system. The model considers a pesticide capture coefficient for the whole aerial plant part without distinction between the different plant organs. This value differs eventually from the interception capacity of ears, which were analysed in this experiment.

These consideration were taken into account to adjust the model with a 60% initial loss at spray time for plant interception. According to this systematic correction and new calculations, the correspondence between calculated initial concentrations and measures can be then observed on Figure 49. The accuracy of this systematic adjustment underlines the high uncertainty of the treatment effectiveness. Climatic factors and spraying technique are confirmed as the main factor segregating measures and computed data for initial concentrations. Final results show logically that the ranking of the substances depends on the initial mass of product spayed and that a good concordance for different substances is obtained in the determination of the initial concentration.

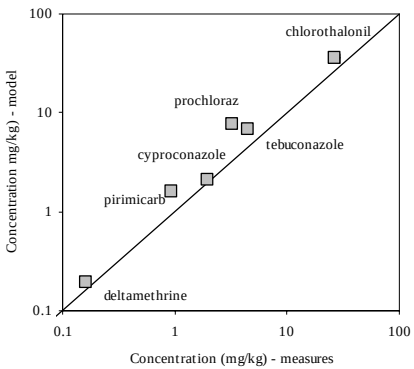



Figure 49. Initial concentrations (mg/kg) of six substances, 6 hours after application on wheat crop, comparison between measures of total ears and calculated values by the model.

### 6.3.3 Evolution of residues

Measures of concentrations in ears logically show a constant dissipation of the substances with the time. For cyproconazole, the precision of the measures remains the same for all dates of sampling with variation coefficients between 15 and 20 %. The imprecision increases for chlorothalonil with time, with a variation coefficient increasing from 10% (first measure at

treatment) to 80, 90 and finally 140% (last measures at harvest). This evolution underlines the difficulty to get good precision for the evaluation of residue a long time after the application and when a low concentration level has to be analysed.

To evaluate the general functioning of the model, transfer rates were calculated and the model was run. Values for initial distribution were not corrected and values for half-life were extrapolated as half of the values in soil. Concentration results are those in the stem compartment. An example of the transfer rates considered is given for cyproconazole in Table 23. For the case of tebuconazole, transfer rate from the formulation deposit to the leaves is generally high so that an important transport of substance may be expected. Transfer rate within phloem from leaves to stem is sufficient to consider that transport in the plant is not a limiting factor for this substance.

Table 23. Transfer rates between source and the receiving plant compartments for tebuconazole according to the model.

| | Source compartments | | | | | |
|---|---|---|---|---|---|---|
| Transfer rates (1/d) to the receiving plant compartments | air | soil | formulation deposit | roots | stem | leaves |
| air | -3.1E+00 | - | 2.1E-03 | - | - | 6.3E-04 |
| soil | 9.6E-02 | -1.2E-02 | 1.8E-01 | 3.2E-01 | - | - |
| formulation deposit | 5.8E-01 | - | -1.9E+02 | - | - | 6.2E-01 |
| roots | - | 3.4E-03 | - | -3.3E-01 | - | - |
| stem | - | 6.8E-05 | - | - | -2.0E-02 | 2.4E-03 |
| leaves | 1.9E+00 | - | 1.9E+02 | - | 1.2E-02 | -6.3E-01 |

Concentrations measured and calculated from time of application to harvest (1, 7, 24 and 30 days after application) are compared in Figure 50. First overview indicates a rather good relation between experimental and calculated results. However a detailed analysis shows new elements about the functioning of the model and the limits of the comparison between the measures and the model. For each substance, the first point of calculated concentration (highest value) corresponds to the intercepted substance with a high fraction in form of deposit. The following points of evolution correspond to the substance accumulated in the plant tissue after transfers. The difference between the first and the second point is high, indicating that the transition is artificially abrupt between the concentration in form of deposit and the concentration of accumulated substance in plant tissue. It also appears that few days after the application time (second point, that is 7 days after application), the substance in the plant is generally underestimated by the model. Afterwards, concentration decrease is slower in the model than given by the measures. This compared evolution indicates that the accumulation in plant is eventually slower and lower in the model or that substance in form of deposit present in the analysed ears is missing in the calculated values. Additionally, the residence time used is probably overestimated by the model, and that the extrapolated half-life in plant is quite conservative.

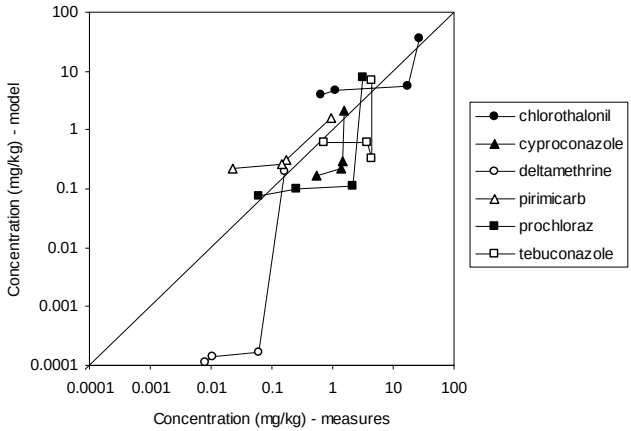



Figure 50. Compared concentrations (mg/kg) during evolution of six compounds at harvest of wheat crop; comparison of calculated values and measures of ears, 1, 7, 24 and 30 days after treatment.

### 6.3.4 Residues at harvest

At harvest the measured concentrations vary by a factor 500 between extreme concentrations of substances. The calculated concentrations show apparently a rather light correspondence to the measures (Figure 51). Two substances show a bad correspondence leading to following points of discussion. The high persistence of chlorothalonil in the air and of pirimicarb in soil explains a large part of the overestimation by the model. The case of pirimicarb may be explained by the conservative choice of half-life in soil for the value in plant. The half-life in the air for chlorothalonil is exceptionally high, so that the absence of losses due to advection (wind) in the model is a probable source of overestimation. This would ask to consider this process for a better correspondence between practical measures and the model. However according to the methodological framework of LCA, an advective “loss” is exported to another place, but remains available for accumulation in plant or in another media. In the particular case, the model considers the substance to remain effectively available for plant accumulation, which does not corresponds well to experimental conditions. Advection will be properly addressed once the plant module will be incorporated in a full multi-media model including advection. A first screening test indicates that adding advection with a wind speed of 1 m/s to the model reduces the accumulated mass in harvest by a factor 7 for chlorothalonil, whereas practically no influence is observed for pirimicarb.

The low calculated concentration of deltamethrine is explained its limited systemic transport from leaf to stem (and grains). This substance has a high $K_{ow}$ and so its mobility in the plant is slow compared to other substances.

The main factor of variation is the half-life of the substance, especially in the plant. The use of half-life in soil to extrapolate the degradation in plant appears as a good approximation.

Approximating plant degradation by air half-life would lead to an important underestimation so that this assumption is not to be considered.

The application of the model for substances applied at the same moment give a rather good concordance, considering the fact that the model complexity includes a variety of potentially determining processes that could artificially or inconsistently create high differences between substances. According to the confidence factors determined for each substance (see the uncertainty analysis Chapter 6.2.4 Uncertainty analysis of single substances) the results of the model are generally in included in the range of uncertainty. The low distribution range for uncertainty around the calculated result for chlorothalonil and pirimicarb is mainly explained by the low sensitivity values of the uncertain parameters (partition coefficients, half-life).

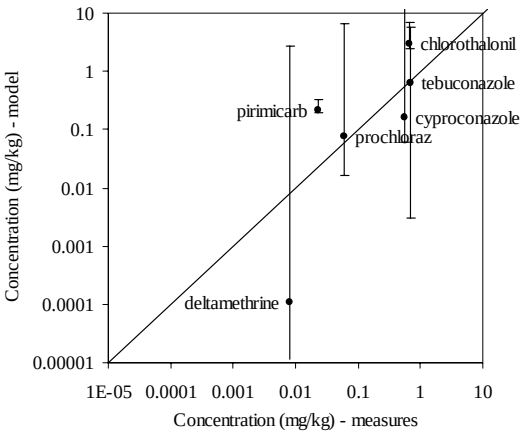



Figure 51. Concentrations (mg/kg) of six compounds at harvest of wheat crop, comparison of calculated values and measures of ears. Confidence interval determined on the basis of confidence factors.

### 6.3.5 Half-life and residence time in plant

The residence time of the substances in plant and the half-life in plant, calculated after deduction of dilution due to plant growing, were determined from the measures using first and last measure and for the model as a function of the removal rate of the stem compartment. Table 24 gives an overview about both values , compared with data chosen from literature.

Table 24. Residence time and half-life for the substance obtained from experimentation and chosen data from literature.

| | Residence time in plant (days) | | Half-life in plant (days) | | Half-life, literature (days) | | |
|---|---|---|---|---|---|---|---|
| | measures | model | measures | model | air | soil | water |
| Cyproconazole | 22 | 8.6 | 16 | 13.5 | 1 | 27 | 1460 |
| Chlorothalonil | 11.5 | 9.2 | 8 | 18 | 584 | 36 | 49 |
| Prochloraz | 7 | 14.7 | 5 | 11 | 1 | 22 | 30 |
| Tebuconazole | 83 | 35.1 | 59 | 42.5 | 1 | 85 | 365 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Pirimicarb | 7.5 | 2.0 | 6.5 | 60 | 1 | 120 | 60 |
| Deltamethrine | 8.5 | 15.1 | 6 | 10.5 | 1 | 21 | 60 |

This comparison illustrates the difficulty to get consistent values for degradation processes. The residence time and half-life values give similar information The half-life value for plant are effectively situated between those of soil (upper) and those of air (lower). The experimental values of half-life in plant are to be considered with precaution for the following reasons: no distinction was made between the concentration in grain and on the surface of ears. Substances as surface deposit have a probable higher degradation rate and are exposed to other dissipation processes than degradation. The other plant organs have not been analysed and no control is possible for the translocation of substance in plant. However these data of residence time and of half-life in plant give a useful overview about degradation in the plant. They confirm that a rough estimation of half-life in plant can be extrapolated from the half-life in the soil, in absence of available data.

### 6.3.6 Discussion

Indications for accuracy of the model and for further needs in process development made this experimental part particularly interesting, as it was carried out during the development of the model.

The good concordance for different substances to evaluate the initial concentration especially confirmed the approach highlighting the initial conditions and the further dynamic evolution. The adjustment according to climatic data or more generally the efficiency of the plant treatment application also gives a possibility to get nearer to experimental conditions and real conditions. Further developments on the initial processes would be necessary to get more precision for practical agricultural conditions: However, these developments are not directly needed in the targeted evaluation and comparison of substances.

The importance of the degradation in plant is clearly illustrated here. The assumption to use the data for soil in order to obtain a first order of magnitude is confirmed as a potential way in case of lack of data.

Finally the good overview given by the simulation confirms the potential of the model to help analytical approaches for the evaluation of substances behaviour and residues in harvest.

## 6.4 Concentration at harvest and tolerance value

The tolerance values could also enable a preliminary control of the model results. A tolerance value is the maximum concentration that may be observed in one part of the plant assuming good agricultural practices. The value is specific to the substance and the harvested part of the crop. Calculated concentrations at harvest obtained by the model are compared here with tolerance values.

Some harvest fractions are high which indicates mostly high concentrations in harvest. For example chlorothalonil has the following results: dose applied 1.5 kg/ha, harvest fraction 0.0068 kg/kg applied, concentration of 1.5 mg substance / kg grains for a yield of 6000 kg / ha. The tolerance value for chlorothalonil varies between 0.05 and 3.5 mg/kg depending on

the agricultural product; it is fixed by 0.2 mg/kg for wheat grain. According to this substance, it appears that the evaluation by the model is relatively overestimated. In the case of chlorothalonil, a very high half-life in air, including degradation by OH radicals and deposition (584 days), is a source of the overestimation, since no other losses or nor transfers to the environment are considered from this compartment. Potentially the adding of advection would effectively contribute to better results for substances with particularly high half-life in air, similarly as previously demonstrated in the experimental part of this study. The rather high persistence in soil (35 days) is also a contribution of a high concentration level at harvest, since the degradation in plant is directly extrapolated from this value.

Pirimicarb also shows a result slightly over the tolerance value, due to a high half-life in soil and in plant. The residence time of tebuconazole and cyproconazole were also high in the experimental part of the study (Table 24) and the high concentration at harvest is therefore not surprising. However, the comparison of these concentrations with the tolerance value underlines the potential risk for an application shortly before harvest. The other substances are situated under the legal limits.

This comparison to the tolerance value represents a pertinent method of control for substances with high persistence values and a high harvest fraction. Inversely no inferior limit is available for low harvest fractions.

Table 25. Concentration in grain calculated by the model and tolerance value for substances used in wheat.

| | Substances | Grain concentration mg/kg | | Tolerance value mg/kg |
|---|---|---|---|---|
| | | model | measures | |
| Herbicides | Diflufenican | 0.02 | | 0.02 |
| | Ioxynil | 0.004 | | 0.1 |
| | Isoproturon | 0.02 | | 0.05 |
| | Pendimethalin | 0.003 | | 0.05 |
| Growth regulators | Chlormequat chloride | 0.0006 | | 2.0 |
| | Ethephon | 0.0001 | | 0.2 |
| | Trinexapac-ethyl | <0.00001 | | 0.2 |
| Insecticides | Deltamethrine | 0.00001 | 0.008 | 1.0 |
| | Lambda-cyhalothrin | <0.00001 | | 0.02 |
| | Pirimicarb | 0.065 | 0.023 | 0.01 |
| | Teflubenzuron | 0.004 | | 0.05 |
| Fungicides | Azoxystrobin | 0.0008 | | 0.3 |
| | Chlorothalonil | 1.5 | 0.09-0.66 | 0.2 |
| | Cyproconazole | 0.02 | 0.54 | 0.05 |
| | Prochloraz | 0.02 | 0.06 | 0.2 |
| | Tebuconazole | 0.62 | 0.71 | 0.05 |

## 6.5 Qualitative comparison with other models

The present model offers a new alternative to existing models for the evaluation of the pesticides toxicity. Its validity is discussed hereafter compared to environment multi-media models and compared to alternative methods for assessment of pesticides. The comparison to alternative models is of interest for several reasons. First, the comparison with methodologies

of same type is useful to put in evidence improvements and further needed developments. Then, the comparison with other models is a possibility to test the accuracy of the present approach to attain the targeted objectives or to point out similarities to other types of models with different objectives.

Actually other methods in the frame LCA do not offer an effective potential for comparison. Confronted to the same problem of comparison and to underline new initiated methodological approaches, Margni et al., (2003) highlighted different types of insufficiency in existing methods: they usually concentrate on general behaviour of substances in the environment; ranking methods lack a clear weighting between impacts. LCA methods are mainly based on toxicological data with rough basis for pesticides without consideration of residues; improved LCA methods do effectively combine the fate and exposure but with effect factors, without consideration of agricultural conditions. Existing models for evaluation of transport in plant can be added to this list. However, these models, particularly multi-media models and plant models, stand for potential points for the comparison of specific elements or for discussing the pertinence in the approach of the present model.

Consequently the following types of methods are identified for comparison and discussion: methodology dedicated to pesticides, environmental multi-media models and agricultural plant models.

### 6.5.1 Methodology dedicated to pesticides

Methodologies to assess the toxicity of pesticides through the food chain are not numerous in the framework of LCA. Margni (2003) first developed a method according to the following principles: the method assesses the impact on human health, but also aquatic and terrestrial ecosystems. Intermedia transfers are modelled and the results are based on a clear distinction and combination of fate, exposure and effect assessment. This work was initiated as existing methodologies for evaluation of pesticides were generally not satisfying LCA requirements. The developed methodology is effectively based on the applied amount of pesticide; the fate and exposure is based on the intake fraction, that is the ratio of total human intake to the total emission; finally the effect factor corresponds to a measure of toxicity of the substance. Concerning the fate of the substance in the agriculture and food chain up to its ingestion by humans, the substance is evaluated according to a measure of residues in agricultural plant, the tolerance value, corrected by factors for the transfer from agriculture to food. The use of the tolerance value to estimate the fate of the substance during the agricultural life cycle of the substance is recognised de facto as an overestimation of the real concentrations. However this method constitutes a precise step in the aim at assessing the fate and impact of pesticides. For this reason it is used here for a comparison.

The harvest fraction for the substances used in wheat is calculated in order to compare the present approach with the method by Margni et al. (2003). The present approach models the fate of the substance, whereas Margni et al. (2003) consider the tolerance value for this evaluation. Figure 52 compares both results. It underlines the difference between a method based on a threshold, in a range of order that allows analytical attestation, and a model approach calculating the fate of the substance and independent from measurable orders. The use of the tolerance value reduces the variability between substances, whereas no limit is fixed by modelling the fate of the substance. Consequently the possibility to differentiate between substances is clearly increased by considering the fate of the substance. On the other

side, the possibility of an effective high concentration of a substance in harvest is better preserved by using a threshold like the tolerance value.

Two groups of substances are identified according to the comparison of both methods. Some substances obtain similar results according to both methods due to a tolerance value probably near realistic levels of residues at harvest. The calculated concentrations harvest fraction is much lower and does not correspond to the tolerance value for substances which fate is dominated by a high dissipation rate or characterised by the absence of transport to the harvest organs. Part of these substances has a tolerance value corresponding to an analytical threshold.

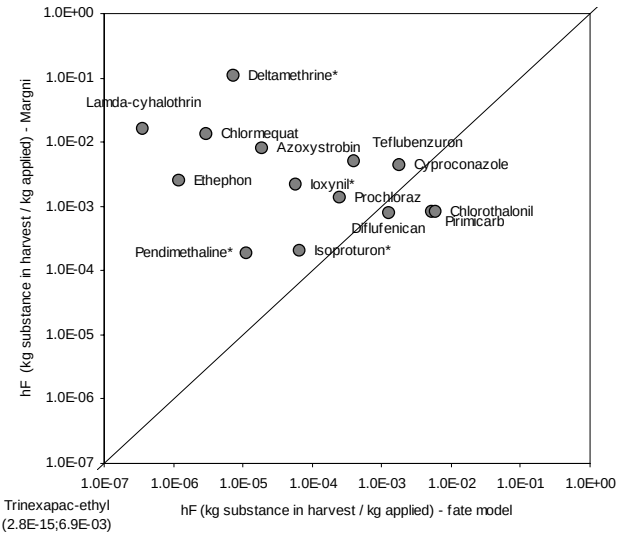



Figure 52. Comparison of harvest fraction (kg substance in harvest / kg substance applied) between the fate model and method by Margni et al. (2003). * Not detectable values

### 6.5.2 Environmental multi-media models

The similarity of the present model with environmental models has been mentioned during the descriptions of the processes to be included in the model. Whereas partly built on same processes, a direct comparison with these models is not pertinent, as they are built according to a different framework and for different objectives. Besides none of them consider the particular conditions of agricultural practice. Environmental models are built in multi-media systems and are suitable to assess the behaviour of substances (among them pesticides) in soil, water or air. However, all aim principally at assessing the behaviour and effect of substances in aquatic and terrestrial ecosystems or at assessing the risk of human toxicity by the fate of pollutants in the environment. Many of them have also been improved with a vegetation medium. The pertinence to include vegetation in multi-media models is discussed by different studies. For some substances, the vegetation is the dominant transfer pathway and

its modelling is needed to explain their fate. Significant effects by vegetation are awaited for substances that are taken up following atmospheric deposition and those that are taken up by transportation stream (Cousins and Mackay, 2001). For air exchanges, this study indicates substances with a $K_{oa}$ greater than 6 and a log $K_{aw}$ greater than –6. Plant uptake from the soil concerns mainly substances with log $K_{ow}$ less than 2.5 and a log $K_{aw}$ less than –1. In the present model an optimum transfer rate to the plant is considered for substances with a log $K_{ow}$ between –0.5 and 4.5; in addition the lipophilic character of the substance determines the capacity of the substance to be preferably bound to the soil than to be mobile and available for the plant.

Severinsen and Jager (1998) added vegetation to a multi-media model and showed that this media comprised important processes determining the regional fate of xenobiotics. Particularly the metabolism and harvest of aerial plant parts appeared as important elements of the vegetation compartment; stomatal exchanges were not significantly modifying the fate of xenobiotics, or the compartment of root. According to these observations the possibility to ignore the root is confirmed, together with the need to give particular attention to the choice of the half-life on and in the plant.

The evaluation of semi volatile organic compounds showed that the first effect of a vegetation canopy was the reduction of air concentration due to an increase of deposition (Wania and McLachlan, 2001). Chemicals with log Koa around 9 and 10 and log Kaw between –2 and –3 were mainly concerned. According to this point a better description of the processes from the air to plant could be developed. However the storage capacity of the soil for substances mainly explains the influence of vegetation. The high degradation rate of substance on the surface of plant also leads to an important sink effect by vegetation.

A recent study achieved a models comparison for the uptake of organic chemicals by plants (Collins and Fryer, 2003). The study evaluated the performance of a range of 9 models against experimental data sets. Very different types of models were selected described as dynamic, regression-based, steady state and equilibrium models. The models showed a variation in terms of scope, methodological approach and complexity. All were predicting the uptake, translocation and elimination of organic contaminants by plants. Accumulation occurred from the soil and from the air. The validation of these models to real world data appeared generally as deficient and motivated part of that study. The results of the analysis showed that dynamic prediction of chemical fate gave advantages for acute exposure durations and for rapid changing environmental media. Other models, like steady state, performed better for chronic exposure durations. The choice of a model is consequently dependent on the requirements of the assessment, the nature of the environmental media and the duration of the source term. Concerning the dynamic models, a certain complexity of the system structure appeared as necessary, in particular the choice and number of plant organs. According to the dynamic, and generally more complex, models, the inclusion of the soil – air – plant transfer route was demonstrated as important. The study also showed that a high quality of independent data sets were still required, particularly for exposure durations equivalent to entire growing seasons. According to the detailed analysis achieved by Collins and Fryer (2003), different elements are useful for the discussion of the present model. None of these models include the conditions of agricultural practices and residues following direct application of pesticides, although the dynamic models would be suitable for such supplements. If some models are suitable for chronic exposure, the phytosanitary conditions and the route of substance accumulation from surface deposit to the plant are lacking. In addition the identification of the harvested part of the plant is generally not detailed. Finally the difficulty to test such models against real world appears as a recurring difficulty, for

which appropriate alternative methods are necessary or specific analytical development should remediate.

According to multi-media models, the exposure for human toxicity by pesticide is dominated by the food chain; the human toxic exposure through drinking water or air inhalation appears as less important. Comparison between direct residues and indirect air – soil – plant interaction has been studied showing underestimation of intake fraction by factors 100 (Humbert, 2002; Margni et al., 2003).

The comparison of the results obtained by the environmental multimedia model Impact 2002+ and by the dynamic plant model illustrates well the significance of the present model for the evaluation of pesticide fate in agricultural commodities. Humbert (2002) compares both approaches for the evaluation of pesticides used in banana and shows the absence of concordance between their results (Figure 53). These differences are explained by the importance of the time between the application and the harvest, that cannot be accounted for in steady state resolution.

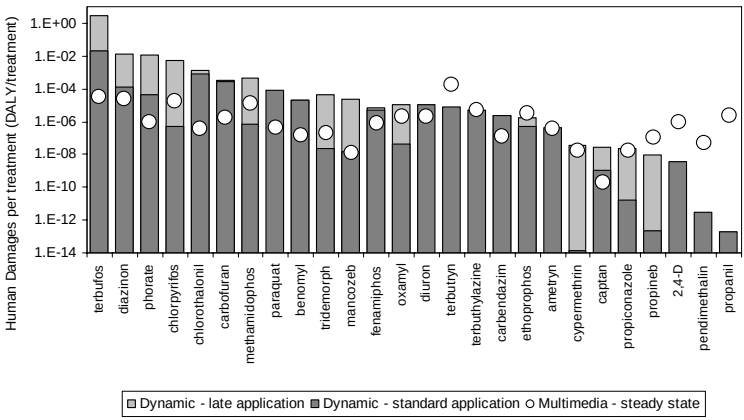



Figure 53. Comparison of Human Damages per treatment (DALY/treatment) for substances used in banana, applying the multimedia model Impact 2002+ and the dynamic plant model for different periods of application in accordance with the type of substances. Based on Data by Humbert 2002.

### 6.5.3 Agricultural plant models

Different plant models have been already described or used as references for the description of transfers (Trapp and Matthies, 1995, Riederer, 1995). These models were mainly set to environmental purposes as previously largely discussed. According to a broad review on the stand of knowledge on the foliar uptake of agrochemical formulations (Zabkiewicz, 2003), only one (easily available published) recent model has collected and synthesised detailed, single described, processes into a model for the purpose of pesticides development and evaluation. Satchivi et al. (2000a, 2000b, 2001) have developed a non-linear dynamic

simulation model for xenobiotics transport. The processes of the model are complex, due to the need of predictive allocation of xenobiotics in the whole plant. In particular the model is dominated by the uptake of substance from foliar xenobiotics. Additionally the transport processes in xylem and phloem sap are described in detail. The compartments and transports are built according to anatomical, physiological and biochemical characteristics, which makes the model complex, but more reliable in accordance to actual knowledge on biological processes. Particularly the description of the transport of xenobiotics in the plant includes detailed elements about the transfers between plant tissues. These elements are based on a specific model for the phloem mobility of xenobiotics (Kleier, 1988; Hsu et al., 1996). These references could be useful to specify effective systemic translocation of substances in the plant. The mobility in phloem is an important factor that explains the presence of substances in the harvested plant part. In particular the mobility of herbicide is recognised as mostly high (Hsu and Kleier, 1996). However the functioning of these models is too complex to be used as references in the framework of the present methodological developments, due to the level of detail designed. Additionally they are mostly built to evaluate substances for very short time duration.

The verification of the effective selectivity of the treated crop is a complementary important element to be verified and documented, particularly for herbicides. Different mechanisms explain the resistance or the absence of reaction of a crop to the received herbicide: the incapacity of the substance to penetrate into the plant, the detoxification of the substance in the plant or the insensitivity of the organs targeted by the active substance. If the model is able to calculate the fate of the substance, the mechanisms of selectivity are not comprised in it, or indirectly in the value of half-life in plant. According to this, the effective transport of the herbicide into the plant and the mechanisms of selectivity should be verified.

Difficulty is foreseen in detailing mathematically the metabolism in plant (Komossa et al., 1995) and actually no model is available. According to Satchivi et al. (2000b), the collected values for the metabolism of substances in plant show relatively high variations, from a short half-life of some days up to high values (30 days), depending on the substance or on the type of plant for a single substance (herbicide in different weeds).

## 6.6 Validity range and achievements

The validity range of the model and achievements are resumed conclusively to this evaluation of the model.

The literature studies and the developments throughout the building of the model, so as the qualitative comparison with other models, have highlighted how the model validity must be understood and what are the limits. Main critical elements are resumed hereafter (Table 26), with the assumed validity and the identified limits. According to theses elements, consequences and perspectives are identified for verifications and new methodological developments. These indications are in particular useful to provide the frame and requirements for the model application.

Table 26. Validity, limits for the model application and corollary for verifications and new methodological developments.

| Validity | Limits | Perspectives |
|---|---|---|
| Substances are considered as non polar, | Light or major transformations of the substances may occur during the fate | A preliminary control from literature would be needed concerning the |

| Validity | Limits | Perspectives |
|---|---|---|
| non dissociating and neutral organics, especially substances with a lipophilic character. | in the different compartments, notably in soil and in plant. A fraction of the substances may dissociate. The validation of these models does not systematically include the full range of characteristics variability that may be found within pesticides. | substances state during the transport processes and in the different compartments. An adaptation or an additional run of the model would be needed to evaluate dissociated substances using the cascade model. Further methodological developments provided by Trapp (2000) show one way to account for substances dissociation. |
| Only active substances from treatment products are evaluated without consideration of metabolites. | Substances are transformed during degradation processes. Resulting metabolites may also require an evaluation of fate similarly to the original pesticide. | The occurrence of metabolites at the harvest time may be evaluated with an additional run of the model accounting for the transformation rate of substances in each compartment. |
| The evaluation of fate is based on the behaviour of the pure active substances present in sprayed products. | The improvement of transport efficiency provided by adjuvant is not considered by the model. Consequently the transport velocity from surface residue to plant inner may be underestimated. The protecting effect against losses provided by adjuvant substances is neither considered, although by the level of losses from formulation deposit on plant considered by the model is low. | Where needed transfer rates could be adapted by considering the effects of adjuvant, particularly on transfer processes from formulation deposit. Elements and bibliographic references are provided for instance by Schönherr and Baur (1996), Baur et al. (1999), Knoche and Bukovac (1999). |
| Partition coefficients and half-life values are main parameters describing the substances. These data are selected from various databases. Half-life in plant is extrapolated from data in soil. | The choice of data may be sensitive, since the sources of data are very variable and sometimes missing. The extrapolation of half-life in the plant from value in soil contributes to a high imprecision of the results. The use of equilibrium partition coefficients in time dynamic processes is questionable for very short time period. | Criteria for selection of data are needed. Availability of half-life in plant must be improved. A better knowledge about limits and consequences of extrapolations is needed. Additional studies would be needed to precise the velocity of substances to reach the equilibrium in compartments relatively to the transfer rates to ensure that equilibrium is reached in much shorter period than e.g. the elapsed time between application and harvest. |
| Good agricultural practices are considered including favourable climatic conditions for spraying. Minimal losses out of the system are considered. Maximal efficiency of application is supposed. | High faction of substance applied are considered to remain in the agricultural system. Losses to environment are on the lowest level in comparison to probable current practical conditions. Low losses from soil compartment lead to a high persistence of the substances in the soil and long availability for accumulation in plant. | The increment of additional processes between plant and environment shall reduce the risk of underestimating transfers out of agricultural system. The present integration of the present model in the environmental multimedia model Impact 2002 (Pennington, 2004) also helps to better consider the other pesticides exposure pathways to human, but also to ecotoxicological problems. |

| Validity | Limits | Perspectives |
|---|---|---|
| The agricultural system is the annual field crop. The harvested commodity may be a plant organ exposed or unexposed to formulation residues, in equilibrium the stem or leaf. | The rough plant architecture does not allow to evaluate detailed distribution of pesticides into the plant. Evaluation of fruits from trees or bushes are not possible. The model considers a parallel development of all plant organs. The basipetal transport into fine roots is not taken into account. | The increment of new plant organs would make the results more detailed, according to diverse plant architecture. To study perennial vegetation, adaptations of the plant model and of some processes would be needed. For instance developments by Satchivi et al. (2000a, 2000b, 2001) could help to enhance the detailed model of the plant architecture and functioning. |
| The model calculates the fate of the substances, inclusive herbicides, without refereeing to particular barriers or enzymatic processes related to specific physiological plant processes. | The mechanisms of selectivity of herbicides are not comprised in the model, or indirectly in the value of half-life in plant. | The effective transport of the herbicide into the plant and the absence of reaction of the plant to an herbicide should be verified from literature. Following processes may need specific implements in the model: the incapacity of the substance to penetrate, the detoxification of the substance in the plant or the insensitivity of the organs targeted by the active substance. |

Finally, the present key points resume the original elements brought by the present approach of the system of phytosanitary measures – plant - environment.

- The system is dynamic and is evolving during a definite period.
- The initial system is determined by conditions specific to agricultural situations: the vegetation is a crop at a definite growth stage, which determines the distribution of released substance in the system. The substance applied into the system is a punctual single amount.
- The transport processes between the media take into account the crop development during the system evolution, which is limited to the period between spray and harvest.
- The transfer of formulation deposit on the surface of leaves into the plant is described by processes specifically identified for pesticides.
- The plant system is composed of different compartments, which allows differentiating between the exchanges from the sources of substances to the harvested organs and the other dissemination routes of the substance in the various compartments building the system.

# 7. Harvest fraction and human toxicity

The model is applied here for an ultimate presentation and interpretation, synthesising all elements brought in the development of the model and combining the results with the evaluation of the toxicity on humans. The model is first applied to the set of test substances used in wheat and then to a larger set of substances used in field crops.

## 7.1 Set of substances used in wheat

Final evaluation of harvest fraction and human toxicity is presented here for the set of substances used in the present study. The model is used to determine the harvest fraction of the substances in accordance with the Chapter 5 Understanding the functioning of the system. The toxicity on humans is evaluated according to the methodology introduced at the beginning of the present work in the Chapter 2.2 Effect factor and impact evaluation.

### 7.1.1 Harvest fraction

The harvest fraction is the main result delivered by the model. Complementary elements describing the system evolution are also displayed, useful for the interpretation of the results as well as for extrapolations: the harvest fraction of each single source (soil, formulation deposit and air), the maximum level of the harvest fraction of each single source, the time to reach this level and the dissipation rate from this point. These last parameters are used to extrapolate other harvest fractions for each single source at other application time. The extrapolation is based on the equation 62 determining the maximum mass accumulated in the plant compartment. The following equation is obtained:

$$hF_i(t) \approx hF_{i,\max} \exp(-\mu_{i,2}(t - t_{i,\max})) \qquad 142$$

with $hF_i$ (kg in harvest / kg applied in source i) the harvest fraction of single source i, $hF_{i,\max}$ the maximum level based on equation 81, $\mu_{i,2}$ (1/days) the dissipation rate in harvest compartment, $t_{i,\max}$ (days) the time to reach the $hF_{i,\max}$ based on equation 79, t (days) the time from the application of substance to the harvest. Table 27 presents these results for the studied substances with the overall harvest fraction obtained, the harvest fraction of each single source and the determining parameters for extrapolations.

Table 27. Harvest fraction and parameters for simplified resolution. Time from application of substance to harvest (days), and harvest fraction (hF, kg in harvest /kg applied). Harvest fraction of single source ($hF_i$ kg substance in harvest / kg applied in source i) and parameters for simplified resolution for soil (s), formulation deposit (fd), air (a): maximum harvest fraction ($hF_{i,max}$, kg in harvest /kg applied in source i), time to reach the $hF_{i,max}$ ($t_{i,max}$, days) and dissipation rate ($\mu_{i,2}$, 1/days).

| substances | time | hF | soil | | | | form.deposit | | | | air | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $hF_s$ | $hF_{s,max}$ | $t_{s,max}$ | $\mu_{s,2}$ | $hF_{fd}$ | $hF_{fd,max}$ | $t_{fd,max}$ | $\mu_{fd,2}$ | $hF_a$ | $hF_{a,max}$ | $t_{a,max}$ | $\mu_{a,2}$ |
| | d | kg/kg | | kg/kg | d | 1/d | | kg/kg | d | 1/d | | kg/kg | d | 1/d |
| Diflufenican | 127 | 1.3E-03 | 1.0E-04 | 2.1E-04 | 156 | -4.5E-03 | 4.3E-03 | 1.4E-03 | 21 | -8.9E-03 | 3.0E-03 | 1.4E-03 | 21 | -9.9E-03 |
| Ioxynil | 127 | 5.9E-05 | 4.8E-06 | 3.2E-03 | 10 | -7.0E-02 | 1.2E-04 | 1.7E-01 | 6 | -1.4E-01 | 3.0E-04 | 1.1E-01 | 6 | -2.7E-02 |
| Isoproturon | 127 | 6.6E-05 | 7.5E-05 | 1.8E-02 | 19 | -3.7E-02 | 8.8E-06 | 1.2E-01 | 9 | -7.0E-02 | 7.3E-06 | 4.9E-02 | 4 | -7.2E-02 |
| Chlormequat | 95 | 2.9E-06 | 2.8E-06 | 7.8E-04 | 14 | -4.8E-02 | 9.2E-08 | 1.7E-03 | 9 | -9.6E-02 | 6.6E-06 | 9.3E-02 | 2 | -9.6E-02 |
| Ethephon | 95 | 1.2E-06 | 3.1E-07 | 5.5E-05 | 14 | -4.8E-02 | 9.4E-08 | 8.2E-04 | 9 | -9.6E-02 | 1.7E-05 | 2.7E-01 | 4 | -9.6E-02 |
| Trinexapac | 95 | 2.8E-15 | 2.1E-32 | 5.5E-04 | 1 | -6.9E-01 | 1.3E-14 | 3.5E-02 | 2 | -2.1E-01 | 3.6E-36 | 3.4E-02 | 2 | -1.0E-01 |
| Deltamethrine | 75 | 7.4E-06 | 3.4E-09 | 2.1E-08 | 21 | -3.3E-02 | 1.4E-05 | 2.2E-04 | 10 | -6.6E-02 | 4.0E-06 | 3.8E-05 | 2 | -6.6E-02 |
| Pirimicarb | 75 | 5.2E-03 | 2.0E-03 | 2.9E-02 | 115 | -6.4E-03 | 9.1E-03 | 2.7E-01 | 15 | -1.2E-02 | 1.4E-03 | 1.1E-02 | 1 | -2.7E-02 |
| Teflubenzuron | 75 | 3.9E-04 | 5.0E-06 | 1.4E-05 | 34 | -2.0E-02 | 7.0E-04 | 1.7E-03 | 13 | -4.0E-02 | 6.5E-04 | 1.1E-03 | 8 | -4.0E-02 |
| Azoxystrobin | 65 | 1.9E-05 | 2.2E-05 | 2.4E-03 | 10 | -6.7E-02 | 1.1E-05 | 5.4E-02 | 7 | -1.3E-01 | 1.1E-05 | 1.2E-02 | 1 | -1.3E-01 |
| Chlorothalonil | 65 | 5.9E-03 | 4.4E-04 | 2.5E-03 | 35 | -2.0E-02 | 1.0E-02 | 5.8E-02 | 12 | -3.9E-02 | 1.2E-02 | 1.2E-01 | 32 | -5.7E-03 |
| Cyproconazole | 65 | 1.8E-03 | 4.9E-04 | 4.2E-03 | 26 | -2.6E-02 | 2.1E-03 | 5.0E-02 | 11 | -5.2E-02 | 1.7E-03 | 1.6E-02 | 4 | -5.5E-02 |
| Prochloraz | 65 | 2.4E-04 | 9.1E-06 | 8.9E-05 | 22 | -3.2E-02 | 1.1E-04 | 3.8E-03 | 10 | -6.3E-02 | 2.5E-05 | 2.8E-04 | 1 | -6.5E-02 |

### 7.1.2 Human toxicity

The methodology to assess the human toxicity has been presented in the Chapter 2 Methodology for assessment of human toxicity potential and is applied here. The Human Toxicity Potential (HTP) is the combined result of fate and effect of the substance. The ultimate expression of fate corresponds to the intake fraction. It is derived from the harvest fraction according to the successive processing steps to transform the agricultural commodity to food. Eilrich (1991) shows for chlorothalonil and wheat a factor 0.185 from the harvest to the food fraction (bread). As these steps are not the subject of this study, the intake fraction is assumed to be equal to the harvest fraction in the results presented here.

The effect factor is evaluated on the base of a benchmark dose. Results of the human toxicity evaluation of tested substances are presented in Table 28 according to the intake fraction and damage factors. Several data of benchmark dose are not presently available for the substances tested here.

Table 28. Toxicity evaluation of intake fraction (iF, kg substance ingested / kg applied) for substances used in wheat. Effect factor for cancer and non cancer (EF, DALY / kg substance absorbed), Human Damage Factor (HDF, DALY/ kg substance applied) and Human Toxicity Potential characterised by chloroethylene ($HTP_{chlo}$ , in kg equivalent chloroethylene / kg applied, with 1.45E-06 DALY/kg chloroethylene). I*n italic HTP without cancer effect.*

| Substances | iF kg/kg | EF non cancer DALY/kg | EF cancer DALY/kg | HDF DALY/kg | $HTP_{chlo}$ kg/kg |
|---|---|---|---|---|---|
| Diflufenican | 1.3E-03 | - | - | - | - |
| Ioxynil | 5.9E-05 | 4.7E-02 | 4.7E-01 | 3.0E-05 | 2.1E+01 |
| Isoproturon | 6.6E-05 | - | - | - | - |
| Chlormequat | 2.9E-06 | - | - | - | - |
| Ethephon | 1.2E-06 | 8.2E-01 | - | *1.0E-06* | *7.0E-01* |
| Trinexapac-ethyl | 2.8E-15 | - | - | - | - |
| Deltamethrine | 7.4E-06 | 2.3E-02 | 2.3E-01 | 1.9E-06 | 1.3E+00 |
| Pirimicarb | 5.2E-03 | - | - | - | - |
| Teflubenzuron | 3.9E-04 | - | - | - | - |
| Azoxystrobin | 1.9E-05 | - | - | - | - |
| Chlorothalonil | 5.9E-03 | 1.9E-02 | 3.7E-02 | 3.3E-04 | 2.3E+02 |
| Cyproconazole | 1.8E-03 | - | - | - | - |
| Prochloraz | 2.4E-04 | 4.1E-02 | 2.8E-01 | 7.9E-05 | 5.4E+01 |

## 7.2 Phytosanitary measures in field crops

The list of potentially used substances is long and the building of a phytosanitary strategy obeys multiple criteria. Consequently, practical information is needed to complement the data concerning agricultural practices required by law or described in technical books: used substances, effective amount per application and frequency of application per crop. Different complementary results are proposed for the evaluation of phytosanitary measures in field crops. Substances are assessed per unit quantity applied and per single treatment made under good agricultural practices. The evaluation is also made per unit crop area by accounting for the average dose per crop. According to these evaluations, differences between substances are put in evidence and problematic treatments are identified.

There is no statistic or available information about the effective use of substances. Consequently the use of data collected directly in practical conditions is the only source of data in order to notify the used substances and phytosanitary practices for each crop. The present evaluation accounts for the effective practices by farmers on the base of observed practices in a determined region.

### 7.2.1 Method

The use of pesticides was evaluated according to data collected on network of farms in Western Switzerland, provided by the Service Romand de vulgarisation agricole, an extension service (Zimmermann, 2001) and emphasized in accordance to the present study (Charles and Zimmermann, 2001). Data describing the agricultural practices were collected during three years (1998 – 2000) on 41 farms. All activities were recorded at field level, representing between 430 and 513 observed field crops each year. According to these observations, the phytosanitary practices could be described for each crop. The following crops are evaluated:

winter wheat, spring wheat, winter barley, spring barley, winter rye, winter triticale, winter oat, grain maize, forage maize, sugar and forage beet, potatoes, winter rape, soybean, sunflower, spring pea, meadow. The applications occur mostly after the winter. Some substances are applied in fall, so that the consideration of the wintertime would need some complements no developed in the present study. As most of these substances are also applied in late winter or early spring, this later case is considered for the evaluation.

The first basic results of the substances evaluation deliver the harvest fraction, the dose taken in per unit quantity applied (kg/kg) and the harvest dose per single application (kg/ha), according to good agricultural practices. The later is obtained by multiplying the harvest fraction by the quantities of the considered phytosanitary substances authorized for crops. The quantities per application are based on the official list of plant protection products (OFAG, 2002). Finally the results of harvested dose per unit area for the whole crop (per ha crop) are obtained by multiplying the harvest fraction by the average dose applied per unit area for the whole crop. Ti accounts for the effective amount of substance per application and the frequency of application for the considered crop. The harvested dose per unit area and crop corresponds to the average quantity of each substance that should be found in wheat produced per unit area (6000 kg/ha). It can also be noticed that the final concentration in the wheat (kg substance / kg wheat) can calculated as the product of quantity applied by the harvest fraction.

The periods of spray are highly varying, as substances may be used at different time of crop development. Consequently, effective collected agricultural practices are used to determine the time of spray.

Only the current method based on a benchmark dose is applied for this concluding toxicity evaluation. Several data of benchmark dose (or effect dose 10%) are not presently available, so that some Human Damage Factors (HDF) are missing or include only the non-cancer effect. This could be completed later, as benchmark dose can be extrapolated from the same toxic measures than Acceptable Daily Intake or reference Doses.

### 7.2.2 Phytosanitary data and harvest fraction

The observed data of agricultural practices and results of harvest fractions and human toxicity evaluations are given in Table 29 and Table 30 for wheat crop and in Appendix G. Harvest fraction and human toxicity for other field crops. The Figure 54 illustrates main results on human damages due to treatment on wheat crop.

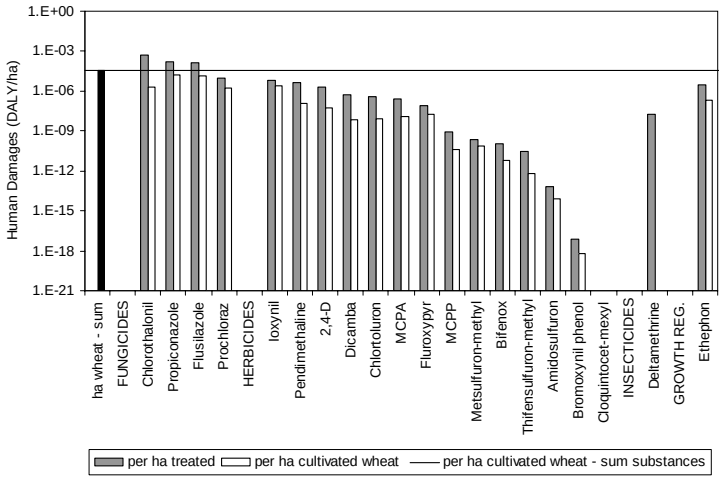



Figure 54. Human Damages per ha (DALY/ha) for substances used in wheat. Evaluation per ha treated (maximum authorised dose), per ha cultivated wheat and per ha cultivated wheat summing all substances.

More than 40 substances are used in wheat. Some substances have a high application rate 1.5 kg/ha (chlorothalonil), 1.6 kg/ha (MCPP, pendimethaline) and 2.8 kg/ha (chlortoluron), contrasting with lower rates equal or inferior to 0.01 kg/ha (metsulfuron, sulfosulfuron, deltamethrine). The dates of treatment are also variable, with an already demonstrated effect on the harvest fraction.

Human Damages per treatment depend on the combination between application rate, harvest fraction and effect factor. The differences between substances are due to the variability of agricultural practices, of substances physicochemical properties and of their toxicological effects. The comparison of the variability of the harvest fractions and of the effect factors demonstrates that the fate process is the main source of differences between substances (typically 6 orders of magnitude), as it was already assumed for the test substances. Variations of 4 orders of magnitude are observed on effect factors. These Human Damages result from the combination of several parameters, as demonstrated in the evaluation of the core model and in the first evaluation of human toxicity. Consequently the results need to be interpreted with care.

On the one hand, results of the Human Damages show that the differences in impact between substances are large, enabling to substitute problematic treatments or to try to avoid them. On the other hand, the difference between minimum and maximum application rate for the same substance only offer a limited improvement potential. The Human Damages per treatment tend to be the highest for fungicides by comparison to herbicides, indicating the risk of late applications. Available data do not offer the possibility to evaluate the effect factors as a function of the type of substance. Substitutions are difficult to evaluate for fungicides due to the present lack of toxicity data for several compounds. However, the results of harvested fractions suggest some potential substitutions. This potential is larger among herbicides attributable to some substances with Human Damages per treatment and partly explained by

the earliness of the treatments. Each substitution should additionally be confirmed by the effective similar agricultural efficiency for both compared substances.

The sum of Human Damages per unit crop area for all substances corresponds to the overall Human Damages per unit cultivated area. The variability of the dose per crop depends on the variability of the application rate and the frequency in the use of the substance. Due to a low application frequency, chlorothalonil shows a low dose per ha crop (0.007 kg/ha), although the application rate is high (in practice around 1.5 kg/ha). On the contrary, Isoproturon is very often used and its dose per crop area 0.8 kg/ha wit an application rate between 1.2 and 1.5 kg/ha. The use of insecticide is practically insignificant.

The results of Human Damages per crop area highlight some substances responsible for the most part of the toxicity. These substances are all fungicides, for which a substitution should be found or that should be avoided. However a lot of substances are not evaluated and could contribute to a large part of the total Human Damages , for instance isoproturon.

Finally the Human Damages by eating bread, due to the application of pesticides in the production of wheat, are equal to 3.7E-05 year per ha wheat. Accounting for an area of 100’000 ha wheat for bread making in Switzerland (self-production), these Human Damages are equal to 1350 days for 7.5 millions people or to 15 seconds per person. This result that represents an order of magnitude is obtained on the sole basis of the substance with available toxicological data. It could therefore be underestimated. Extrapolations for other substances lead to 7 minutes per person in the most unfavourable case.

Table 29. Description of substances used in wheat and harvest fractions. Date of treatment according to data collected during three years (1998 – 2000) on 41 farms in Western Switzerland. Minimum and maximum application rate (kg/ha) according to the official list of plant protection products (OFAG, 2002), and average application per crop (kg/ha) according to collected data. Time (days) between treatment and harvest, harvest fraction according to the model (hF, kg substance in harvest / kg applied). Harvest fraction for single source ($hF_i$ kg substance in harvest / kg applied in source i) and parameters for simplified resolution for each source soil (s), formulation deposit (fd), air (a):, maximum harvest fraction ($hF_{i,max}$, kg in harvest /kg applied in source i), time to reach the $hF_{i,max}$ ($t_{i,max}$, days) and dissipation rate ($\mu_{i,2}$, 1/days).

| Substance | Application rate / treatment | | Average appl. | Date | Time | hF | Soil | | | | Formulation deposit | | | | Air | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | min | max | / ha crop | treat. | | | $hF_s$ | $hF_{s,max}$ | $t_{s,max}$ | $\mu_{s,2}$ | $hF_{fd}$ | $hF_{fd,max}$ | $t_{fd,max}$ | $\mu_{fd,2}$ | $hF_a$ | $hF_{a,max}$ | $t_{a,ma}x$ | $\mu_{a,2}$ |
| | kg/ha | kg/ha | kg/ha | | days | kg/kg | kg/kg | kg/kg | days | 1/days | kg/kg | kg/kg | days | 1/days | kg/kg | kg/kg | days | 1/days |
| FUNGICIDES | | | | | | | | | | | | | | | | | | |
| Acibenzolar-S-methyl | 0.030 | 0.030 | 0.021 | 16.3 | 121 | 1.0E-06 | 1.3E-06 | 2.9E-04 | 14 | -5.0E-02 | 3.5E-08 | 1.3E-02 | 8 | -9.9E-02 | 1.5E-08 | 6.5E-03 | 5 | -1.2E-01 |
| Azoxystrobin | 0.200 | 0.250 | 0.044 | 25.5 | 51 | 5.7E-05 | 5.7E-05 | 1.2E-03 | 10 | -6.8E-02 | 4.6E-05 | 1.8E-02 | 7 | -1.3E-01 | 5.8E-05 | 1.8E-02 | 5 | -1.3E-01 |
| Chlorothalonil | 1.500 | 1.500 | 0.007 | 1.6 | 44 | 6.1E-03 | 3.4E-04 | 8.3E-04 | 35 | -2.0E-02 | 9.0E-03 | 1.9E-02 | 12 | -3.9E-02 | 1.1E-02 | 4.0E-02 | 33 | -6.5E-03 |
| Cyproconazole | 0.060 | 0.080 | 0.024 | 22.5 | 54 | 1.9E-03 | 6.9E-04 | 2.3E-03 | 26 | -2.7E-02 | 2.8E-03 | 1.7E-02 | 11 | -5.2E-02 | 2.4E-03 | 6.0E-03 | 5 | -5.4E-02 |
| Cyprodinil | 0.600 | 0.600 | 0.050 | 25.4 | 81 | 2.4E-06 | 1.9E-06 | 4.1E-05 | 13 | -5.3E-02 | 4.2E-06 | 1.9E-03 | 8 | -1.1E-01 | 1.6E-07 | 7.0E-05 | 1 | -1.1E-01 |
| Difenoconazole | 0.125 | 0.125 | 0.004 | 2.6 | 43 | 1.3E-03 | 9.8E-05 | 1.1E-04 | 36 | -1.9E-02 | 1.9E-03 | 1.2E-03 | 13 | -3.8E-02 | 1.8E-03 | 8.7E-04 | 10 | -3.8E-02 |
| Epoxiconazole | 0.063 | 0.125 | 0.032 | 25.5 | 51 | 8.8E-03 | 4.6E-04 | 7.7E-04 | 75 | -9.3E-03 | 1.4E-02 | 7.5E-03 | 16 | -1.8E-02 | 1.3E-02 | 3.9E-03 | 10 | -1.9E-02 |
| Famoxadone | 0.150 | 0.280 | 0.009 | 24.5 | 52 | 3.8E-06 | 7.1E-07 | 5.1E-06 | 11 | -6.3E-02 | 7.1E-06 | 2.9E-04 | 8 | -1.3E-01 | 2.1E-06 | 4.1E-05 | 1 | -1.3E-01 |
| Fenpropimorphe | 0.188 | 0.375 | 0.030 | 1.6 | 44 | 6.1E-04 | 5.0E-05 | 5.7E-05 | 38 | -1.8E-02 | 1.1E-03 | 1.6E-03 | 13 | -3.6E-02 | 2.8E-05 | 6.0E-05 | 1 | -4.1E-02 |
| Fludioxonil | 0.009 | 0.009 | 0.001 | 5.10 | 136 | 1.5E-07 | 3.3E-07 | 3.7E-05 | 16 | -4.4E-02 | 1.5E-07 | 6.8E-04 | 9 | -8.8E-02 | 1.5E-07 | 1.2E-04 | 2 | -8.8E-02 |
| Flusilazole | 0.250 | 0.300 | 0.033 | 4.5 | 72 | 2.2E-03 | 5.1E-04 | 7.9E-04 | 122 | -5.7E-03 | 5.1E-03 | 3.9E-03 | 20 | -1.1E-02 | 1.8E-03 | 2.0E-03 | 11 | -1.9E-02 |
| Kresoxim-methyl | 0.126 | 0.126 | 0.028 | 24.5 | 52 | 1.1E-06 | 2.3E-06 | 3.4E-04 | 6 | -1.2E-01 | 2.3E-07 | 3.1E-03 | 5 | -1.4E-01 | 9.6E-08 | 7.5E-04 | 1 | -2.4E-01 |
| Metconazole | 0.090 | 0.090 | 0.010 | 26.5 | 50 | 6.7E-03 | 4.6E-04 | 7.2E-04 | 112 | -6.2E-03 | 1.1E-02 | 3.2E-03 | 19 | -1.2E-02 | 8.8E-03 | 9.7E-04 | 7 | -1.3E-02 |
| Prochloraz | 0.464 | 0.464 | 0.079 | 1.5 | 75 | 6.7E-05 | 1.3E-05 | 4.6E-05 | 22 | -3.2E-02 | 1.7E-04 | 1.4E-03 | 10 | -6.3E-02 | 3.9E-05 | 1.1E-04 | 1 | -6.5E-02 |
| Propiconazole | 0.125 | 0.125 | 0.012 | 25.4 | 81 | 4.0E-03 | 7.7E-04 | 1.3E-03 | 83 | -8.4E-03 | 1.0E-02 | 5.7E-03 | 17 | -1.7E-02 | 5.9E-03 | 1.1E-03 | 4 | -1.9E-02 |
| Spiroxamine | 0.200 | 0.375 | 0.026 | 16.5 | 60 | 3.8E-07 | 6.5E-07 | 1.1E-04 | 7 | -1.0E-01 | 1.5E-07 | 1.0E-02 | 6 | -1.5E-01 | 5.5E-09 | 7.3E-04 | 1 | -2.2E-01 |
| Tebuconazole | 0.125 | 0.250 | 0.023 | 22.5 | 54 | 7.0E-03 | 6.3E-04 | 9.3E-04 | 85 | -8.2E-03 | 1.2E-02 | 4.5E-03 | 17 | -1.6E-02 | 1.0E-02 | 1.9E-03 | 9 | -1.7E-02 |
| HERBICIDES | | | | | | | | | | | | | | | | | | |
| 2,4-D | 0.900 | 1.200 | 0.036 | 22.4 | 84 | 4.1E-06 | 6.4E-06 | 1.2E-02 | 9 | -8.5E-02 | 2.3E-07 | 5.1E-02 | 6 | -1.5E-01 | 1.5E-07 | 7.2E-02 | 4 | -1.5E-01 |
| Amidosulfuron | 0.015 | 0.030 | 0.003 | 23.3 | 114 | 2.4E-08 | 3.1E-08 | 4.8E-02 | 7 | -1.2E-01 | 9.7E-10 | 5.1E-02 | 6 | -1.5E-01 | 3.0E-12 | 2.7E-03 | 0 | -1.8E-01 |
| Bifenox | 0.750 | 0.900 | 0.044 | 22.3 | 115 | 1.3E-08 | 7.3E-09 | 4.7E-06 | 10 | -6.8E-02 | 2.1E-08 | 5.5E-04 | 7 | -1.4E-01 | 4.2E-08 | 8.4E-04 | 12 | -4.7E-02 |
| Bromoxynil phenol | 0.240 | 0.480 | 0.041 | 23.3 | 114 | 5.3E-16 | 6.9E-16 | 5.7E-04 | 3 | -2.5E-01 | 3.5E-26 | 7.5E-03 | 3 | -1.6E-01 | 4.6E-26 | 9.4E-03 | 5 | -6.4E-02 |
| Chlortoluron | 1.200 | 2.800 | 0.065 | 9.11 | 136 | 1.9E-04 | 2.8E-04 | 1.4E-01 | 16 | -4.2E-02 | 1.9E-04 | 2.2E-02 | 12 | -4.2E-02 | 1.9E-04 | 3.2E-03 | 2 | -5.6E-02 |

| Substance | Application rate / treatment | | Average appl. | Date | Time | hF | Soil | | | | Formulation deposit | | | | Air | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | min | max | / ha crop | treat. | | | $hF_s$ | $hF_{s,max}$ | $t_{s,max}$ | $\mu_{s,2}$ | $hF_{fd}$ | $hF_{fd,max}$ | $t_{fd,max}$ | $\mu_{fd,2}$ | $hF_a$ | $hF_{a,max}$ | $t_{a,max}$x | $\mu_{a,2}$ |
| | kg/ha | kg/ha | kg/ha | | days | kg/kg | kg/kg | kg/kg | days | 1/days | kg/kg | kg/kg | days | 1/days | kg/kg | kg/kg | days | 1/days |
| Clodinafop-propargyl | 0.060 | 0.084 | 0.003 | 30.3 | 107 | 2.1E-07 | 2.7E-07 | 1.4E-04 | 10 | -6.9E-02 | 1.7E-08 | 2.3E-03 | 7 | -1.4E-01 | 9.7E-09 | 6.7E-04 | 2 | -1.4E-01 |
| Cloquintocet-metyl | 0.012 | 0.021 | 0.001 | 30.3 | 107 | 1.0E-20 | 1.4E-20 | 8.1E-08 | 2 | -2.9E-01 | 8.3E-30 | 4.6E-05 | 3 | -1.4E-01 | 5.7E-30 | 2.0E-05 | 1 | -5.8E-01 |
| Dicamba | 0.119 | 0.119 | 0.002 | 31.5 | 45 | 9.7E-05 | 1.7E-04 | 1.5E-02 | 8 | -9.2E-02 | 3.7E-05 | 2.2E-02 | 6 | -1.6E-01 | 4.9E-05 | 9.5E-02 | 5 | -1.6E-01 |
| Diflufenican | 0.050 | 0.075 | 0.034 | 26.3 | 111 | 6.9E-04 | 7.0E-05 | 8.2E-05 | 156 | -4.5E-03 | 2.9E-03 | 5.0E-04 | 21 | -8.9E-03 | 2.0E-03 | 4.9E-04 | 21 | -9.9E-03 |
| Fluroxypyr | 0.104 | 0.130 | 0.034 | 19.4 | 87 | 3.8E-03 | 3.7E-03 | 3.0E-02 | 42 | -2.0E-02 | 3.4E-03 | 9.0E-02 | 11 | -2.9E-02 | 3.9E-03 | 5.9E-02 | 8 | -2.9E-02 |
| Ioxynil | 0.213 | 0.355 | 0.129 | 26.3 | 111 | 3.7E-05 | 5.2E-06 | 1.7E-03 | 10 | -7.1E-02 | 2.8E-05 | 6.9E-02 | 5 | -1.4E-01 | 2.0E-04 | 4.6E-02 | 7 | -3.0E-02 |
| Isoproturon | 1.245 | 1.494 | 0.820 | 21.3 | 116 | 8.8E-05 | 1.1E-04 | 9.5E-03 | 19 | -3.9E-02 | 1.5E-05 | 4.3E-02 | 9 | -7.0E-02 | 1.4E-05 | 2.1E-02 | 5 | -7.1E-02 |
| MCPA | 0.660 | 1.485 | 0.068 | 25.4 | 81 | 4.2E-07 | 6.7E-07 | 1.2E-02 | 7 | -1.1E-01 | 6.5E-08 | 3.8E-02 | 5 | -1.9E-01 | 2.2E-09 | 3.8E-02 | 3 | -2.0E-01 |
| MCPP | 1.400 | 1.600 | 0.075 | 22.3 | 115 | 2.0E-07 | 2.6E-07 | 6.7E-03 | 9 | -7.8E-02 | 1.3E-10 | 8.0E-02 | 5 | -1.5E-01 | 1.3E-13 | 2.2E-02 | 2 | -2.3E-01 |
| MCPP-P | 0.650 | 0.780 | 0.114 | 3.4 | 103 | 2.9E-06 | 4.0E-06 | 1.0E-02 | 10 | -7.0E-02 | 2.1E-08 | 2.0E-02 | 7 | -1.3E-01 | 2.2E-08 | 3.2E-02 | 3 | -1.3E-01 |
| Metsulfuron-methyl | 0.005 | 0.005 | 0.002 | 5.4 | 101 | 7.9E-06 | 5.9E-06 | 4.0E-04 | 20 | -3.5E-02 | 3.8E-09 | 3.7E-05 | 10 | -6.9E-02 | 3.7E-05 | 7.6E-02 | 3 | -6.9E-02 |
| Pendimethaline | 1.200 | 1.600 | 0.043 | 9.11 | 136 | 7.5E-05 | 2.9E-05 | 9.6E-05 | 67 | -1.0E-02 | 7.5E-05 | 9.7E-05 | 16 | -2.1E-02 | 7.3E-05 | 1.3E-05 | 3 | -2.1E-02 |
| Pyridate | 0.800 | 0.800 | 0.010 | 30.3 | 107 | 2.1E-11 | 2.7E-13 | 1.6E-03 | 3 | -2.1E-01 | 2.5E-11 | 1.2E-03 | 4 | -1.4E-01 | 1.5E-21 | 2.0E-02 | 2 | -4.1E-01 |
| Sulfosulfuron | 0.010 | 0.020 | 0.001 | 4.4 | 102 | 7.2E-05 | 9.7E-05 | 3.9E-03 | 23 | -3.0E-02 | 5.9E-08 | 2.4E-04 | 11 | -5.8E-02 | 1.6E-05 | 7.5E-03 | 1 | -5.8E-02 |
| Thifensulfuron-methyl | 0.061 | 0.061 | 0.002 | 4.4 | 102 | 3.8E-09 | 5.2E-09 | 9.0E-05 | 8 | -9.0E-02 | 5.9E-12 | 2.8E-05 | 6 | -1.4E-01 | 6.9E-10 | 1.1E-01 | 4 | -1.8E-01 |
| INSECTICIDE | | | | | | | | | | | | | | | | | | |
| Deltamethrine | 0.008 | 0.008 | 0.000 | 15.5 | 61 | 8.8E-06 | 8.3E-10 | 1.8E-09 | 21 | -3.3E-02 | 2.0E-05 | 7.3E-05 | 10 | -6.6E-02 | 5.1E-06 | 1.1E-05 | 2 | -6.6E-02 |
| Pirimicarb | 0.075 | 0.075 | 0.000 | 15.5 | 61 | 5.2E-03 | 1.9E-03 | 1.4E-02 | 112 | -6.7E-03 | 6.4E-03 | 9.5E-02 | 15 | -1.2E-02 | 1.6E-03 | 4.7E-03 | 1 | -2.1E-02 |
| Teflubenzuron | 0.060 | 0.060 | 0.002 | 15.5 | 61 | 3.2E-04 | 9.4E-06 | 1.2E-05 | 34 | -2.0E-02 | 6.4E-04 | 5.8E-04 | 13 | -4.0E-02 | 5.5E-04 | 5.6E-04 | 12 | -4.0E-02 |
| GROWTH REG. | | | | | | | | | | | | | | | | | | |
| Chlormequat chloride | 0.230 | 1.150 | 0.010 | 23.4 | 83 | 2.2E-06 | 4.4E-07 | 3.3E-05 | 14 | -4.8E-02 | 7.9E-08 | 7.5E-04 | 9 | -9.6E-02 | 1.8E-05 | 1.0E-01 | 4 | -9.6E-02 |
| Ethephon | 0.360 | 0.720 | 0.056 | 2.5 | 74 | 4.9E-06 | 7.6E-09 | 3.7E-07 | 14 | -4.8E-02 | 9.1E-08 | 3.1E-04 | 9 | -9.6E-02 | 4.9E-05 | 1.6E-01 | 6 | -9.6E-02 |
| Trinexapac-ethyl | 0.100 | 0.150 | 0.095 | 28.4 | 78 | 6.1E-14 | 1.3E-27 | 2.8E-04 | 1 | -7.0E-01 | 3.8E-10 | 1.3E-02 | 2 | -2.1E-01 | 1.9E-50 | 3.0E-03 | 0 | -1.5E+00 |

Table 30. Toxicity evaluation for substances used in wheat. Intake fraction (iF, kg substance ingested / kg applied)[1], Effect factor (DALY / kg substance absorbed) for cancer and non cancer, Human Damage Factor in DALY per unit quantity applied (DALY / kg substance applied); Human Damages per treatment (DALY / kg ha treated) and per unit wheat area (DALY / ha crop cultivated), *in italic substances for which there is no Effect Factor for cancer effect.*

[1] The present intake fraction is assumed equal to the harvested fraction. Eilrich (1999) shows that Chlorothalonil, the intake fraction can be typically reduced by a factor 5 compared to the intake fraction, by the washing, peeling and cooking processes. By default, this factor 5 should be applied for all substances, further studies being required to study the reduction linked to these processes.

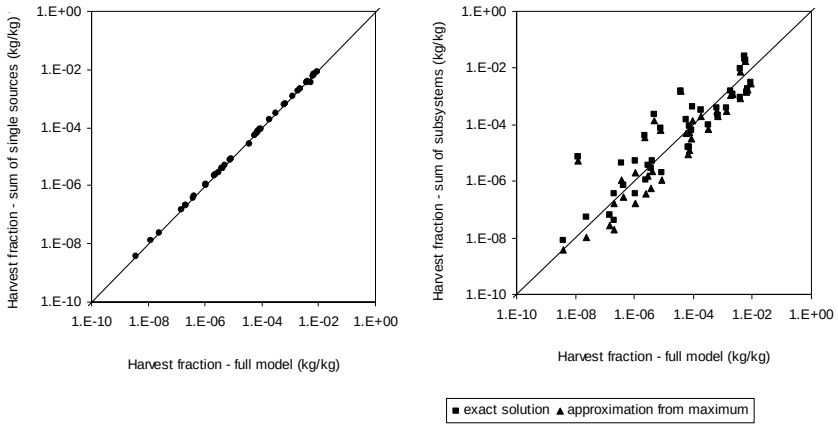
| Substances | Crop | Intake fraction | Effect Factor | | Human Damages | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | oral | non cancer | cancer | non cancer | cancer | per treat.min | per treat.max | per ha cult. crop |
| | | kg/kg | DALY/kg | DALY /kg | DALY /kg | DALY /kg | DALY /ha treat. | DALY /ha treat. | DALY /ha cult. |
| FUNGICIDES | | | | | | | | | |
| Chlorothalonil | wheat winter | 6.1E-03 | 1.9E-02 | 3.7E-02 | 1.1E-04 | 2.3E-04 | 5.1E-04 | 5.1E-04 | 2.3E-06 |
| Flusilazole | wheat winter | 2.2E-03 | 1.9E-01 | - | 4.1E-04 | - | *1.0E-04* | *1.2E-04* | *1.4E-05* |
| Prochloraz | wheat winter | 6.7E-05 | 4.1E-02 | 2.8E-01 | 2.8E-06 | 1.9E-05 | 1.0E-05 | 1.0E-05 | 1.7E-06 |
| Propiconazole | wheat winter | 4.0E-03 | 3.0E-02 | 3.0E-01 | 1.2E-04 | 1.2E-03 | 1.7E-04 | 1.7E-04 | 1.6E-05 |
| HERBICIDES | | | | | | | | | |
| 2,4-D | wheat winter | 4.1E-06 | 1.4E-01 | 2.5E-01 | 5.9E-07 | 1.0E-06 | 1.5E-06 | 1.9E-06 | 5.8E-08 |
| Amidosulfuron | wheat winter | 2.4E-08 | 9.5E-05 | - | 2.3E-12 | - | *3.4E-14* | *6.9E-14* | *7.9E-15* |
| Bifenox | wheat winter | 1.3E-08 | 9.4E-04 | 9.4E-03 | 1.2E-11 | 1.2E-10 | 9.8E-11 | 1.2E-10 | 5.8E-12 |
| Bromoxynil phenol | wheat winter | 5.3E-16 | 2.8E-02 | - | 1.5E-17 | - | *3.5E-18* | *7.1E-18* | *6.1E-19* |
| Chlortoluron | wheat winter | 1.9E-04 | 7.5E-04 | - | 1.4E-07 | - | *1.7E-07* | *3.9E-07* | *9.0E-09* |
| Cloquintocet-metyl | wheat winter | 1.0E-20 | 2.7E-03 | - | 2.7E-23 | - | *3.3E-25* | *5.7E-25* | *2.1E-26* |
| Dicamba | wheat winter | 9.7E-05 | 4.9E-02 | - | 4.7E-06 | - | *5.6E-07* | *5.6E-07* | *7.5E-09* |
| Fluroxypyr | wheat winter | 3.8E-03 | 1.5E-04 | - | 5.9E-07 | - | *6.1E-08* | *7.6E-08* | *2.0E-08* |
| Ioxynil | wheat winter | 3.7E-05 | 4.7E-02 | 4.7E-01 | 1.8E-06 | 1.8E-05 | 4.1E-06 | 6.9E-06 | 2.5E-06 |
| MCPA | wheat winter | 4.2E-07 | 2.5E-01 | 1.9E-01 | 1.1E-07 | 7.9E-08 | 1.2E-07 | 2.7E-07 | 1.3E-08 |
| MCPP | wheat winter | 2.0E-07 | 2.9E-03 | - | 5.9E-10 | - | *8.2E-10* | *9.4E-10* | *4.4E-11* |
| Metsulfuron-methyl | wheat winter | 7.9E-06 | 5.6E-03 | - | 4.5E-08 | - | *2.2E-10* | *2.2E-10* | *7.8E-11* |
| Pendimethaline | wheat winter | 7.5E-05 | 3.0E-03 | 3.7E-02 | 2.2E-07 | 2.8E-06 | 3.6E-06 | 4.9E-06 | 1.3E-07 |
| Thifensulfuron-methyl | wheat winter | 3.8E-09 | 1.1E-01 | - | 4.3E-10 | - | *2.6E-11* | *2.6E-11* | *6.8E-13* |
| INSECTICIDES | | | | | | | | | |
| Deltamethrine | wheat winter | 8.8E-06 | 2.3E-02 | 2.3E-01 | 2.1E-07 | 2.1E-06 | 1.7E-08 | 1.7E-08 | 0.0E+00 |
| GROWTH REG. | | | | | | | | | |

| Substances | Crop | Intake fraction | Effect Factor | | Human Damages | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | oral | non cancer | cancer | non cancer | cancer | per treat.min | per treat.max | per ha cult. crop |
| | | kg/kg | DALY/kg | DALY /kg | DALY /kg | DALY /kg | DALY /ha treat. | DALY /ha treat. | DALY /ha cult. |
| Ethephon | wheat winter | 4.9E-06 | 8.2E-01 | - | 4.1E-06 | - | *1.5E-06* | *2.9E-06* | *2.3E-07* |
| TOTAL | wheat winter | | | | | | | | *3.7E-05* |

## 7.3 Interpretation

A short interpretation of the results obtained for the set of substances used in wheat and more particularly for the phytosanitary measures in wheat is made here in relation with the lasts steps in the application of the method.

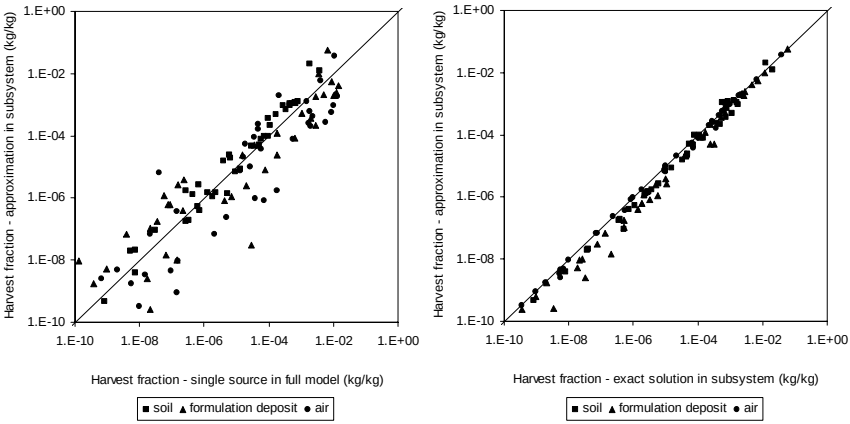
First results consist in the harvest fraction given by the full model, the harvest fraction of each single source and the parameters for simplified resolution. Figure 55A first compares the harvest fraction given by the full model with the sum of harvest fractions from single sources. It shows that there is no loss of precision by the aggregating the evaluations of each single source, by comparison to the full application of the model in one step. The loss of precision is obvious by a resolution with subsystems, as shown in Figure 55B. In that case, the deviation attains a factor 10 to 100 and more.




A. Single sources B. Subsystems

Figure 55. Harvest fraction for substance applied in the full system compared in A. with the sum of harvest fractions for substance applied as single source in air, soil and surface deposit using the full model, in B. with sum of harvest fractions from subsystems, according to exact solution and to approximation given by the dissipation of the maximum accumulated mass. Harvest fraction expressed as kg substance in harvest / kg substance applied in the system, respectively in the single medium. Data from Table 29.

Figure 56A. shows that the loss of precision due to the resolution with subsystems concerns all the sources: soil, air and formulation deposit. However, this deviation is not much enhanced by the approximation considering the dissipation of the maximum accumulated mass, as shown in Figure 56B. This indicates a relative unreliability of the model simplification into subsystems, but beyond this deviation a possibility of system interpretation and approximated resolution considering the maximum accumulated mass.




A. Full model and subsystems

B. Approximation in subsystems

Figure 56. A. Harvest fraction for each single source in air, soil and formulation deposit using the full model compared with harvest fraction for each single source approximated by the exact resolution of the subsystems. B. Harvest fraction for each single source given by the exact resolution of the subsystems compared with the harvest fraction for each single source given by the approximation considering the dissipation of the maximum accumulated mass. Harvest fraction expressed as kg substance in harvest / kg substance applied in the single medium. Data from Table 29

No uncertainty analysis is carried out for the set of substances evaluated here. Confidence factors identified in chapter 6.2 Uncertainty analysis in particular in Table 21 give an indicative value by considering a confidence factor of about 5 for a partial uncertainty evaluation, without the effect of system evolution. The overall uncertainty can be evaluated from Figure 45 in accordance with the propagation of the confidence factor as function of time from application to harvest.

The evaluation of the toxicity concludes the application of the method. Evaluation of the substances per application on 1 hectare, by taking into account the rate of application, allows a comparison of the substances according to the effective conditions of utilisation. Figure 57 illustrates the results of harvest fraction and human toxicity. The restricted choice of substances presented here does probably not represent the maximum range of Human Damages levels, but indicates a grouping of several substances with similar results, and some divergent substances. For a similar function, substances show differences of some orders of magnitude. Highest harvest fractions concern mainly the latest applied substances such as fungicides (chlorothalonil, propiconazole). The relative high persistence and the high toxicity effect of some herbicides (pendimethaline, ioxynil) explain the relative high level of Human Damages for theses substances. However, the results have to be interpreted according to some limits of the model previously discussed for herbicides evaluation (persistence, phloem mobility, selectivity).

The results of the Human Toxicity Potential show variability largely dependent on the variation between the substances fate. According to the substances studied here, the variability between substances is higher for the fate factor (iF) than for the effect factor (EF). The range of effect factors varies by 4 orders of magnitude between substances, but reaches about 20 for the intake fractions. Conclusively, the fate contributes mainly to the differences between substances. The variability of Human Damages per treatment allows identifying substitutions between substances with same function as plant treatment products.

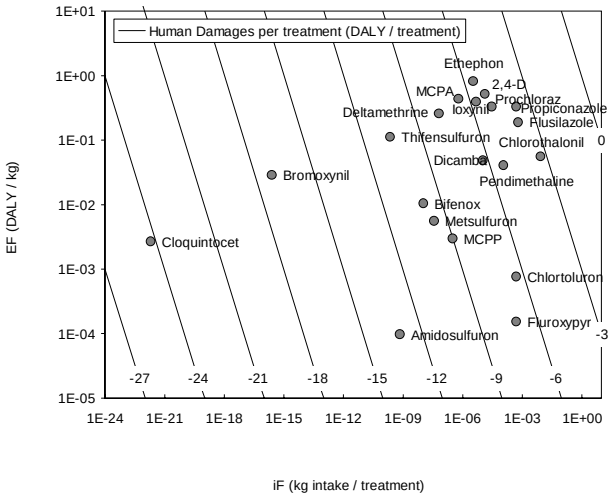



Figure 57. Distribution of substances as a function of intake fraction (iF, kg intake / treatment) and to Effect Factor (EF, DALY / kg substance absorbed), and levels of Human Damage Factor per application according to both factors (Human Damages isolines, DALY / treatment).

# 8. Conclusions

This study has developed the assessment of pesticides residues in harvested crops. Conclusions are brought here by answering to the different challenges and questions scheduled in the introduction (chapter 1.4). Prospects for additional developments are also drawn up.

- **Process description and modelling phytosanitary measures**

**How can the fate of pesticides be described, what are the involved processes and in which system ?**

The fate of pesticides is described by a model representing the system phytosanitary measures – plant – environment and describing the main transport and dissipation processes. These processes are dynamic, as a function of the elapsed time between pesticide application and crop harvest. The initial concentrations of substance in the soil, the air and the formulation deposit on plants are determined by the distribution of pesticide in the system at spraying. The initial distribution depends notably on the crop stage.

Main transport processes are in form of advection and diffusion. Degradation of substance and plant growth are additional processes to be accounted for. Each transport is described by a transfer rate accounting for the process and for the equilibrium partitioning between the two exchanging phases or compartments. Partition coefficients describe the substance behaviour and distribution between different phases. These parameters show a high variation between substances, are sources of an important sensitivity of the system and contribute largely to the uncertainty of the results. However, their contribution to the behaviour of substances is highly variable, may be determinant or negligible, with increasing or limiting effect on mobility depending on other properties. Consequently a direct relationship between partition coefficients and residues at harvest cannot be put in evidence.

Parameters linked with the system dynamics are important factors determining the fate and have an important influence on the sensitivity and on propagation of uncertainty of the results. Particularly, half-life values and elapsed time between application and harvest determine the persistence of the substance. These parameters represent the most determining parameters and their influences on the dynamic evolution of the system are the easiest to interpret.

The organisation of the system describing the environment and the plant is chosen in order to include only determining compartments, to insure the understanding and interpretation of the model functioning. Air, soil and formulation deposit are the primer compartments receiving the sprayed substance and are subsequently sources for further transfer and accumulation in plant. Plant compartments included in the system are identified as a function of the sources of pesticides from the environment and of internal transport processes. Fine roots, stem and leaves are the main plant compartments; fruits are in equilibrium with the stem or the leaf depending on the exposure of this plant organ to the applied substance.

**What is the importance of direct application of a substance on plant compared to release in soil and air for the occurrence of residues, and how can fate processes be modelled ?**

Initial conditions of the system determine the first distribution of substance: the plant canopy and the losses of substances during application. A large difference is observed between herbicides and fungicides, that is between soon and late applied pesticides. Early applied herbicides tend to have their major effect through releases to soil, whereas residues of late applied fungicides are mainly due to formulation deposits on plants. Consequently the importance of the direct application on plants is high, particularly with pesticides applied during crop growth and just before harvest. For this reason the model needs to account for the plant stage and instant leaf area index at application time.

The residence time of the substance is a central factor to determine the relevant pathway (air, soil, formulation deposit). The degradation in air is very fast for most pesticides, whereas the persistence of substance in soil may be very long. The half-life of substance deposited on plant is limited to a few days, but the transfer is fast from formulation deposit to the inner plant, where degradation is generally much slower. Consequently the direct application is an important source for accumulation in plant. It concerns particularly substances rapidly transported into the plant tissue instead of being degraded as deposit on plant surface.

The recent publications concerning the understanding and the modelling of pesticides transfer from deposit through the cuticular waxes and membrane offer new possibilities to model pesticide fate in agricultural systems and to account for the contribution of direct application to the occurrence of residues. Particularly the description and quantification of the substance mobility in the cuticular membrane represents an essential factor for the evaluation of pesticide fate and a potential improvement for environmental multimedia models (Impact 2002+).

**How does dynamic behaviour affect the final residues in plants depending on the time interval between application and harvest ?**

The dynamic behaviour first affects the initial distribution of substance between the air, the soil and the deposit on plant surface as a function of the dynamic development of the crop, including the growth and the leaf area index evolution. However, the dynamic behaviour principally relates to the time interval between application and harvest. The initial transport processes, during the first days after the application distribute the substance in the different system compartments. Once residues in each plant compartment have reached a maximum amount, a dissipation phase occurs up to the moment of harvest. The duration of these determining periods, from application to maximum residues and from maximum residues to harvest, is determinant for the level of residues. These processes directly depend on the half-lives of the substance in the initial compartment and inside the plant. It also depends on the transfer rates between the compartments. The consideration of this dynamic behaviour is an essential factor that makes the modelling of pesticides residues distinct from other applications of multi-media models.

- **System understanding.**

**What are the procedure and requirements to simulate the dynamic functioning of the whole system ?**

The level of complexity of the model determines the way to solve it mathematically. It also opens the possibility to complement the detailed results with simpler tools to understand the functioning of the system, to interpret the results and to approximate them.

The model is based on initial amounts of substance in the source compartments, on transfer rates linking the compartments and on a dynamic modelling of the system, as a function of the time interval between application and harvest. Each compartment is described by a linear differential equation defining the variation in accumulated mass and its dissipation. The capacity to express each process by the determining factors is the major challenge in building the model.

The low availability and partly unsatisfying quality of data for pesticides description is a major complication for the methodology development and application. To be significant, high differences between the results are needed particularly caused by the uncertainty of the partition coefficients and the half-life values. Besides, the lack of data for half-life in plant tissue leads to a strong extrapolation for a determinant factor. Consequently the results need to be handled with precaution, as much more as a detailed verification of the functioning of the model with analytical data is mostly unachievable.

**What are the most significant relationships describing the functioning of the system ? What are the corresponding pertinent approximations ?**

Most significant relationships describing the functioning of the system are identified by decomposing the system and simplifying its resolution. These developments also consist in potential approximations for the resolution of the full system. The simplification of the system into source subsystems (air, soil, formulation deposit) and the receiving plant compartment (stem), put in evidence a strong direct relationship between both source and receiving compartments. The possibility, under conditions, to further simplify the subsystem by ignoring the transfer back from receiving to the source compartment confirms the low contribution of feedback in the functioning of this complex system.

Determinant pathways for substance accumulation in plant are identified. The formulation deposit is an important source, particularly for late applied pesticides. Due to the higher persistence in ground, the soil is logically determinant for early applied pesticides, for substances with low degradation rate and for long-term evolutions. The contribution of substance from the air is mostly negligible.

The evolution of each subsystem is characterised by a maximum accumulated mass. The capacity to quantify this maximal accumulated mass and the time to reach it is a major contribution for the understanding of the system functioning. This point corresponds to equilibrium, when the flux of transfer from the source compartment is equal to the flux of dissipation from the receiving plant compartment. The time of maximum accumulation is logically followed by a degradation process, for which the dissipation rate and the long-term evolution are quantified.

Finally, the simplification in subsystems contributes to the development of additional tools. Particularly, a simplified resolution consists in considering the maximum accumulated substance and the time of maximum accumulation to harvest together with long-term dissipation. The sum of the subsystems results gives a pertinent approximation of the total system.

- **Assessment of pesticides in agricultural products and practices.**

**What are the residues at harvest for different application times and substances?**

The residues at harvest are in principle lower than the tolerance value, which constitutes a control of the pertinence of the results obtained by modelling. Some exceptions indicate that the model functioning is rather conservative with low losses, but also that high residue levels may be potentially reached with a few substances. Harvest fractions tend to be the highest for fungicides, due to late applications. The persistence of herbicides in soil may lead to high harvest fraction, although these substances have a long delay between application and harvest. Very high and low residue levels are found among all types of substances highlighting a very large variability in fate.

**What are the optimisation factors for pesticide use and the possibility of substance substitutions according to fate, exposure and effect factors of the toxicity ?**

The result of 15 seconds or even 7 minutes of life lost due to pesticides absorbed with bread can be seen as rather limited compared to the benefice of eating bread. Admitting this valuation, it underlines that the presence of residues has probably a greater impact on the societal value of food as on its toxicity on humans. It confirms the legal admittance of pesticides occurrence in food on a strictly human toxicological point of view. However, the variability between substances indicates effective optimisation potentials to limit occurrence of residues in food and risk of toxicity. Problematic substances may be substituted on the basis of the actual available list of Human Damages per treatment. The fate process represents the highest source of variation for the toxicity, larger than the effect of the substance for the present dataset. However the toxicity evaluation needs to account for both factors, as only their combination effectively allows evaluating the toxicity. In opposite the application rate does not explain the high variation in residue levels at harvest. Eventually, the time of application may represent an optimisation potential, particularly for late treatments.

- **Final considerations and perspectives**

According to these answers, the objectives of the study have been achieved: identification and description of main processes in environment – plant exchanges, building of a model to assess the residue concentration at harvest in agricultural commodities, understanding of the functioning of the system phytosanitary measures - plant – environment, characterisation of pesticides used in field cropping systems and identification of optimisation potentials in phytosanitary measures. The methodology for the evaluation of pesticide fate in agricultural commodities is improved by the consideration of dynamic processes, of agricultural conditions and of direct applications on plants. This opens new perspectives in the frame of life cycle assessment in agriculture, in particular concerning the effective relevance of pesticides in agricultural products on a toxicological point of view. Further research is also needed to improve the model. It concerns factors describing the transfer, the quality of the data, the toxicity evaluation, some factors not accounted for, and potential collaborations with scientists from other domains.

There is a specific need to improve the description of determinant transfers between environment and vegetation. Particularly, knowledge is continuously improved concerning the pesticides mobility in cuticular membrane and the substance partitioning between the different media from the formulation deposit to the plant inner. Developments concern also the other pathways for accumulation in plant, from the soil and from the air. The present results have shown that the soil may be an important source for accumulation, particularly on a long time perspective. A better knowledge should be obtained for the balance between the accumulation to the plant and the losses from the agricultural soil to other environmental compartments. Concerning the air, major improvements should contribute to evaluate with

more details losses at application time and in the period just after. The use of environmental literature for the development of the model and its subsequent integration in an environmental multimedia model has already begun, which should bring additional synergies between both approaches.

The quality of data should be a permanent survey. Particularly, half-life data are determinant for the functioning of the present model. No data are available for the degradation in plant and degradation on plant surface is assumed as non-specific to the substance. A procedure for extrapolations should be developed, since no availability is rendered possible. The general quality of other half-life data is also problematic. The methodology developed here has shown how to handle with the results to avoid misinterpretations, but a lower uncertainty level could be obtained by a better quality of half-life data. New measurement methods such as those recently presented by Wild et al. (2004) could enable to better measure the dynamic behaviour in plant and determine these half-lives in the plant. Reciprocally, the developed models in the present work could help interpreting results of these measurements.

Concerning the toxicity evaluation, a better knowledge is needed for the pesticide fate between the harvest in agricultural field and the ingested food. The comparison of the different ways of exposure to pesticides belongs also to such developments, in particular concerning direct ingestion with food, less direct exposure pathways by inhalation and by absorption with water, and even exposure for agricultural workers. Finally the availability of new data for toxicity effect would enlarge the applicability of the present model.

Some factors are not considered in the present method due to the lack of descriptive and quantitative methodology or in accordance with the frame of the present study. The formulation of plant treatment products is a major source of controlling the fate of the active substances, despite their physico-chemical characteristics. The incidence of the formulants on the fate and its variability need to be better controlled. In parallel, the way to consider the climatic factors and the good agricultural practices has to be continuously reassessed. The evaluation of metabolites resulting from substances degradation belongs to further improvements, for the fate analysis as for the effect evaluation.

Finally, beyond the frame of life cycle assessment, the present model open possibilities for collaboration between different domains. The analytical surveys of substances in agricultural commodities need solutions for recurring problematic substances or help in the analysis and understanding of some complex cases. Analytical results are also possibilities to further test the model functioning. The present model represents also a development in the modelling of dynamic processes, in this case typical for the use of plant treatment products. The extension of the model to a system representing the agricultural field and its near environment could be a useful tool to assess the dynamic fate of pesticides in the near environment in particular in proximate soil and water systems.

# References

Abraham, M.H., McGowan, J.C., 1987. The use of Characteristic volumes to measure cavity terms in reversed phase liquid chromatography. Chromatographia, 23: 243-246.

Baur, P., 1997. Surfactants effects on cuticular penetration of neutral polar compounds: dependence on humidity and temperature. J. Agric. Food Chem. 47: 753-761.

Baur, P., Marzouk, H., Schönherr, J., Grayson, B.T. 1997. Partition coefficients of active ingredients between plant cuticle and adjuvants as related to rates of foliar uptake. J. Agric. Food Chem. 45: 3659-3665.

Baur, P., Marzouk, H., Schönherr, J. 1997. Estimation of path lengths for diffusion of organic compounds through leaf cuticles. Plant, Cell and Environment 22: 291-299.

Baur, P., Schönherr, J., Grayson, B.T., 1999. Polydisperse ethoxylated fatty alcohol surfactants as accelerators of cuticular penetration. 2: Separation of effects on driving force and mobility and reversibility of surfactant action. Pestic. Sci. 55: 831-842.

Bennett, D.H., McKone, T.E., Evans, J.S., Nazaroff, W.W., Margni, M., Jolliet, O., Smith, K.R., 2002a. Defining intake fraction. Environ. Sci. Technol. 36: 207A-211A.

Bennett, D.H., Margni, M., McKone, T.E., Jolliet, O., 2002b. Intake fraction for multi-media pollutants. a tool for Life Cycle Analysis and comparative Risk Assessment. Risk Analysis 22: 903-916.

Böhme, F., Welsch-Pausch, K., McLachlan, M. 1999. Uptake of Airborne Semivolatile Organic Compounds in Agricultural Plants: Field Measurements of Interspecies Variability. Environ. Sci. Technol. 33: 1805-1813.

Briggs, G.G., Bromilow, R.H., Evans, A.A. 1982. Relationships Between Lipophilicity and Root Uptake and Translocation of Non-ionised Chemicals by Barley. Pestic. Sci., 13: 495-504.

Briggs, G.G., Bromilow, R.H., Evans, A.A., Williams, M. 1982. Relationships Between Lipophilicity and the distribution of non-ionised chemicals in barley shoots following uptake by the roots. Pestic. Sci. 14, 492-500.

Bromilow, R.H., Chamberlain, K., 1995. Principles governing uptake and transport of chemicals. *In* S. Trapp and J.C. Mc Farlane. Plant Contamination. Modelling and Simulation of Organic Chemical Processes. Lewis Publishers, Boca Raton, USA, 37-68.

Buchholz, A., Baur, P., Schönherr, J. 1998. Differences among plant species in cuticular permeabilities and solute mobilities are not caused by differential size selectivities. Planta, 206: 322-328.

Burken. J.G., Schnoor, J.L. 1998. Predictive relationships for uptake of organic contaminants by hybrid poplar trees. Environ. Sci. Technol. 32, 3379-3385.

Campbell, G.S. 1985. Soils physics with BASIC: transport models for soil-plant systems, Elsevier, Amsterdam.

Cao, T., 2001. Fate and a prediction model of pesticides residues evolution in plants. Cycle postgrade en Sciences de l'Environnement: EPFL – Lausanne.

Charles, R., Cao, T.T. and Jolliet, O., 2001. Fate of pesticides in plant and Human Toxicity Potential. Proceedings of the International Conference on LCA in Foods, Gothenburg, Sweden, p. 42-47.

Charles, R., Zimmermann, A., 2001. Utilisation des produits de traitement des plantes 1998-2000. Réseau d'exploitations du SRVA. Rapport interne. Agroscope RAC, Nyon, Suisse.

Charles, R., Jolliet, O., 2001. Toxizität von Pestiziden und Schwermetallen. Schriftreihe der FAL 38, 25-27.

Charles, R., Jolliet, O., 2002. Fate of pesticides in plants, 10th IUPAC International Congress on the chemistry of Crop Protection, Basel 2002 2, 255.

Charles, R., Margni, M., Jolliet, O,. 2003. Pesticides and pollutants fate in agricultural plants. Proceeding of the 13th meeting of SETAC-Europe, Hamburg, Germany. http://abstracts.co.allenpress.com/pweb/setaceu2003/document/?ID=23030

Charles, R., Jolliet, O., 2004. Pesticides in plant and related impacts on human health. Proceeding of the 14th meeting of SETAC-Europe, Prague, Czech Republic.

Chatelain C., 1999. Résidus de pesticides et analyse de cycle de vie. Travail de semestre interdisciplinaire. Gestion des écosystèmes, EPFL – Lausanne.

Chiou, C.T., Sheng, G., Manes, M. 2001. A partition-limited model for the plant uptake of organic contaminants from soil and water. Environ. Sci. Technol. 35, 1437-1444.

Cousins, I. T.; Mackay, D. 2001. Strategies for including vegetation compartments in multi-media models. Chemosphere 44, 643-654.

Cousins, I.T., Mackay,. D., 2001. Transport parameters and mass balance equations for vegetation in Level III fugacity models. Internal report published on the website of the Canadian Environmental Modelling Centre (http://www.trentu.ca/envmodel).

Crettaz, P. 2001. From toxic releases to damages in human health: a method for life cycle impact assessment, with a case study on domestic rainwater use. Dissertation 2212 (2000), Swiss Federal Institute of Technology, CH-1015 Lausanne. Also available http://gecos.epfl.ch/lcsystems/ .

Crettaz, P., Pennington, D., Rhomberg, L., Brand, B., Jolliet, O., 2002. Assessing human health response in life Cycle Assessment using ED10s and DALYs: Part 1-Cancer effects. Risk Analysis 22: 931-946.

Eilrich, G.L., 1991. Tracking the fate of residues from the farm gate to the table. In Pesticide residues and food safety, American Chemical Society, 202-212.

Ganzelmeier H., Rautmann D., Spangenberg R., Streloke M. 1995. Studies on the Spray Drift of Plant Protection Products. Mitteilungen aus der Biologischen Bundesanstalt für Land- und Forstwirtschaft Berlin-Dahlem, Heft 305, 1995, Blackewll Wissenschafts-Verlag GmbH Berlin/Wein.

Geisler G., 1988. *In* Keller, E., Hanus H., Heyland K.-U.1997. Grundlagen der Pflanzenproduktion. Verlag Eugen Ulmer, Stuttgart, 860 p.

Goedkoop, M. 1995. Eco-indicator 95, weighting method for environmental effects that damage ecosystems or human health on a European scale. Final Report, RIVM.

Goedkoop, M., Spriennsma, R. 1999. The Eco-indicator 99: a damage oriented method for Life Cycle Impact Assessment; Pré Consultant.

Gyldenkaerne, S., Secher B.,JM., Nordbo, E. 1999. Ground deposit of pesticides in relation to the cereal canopy density. Pestic. Sci. 55 :1210 – 1216.

Heijungs, R. 1992. Environmental Assessment of products, background and guide. Centre of Environmental Science (CML), NL-2300 RA Leiden.

Hood, G., 2002. Poptools. Csiro, Australia. http://www.cse.csiro.au/poptools/index.htm.

Hsu F. C., Kleier D. A., 1996. Phloem mobility of xenobiotics. VIII. A short review. Journal of Experimental Botany 47: 1265-1271.

Hsu F.C., Marxmiller R.L., Yang A.Y.S., 1990. Study of root uptake and xylem translocation of cinmethylin and related compounds in detopped soybean roots using pressure chamber technique. Plant Physiol.. 93, 1573-1578.

Huijbregts P., 1999. Priority Assessment of Toxic Substances in LCA. Application of the Uniform System for the Evaluation of Substances 2.0. IVAM report, University of Amsterdam, part of updated CML guide on LCA.

Huijbregts M.A.J., Thissen U., Jager T., van de Meent D., Ragas A.M.J., 2000. Priority assessment of toxic substances in life cycle assessment. Part II: assessing parameter uncertainty and human variability in the calculation of toxicity potentials. Chemosphere, 41: 575-588.

Humbert S., 2002. Life cycle impacts on human health and ecosystems of the most used pesticides in Costa Rica. EPFL-ENAC-GECOS, CH-1015 Lausanne, 38 pp.

Hung H., Mackay, D. 1997. A novel and simple model of the uptake of organic chemicals by vegetation from air and soil. Chemosphere, 35 (5), 959-978.

INRA, 2003. Agritox - Base de données sur les substances actives phytopharmaceutiques. http://www.inra.fr/agritox/listesa/listesa.html .

Jolliet, O., Crettaz, P., 1997. Critical Surface-Time 95. A life cycle impact assessment methodology including fate and exposure. EPFL-ENAC-GECOS, CH-1015 Lausanne, 79 pp.

Jolliet, O., Crettaz, P., 2000. Human toxicity and ecotoxicity – modelling versus scoring. LCA sophistication. An international Workshop on Life Cycle Impact Assessment Sophistication. US-EPA. EPA/600/R-00/023, Washington, DC, US, p. 42-52.

Jolliet, O., Margni, M., Charles, R., Humbert, S., Payet, J., Rebitzer, G., Rosenbaum, R., 2003. IMPACT 2002+: a new life cycle impact assessment methodology. Int. J. LCA 8 (6), 324-330.

Kerler, F., Schönherr, J. 1988. Accumulation of Lipophilic Chemicals in Plant Cuticles: Prediction From Octanol/Water Partition Coefficients. Arch. Environ. Contam. Toxicol. 17: 1-6.

Kerler, F., Schönherr, J. 1988b. Permeation of lipophilic chemicals across plant cuticles: prediction from partition coefficients and molar volumes. Arch. Environ. Contam. Toxicol. 17: 7-12.

Kirkwood, R.C., 1999. Recent developments in our understanding of the plant cuticle as a barrier to the foliar uptake of pesticides. Pestic Sci. 55: 69-77.

Kleier, D.A., 1988. Phloem mobility of xenobiotics. I. Mathematical model unifying the weak acid and intermediate permeability theories. Plant Physiol. 86: 803-810.

Knoche, M., Bukovac, M., 1999. Spray application factors and plant growth regulator performance: II Foliar uptake of gibberellic acid and 2,4-D. Pestic. Sci. 55:166-174.

Knoche, M., Petracek, P.D., Bukovac, M., 2000. Finite dose diffusion studies I. Characterizing cuticular penetration in a model system using NAA and isolates tomato fruit cuticles. Pest. Manag. Sci. 56: 1005-1015.

Komossa, D., Langebartels, C. Sandermann, H., 1995. Metabolic processes for organic chemicals in plants. *In* S. Trapp and J.C. Mc Farlane. Plant Contamination. Modelling and Simulation of Organic Chemical Processes. Lewis Publishers, Boca Raton, USA, 69-103.

Könneke, 1967. *In* Keller, E., Hanus H., Heyland K.-U.1997. Grundlagen der Pflanzenproduktion. Verlag Eugen Ulmer, Stuttgart, 860 p.

Leonard, R.A., Knisel, W.G., Still, D.A., 1987. GLEAMS: ground water loading effects of agricultural management systems. Trans. Amer. Soc. of Agric. Engrs. 30, 1403-1418.

Leonard, R.A., Knisel, W.G., Davis,F.M., 1995. Modelling pesticide fate with GLEAMS. Eur. J. Agron. 4, 485-490.

Linders, J., Mensik, H., Stepehson, G., Wauchope, D., Racke, K., 2000. Foliar interception and retention values after pesticide application. A proposal for standardised values for environmental risk assessment. Pure Appl. Chem., 72: 2199-2218.

MacLeod, M.J., 2002. Contaminant fate models to support the sustainable use of chemicals in North America. Doctoral thesis, Watershed Ecosystems Graduate Program, Trent University, Peterborough, Ontario.

Margni, M., Rossier, D., Crettaz,P., Jolliet, O., 2002. Life cycle impact assessment of pesticides on human health and ecosystems. Agriculture, Ecosystems and Environment, 93:379-392.

Margni, M., Pennington, D., Bennett, D.H., Jolliet, O., 2003. Cyclic exchanges between environmental media: understanding the importance of intermedia feedbacks in multi-media models. Submitted to Agriculture, Ecosystems and Environment.

Marzouk, H., Baur, P., Schönherr, J., 1998. Relative Solubilities of bifenox and 1-Naphthylacetic (NAA) in plant cuticles and in selected pure or aqueous glycol additives. Pestic. Sci. 53: 278-284.

McLachlan, M. S., 2000. Vegetation-air partition coefficient. *In* Handbook of Property Estimation Methods for Chemicals: Environmental and Health Sciences. Boethling, R.S. and Mackay, D. (Eds.). Lewis Publishers, Boca Raton, FL, 115-123.

Morgan, M.G., Henrion, M., 1990. Uncertainty: A guide dealing with uncertainty in quantitative risk and policy analysis. Cambridge University Press, Cambridge, England.

Newman, A., 1995. Ranking pesticides by environmental impact. Environ. Sci. Technol. 29, 324-326.

Nobel, P.S., 1991. Physicochemical and environmental plant physiology. Academic Press, SanGiego, California, 634 p.

OFAG, 2002. Produits phytosanitaires. Index 2002. Office fédéral de l'agriculture, Berne.

Paterson, S., Mackay, D., McFarlane, C. 1994. A model organic uptake by plants from soil and the atmosphere. Environ. Sci. Technol. 28, 2259-2266.

Pennington, D., Margni, M., Ammann, T., Jolliet, O., 2004. Multimedia fate and human intake modelling : spatial versus non-spatial insights for chemical emissions in Western Europe. Environmental Science & Technology accepted.

Pennington, D., Crettaz, P., Tauxe, A., Rhomberg, L., Brand, B., Jolliet, O., 2002. Assessing human health response in life Cycle Assessment using ED10s and DALYs: Part 2-Noncancer effects. Risk Analysis 22: 947-963.

Pennington, D., Margni, M., Payet, J., Tauxe, A., Charles, R., Ammann, C., Pelichet, T., Jolliet, O., 2002. Time and Space Integrated Risk and Potential Consequences of Toxicological Impacts: IMPACT 2002. Proceeding of the 12th meeting of SETAC-Europe, Vienna, Austria. http://abstracts.co.allenpress.com/pweb/setaceu2002/document/?ID=1006.

Riederer, M. 1995. Partitioning and transport of organic chemicals between the atmospheric environment and leaves. *In* S. Trapp and J.C. Mc Farlane. Plant Contamination. Modelling and Simulation of Organic Chemical Processes. Lewis Publishers, Boca Raton, USA, 153-190.

Riederer, M., Schreiber, L., 2001. Protecting against water loss: analysis of the barrier properties of plant cuticles. Journal of Experimental Botany, 22:2023-2032.

Rosenbaum, R., Charles, R., 2004. Implementation of the vegetation module, OMNIITOX project report – D41A Part V. EPFL-ENAC-GECOS, CH-1015 Lausanne.

Satchivi, N.M., Stoller, E.W., Wax, L.M., Briskin, D.P., 2000. A nonlinear dynamic simulation model for xenobiotics transport and whole plant allocation following foliar application. I. Conceptual Foundation of Model Development. Pesticide Biochemistry and Physiology 68: 67-84.

Satchivi, N.M., Stoller, E.W., Wax, L.M., Briskin, D.P., 2000. A nonlinear dynamic simulation model for xenobiotics transport and whole plant allocation following foliar application. II. Model validation. Pesticide Biochemistry and Physiology 68: 85-95.

Satchivi, N.M., Stoller, E.W., Wax, L.M., Briskin, D.P., 2001. A nonlinear dynamic simulation model for xenobiotics transport and whole plant allocation following foliar application. III. Influence of chemical properties, plant characteristics and environmental parameters on xenobiotic absorption and translocation. Pesticide Biochemistry and Physiology 71: 77-87.

Schönherr, J., Baur, P., Buchholz, A., 1999. Modelling foliar penetration: its role in optimising pesticide delivery. In Pesticide Chemistry and Bioscience: The Food-Environment Challenge, Brooks G.,T. and Roberts T.R., Royal Society of Chemistry, 1999, 134-151.

Schönherr, J., Baur, P. 1994. Modelling Penetration of Plant Cuticles by Crop Protection Agents and Effects of Adjuvants on their Rates of Penetration. Pestic. Sci., 42: 185-208.

Schönherr, J., Baur, P. 1996. Effects of temperature, surfactants and other adjuvants on rates of uptake of organic compounds. In Plant cuticles, G. Kerstiens. BIOS Scientific Publishers Ltd, Oxford, 135-155.

Schönherr, J., Riederer, M. 1989. Foliar penetration and accumulation or organic chemicals in plant cuticles. In *Reviews of environmental contamination and toxicology* (Ware G.W. ed.), vol. 108, Springer-Verlag New York Inc. 1-70.

Schwarzenbach, R., Gschwend, P., Imboden, D. 1993. Environmental organic chemistry. John Wiley and Sons, New York.

Schwartz, S., 2000. Quality assurance of exposure models for environmental risk assessment of substances. Doctoral thesis, Institute of environmental systems research, Osnabrück, Germany. 186 p.

Severinsen, M., Jager, T., 1998. Modelling the influence of terrestrial vegetation on the environmental date of xenobiotics. Chemosphere, 37: 41-62.

Strom D.J., Stanbury, P.S., 2000. Determining parameters of lognormal distribution from minimal information. AIHAJ, 61:887-880.

Syracuse Research Corporation, 2003. Databases. Syracuse Research Corporation http://esc.syrres.com

Tomlin, C.D.S. (1997). The Pesticide Manual World Compendium, Tomlin, C.D.S. , Ed., Surrey, England, British Crop Protection Council.

Trapp, S., 2002. Dynamic root uptake model for neutral lipophilic organics. Environmental Toxicology and Chemistry, 21: 203-206.

Trapp, S., 2000. Modelling uptake into roots and subsequent translocation of neutral and ionisable organic compounds. Pest Manag Sci 56, 767-778.

Trapp, S. 1995. Model for uptake of xenobiotics into plants. *In* S. Trapp and J.C. Mc Farlane. Plant Contamination. Modelling and Simulation of Organic Chemical Processes. Lewis Publishers, Boca Raton, USA, 107-151.

Trapp, S., Matthies, M. 1995. Generic one-compartment model for uptake of organic chemicals by foliar vegetation. Environ. Sci. Technol. 29: 2333-2338; 30, 360.

Trapp, S., Matthies, M. 1998. Chemodynamics and Environmental modeling. An introduction. Springer Verlag, 285 p.

Trapp, S., Mc Farlane C., Matthies M., 1994. Model for uptake of xenobiotics into plants: validation with bromacil experiments. Environ. Toxicol. and Chem. 13, 413-422.

Trapp, S., Mc Farlane, J.C. 1995. Plant Contamination. Modelling and Simulation of Organic Chemical Processes. Lewis Publishers, Boca Raton, USA.

Trapp, S., Pussemier, L. 1991. Model calculations and measurements of uptake and translocation of carbamates by bean plants. Chemosphere 22, 3-4, 327-339.

Travis, C., Arms, A., 1988. Bioconcentration of organics in beef, milk and vegetation. Environ. Sci. Technol., 22: 271-274.

U.S. EPA. 1999. U.S. Environmental Protection Agency. The Total Risk Integrated Methodology. Technical Support Document, Volume II: Description of Chemical Transport and Transformation Algorithms. External Review Draft. EPA-453/D-99-002B U.S. EPAOffice of Air Quality Planning and Standards.

Van de Berg, F., Kubiak, R., Benjey, W.G., Majewski, M.S., Yates, S.R., Reeves, G.L., Smelt, J.H., Van der Linde, A.M.A., 1999. Emissions of pesticides into the air. Water, Air, and Soil Pollution 115:195-218.

Wania, F., McLachlan, M.S., 2001. Estimating the influence of forests on the overall fate of semivolatile organic compounds using a multi-media fate model. Environ. Sci. Technol. 35: 582-590.

Weiss, G., 2001. Effets des modes d'interventions phytosanitaires et des types de pesticides sur leur répartition dans la plant sous forme de résidus et dans l'environnement immédiat. Cycle postgrade en Ingénierie et systèmes de management de l'environnement: EPFL – Lausanne. 83 p.

Wild, E., Dent, J., Barber, J. L., Thomas G. O. and Jones, K. C., 2004. Visualising and Tracking Organic Chemicals Within Living Plants. Proceedings of the SETAC-Europe conference, Prague, 2004

Willis, G.H., McDowell, L., 1987. Pesticide persistence on foliage. Reviews of Environmental Contamination and Toxicology 100., 23-73.

Zimmermann, A., 2001. Réseau des exploitations pilotes du Service romand de vulgarisaiton agricole, base de données 1998-2000. Rapport Interne. SRVA, Lausanne, Suisse.

Zabkiewicz, J.A., 2003. Foliar interactions and uptake of agrichemical formulations – Present limits and future potential. In Chemistry of crop protection. Progress and prospects in science and regulation. G. Voss and G. Ramos eds, Wiley-VCH, Weinheim, 237-251.

# Curriculum Vitae

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## Education

| | |
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| 2000-2004 | Swiss Federal Institute of Technology, Lausanne, Laboratory of Life Cycle Systems – Industrial Ecology. Dissertation in Life Cycle Impact Assessment in Agriculture. |
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| | |
|---|---|
| 1994 up to now | Swiss Federal Research Station for Plant Production, Agroscope RAC Changins, Nyon. In charge of the service Field crops systems, beet, forage cereals and grain crops. Responsible for the project Field Crops Systems. Research activities in the development and the assessment of production systems in field crops. Responsible for the variety testing and crop management of grain legumes. |

## Languages

Mother language: French

German: fluent (5 years study at ETH Zurich)

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## Personnal

Member of Club en Fauteuil Roulant de La Côte, participation to sport activities, and active as referee for quadrugby

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## Publications and communications **in relation with LCA**

Charles, R., Jolliet, O., 2004. Pesticides in plant and related impacts on human health. Proceeding of the 14th meeting of SETAC-Europe, Prague, Czech Republic.

Rosenbaum, R., Charles, R., 2004. Implementation of the vegetation module, OMNIITOX project report – D41A Part V. EPFL-ENAC-GECOS, CH-1015 Lausanne.

Charles, R., Margni, M., Jolliet, O,. 2003. Pesticides and pollutants fate in agricultural plants. Proceeding of the 13th meeting of SETAC-Europe, Hamburg, Germany.

Jolliet, O., Margni, M., Charles, R., Humbert, S., Payet, J., Rebitzer, G., Rosenbaum, R., 2003. IMPACT 2002+: a new life cycle impact assessment methodology. Int. J. LCA 8 (6), 324-330.

Nemecek T., Kufrin P., Menzi M., Hebeisen T. und Charles R., 2003. Ökobilanzen verschiedener Anbauvarianten wichtiger Ackerkulturen. VDLUFA-Schriftenreihe 58, 564-572.

Charles, R. and Nemecek, T., 2002. A standardised method to assess the environmental impact of grain legumes. Grain Legumes 36 (2), 18-19.

Charles, R. and Gosse, G., 2002. Environmental impact related to nitrogen emissions from crops of peas and wheat. Grain Legumes 36 (2), 20-20.

Charles, R. and Jolliet, O., 2002. Toxizität von Pestiziden und Schwemetallen. Schriftreihen FAL 38, 25-27.

Charles, R., Jolliet, O., 2002. Fate of pesticides in plants, 10th IUPAC International Congress on the chemistry of Crop Protection, Basel 2002 2, 255.

Charles R. et Nemecek T., 2002. Bilan écologique de la betterave à sucre. In: Fachtagung für Zuckerrübenanbau SFZ. FAL 1.3.2002 und RAC 8.2.2002.

Pennington, D., Margni, M., Payet, J., Tauxe, A., Charles, R., Ammann, C., Pelichet, T., Jolliet, O., 2002. Time and Space Integrated Risk and Potential Consequences of Toxicological Impacts: IMPACT 2002. Proceeding of the 12th meeting of SETAC-Europe.

Charles, R., Cao, T.T. and Jolliet, O., 2001. Fate of pesticides in plant and Human Toxicity Potential. Proceedings of the International Conference on LCA in Foods, Gothenburg, Sweden, p. 42-47.

Gaillard G., Alföldi Th, Charles R., Dubois D., Gysi Ch., Mouron P., Nemecek Th., Oberholzer H.-R., Rossier D., Schmid O., Stadelmann F.X. and Zimmermann A., 2000. Environmental life cycle assessment (LCA) of organic farms. In: The World Grows Organic. Alföldi T. et al. (eds.). Proceedings of the 13th IFOAM Scientific Conference, 28.-31.8.2000, Basel, vdf ETH Zürich,156.

# Appendices

# A. Environmental analysis of intensity level in wheat crop production using life cycle assessment

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## *A.1 Abstract*

An environmental assessment of wheat for bread making was performed to optimise agricultural fertilization which most characterises intensity of arable production systems, quality of agricultural products and environmental damages. To assess and compare different intensities of production, adequate functional units were developed to take into account the main functions of agricultural activity: production and upkeep of farmland. The limits of these functional units were identified and the influence of the choice of functional unit was analysed.

Assessment per ton of grain for a given variety and with variation in quality shows that fertilisation intensification needs a sufficient increase in yield to compensate additional emissions and to be environmentally favourable. To compare different systems of production managed by fertilisation intensities, it is necessary to take into account quality in the functional unit and to bring a correction in yield for an equivalent quality at each intensity of fertilisation. Methodological development was brought using variations in variety concerning fertilisation-yield and yield-protein content relations to assess wheat production system per ton of grain with a constant 13% protein content. This new functional unit identified high fertilisation intensity as favourable for most impact categories and demonstrated sufficient yield increase with a change in variety at each level of fertilisers. On the other hand, impact per hectare increases with fertilisation intensification for all environmental categories except land utilisation. This functional unit helps to explicitly point out impact most affected by agricultural activity: energy consumption, greenhouse effect, acidification, terrestrial ecotoxicity and human toxicity. Assessment of fertilisers exposed important differences between types and improvement potentials due to heavy metals content and impact on terrestrial ecotoxicity and human toxicity. Optimal combinations of variety, fertilisation and land utilisation are discussed to design best production strategies from an environmental point of view.

**Keywords:** Life Cycle Assessment, Cropping System, Wheat, Fertilisation, Grain Quality.

## *A.2 Introduction*

### A.2.1 Context

The present paper addresses the environmental impact of a wheat crop in relation to cultivation intensities. Agriculture is an important source of pollutant emissions in Western Europe, wheat crop being one of the dominant species in arable cropping systems. To produce wheat for bread making, different cultural techniques are commonly used in European agriculture, leading to related variations in cultivation intensities, yield quantities and qualities and environmental impacts. High-yield production systems maximising yield with high fertiliser supply and crop protection intervention are economically advantageous in many European agricultural areas. Kuesters and Lammel (1999) showed that the economic optimum for winter wheat yield and maximum net energy yield were obtained at similar high production intensity. On the one hand, this could mean that these intensive systems can be both economically and environmentally of interest thanks to a global high productivity. On the other hand, these highly intensive systems are usually recognised as exposing the environment to damaging nitrogen, phosphor and pesticides emissions. Similarly, the a priori thinking that a low intensity crop is environmentally favourable could be questioned regarding the reduction in productivity, which could simply lead to pollution shifting to other regions. These different factors have often been studied independently, looking at either agriculture production or environmental impacts separately. As cultivation practices generally refer to a complex cropping system, these different factors interact, therefore making a combined assessment necessary. The following questions will be addressed in priority:

a) How do yield quantities, yield qualities and environmental impacts interact, and what are the main factors characterising cultivation intensity ?

b) On which common basis should different agriculture scenarios be compared in an environmental assessment and how can both yield quantity and yield quality be accounted for?

c) What is the best intensity of production for wheat crop from an environmental point of view, with regards to fertilisation?

d) What are the key factors influencing the environmental performances of a wheat crop?

To address these questions, only an overall assessment which takes into account main functions of an agricultural system, as well as emissions and impacts to the environment can aim to determine the best-balanced system and remove a priori judgements. Therefore, a life cycle assessment (LCA) methodology has been applied (ISO, 2001), as it can relate environmental impacts to the main function of the considered system, while taking into account supply chain, direct field emissions and potential pollution shift to other regions. The present study is structured as follows: after a short review of existing LCA studies of agriculture and more specifically wheat production, the basis for scenario comparison, namely the limits of the system and the functional units, are chosen according to the identification of main factors in wheat production influencing yield, quality and environmental impacts. According to the subsequent LCA phases (goal definition, inventory, impact assessment and

interpretation), we analyse the environmental impacts of a wheat crop as a function of the crop intensity level, starting with amounts and types of fertilizers.

### A.2.2 Existing environmental assessments of wheat crop

Recent developments in Life Cycle Assessment (LCA) methodology have brought a tool to assess agricultural systems of production. Audsley et al. (1997) reviewed wheat production to bring methodological harmonisation. In particular, British and Swiss wheat production systems have been compared. Variations in production intensities due to nitrogen fertilisation and crop protection products have been shown to cause different environmental burdens. Gaillard et al. (2002) showed that low input systems were environmentally better as long as a sufficient yield level was obtained. Brentrup (2003) studied various intensities of nitrogen fertiliser rates in cereal production. This study identified that the greatest potential to minimise the environmental impact per ton of grain was to achieve high yields per unit of land and simultaneously low losses of some precise emissions (nitrate leaching).

However, theses studies have not proposed an optimisation of production practices, which considers the overall system and which is based on existing variations, notably about best choice of variety and fertilisation level. Consequently, wheat crop needs to be considered as a complex system and it is important to analyse key interactions and the main influential factors.

### A.2.3 Main factors influencing yield, quality and environmental impacts

Negative correlations between yield potential and quality of grain among wheat varieties are broadly reported. This relation is influenced by cropping techniques. Many works refer to this inverse yield – quality relationship and discuss potential developments (Bänzinger et al., 1992, Debaeke et al., 1996, Feil, 1998; Le Gouis et al., 2000). Wheat varieties are characterised either by a high quality with a low yield or by a high yield with a lower quality. Nitrogen fertilisation is one of the main factors regulating yield level and quality of the grains specific to each variety. Optimum fertilisation level should lead to an equilibrium between yield increase and grain quality formation. Different realistic or potential scenarios of wheat production systems may be built based on the genetic variation of yield potential and on the possibility to achieve control of the inverse yield – protein relationship by fertilisation to obtain a high equivalent quality of grain.

Existing varieties also provide the possibility of obtaining high quality with restricted inputs of fertilisers, eventually combined with a limited use of plant protection products. These extensive crop management systems have lower yields than conventional cropping systems but are appropriated in agricultural conditions with low growing potentials (Feil, 1996; Collaud, 2000). They are also economically relevant in sponsored environmental programs.

Finally, variety constitutes one of the determining elements characterising a production system. Choice of an adapted variety depends on agronomic and local growing conditions. It also determines cultural practices, amount of fertilisers, need for crop protection, harvest yield and quality. In intensive systems, wheat production requires a significant use of mineral fertilisers. In particular, nitrogen fertilisers contribute to the productivity of these systems and have an influence on the quality of wheat grain.

Therefore, qualitative assessment is not sufficient and there is clearly a need to combine yield and grain quality and as well as quantify their interactions with cultivation techniques in order to build a consistent basis for the environmental comparison. Environmental assessment of wheat production systems should first concentrate on differences between intensive and extensive production systems and attempt to determine the optimal equilibrium between the quantity of fertilisers applied and impact to the environment. Besides, production and composition of fertilisers vary greatly, so that identifying high contrasts could be helpful to determine environmental priority between fertilisation intensity and types of mineral fertiliser through a sensitivity analysis.

## *A.3 Objectives*

This environmental analysis of wheat production aims at finding the key factors and optimal intensity level in the production techniques regarding fertilisation, according to the antagonistic requirements for yield quantity and grain quality. For this purpose it specifically aims at:

- Defining a common basis of assessment and comparison through the identification of the functions of the wheat production system and the corresponding appropriate functional units.
- Analysing the impact variation with applied fertiliser quantities.
- Performing a sensitivity study of fertiliser types.

## *A.4 Definition of system, scenarios and functional units*

System definition, scenario description and choice of functional unit are closely related and directly linked to the function of the considered crop (the offered service). The basis for scenario comparison is the functional unit which is the common unit representing this function. Emissions and extractions in the inventory phase and resulting impacts are then calculated per functional unit. Rossier (1999) studied different appropriate functional units that may be considered for agricultural activities: one hectare, one ton of products, one human-digestible energy unit. For wheat system, functions are multiple. Consequently, different functional units can be considered as an adequate basis to compare the various analysed systems, taking into account the more or less complex relating area, yield and quality. Data for cultivation corresponds to good agricultural practice, reproduced from Swiss conditions and described by Gaillard et al. (2002). Time limit is one year from harvest of a theoretical previous wheat crop to the harvest of the assessed crop. Only grain is harvested; straw remains in the field. The two main optimisation possibilities are defined in the objectives, namely fertilisation quantities and types.

### A.4.1 Scenario definition for fertilisation intensity

Four treatments of NPK fertilisation are analysed for their environmental impact. Provisions of nitrogen, in the form of ammonium nitrate (27.5%), are split in 40 and 60 kg N for a total amount of 100 kg N/ha (N100), in 40, 60, 40 kg N for 140 kg N/ha (N140), in 3 times 60 kg N for 180 kg N/ha (N180), and in 60, 60, 60 and 40 kg N for 220 kg N/ha (N220). For each nitrogen intensity, amounts of phosphorus (supertriple, 46% $P_2O_5$) and potassium fertilisers (potash, 60% $K_2O$) are adjusted as a function of yield level, in a proportional relation with the export of nutrients by the grain (Ryser et al., 2001). Standard intensity level, identified as

standard treatment, receives 140 kg N/ha, 65 kg $P_2O_5$/ha and 95 kg $K_2O$/ha and a full crop protection.

Optimisation of fertilizer intensity is analysed considering three functions of agriculture: farmland upkeep, production and finally production with quality requirements. This section develops the methodology to determine the corresponding functional units for the different scenarios.

### A.4.2 Base for comparison and functional unit

#### A.4.2.1 *Impact per hectare*

In a first approach, the assessment is performed according to the farmland upkeep function and the functional unit is identified as one hectare. Farmland upkeep assumes a function of the agricultural activity. Impacts are reported per hectare. The system is limited to the agricultural surface and includes all cultivation activities involved. In optimisation processes, this functional unit provides explicit information about the intensity in the use of agricultural inputs.

#### *A.4.2.2 Impact per ton of grain*

In a second approach, the assessment is performed according to the production function. Basic assessment of this function can be expressed per ton of grain produced. This functional unit is limited to the effect of cultural techniques on grain yield. This approach helps to identify the optimal level of production intensity for confined purposes such as the response of one crop to the fertilisation intensification at the field level.

To calculate this, the relationship between yield and fertilization intensity is required. Trials representative for wheat growth response to nitrogen fertilisation (Pellet, 1997) have been performed to model production scenarios, grain yield of a standard variety "Runal" ($G_{standard}$, t/ha) as a function of Nitrogen fertilisers rate (N, kg N/ha) (fig. 1).

$$G_{standard}(N) = -0.00006\ N^2 + 0.031\ N + 3.1 \quad (1)$$

This first approach of the production system concentrates exclusively on quantitative relations. It is directly dependent on one single relation fertilisation – yield given by equation 1. However variations in qualitative parameters according to fertilisation intensity are neglected in this analysis. According to the same trials (Pellet, 1997) the protein content of the standard variety "Runal" ($P_{standard}$, %) also varies with fertilizer intensity as follows (fig.2 ):

$$P_{standard}(N) = 0.026\ N + 9.5 \quad (2)$$

The per kg analysis is therefore not suitable on its own to assess wheat production systems and strategies, hence the need for a new approach.

#### *A.4.2.3 Impact per ton of grain with constant quality*

If the specific function is bread making, determination of optimisation potentials needs to be based on products with identical quality regarding their ability to produce bread. This is especially important when interactions occur between agricultural techniques, yield and grain quality. Differences in the quality of wheat grain resulting from variations in intensity of production were not fully taken into account in previous studies on wheat production, limiting the reliability for assessment of different production intensities. This third approach was developed to take into account the quality in the functional unit and proposes to do the assessment per ton of grain with constant quality. Expanding first approach and scenario of the system, a model of the wheat production was developed to express both yield and quality as a function of fertilisation, so that it is possible to use this functional unit. As interactions between fertilisation, yield and quality are mainly controlled by the choice of variety, variations in variety were considered in the development of the adequate methodology. Protein content has been chosen to characterise quality, as one of the main qualitative requirements for bread making. Interestingly, this parameter strongly depends on agricultural practices. A level of 13% protein in dry grain is retained as a good quality for bread making satisfying bakery requirements and the functional unit can be defined as a ton of grain with 13% protein. In reality, more traits are required to characterise wheat grain quality for bread making and must be kept in mind in the qualitative discussion of results.

To achieve this, we need to determine the ton of grain with 13% protein content, which can be produced per ha. As described above, Equation (2) shows that for a given variety, the protein content increases with fertiliser intensity. A correction is therefore needed in the first production scenario, to ensure a constant level of protein. This constant level can be achieved by choosing the variety which can produce 13% protein at each fertilisation level, as discussed in section 2.3. As variety also affects productivity, Equation (1) must be corrected by introducing the change in yield ($\Delta G$) linked to the change in variety, high protein levels corresponding to variety with low productivity:

$$G^{pref}(N) = G_{standard}(N) + \Delta G$$

To calculate this correction ($\Delta G$), relations between yield and quality for different varieties have therefore been studied on data from variety trials (RAC, 1997). Different varieties i observed at a constant fertilisation level show a protein content linearly decreasing with yield (fig. 3):

$$P_i^n(G_i^n) = -0.85\, G_i^n + 19.0 \qquad (3)$$

where:

$P_i^n$ = protein content of variety i by fertilisation level n (%)

$G_i^n$ = grain yield of variety i by fertilisation level n (t/ha)

Assuming that this correlation between change in yield and change in protein remains the same at different levels of fertilisation, one obtains: $\Delta G = (P_{ref} - P_{standard}(N)) / -0.85$

and therefore yield for a fixed protein content is given by:

$$G^{pref}(N) = G_{standard}(N) + (P_{ref} - P_{standard}(N)) / -0.85 \qquad (4)$$

Assuming Pref=13% and introducing equations 1 and 2 in equation 4, one obtains:

$$G_i^{p=13}(N) = -0.00006\ N^2 + 0.062\ N - 1.01 \quad (5)$$

Figure 1 illustrates that correcting yield to ensure a fixed protein content of 13% (figure 2: black line) leads to a much stronger dependence between yield and fertilizer level (Figure 1: black line against conventional yield in grey).

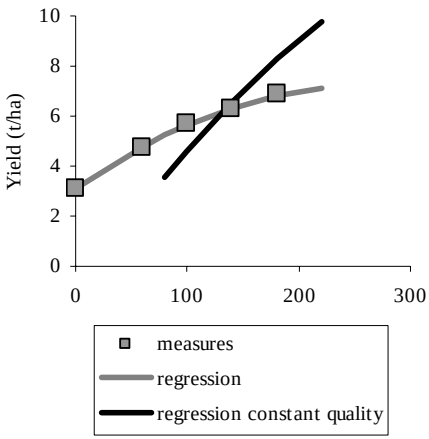


Figure 1. Yield of winter wheat as a function of fertilisation intensity. Four NPK fertilisation intensities expressed as nitrogen rates from 0 kg N/ha to 220 kg N/ha. Results of yield measures, corresponding yield regression given by equation (1) and corrected regression for constant quality 13% protein given by equation (5).

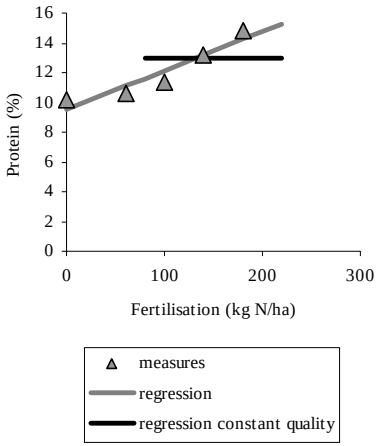


Fig.2. Protein content of winter wheat as a function of fertilisation intensity. Four NPK fertilisation intensities expressed as nitrogen rates from 0 kg N/ha to 220 kg N/ha. Results of protein measures, corresponding regression given by equation (2) and corrected regression for constant quality at 13% protein.

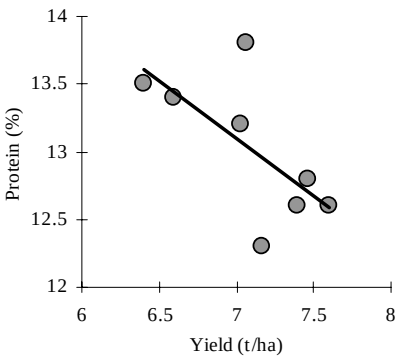


Figure 3. Relation between yield and quality for a range of varieties at a constant fertilisation level (140 kg N/ha).

We have demonstrated the practical solution to ensure constant quality at each fertilisation level. The complex system can be finally illustrated by figure 4: relations between yield and quality are given according to a range of varieties and to different fertilisation intensity levels. Going from the linear regression between yield and quality for a range of varieties at a constant fertilisation level (fig. 3), the system is expanded to other fertilisation levels (100, 180 and 220 kg N/ha) and represented in Figure 4.

One can see the necessity of change in variety at each fertilisation level to obtain a constant quality and the resulting evolution in yield, also represented by figure 1. Other possibilities of production scenarios can also be identified according to various quality requirements and to agronomic conditions. Instead of assuming a change in variety, one could assume that yield with low protein content is mixed with a high quality grain obtained with a variety with lower yield. As equation (3) is linear in the considered range, this leads to the same correction as equations (4) and (5) above.

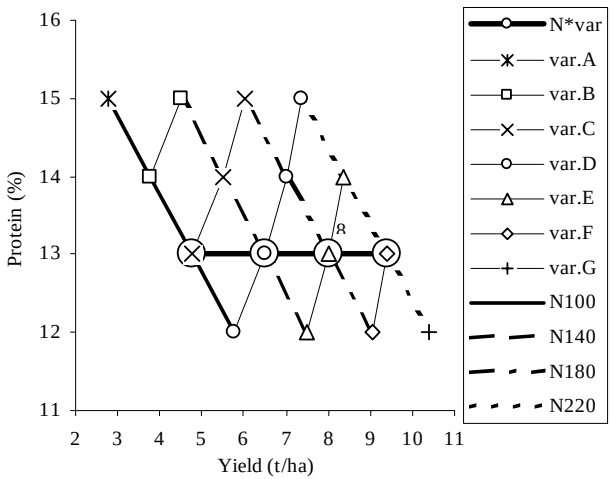


Fig. 4. Relation between yield and quality according to variety and to fertilisation intensity. Seven varieties (A to G) at four NPK fertilisation intensities expressed as nitrogen rates 100, 140, 180 and 220 kg N/ha. System limited to the protein range between 12 and 15% content. In circle: yield given by the variety and fertilisation intensity to obtain 13% protein content.

## *A.5 Emissions inventory*

Agricultural inputs and related emissions are grouped in different categories: field emissions, fabrication and transport of machinery, fuel, fertiliser and miscellaneous. Emission inventory

of agricultural inputs is based on Audsley et al. (1997) and Gaillard et al. (1997a). Direct field emissions were calculated as proposed by Gaillard et al. (1997b).

$NO_3$ emission levels have been assessed for contrasting conditions of leaching using different methods (table 1): reference method considering mineralisation in soil, absorption by plant and leaching of mineral fertilisers (Walther in Gaillard et al., 1997b), balance calculation between inputs (fertiliser, deposition) and outputs (grain, $N_2O$, $NH_3$ and $NO_x$ emissions) and worst case considering reference leaching for 100 kg N /ha and half loss of additional nitrogen applied in higher fertilisation levels.

Table 1. Nitrogen leaching emissions for winter wheat according to different field conditions and fertilisation intensities (100 and 220 kg N/ha).

| | Nitrogen leaching emissions (kg N/ha) | |
|---|---|---|
| | $N_{100}$ | $N_{220}$ |
| Model [a] | 79 | 83 |
| Balanced | 31 | 48 |
| Worst case | 79 | 139 |

[a] Walther (Gaillard et., al. 1997)

## *A.6 Impact assessment*

Impact assessment includes the following environmental categories with characterisation factors: energy consumption (ESU, 1995), land use (ESU, 1994), greenhouse effect 500 years (Heijungs et al., 1992), photo-oxidant formation (Heijungs et al., 1992), acidification (Heijungs et al., 1992), eutrophication P-limiting and N-limiting (Heijungs et al., 1992), aquatic ecotoxicity, terrestrial ecotoxicity and human toxicity (Jolliet et Crettaz, 1997).

### A.6.1 Impact per hectare

Assessing wheat production system as a function of farmland upkeep shows that all environmental classes, except land utilisation, have the lowest impact per hectare by extensive fertilisation (figure 5A). Differences between levels of fertilisation are particularly evident for greenhouse effect, acidification, terrestrial ecotoxicity and human toxicity.

Assessment per hectare leads to assessing the intensity of production so that the lower the activity is, the better the environmental impact appears. According to this point of view, a low fertilisation intensity and a low input system present clear advantages. Assessment per hectare helps explicitly to point out most varying impact classes according to agricultural activities. However, it should not replace the analysis of the production system according to its central accurate function: the production of grain.

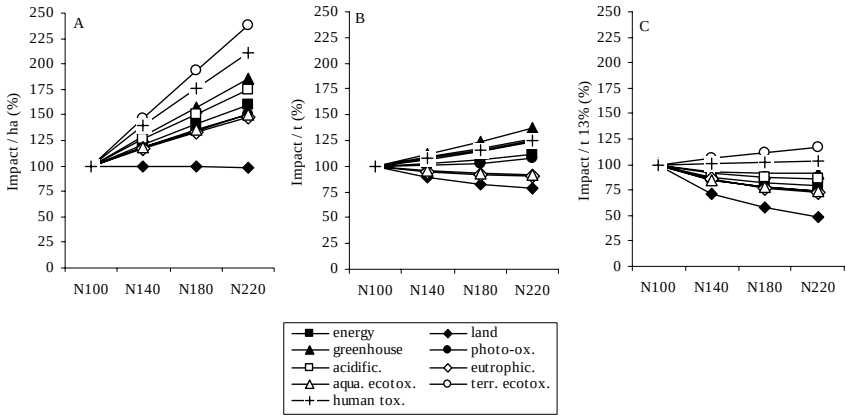


Figure 5. Impact assessment of winter wheat in function of fertilisation intensity. Four NPK fertilisation intensities expressed as nitrogen rates form 100 kg N/ha ($N_{100}$) to 220 kg N/ha ($N_{220}$). Results in relative value to lowest fertilisation intensity ($N_{100}$). A) Impact per hectare producing grain with 13% protein content, with change in variety and constant protein content, B) Impact per ton of grain, with constant variety and varying protein content, C) Impact per ton of grain with 13% protein content, with change in variety and constant protein content.

### A.6.2 Impact per ton of grain

Results of the environmental assessment per ton of grain show that the marginal yield brought by the increase of fertilisation from 140 to 220 kg N/ha is large enough to compensate for additional emissions for aquatic ecotoxicity, land use and eutrophication, but not for greenhouse effect, human toxicity and terrestrial ecotoxicity which are higher at high fertilisation levels (figure 5B). Impacts slightly increase with fertilisation levels for energy consumption, acidification, and photo-oxidant formation. According to equation 1, yield difference between each level of fertilisation diminishes rapidly up 140 kg N/ha, explaining a decrease in fertilisation efficiency. Mainly land utilisation appears clearly to decrease with intensification. Notice that optimal rate of fertilisers from an agronomic point of view is situated at about 140 kg N/ha, which corresponds to average Swiss growing conditions for bread making.

### A.6.3 Impact per ton of grain with constant quality

High fertilisation provides a distinctly better environmental impact per ton grain with constant quality for most impact categories (figure 5C). Specifically, increase in yield is mostly higher than additional impacts due to fertilisation intensification. Particular attention should be paid to variations over 20% of impact on energy consumption, land utilisation, photo-oxidant formation, eutrophication and aquatic ecotoxicity. There are no distinct differences between fertilisation levels for human toxicity: increase in yield just compensates additional emissions

due to heavy metals in fertilizers, so that impact per ton of grain with constant quality remains unchanged. Only terrestrial toxicity is decreased by extensive fertilisation level.

## *A.7 Interpretation and sensitivity study*

### A.7.1 Fertilization intensity

The impact assessment is largely dependent on the choice of the functional unit. Totally opposite conclusions in the identification of optimisation potentials appear according to the function assigned to the system or to the objectives of the evaluation (figure 5, table 2).

Table 2: Environmental impact of standard treatment of winter wheat ($N_{140}$) according to different functional units: per ton of grain (/ t), per ton of grain with constant quality 13% protein (/ $t_{p13\%}$) and per hectare (/ ha).

| | | / ha | / t | / $t_{p13\%}$ |
|---|---|---|---|---|
| Energy consumption | MJ | 21657 | 3402 | 3327 |
| Land utilisation | $m^2$ | 523 | 83 | 80 |
| Greenhouse effect | kg $CO_2$ equ. | 2417 | 381 | 371 |
| Photo-oxidant formation | kg $C_2H_2$ equ. | 7.9 | 1.25 | 1.22 |
| Acidification | kg $SO_2$ equ. | 17.8 | 2.8 | 2.73 |
| Eutrophication | kg $PO_4$ equ. | 3.47 | 0.542 | 0.543 |
| Aquatic ecotoxicity | kg $Zn_{water}$ equ. | 1.76 | 0.274 | 0.27 |
| Terrestrial ecotoxicity | kg $Zn_{soil}$ equ. | 0.0539 | 0.00831 | 0.00827 |
| Human toxicity | kg $Pb_{air}$ equ. | 1115 | 173 | 171 |

There are different results between assessments per hectare and per ton of grain. For wheat, these differences are enhanced if constant quality is taken into account. This demonstrates the importance of the quality parameter in agricultural output. Consequently this parameter must be considered in the system boundaries and in the identification of an adequate functional unit.

Both possibilities of assessment, per hectare and per ton of grain with constant quality, can be considered as complementary analysis with respect to the multifunctional role of agricultural activity. Kuesters and Lammel (1999) who investigated the energy efficiency of winter wheat fertilisation propose a similar comparison per hectare and ton of grain. Efficiency of the wheat production system is taken into account by a functional unit per ton of grain, its intensity by the functional unit per hectare. Variations were observed between different production intensities and growing conditions. In that case, low input system provided the highest energy output/input ratio. The maximum net energy output was obtained by a high intensity and was situated near the economic optimum.

On the one hand, the assessment per ha clearly shows that if the main function is farmland upkeep, the fertilisation intensity should be reduced to a minimum, as expected. As a matter of fact, in that case, alternative crops should be considered to ensure this function in the least polluting way. On the other hand, assessment of wheat systems show that intensification of fertilisation has lower impacts if high yield and required quality are guaranteed by an adequate corresponding fertiliser rate. It has also been demonstrated that as soon as the fertilisation intensity does not provide a sufficient yield increase, impact increases for most

environmental classes. Gaillard et al. (2002) also showed that extensive production systems are more favourable only if a significant yield is obtained.

Intensity of fertilisation plays an important role on most impact categories and is a major source for environmental optimisation opportunities. Important field emissions linked to the use of fertilisers are nutrient related emissions ($N_2O$, $NO_x$, $NH_3$, $PO_4$) with impact on greenhouse effect, acidification and eutrophication, and heavy metals occurring in fertilisers (Cd, Zn, Co, Se, Hg) with impact on aquatic ecotoxicity, terrestrial ecotoxicity and human toxicity (table 3, figure 6).

Table 3. Main contributing field emissions for each environmental impact (% of impact) of winter wheat standard treatment ($N_{140}$).

| Impact classes | Field emissions (impact >5%) |
|---|---|
| Energy consumption | - |
| Land utilisation | "land used for cultivation" (95%) |
| Greenhouse effect | $N_2O$ (46%) |
| Photo-oxidant formation | $NO_x$ (15%) |
| Acidification | $NH_3$ (30%), $NO_x$ (5%) |
| Eutrophication | $PO_4$ (52%) |
| Aquatic ecotoxicity | Cd (41%), Chlorothalonil (33%), Hg (8%), Isoproturon (8%), |
| Terrestrial ecotoxicity | Cd (47%), Zn (41%), |
| Human toxicity | Cd (39%), Co (36%), Se (20%) |

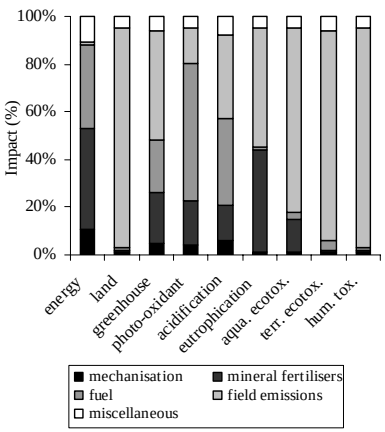


Figure 6. Contribution of each category of inputs to environmental impacts of wheat production standard treatment ($N_{140}$). % of total impact per ton of grain with 13% protein content.

Eutrophication has been considered as P-limiting, so that influence of nitrogen emissions is negligible. As nitrogen is considered as an important factor in fertilisation intensification, calculation for N-limiting situations provides a complementary information for different levels of N-emissions, especially nitrate ones. Eutrophication impact remains in tendency the lowest per ton of grain at high levels of fertilisation (table 4) for each condition calculated (table 1). Differences are all the more important as nitrate emissions are not only influenced by nitrogen fertilisation.

Moreover, fabrication and transport of mineral fertilisers play an important role on energy linked impacts: they determine over 40% of impact on energy consumption (figure 6). Further analysis of types of fertilisers will help to identify potentials for improvement.

Table 4. Impact assessment of winter wheat on eutrophication for P- and N-limiting situations and different N-leaching intensities. Impact per ton of grain with constant quality 13% protein. Two different NPK fertilisation intensities expressed by nitrogen rates (100 and 220 kg N/ha).

| | | Eutrophication / $t_{p13\%}$ | |
|---|---|---|---|
| | | $N_{100}$ | $N_{220}$ |
| Model [a], P-limiting | % | 100 | 75 |
| | kg $PO_4$ equ. | 0.63 | |
| Model [a], N-limiting | % | 100 | 55 |
| | kg $PO_4$ equ. | 8.8 | |
| Balance | % | 100 | 75 |
| | kg $PO_4$ equ. | 4.1 | |
| Worst case | % | 100 | 85 |
| | kg $PO_4$ equ. | 8.8 | |

Model [a] : Walther (Gaillard et., al. 1997)

### A.7.2 Quality and variety

The consideration of quality plays a very significant role in the assessment of wheat for bread making. It has been identified as a determining factor for the entire production system and for the intensity in the use of agricultural inputs. Breeding for yield increase can be considered as environmentally efficient as long as parallel improvement can be obtained for agronomic characters. In this study, the relation between yield and quality shows a 0.85% decrease in protein content per ton of grain increase for the different variety types considered. This level of quality loss appears not to be unfavourable for high yielding varieties, but states that nitrogen fertilisation is able to compensate. This compensation is based on an increase of 0.26% protein per 10 kg N/ha fertilisation. Consequently two methods of optimisation are possible: combining high quality and yield in breeding programs and improving nutrient uptake efficiency by breeding or by cultural techniques. Feil (1996) demonstrated the need to consider together yield potential, quality of grain and food supply problems in breeding strategies for reducing the use of nitrogen fertiliser and for environmental improvement of wheat production. Cultivation of high yielding varieties can ensure high productivity and efficiency of whole wheat systems and can contribute consequently to a better environmental performance with respect to some conditions. Variety type must be chosen in function of growing conditions and cultivation techniques (rates of fertilisers, crop protection) and have to correspond to effective yield potential as well as achieve required quality.

### A.7.3 Sensitivity study: choice of mineral fertilisers

In a sensitivity analysis of fertilisation, the influence of the choice of fertilisers is analysed. Two types of nitrogen and potash fertilisers are compared to evaluate the potential of environmental benefit given by the choice of fertiliser type: ammonium nitrate (27.5%) and urea (46% N), supertriple (46% $P_2O_5$) and Thomas meal (17% $P_2O_5$). Assessment is made per ton of grain with a constant quality. There is no interaction on impact due to the type of fertiliser and its intensity use: differences in impact between fertilisers are the same independent of the fertilisation intensity. Moreover, type of fertiliser has no influence on optimal level of fertilisation, so that results are presented for the standard treatment only.

Choice of mineral fertiliser can have a considerable influence on impacts (figure 7).

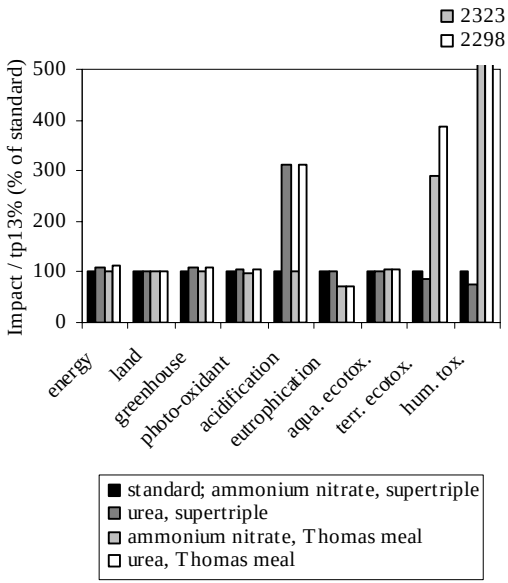


Figure 7. Impact assessment of winter wheat in function of different fertilisers types. Impact per ton of grain with 13% protein content. Standard treatment ($N_{140}$). Results in relative value (log) to standard fertilisers types (ammonium nitrate and supertriple).

On the one hand, substitutions of fertilisers generally have a restricted influence on energy consumption, land utilisation, greenhouse effect, photo-oxidant formation and aquatic ecotoxicity. On the other hand, heavy metals have the highest effects (table 3): Thomas meal emits the most charging emissions, especially chrome. A substantial environmental improvement can be obtained in substituting Thomas meal by supertriple and diminishing impacts on terrestrial ecotoxicity by a factor 6 and human toxicity by a factor 23. Compared to ammonium nitrate, urea produces a higher impact on acidification, because of higher emissions of $NH_3$. This illustrates the need to know the composition of the fertilisers, which provides explicit possibilities to optimise fertilisation practices. In some situations Rossier

(1998) distinguished mineral fertilisers as the main emissions sources for whole farm level and could simply propose a change in type of fertiliser as the main effective improvement solution. Brentrup et al. (2001) identified differences between forms of nitrogen fertilisers due to ammonia volatilisation after application, with impacts on eutrophication and acidification. The Eco-indicator 95 method was chosen for this LCA application.

## *A.8 Conclusion*

This study demonstrates different important steps which can be used for the environmental assessment of wheat production systems and for the identification of optimisation potentials. The information gathered addresses the principal questions raised in the introduction, regarding the main achievements and perspectives for further studies:

a) On which common basis should different agriculture scenarios be compared in an environmental assessment ? Environmental assessment of agricultural activities is particular in that it has a multifunctional role and evolves in complex systems close to the environment. Consequently, the risk is high that the assessment is biased by reductionism in the system boundaries description, the scenario definition, the choice of the functional unit and the considered impact indicators. Conclusively, an assessment based only on impact per cultivated area can lead to a displacement of pollution instead of a real reduction.

b) How can both yield quantity and yield quality be accounted for? This study has been able to characterise not only intensity per hectare and production of grain, but also the product quality. It has shown the importance of the interaction between fertilisation intensity, crop variety and their influence on yield and quality. A method has been developed to determine corrected ton of grain with constant protein content, a functional unit constituting a sound basis to account for quality in Life Cycle Assessment of agriculture crops. However, further research is needed to take into account qualitative parameters other than protein content, such as other bakery requirements for the grain quality and vitamin content.

c) What is the best fertilization intensity of production for wheat crop from an environmental point of view ? Different wheat production systems exist in Europe. Intensive systems are developed in highly fertile regions, where more than 200 kg N / ha fertilisation and high crop protection are practised. Half fertilisation intensity is applied in other areas where wheat is cultivated in extensive systems. Agronomic situations partly explain these differences, which depend on local natural fertility and yield potential. Other circumstances explain these differences linked to economic, environmental or social agricultural policies. Some of these production orientations could be questioned from a strictly environmental point of view (Gaillard et al., 2002). Environmental problems in arable systems are often reduced to nitrogen and pesticides problems, forgetting the specific high efficiency of this agricultural inputs to the whole production system. In any case, the choice of the production intensity remains linked to the site specific potential, at field level, resulting in a combination of intensive and extensive situations. Brentrup (2003) concluded that a good environmental performance was achieved in wheat production notably by maintaining high yields in order to use land most efficiently, to apply fertilisers to crop demand and to limit specific emissions ($NO_3$, $NH_3$ and $N_2O$).

The best combination of variety, fertilisation, crop protection and land utilisation should therefore be explored to design optimal production strategies from an environmental point of view. This study has shown that if quality for bread making is considered, high fertilisation intensity is favourable for most impact categories, demonstrating sufficient yield increase

potential with changes in variety for each level of fertilisers. This conclusion was attested to different types of fertilizer or regions (P or N-limited). On the other hand, impact per ton of grain increases with fertilisation intensification for most environmental categories if variety is not adapted, or more generally, if the intensity level exceeds the production potential. Furthermore, impact per hectare increases with fertilisation intensification for all environmental categories except land utilisation, showing that minimum fertilization or less intensive crops have to be considered for pure land upkeep function.

Several developments could be considered for further studies: the upkeep of released areas due to production intensity, or inversely, the need for additional cultivated areas through extensification should be taken into account. Intensive production showed a substantial reduction of the impact on land utilisation per ton of grain. In this study, an impact of zero has been attributed to land left free by intensification. Effectively constant progress in productivity have modified the affectation of arable surfaces to diminish volumes of production. Different uses have been made of these free areas, removed from the productive surface in the form of fallow or areas for ecological compensation, or attributed to new production forms, such as cultivation of renewable raw materials. Surplus productions of wheat were also denatured for animal feeding (instead of bread making) and became a new form of production resulting in new specific impacts. Further studies about different utilisation strategies of subtracted wheat production area for bread making should complete the identification of optimisation potentials and clarify the real impact.

The evaluation of the land use is a sensitive point due to the coexistence of the two functions, production and land upkeep. The necessity to have a precise goal definition of the study and to identify clearly the system boundaries was underlined through the comparisons of different land use systems by LCA (Gärtner et al., 2001). An improvement in the methodological approach is furthermore necessary, as important quantitative and qualitative differences in land use occur according to the choice of the production intensity. Notably, a recent concept to measure the human influence on ecosystems was developed for the life cycle assessment of land use to characterize different types of land use (Brentrup et al, 2002).

d) What are the key factors influencing the environmental performances of a wheat crop?

Variety, amount and types of fertilisers, as well as heavy metal contents were identified as having a significant influence on the environmental performances. For energy and $CO_2$, Nitrogen fertilizers play a significant role, whereas P-fertilizers are dominant for heavy metals or eutrophication in P-limited area.

The dominating effect of heavy metals on ecotoxicity and toxicity relies on the adopted method Critical Surface-Time (Jolliet et Crettaz, 1997) and on their high persistence, compared to other types of emissions like pesticides. Recent specific methodological improvements have been brought for the assessment of pesticides (Margni et al., 2002) and others could be brought for heavy metals. However, the major challenge concerns the capacity of evaluating simultaneously both types of emissions or differentiating short- and long-term impacts.

As a whole, efficiency of nitrogen fertilisation is high and contributes for a large part to the productivity of wheat systems. However, the optimisation of fertilisation shows that environmental optimisation of wheat production system cannot be reduced to an optimisation of nitrogen on its own. A larger scaled system is needed by taking into account determining

agricultural parameters, such as the interaction between fertilisation and variety, quality requirements and the multiple function of the agricultural system.

## *A.9 Bibliography*

Audsley, E., Alber, S., Clift, R., Cowell, S., Crettaz, P., Gaillard, G., Hausheer, J., Jolliet, O., Kleijn, R., Mortensen, B., Pearce, D., Roger, E., Teulon, H., Weidema, B. and van Zeits, H., 1997. Harmonisation of environmental life cycle assessment for agriculture. Final report for the DG VI Agriculture of the European Commission.

Bänzinger, M., Feil, B., Schmid, J.E. and Stamp, P., 1992. Genotipic variation in grain nitrogen content of wheat as affected by mineral nitrogen supply in the soil. Eur. J. Agron. 1, 155-162.

Brentrup, F., 2003. Life Cycle Assessment to evaluate the environmental impact of arable production. Cuviller Verlag, Göttingen , Germany, .

Brentrup, F., Küsters, J., Kuhlmann, H., Lammel, J., 2001. Application of the Life Cycle Assessment methodology to agricultural production: an example of sugar beet production with different forms of nitrogen fertilisers. Eur. J. Agron. 14, 221-223.

Brentrup, F., Küsters, J., Lammel, J., Kuhlmann, H., 2002. Life Cycle Impact Assessment of land use based on the Hemeroby concept. Int J LCA 7, 339-348.

Collaud, J.F., 2000. Comparaison blé – orge – triticale: agronomie et économie. Revue suisse agric. 32 (5), 211-216.

Debaeke, Ph., Aussenac, Th., Fabre, J.L., Hilaire, A., Pujol, B. and Thuries, L., 1996. Grain nitrogen content of winter bread wheat (*Triticum aestivum* L.) as related to crop management and to previous crop. Eur. F. Agron. 5, 273-286.

ESU, 1995. Ökoinventare für Energiesysteme. Gruppe Energie-Stoffe-Umwelt, ETH-Zürich, PSI Villingen, 520 p.

Feil, B., 1996. Extensivierung der Stickstoffdüngung im Getreidebau. Agrarforschung 3 (6), 271-274.

Feil, B., 1998. Physiologische und pflanzenbauliche Aspekte der inversen Beziehung zwischen Ertrag und Proteinkonzentration bei Getreidesorten: eine Übersicht. Pflanzenbauwissenschaftem, 2 (1), 37-46.

Gaillard, G., Crettaz P., and Hausheer, J., 1997a. Inventaire environnemental des intrants agricoles en production végétale. Rapport FAT 46.

Gaillard, G., Dinkel, F., Waldeck, B., Grub, A., Hausheer, J., Menzi, H., Prasuhn, V., Stauffer, W,. Studer, K., Walther, U. and Weisskopf, P., 1997b. Ressourcenbedarf und ökologische Wirkungen von Stoffflüssen. In : Beurteilung nachwachsender Rohstoffe. Wolfensberger, U. and Dinkel, F. FAT – Carbotech. Bericht im Auftrag des schweizerischen Bundesamtes für Landwirtschaft, Bern 37-88.

Gaillard, G., Nemecek., T., 2002. Ökobilanzierung des Extensoanbaus von Getreide und Raps. Agrarforschung 9 (11-12), 490-495

Gärtner, S.O., Jungk, N.C. Reinhardt G.A., 2001. Food production and land use - an environmental comparison of different land use systems. In Swedish Institute for Food and Biotechnology (ed.): Proceedings of the International Conference on LCA in Foods, Gothenburg 26-27 April 2001, SIK document No. 143, pp. 53-58, Gothenburg 2001.

Heijungs, R., Guinée, J.B., Huppes, G., Lankreisjer, R.M., Udo De Haes, H. A., Sleeswijk, A.W., 1992. Environmental Life Cycle Assessment of Products. R. Haijungs Editor, CML, Leiden.

ISO, 2001. Environmental management - Life cycle assessment - Life cycle impact assessment, International Standard ISO 14042. International Organization for Standardization ISO, Geneva, Switzerland.

Jolliet, O. and Crettaz, P., 1997. Critical Surface-Time 95. A life cycle impact assessment methodology including fate and exposure. EPFL, Institut d'Aménagement des Terres et des Eaux.

Kuesters, J. and Lammel, J., 1999. Investigations of energy efficiency of the production of winter wheat and sugar beet in Europe. Eur. J. Agron. 11, 35-43.

Le Gouis, J., Béghin, D., Heumez, E. and Pluchard, P., 2000. Genetic differences for nitrogen uptake and nitrogen utilisation efficiencies in winter wheat. Eur. J. Agron. 12, 163-173.

Margni, M., Rossier, D., Crettaz, Jolliet, O., P. 2002. Life cycle impact assessment of pesticides on human health and ecosystems. Agriculture, Ecosystems and Environment, 93:379-392.

Pellet, D., 1997. Techniques culturales sur céréales panifiables. Résultats des essais 1997. Rapport Phytotechnie, céréales et plantes industrielles, RAC - Nyon.

RAC, 1997. Blé d'automne. Résultats des essais d'homologations 1995-1996. Rapport interne, Forschungsanstalt für Agrarökologie un Landbau, FAL – Reckenholz, Zürich et Station de recherches en production végétale, RAC – Changins, Nyon.

Rossier, D., 1999. L'écobilan, outil de gestion écologique de l'exploitation agricole ? Revue suisse Agric. 31 (4), 179-185.

Ryser, J.P., Walther, U., Flisch, R., 2001. Données de base pour la fumure des grandes cultures et des herbages. Revue suisse Agric., 33, 1-80.

# B. List of parameters

## *B.1 Indices*

$_{0}$ Indice for system evolution and time: 0 conditions at begin of plant growth

$_{sp}$ Indice for system development: conditions at spray time

$_{d}$ Indice for system development: conditions for dynamic system evolution

$_{h}$ Indice for system development: conditions at harvest time

$_{r}$ Indice for plant compartment: root

$_{st}$ Indice for plant compartment: stem

$_{l}$ Indice for plant compartment: leaf

$_{fd}$ Indice for plant compartment: formulation deposit

$_{a}$ Indice for environmental compartment: air

$_{s}$ Indice for environmental compartment: soil

## *B.2 Time*

$t_i$ Time from begin of plant growth, variable according to event (days)

## *B.3 Plant*

$BM_t$ Dry plant biomass ($kg/m^2_{soil}$ ), variable according to crop and plant development

frpl Fraction root to aerial plant part per default 0.5 kg/kg

flpl Fraction leaf to aerial plant part (kg/kg), variable according to crop

fstpl Fraction stem to aerial plant part (kg/kg), variable according to crop

frpl Fraction root to aerial plant part (kg/kg), variable according to crop

fharl Fraction of harvested part to leaf compartment (kg/kg), variable according to crop

fharst Fraction of harvested part to stem compartment (kg/kg), variable according to crop

$\rho_i$ Bulk density, variable according to plant compartment – per default 0.8 kg/l

$\rho_w$ = 1 kg/l – Water density

$\rho_r$ = 0.8 kg/l – Bulk density root

$V_i$ – Volume compartment($m^3$), variable according to crop and plant development

$LAI_t$ Leaf area index ($m^2$ / $m^2$), variable according to crop and plant development

$A_{sto}$ = 0.02 $m^2$ / $m^2$ – Fraction stomata area to leaf area

$A_r$ Root area [$m^2$]

tc Transpiration coefficient (l/kg), variable according to crop

$w_i$ Water content in plant, variable according to plant compartment, per default 0.8 g/g

$w_r$ = 0.94 g/g – Root water content

$l_i$ Lipid content in plant, variable according to plant compartment, per default 0.02 g/g

$l_r$ = 0.01 g/g – Root lipid content

bl = bst = 0.95 – Correction plant lipid – n-octanol, aerial plant part for leaf and stem (barley)

br = 0.77 – Correction plant lipid - n-octanol, root compartment (barley)

$L_b$ = 0.001 m – Diffusion path length stomata

$L_{sto}$ = 0.000025 m – Diffusion path length stomata

Lls = 0.0000002 m – Diffusion path length of the limiting skin

## *B.4 Environment*

$V_i$ Volume compartment i($m^3$)

$fr_{volw}$ = 0.2 l/l – Volumetric water fraction soil

$fr_{por}$ = 0.5 l/l – Porosity

$\rho_s$ = 1.3 kg/l – Bulk density soil

## *B.5 Transport*

$D_{wO2}$ = 0.000170208 $m^2$/day – Diffusion coefficient $O_2$ in water

$D_w$ – Diffusion coefficient in water [$m^2$/day]

$D_{ws}$ – Diffusion coefficient in water-filled pores [$m^2$/day]

$D_{aH2O}$ = 2.09088 $m^2$/day – Diffusion coefficient $H_2O$ in the air

$D_a$ Diffusion coefficient in air ($m^2$/day)

$D_{as}$ – Diffusion coefficient in air-filled pores [$m^2$/day]

$k^*_0$ = 8.64 1/day – Solute mobility molecule 0

$k^*$ Solute mobility of substance in plant surface deposit (1/day)

$\beta'_{fd}$ = -0.022 mol/$cm^3$ – Size selectivity (= $\beta'$ * 2.3, with $\beta'$ =0.0095 mol/$cm^3$)

$Q_{xy}$ – Flow xylem ($m^3$/day)

$Q_{ph}$ – Flow phloem ($m^3$/day)

$P_c$ Permeance cuticle (m/day)

$G_c$ Conductance cuticle (m/day)

$G_s$ Conductance stomata (m/day)

$G_b$ Conductance boundary layer (m/day)

$G_{i-j}$ Conductance between compartment i and compartment j (m/day)

$k_{itot}$ Total removal rate constant for compartment i (1/day)

$k_{i-j}$ Transfer rate from compartment i to compartment j (1/day)

$k_{ideg}$ Degradation rate in compartment i (1/day)

## *B.6 Substance dependent variables*

MW Molecular weight (g/mol)

$MW_{ref}$ = 342.14 g/mol – Molecular weight of reference substance Bifenox

MV – Molar volume (ml/mol)

$t_{1/2a}$ Half-life in air (days)

$t_{1/2fd}$ Half-life in plant surface deposit (days)

$t_{1/2s}$ Half-life in soil (days)

$t_{1/2veg}$ Half-life in vegetation (days)

$K_{ow}$ Octanol-water partition coefficient (-)

$K_{aw}$ Air-water partition coefficient (-)

$K_{ij}$ Partition coefficient between compartment i and j (-)

TSCF Transpiration Stream Concentration Factor (-)

# C. Substances used for the developments and the tests of the model

Lists of substances used in wheat needed for the developments and the tests of the single processes and of the functioning of the model. *Restricted list of substances used to evaluate the core model, CAS registry number, type of substance. fungicide (F), herbicide (H), insecticide (I), growth regulator (R).

| * | substances | cas | type |
|---|---|---|---|
| | Amidosulfuron | 120923-37-7 | F |
| * | Azoxystrobin | 131860-33-8 | F |
| | Bifenox | 42576-02-3 | H |
| | Bromoxynil | 1689-84-5 | H |
| * | Chlormequat | 999-81-5 | R |
| * | Chlorothalonil | 1897-45-6 | F |
| | Chlortoluron | 15545-48-9 | H |
| | Clodinafop-propargyl | 105512-06-9 | H |
| * | Cyproconazole | 113096-99-4 | F |
| | Cyprodinil | 121552-61-2 | F |
| * | Deltamethrine | 52918-63-5 | I |
| | Dicamba | 1918-00-9 | H |
| | Difenoconazole | 119446-68-3 | F |
| * | Diflufenican | 83164-33-4 | H |
| | Epoxiconazole | 106325-08-0 | F |
| * | Ethephon | 16672-87-0 | R |
| | Fenpropimorphe | 67564-91-4 | F |
| | Fluroxypyr | 69377-81-7 | H |
| | Flusilazole | 85509-19-9 | F |
| * | Ioxynil | 1689-83-4 | H |
| * | Isoproturon | 34123-59-6 | H |
| | MCPA | 94-74-6 | H |
| | MCPP | 7085-19-0 | H |
| | MCPP-P | 16484-77-8 | H |
| * | Lambda-cyhalothrin | 91465-08-6 | I |
| | Metsulfuron-methyl | 74223-64-6 | H |
| * | Pendimethaline | 40487-42-1 | H |
| * | Pirimicarb | 23103-98-2 | I |
| * | Prochloraz | 67747-09-5 | F |
| | Propiconazole | 60207-90-1 | F |
| | Pyridate | 55512-33-9 | H |
| * | Tebuconazole | 107534-96-3 | F |
| * | Teflubenzuron | 83121-18-0 | I |
| | Terbuthylazine | 5915-41-3 | H |
| | Thifensulfuron-methyl | 79277-27-3 | H |
| | Triasulfuron | 82097-50-5 | H |
| * | Trinexapac-ethyl | 95266-40-3 | R |

# D. Understanding the functioning of the system

## *D.1 Transfer rates between compartments*

Transfer rates between compartments air, soil, plant surface deposit, root, stem and leaf; set of substances used in wheat

| substances | Transfer rates (1/day) | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | soil | | | root | | stem | | leaf | | | | air | | | | form.dep. | | | |
| | $k_{sr}$ | $k_{sst}$ | $k_{stot}$ | $k_{rs}$ | $kr_{tot}$ | $k_{stl}$ | $k_{sttot}$ | $k_{la}$ | $k_{lfd}$ | $k_{lst}$ | $k_{ltot}$ | $k_{al}$ | $k_{as}$ | $k_{afd}$ | $k_{atot}$ | $k_{fdl}$ | $k_{fda}$ | $k_{fds}$ | $k_{fdtot}$ |
| Azoxystrobin | 7.0E-03 | 6.3E-04 | 7.4E-02 | 1.3E+00 | 1.4E+00 | 1.5E-01 | 2.8E-01 | 9.5E-07 | | 3.0E-02 | 1.6E-01 | 1.5E+00 | | | 1.7E+00 | 7.5E-02 | | | 2.1E-01 |
| Chlorothalonil | 4.6E-03 | 1.9E-04 | 2.4E-02 | 1.4E+00 | 1.4E+00 | 7.2E-02 | 1.1E-01 | 1.4E-01 | | 1.4E-02 | 1.9E-01 | 1.5E-01 | | | 1.5E-01 | 5.2E+00 | | | 5.3E+00 |
| Cyproconazole | 7.9E-03 | 4.3E-04 | 3.4E-02 | 9.8E-01 | 1.0E+00 | 6.7E-02 | 1.2E-01 | 3.6E-03 | | 1.3E-02 | 6.9E-02 | 1.4E+00 | | | 2.0E+00 | 1.0E+00 | | | 1.2E+00 |
| Prochloraz | 1.1E-03 | 1.1E-05 | 3.3E-02 | 1.5E-01 | 2.1E-01 | 5.1E-03 | 6.8E-02 | 4.5E-03 | | 1.0E-03 | 6.8E-02 | 9.1E-01 | | | 3.9E+00 | 8.4E+00 | | | 8.5E+00 |
| Diflufenican | 1.7E-03 | 3.7E-06 | 6.1E-03 | 5.6E-02 | 6.4E-02 | 1.2E-03 | 1.0E-02 | 6.8E-03 | | 2.3E-04 | 1.6E-02 | 3.1E-01 | | | 4.5E-01 | 1.1E+02 | | | 1.1E+02 |
| Ioxynil | 1.0E-02 | 9.0E-04 | 8.1E-02 | 2.6E+00 | 2.7E+00 | 1.1E+00 | 1.3E+00 | 4.5E-01 | | 2.2E-01 | 8.1E-01 | 9.6E-02 | | | 1.1E-01 | 1.2E-01 | | | 2.6E-01 |
| Isoproturon | 3.1E-02 | 2.5E-03 | 6.9E-02 | 1.8E+00 | 1.8E+00 | 1.9E-01 | 2.6E-01 | 2.0E-03 | | 3.8E-02 | 1.1E-01 | 1.6E+00 | | | 2.0E+00 | 2.4E+00 | | | 2.6E+00 |
| Pendimethaline | 9.5E-03 | 5.4E-07 | 2.0E-02 | 1.5E+00 | 1.5E+00 | 6.3E-04 | 2.1E-02 | 1.5E-01 | | 1.3E-04 | 1.7E-01 | 1.1E-01 | | | 1.4E+00 | 5.1E+02 | | | 5.1E+02 |
| Lamda-cyhalothrin | 2.8E-05 | 6.4E-08 | 3.2E-02 | 1.1E-03 | 6.6E-02 | 9.7E-06 | 6.4E-02 | 1.4E-04 | | 1.9E-06 | 6.5E-02 | 1.2E+00 | | | 1.9E+00 | 1.9E+03 | | | 1.9E+03 |
| Pirimicarb | 7.6E-03 | 6.9E-04 | 1.4E-02 | 2.5E+00 | 2.5E+00 | 5.3E-01 | 5.4E-01 | 1.6E-02 | | 1.1E-01 | 1.3E-01 | 6.5E-01 | | | 7.0E+00 | 1.6E-01 | | | 3.0E-01 |
| Deltamethrine | 1.3E-06 | 2.8E-09 | 3.3E-02 | 1.9E-02 | 8.5E-02 | 3.0E-04 | 6.6E-02 | 3.1E-03 | | 6.0E-05 | 6.9E-02 | 5.6E-01 | | | 2.1E+00 | 4.8E+01 | | | 4.8E+01 |
| Teflubenzuron | 4.5E-04 | 1.2E-06 | 2.1E-02 | 6.9E-02 | 1.1E-01 | 2.0E-03 | 4.2E-02 | 2.1E-06 | | 4.0E-04 | 4.1E-02 | 1.4E+00 | | | 1.6E+00 | 5.8E+01 | | | 5.8E+01 |
| Chlormequat chloride | 2.0E-02 | 1.5E-04 | 6.8E-02 | 4.3E+00 | 4.4E+00 | 1.2E+00 | 1.3E+00 | 2.6E-06 | | 2.3E-01 | 3.3E-01 | 2.3E+00 | | | 2.6E+00 | 5.4E-04 | | | 1.4E-01 |
| Ethephon | 1.3E-03 | 1.0E-05 | 4.9E-02 | 3.9E+00 | 4.0E+00 | 1.2E+00 | 1.3E+00 | 2.2E-06 | | 2.3E-01 | 3.3E-01 | 2.1E+00 | | | 2.2E+00 | 2.6E-04 | | | 1.4E-01 |
| Trinexapac-ethyl | 1.7E-02 | 1.5E-03 | 7.1E-01 | 2.7E+00 | 4.1E+00 | 6.4E-01 | 2.0E+00 | 2.7E-01 | | 1.3E-01 | 1.8E+00 | 1.3E-01 | | | 4.2E+00 | 1.4E-01 | | | 2.8E-01 |

## *D.2 Initial conditions and results of the model*

Initial masses in source compartments, time between spray and harvest, results of the model in form of mass at harvest in the different compartments

| substances | Initial mass (kg/m$^2$ crop) | | | | time (d) | Mass at harvest (kg/m$^2$ crop) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Spray $M_{spray}$ | air $M_{asp}$ | soil $M_{ssp}$ | for.dep. $M_{fdsp}$ | td | $M_a(t)$ | $M_s(t)$ | $M_{fd}(t)$ | $M_r(t)$ | $M_{st}(t)$ | $M_l(t)$ |
| Azoxystrobin | 2.5E-05 | 2.5E-06 | 1.0E-05 | 1.2E-05 | 6.5E+01 | 1.6E-15 | 1.2E-07 | 1.2E-11 | 6.6E-10 | 8.5E-10 | 2.7E-09 |
| Chlorothalonil | 1.5E-04 | 1.5E-05 | 6.1E-05 | 7.4E-05 | 6.5E+01 | 1.1E-05 | 1.7E-05 | 2.1E-25 | 5.5E-08 | 1.6E-06 | 9.8E-06 |
| Cyproconazole | 8.0E-06 | 8.0E-07 | 3.3E-06 | 3.9E-06 | 6.5E+01 | 2.2E-10 | 5.7E-07 | -5.3E-27 | 4.5E-09 | 2.6E-08 | 1.2E-07 |
| Prochloraz | 4.5E-05 | 4.5E-06 | 1.8E-05 | 2.2E-05 | 6.5E+01 | 3.5E-10 | 2.4E-06 | -7.4E-27 | 1.4E-08 | 2.0E-08 | 3.0E-07 |
| Diflufenican | 7.5E-06 | 7.5E-07 | 5.2E-06 | 1.6E-06 | 1.3E+02 | 7.9E-09 | 2.8E-06 | -1.9E-27 | 7.8E-08 | 1.7E-08 | 5.1E-07 |
| Ioxynil | 3.6E-05 | 3.6E-06 | 2.5E-05 | 7.4E-06 | 1.3E+02 | 1.2E-07 | 3.1E-09 | 2.9E-20 | 1.2E-11 | 3.8E-09 | 2.1E-08 |
| Isoproturon | 1.5E-04 | 1.5E-05 | 1.0E-04 | 3.1E-05 | 1.3E+02 | 5.2E-11 | 8.0E-07 | -8.4E-28 | 1.4E-08 | 1.8E-08 | 5.0E-08 |
| Pendimethaline | 1.6E-04 | 1.6E-05 | 1.1E-04 | 3.3E-05 | 1.3E+02 | 1.5E-12 | 2.9E-05 | 1.1E-29 | 1.8E-07 | 3.2E-09 | 1.4E-11 |
| Lamda-cyhalothrin | 7.5E-07 | 7.5E-08 | 3.5E-07 | 3.3E-07 | 7.5E+01 | 2.3E-13 | 3.1E-08 | 1.5E-31 | 2.4E-11 | 4.9E-13 | 3.0E-09 |
| Pirimicarb | 7.5E-06 | 7.5E-07 | 3.5E-06 | 3.3E-06 | 7.5E+01 | 7.6E-10 | 2.1E-06 | 5.3E-16 | 6.4E-09 | 7.0E-08 | 3.3E-07 |
| Deltamethrine | 7.5E-07 | 7.5E-08 | 3.5E-07 | 3.3E-07 | 7.5E+01 | 3.2E-12 | 2.9E-08 | 5.6E-31 | 7.3E-13 | 1.0E-11 | 2.1E-09 |
| Teflubenzuron | 6.0E-06 | 6.0E-07 | 2.8E-06 | 2.6E-06 | 7.5E+01 | 2.0E-13 | 6.0E-07 | 3.7E-29 | 3.0E-09 | 4.2E-09 | 1.5E-07 |
| Chlormequat chloride | 1.2E-04 | 1.2E-05 | 6.5E-05 | 3.9E-05 | 9.5E+01 | 2.7E-15 | 6.6E-07 | 7.0E-11 | 3.0E-09 | 6.1E-10 | 2.7E-09 |
| Ethephon | 7.2E-05 | 7.2E-06 | 4.1E-05 | 2.4E-05 | 9.5E+01 | 8.2E-16 | 4.3E-07 | 4.5E-11 | 1.4E-10 | 1.6E-10 | 7.8E-10 |
| Trinexapac-ethyl | 1.5E-05 | 1.5E-06 | 8.5E-06 | 5.0E-06 | 9.5E+01 | 7.0E-20 | 1.3E-34 | 1.0E-17 | 6.4E-37 | 7.5E-20 | 1.0E-18 |

# E. Sensitivity analysis

## *E.1 Sensitivity analysis: change in input by 0.1%*

Sensitivity analysis of transfer rate as a function of main parameters of the model. Median, minimum and maximum sensitivity for a change in input by 0.1%.

| median | Kaw | Kow | Koc | MW | MV | t0.5g | t0.5s | t0.5fd | t0.5sp | kpdeg | kfddeg | ksdeg | kadeg | td | Tg | Vstd | Vld | Vrd | Vfdd |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ksr | 9.7E-04 | 0.0E+00 | -9.8E-01 | -4.6E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 8.7E-01 | 2.2E+00 | 0.0E+00 | 0.0E+00 | 9.3E-01 | 0.0E+00 |
| ksst | -7.1E-10 | 0.0E+00 | -9.8E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 8.7E-01 | 2.2E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstot | 1.8E-04 | 0.0E+00 | -1.7E-01 | -7.5E-02 | 0.0E+00 | 0.0E+00 | -8.3E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 8.3E-01 | 0.0E+00 | 1.4E-01 | 3.7E-01 | 0.0E+00 | 0.0E+00 | 1.5E-01 | 0.0E+00 |
| krs | 1.0E-03 | -4.2E-01 | 0.0E+00 | -5.0E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.1E-13 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krtot | 9.9E-04 | -3.4E-01 | 0.0E+00 | -4.7E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -5.1E-02 | 5.1E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.3E-13 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstl | 0.0E+00 | -8.5E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 8.6E-14 | 9.0E-14 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksttot | 0.0E+00 | -1.3E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -4.5E-01 | 4.5E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -5.5E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kla | 9.3E-01 | -6.4E-01 | 0.0E+00 | -4.6E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 3.7E-01 | -2.2E+00 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 |
| klst | 0.0E+00 | -8.5E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 6.1E-14 | 6.5E-14 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 |
| kltot | 3.5E-02 | -1.3E-01 | 0.0E+00 | -1.8E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -6.9E-01 | 6.9E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.4E-02 | -1.1E-01 | 0.0E+00 | -3.1E-01 | 0.0E+00 | 0.0E+00 |
| kal | -7.5E-02 | 5.3E-02 | 0.0E+00 | -4.6E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.2E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| katot | -4.3E-02 | 3.1E-02 | 0.0E+00 | -3.1E-01 | 0.0E+00 | -2.8E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.8E-01 | 8.8E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kfdl | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | -4.6E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.2E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.0E+00 |
| kfdtot | 0.0E+00 | 9.1E-01 | 0.0E+00 | 0.0E+00 | -3.5E+00 | 0.0E+00 | 0.0E+00 | -8.7E-02 | 0.0E+00 | 0.0E+00 | 8.7E-02 | 0.0E+00 | 0.0E+00 | 8.6E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -9.1E-01 |
| Mst | -5.0E-03 | -7.3E-02 | -5.4E-02 | -8.0E-03 | -4.7E-02 | 7.0E-02 | 5.0E-02 | 3.5E-02 | 3.0E+00 | -3.0E+00 | -3.5E-02 | -5.0E-02 | -7.0E-02 | -3.6E+00 | 2.9E-01 | 6.5E-01 | -8.2E-01 | -5.6E-04 | -1.7E-02 |
| min | Kaw | Kow | Koc | MW | MV | t0.5g | t0.5s | t0.5fd | t0.5sp | kpdeg | kfddeg | ksdeg | kadeg | td | Tg | Vstd | Vld | Vrd | Vfdd |
| ksr | 2.0E-08 | -2.7E-02 | -1.0E+00 | -4.9E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 6.1E-01 | 2.2E+00 | 0.0E+00 | 0.0E+00 | 8.7E-01 | 0.0E+00 |
| ksst | -1.5E-07 | -8.3E-01 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 6.1E-01 | 2.2E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstot | 5.2E-10 | 0.0E+00 | -5.8E-01 | -2.6E-01 | 0.0E+00 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 4.1E-01 | 0.0E+00 | 3.0E-05 | 8.7E-05 | 0.0E+00 | 0.0E+00 | 3.6E-05 | 0.0E+00 |
| krs | 2.2E-08 | -7.6E-01 | 0.0E+00 | -5.0E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.8E-13 | -1.8E-13 | 0.0E+00 | 0.0E+00 | -1.8E-13 | 0.0E+00 |
| krtot | 2.1E-08 | -6.5E-01 | 0.0E+00 | -5.0E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -7.8E-01 | 4.5E-03 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -2.2E-13 | -2.2E-13 | 0.0E+00 | 0.0E+00 | -2.2E-13 | 0.0E+00 |
| kstl | 0.0E+00 | -9.5E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -2.5E-13 | -4.0E-13 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksttot | 0.0E+00 | -5.9E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -9.9E-01 | 2.1E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.8E-13 | -3.5E-13 | -9.8E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kla | 4.3E-01 | -9.5E-01 | 0.0E+00 | -5.0E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.6E-01 | -2.2E+00 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 |
| klst | 0.0E+00 | -9.5E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -3.6E-13 | -3.7E-13 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 |
| kltot | 5.8E-06 | -6.5E-01 | 0.0E+00 | -3.2E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -9.9E-01 | 8.6E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.5E-06 | -1.6E+00 | 0.0E+00 | -9.1E-01 | 0.0E+00 | 0.0E+00 |
| kal | -5.7E-01 | 2.9E-05 | 0.0E+00 | -5.0E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 8.7E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| katot | -3.9E-01 | 1.2E-05 | 0.0E+00 | -4.5E-01 | 0.0E+00 | -9.3E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.8E-03 | 7.7E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kfdl | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | -7.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 8.7E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.0E+00 |
| kfdtot | 0.0E+00 | 1.9E-03 | 0.0E+00 | 0.0E+00 | -7.0E+00 | 0.0E+00 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 1.3E-03 | 0.0E+00 | 0.0E+00 | 2.7E-03 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.0E+00 |
| Mst | -3.8E-01 | -1.4E+00 | -6.9E-01 | -4.9E-02 | -1.4E+00 | 6.7E-03 | 3.8E-04 | 9.2E-04 | 7.3E-01 | -8.0E+00 | -6.6E-01 | -3.5E+00 | -4.0E+00 | -2.6E+01 | -3.9E+00 | 1.1E-02 | -2.6E+00 | -6.8E-02 | -3.3E-01 |

| max | Kaw | Kow | Koc | MW | MV | t0.5g | t0.5s | t0.5fd | t0.5sp | kpdeg | kfddeg | ksdeg | kadeg | td | Tg | Vstd | Vld | Vrd | Vfdd |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ksr | 2.9E-01 | 2.3E-02 | -9.2E-01 | -4.4E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.4E+00 | 2.2E+00 | 0.0E+00 | 0.0E+00 | 9.7E-01 | 0.0E+00 |
| ksst | 0.0E+00 | 3.2E-01 | -9.2E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.4E+00 | 2.2E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstot | 7.8E-02 | 0.0E+00 | -4.0E-05 | -1.8E-05 | 0.0E+00 | 0.0E+00 | -4.1E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 7.1E-01 | 1.3E+00 | 0.0E+00 | 0.0E+00 | 5.3E-01 | 0.0E+00 |
| krs | 3.2E-01 | -1.6E-04 | 0.0E+00 | -5.0E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.3E-13 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.8E-13 | 0.0E+00 |
| krtot | 2.8E-01 | -1.6E-04 | 0.0E+00 | -1.1E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -4.5E-03 | 7.8E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.2E-13 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.2E-13 | 0.0E+00 |
| kstl | 0.0E+00 | -1.9E-04 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.2E-13 | 4.2E-13 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksttot | 0.0E+00 | -1.8E-04 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -2.1E-02 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.5E-13 | 3.9E-13 | -4.5E-03 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kla | 1.0E+00 | 2.0E-02 | 0.0E+00 | -2.1E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 5.9E-01 | -2.2E+00 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 |
| klst | 0.0E+00 | -1.9E-04 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 3.9E-13 | 3.9E-13 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 |
| kltot | 6.4E-01 | -1.4E-04 | 0.0E+00 | -2.9E-06 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -8.6E-02 | 9.9E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 3.3E-01 | -1.3E-05 | 0.0E+00 | -9.9E-03 | 0.0E+00 | 0.0E+00 |
| kal | -4.1E-05 | 4.0E-01 | 0.0E+00 | -2.1E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| katot | -1.7E-05 | 2.8E-01 | 0.0E+00 | -1.6E-02 | 0.0E+00 | -1.8E-03 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 9.3E-01 | 1.9E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kfdl | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | -1.8E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.0E+00 |
| kfdtot | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | -3.4E-03 | 0.0E+00 | 0.0E+00 | -1.3E-03 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 2.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.9E-03 |
| Mst | 2.2E+00 | 4.6E-01 | -2.2E-04 | 3.2E+00 | 2.0E-01 | 4.1E+00 | 3.5E+00 | 6.6E-01 | 8.1E+00 | -7.3E-01 | -9.2E-04 | -3.8E-04 | -6.7E-03 | 1.5E-02 | 2.0E+00 | 9.7E-01 | -1.7E-01 | -1.0E-08 | 4.6E-02 |

| median | Qxy | Qph | klai | Tlai | LAId | As | ls | lb | Ar | lro | rr | br | wr | lr | rst | bst | wst | lst | Va |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ksr | 7.1E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 9.3E-01 | -9.3E-01 | -9.3E-01 | 0.0E+00 | 1.8E+01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksst | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstot | 1.8E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.5E-01 | -1.5E-01 | -1.5E-01 | 0.0E+00 | 2.9E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krs | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | -1.0E+00 | -1.0E+00 | -2.7E+00 | -4.5E-01 | -5.5E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krtot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 9.5E-01 | -9.5E-01 | -9.5E-01 | -2.1E+00 | -4.2E-01 | -4.4E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstl | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.0E-13 | -5.3E+00 | -4.1E+00 | -8.9E-01 | 0.0E+00 |
| ksttot | 5.5E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.5E-13 | -9.5E-01 | -2.2E+00 | -1.4E-01 | 0.0E+00 |
| kla | 0.0E+00 | 0.0E+00 | 0.0E+00 | 3.0E+00 | 1.0E+00 | 1.2E-02 | -1.2E-02 | -7.1E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.6E-13 | -5.3E+00 | -4.1E+00 | -8.9E-01 | 0.0E+00 |
| klst | 1.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.4E-13 | -5.3E+00 | -4.1E+00 | -8.9E-01 | 0.0E+00 |
| kltot | 1.6E-01 | 1.6E-01 | 0.0E+00 | 1.4E-01 | 4.9E-02 | 7.7E-04 | -7.7E-04 | -2.5E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.3E-13 | -7.9E-01 | -1.3E+00 | -1.4E-01 | 0.0E+00 |
| kal | 0.0E+00 | 0.0E+00 | 0.0E+00 | 3.0E+00 | 1.0E+00 | 1.2E-02 | -1.2E-02 | -7.1E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.0E+00 |
| katot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.1E+00 | 7.2E-01 | 3.3E-03 | -3.3E-03 | -3.0E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -7.2E-01 |
| kfdl | 0.0E+00 | 0.0E+00 | -7.4E-01 | 1.7E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kfdtot | 0.0E+00 | 0.0E+00 | -6.1E-01 | 1.5E+00 | 9.1E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| Mst | 3.9E-01 | 8.4E-01 | 3.5E-01 | 4.5E-01 | 2.9E-02 | 5.1E-07 | -5.1E-07 | -5.9E-03 | 8.5E-06 | -8.5E-06 | -8.5E-06 | -4.5E-04 | -1.1E-02 | -1.1E-04 | -1.3E-13 | -7.5E-01 | -1.1E+00 | -1.8E-01 | -5.3E-02 |

| min | Qxy | Qph | klai | Tlai | LAId | As | ls | lb | Ar | lro | rr | br | wr | lr | rst | bst | wst | lst | Va |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ksr | 2.5E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 8.7E-01 | -9.7E-01 | -9.7E-01 | 0.0E+00 | 1.7E+01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksst | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstot | 4.3E-06 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 3.6E-05 | -5.3E-01 | -5.3E-01 | 0.0E+00 | 7.0E-04 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krs | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | -1.0E+00 | -1.0E+00 | -9.5E+00 | -1.0E+00 | -9.9E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krtot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.2E-01 | -9.9E-01 | -9.9E-01 | -7.3E+00 | -9.8E-01 | -8.5E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstl | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.7E-13 | -1.2E+01 | -5.0E+00 | -1.0E+00 | 0.0E+00 |
| ksttot | 4.5E-03 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -3.8E+00 | -4.6E+00 | -6.3E-01 | 0.0E+00 |
| kla | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.9E+00 | 1.0E+00 | 1.4E-10 | -9.0E-01 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.2E+01 | -5.0E+00 | -1.0E+00 | 0.0E+00 |
| klst | 1.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -2.1E-13 | -1.2E+01 | -5.0E+00 | -1.0E+00 | 0.0E+00 |
| kltot | 8.7E-04 | 8.7E-04 | 0.0E+00 | 1.7E-05 | 5.8E-06 | 0.0E+00 | -5.8E-01 | -1.1E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -4.7E+00 | -4.1E+00 | -7.4E-01 | 0.0E+00 |
| kal | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.9E+00 | 1.0E+00 | 1.4E-10 | -9.0E-01 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.0E+00 |
| katot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.2E-01 | 7.3E-02 | 5.7E-11 | -8.2E-01 | -8.4E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.0E+00 |
| kfdl | 0.0E+00 | 0.0E+00 | -8.7E-01 | 1.6E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kfdtot | 0.0E+00 | 0.0E+00 | -8.7E-01 | 3.3E-03 | 1.9E-03 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| Mst | 8.6E-02 | 4.2E-01 | -3.5E-01 | -2.0E+01 | -6.9E+00 | -5.9E+00 | -3.4E-02 | -9.7E-02 | -1.7E-04 | -1.8E-03 | -1.8E-03 | -1.5E-01 | -1.3E+00 | -3.3E-02 | -3.4E-12 | -1.1E+01 | -1.1E+01 | -1.1E+00 | -1.6E-01 |
| max | Qxy | Qph | klai | Tlai | LAId | As | ls | lb | Ar | lro | rr | br | wr | lr | rst | bst | wst | lst | Va |
| ksr | 1.3E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 9.7E-01 | -8.7E-01 | -8.7E-01 | 0.0E+00 | 1.9E+01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksst | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstot | 6.2E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 5.3E-01 | -3.6E-05 | -3.6E-05 | 0.0E+00 | 1.0E+01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krs | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | -1.0E+00 | -1.0E+00 | 1.8E-03 | -6.2E-03 | -2.1E-04 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krtot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | -2.2E-01 | -2.2E-01 | 1.7E-03 | -1.4E-03 | -2.1E-04 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstl | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 5.4E-13 | 2.7E-03 | -4.0E+00 | -2.0E-04 | 0.0E+00 |
| ksttot | 9.8E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 4.1E-13 | 2.5E-03 | -1.8E-02 | -1.9E-04 | 0.0E+00 |
| kla | 0.0E+00 | 0.0E+00 | 0.0E+00 | 3.0E+00 | 1.0E+00 | 9.1E-01 | -1.4E-10 | -7.6E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.5E-13 | 2.7E-03 | -4.0E+00 | -2.0E-04 | 0.0E+00 |
| klst | 1.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 4.5E-13 | 2.7E-03 | -4.0E+00 | -2.0E-04 | 0.0E+00 |
| kltot | 8.0E-01 | 8.0E-01 | 0.0E+00 | 2.1E+00 | 7.3E-01 | 5.8E-01 | 0.0E+00 | -5.8E-06 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 4.1E-13 | 1.9E-03 | -4.0E-02 | -1.4E-04 | 0.0E+00 |
| kal | 0.0E+00 | 0.0E+00 | 0.0E+00 | 3.0E+00 | 1.0E+00 | 9.1E-01 | -1.4E-10 | -7.6E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.0E+00 |
| katot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.9E+00 | 1.0E+00 | 8.3E-01 | -5.7E-11 | -2.6E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -7.3E-02 |
| kfdl | 0.0E+00 | 0.0E+00 | -6.6E-01 | 2.2E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kfdtot | 0.0E+00 | 0.0E+00 | -1.5E-03 | 2.2E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| Mst | 9.9E-01 | 1.0E+00 | 6.6E-01 | 1.2E+00 | 1.1E-01 | 3.4E-02 | 5.9E+00 | 5.5E-01 | 1.8E-03 | 1.7E-04 | 1.7E-04 | 2.7E-05 | -2.0E-07 | -2.9E-09 | 1.8E-12 | 1.5E+00 | 3.6E+00 | 4.1E-01 | 8.7E+00 |

| mediane | Dah2o | rsm | OC | spor | svolw | Vsb | Dwo2 | Pc | Gal | Kbw | Ds | TSCF | Kbm | Kba | k*0 | bfd | lfd | Gfdl | Kwxfd |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ksr | 9.7E-04 | -9.8E-01 | -9.8E-01 | -1.8E+00 | 2.9E+00 | -1.0E+00 | 9.0E-01 | 0.0E+00 | 0.0E+00 | -1.0E+00 | 9.3E-01 | -3.2E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksst | 0.0E+00 | -9.8E-01 | -9.8E-01 | -1.2E-09 | -1.4E-02 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstot | 1.8E-04 | -1.7E-01 | -1.7E-01 | -1.5E-01 | 3.5E-01 | -1.7E-01 | 1.2E-01 | 0.0E+00 | 0.0E+00 | -1.7E-01 | 1.5E-01 | 0.0E+00 | -1.6E-04 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krs | 1.0E-03 | 0.0E+00 | 0.0E+00 | -2.0E+00 | 3.3E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krtot | 9.9E-04 | 0.0E+00 | 0.0E+00 | -1.6E+00 | 2.8E+00 | 0.0E+00 | 8.8E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 9.5E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstl | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksttot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kla | 9.3E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 7.5E-02 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| klst | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kltot | 3.5E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 9.3E-03 | 4.9E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kal | 9.3E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 7.5E-02 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| katot | 6.3E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 4.3E-02 | 7.2E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kfdl | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | -4.6E+00 | 1.0E+00 | 1.0E+00 | 1.0E+00 |
| kfdtot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 9.1E-01 | -3.5E+00 | 9.1E-01 | 9.1E-01 | 9.1E-01 |
| Mst | 1.6E-02 | -5.4E-02 | -5.4E-02 | -1.3E-05 | -3.9E-04 | -5.5E-02 | 8.0E-06 | 6.9E-05 | 2.2E-02 | -5.5E-02 | 8.5E-06 | 5.6E-02 | 1.9E-05 | 0.0E+00 | 1.7E-02 | -4.7E-02 | 1.7E-02 | 1.7E-02 | 1.7E-02 |
| min | Dah2o | rsm | OC | spor | svolw | Vsb | Dwo2 | Pc | Gal | Kbw | Ds | TSCF | Kbm | Kba | k*0 | bfd | lfd | Gfdl | Kwxfd |
| ksr | 2.0E-08 | -1.0E+00 | -1.0E+00 | -1.9E+00 | 1.4E+00 | -1.0E+00 | 6.0E-01 | 0.0E+00 | 0.0E+00 | -1.0E+00 | 8.7E-01 | -9.1E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksst | 0.0E+00 | -1.0E+00 | -1.0E+00 | -2.5E-07 | -8.4E-02 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstot | 5.2E-10 | -5.8E-01 | -5.8E-01 | -1.0E+00 | 5.8E-05 | -5.9E-01 | 2.5E-05 | 0.0E+00 | 0.0E+00 | -5.9E-01 | 3.6E-05 | -1.2E-13 | -8.8E-04 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krs | 2.2E-08 | 0.0E+00 | 0.0E+00 | -2.0E+00 | 1.5E+00 | 0.0E+00 | 6.8E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krtot | 2.1E-08 | 0.0E+00 | 0.0E+00 | -2.0E+00 | 3.6E-01 | 0.0E+00 | 1.5E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.2E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstl | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksttot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kla | 4.3E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 4.1E-05 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| klst | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kltot | 5.8E-06 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.4E-10 | 5.8E-06 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kal | 4.3E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 4.1E-05 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| katot | 3.3E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.7E-05 | 7.3E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kfdl | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | -7.0E+00 | 1.0E+00 | 1.0E+00 | 1.0E+00 |
| kfdtot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.9E-03 | -7.0E+00 | 1.9E-03 | 1.9E-03 | 1.9E-03 |
| Mst | -6.4E+00 | -6.9E-01 | -6.9E-01 | -3.6E-03 | -4.4E-02 | -7.1E-01 | -1.2E-04 | -4.3E-01 | -6.9E+00 | -7.1E-01 | -1.7E-04 | 2.3E-04 | 5.3E-09 | 0.0E+00 | -4.6E-02 | -1.4E+00 | -4.6E-02 | -4.6E-02 | -4.6E-02 |

| max | Dah2o | rsm | OC | spor | svolw | Vsb | Dwo2 | Pc | Gal | Kbw | Ds | TSCF | Kbm | Kba | k*0 | bfd | lfd | Gfdl | Kwxfd |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ksr | 2.9E-01 | -9.2E-01 | -9.2E-01 | -1.9E-01 | 3.2E+00 | -1.0E+00 | 9.7E-01 | 0.0E+00 | 0.0E+00 | -1.0E+00 | 9.7E-01 | -2.1E-03 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksst | 0.0E+00 | -9.2E-01 | -9.2E-01 | 0.0E+00 | -3.1E-06 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstot | 7.8E-02 | -4.0E-05 | -2.0E-04 | -9.8E-06 | 1.7E+00 | -2.0E-04 | 5.3E-01 | 0.0E+00 | 0.0E+00 | -4.0E-05 | 5.3E-01 | 0.0E+00 | -7.2E-06 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krs | 3.2E-01 | 0.0E+00 | 0.0E+00 | -2.1E-01 | 3.3E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krtot | 2.8E-01 | 0.0E+00 | 0.0E+00 | -6.1E-02 | 3.3E+00 | 0.0E+00 | 9.9E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstl | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksttot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kla | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 5.7E-01 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| klst | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kltot | 6.4E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 2.4E-01 | 7.3E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kal | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 5.7E-01 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| katot | 8.9E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 4.0E-01 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kfdl | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | -1.8E+00 | 1.0E+00 | 1.0E+00 | 1.0E+00 |
| kfdtot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | -3.4E-03 | 1.0E+00 | 1.0E+00 | 1.0E+00 |
| Mst | 9.7E-02 | -2.2E-04 | -2.2E-04 | 2.3E-04 | -1.3E-08 | -2.2E-04 | 1.8E-03 | 1.9E-02 | 9.8E-02 | -2.2E-04 | 1.8E-03 | 7.4E-01 | 4.9E-04 | 0.0E+00 | 3.3E-01 | 2.0E-01 | 3.3E-01 | 3.3E-01 | 3.3E-01 |
| mediane | Krw | Kstts | Klw | Kla | Kwc | ksr | ksst | kstot | krs | krtot | kstl | ksttot | kla | klst | kltot | kal | katot | kfdl | kfdtot |
| ksr | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksst | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krs | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krtot | -9.5E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstl | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksttot | 0.0E+00 | -5.5E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kla | 0.0E+00 | 0.0E+00 | -1.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| klst | 0.0E+00 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kltot | 0.0E+00 | 0.0E+00 | -3.1E-01 | -4.9E-02 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kal | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| katot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 |
| kfdl | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 |
| kfdtot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 |
| Mst | -5.8E-04 | 6.5E-01 | -8.2E-01 | 3.8E-03 | 0.0E+00 | 1.0E-02 | 5.7E-02 | -8.2E-02 | 1.0E-02 | -1.0E-02 | 3.3E-01 | -2.3E+00 | 3.2E-02 | 1.1E+00 | -3.0E+00 | 2.1E-01 | -2.1E-01 | 7.3E-01 | -7.9E-01 |

| min | Krw | Kstts | Klw | Kla | Kwc | ksr | ksst | kstot | krs | krtot | kstl | ksttot | kla | klst | kltot | kal | katot | kfdl | kfdtot |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ksr | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksst | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krs | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krtot | -9.9E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstl | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksttot | 0.0E+00 | -9.8E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kla | 0.0E+00 | 0.0E+00 | -1.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| klst | 0.0E+00 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kltot | 0.0E+00 | 0.0E+00 | -9.1E-01 | -7.2E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kal | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| katot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 |
| kfdl | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 |
| kfdtot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 |
| Mst | -7.0E-02 | 1.1E-02 | -2.6E+00 | -1.8E+00 | 0.0E+00 | 3.8E-09 | 2.3E-04 | -6.9E+00 | 3.8E-09 | -3.1E+00 | 1.7E-05 | -1.8E+01 | 8.0E-06 | 9.4E-01 | -2.3E+01 | 3.8E-02 | -1.6E+01 | 1.7E-02 | -1.0E+00 |
| max | Krw | Kstts | Klw | Kla | Kwc | ksr | ksst | kstot | krs | krtot | kstl | ksttot | kla | klst | kltot | kal | katot | kfdl | kfdtot |
| ksr | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksst | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krs | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| krtot | -2.2E-01 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kstl | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| ksttot | 0.0E+00 | -4.5E-03 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kla | 0.0E+00 | 0.0E+00 | -1.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| klst | 0.0E+00 | 0.0E+00 | -1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kltot | 0.0E+00 | 0.0E+00 | -9.9E-03 | -5.8E-06 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| kal | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 |
| katot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 | 0.0E+00 |
| kfdl | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 | 0.0E+00 |
| kfdtot | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 0.0E+00 | 1.0E+00 |
| Mst | -2.9E-09 | 9.7E-01 | -1.7E-01 | 7.5E-01 | 0.0E+00 | 3.1E+00 | 9.5E-01 | -3.8E-04 | 3.1E+00 | -3.8E-09 | 1.6E+01 | -6.4E-01 | 8.2E+00 | 1.7E+01 | -9.2E-01 | 8.7E+00 | -3.9E-02 | 9.4E-01 | -4.0E-02 |

## *E.2 Sensitivity analysis: maximum relative output*

Sensitivity analysis of transfer rate as a function of main parameters of the model. Maximum relative difference in output due to a change in input (%). Results of the short list of substances used in wheat.

| max | Kaw | Kow | Koc | MW | MV | t0.5g | t0.5s | t0.5fd | t0.5sp | kpdeg | kfddeg | ksdeg | kadeg | td | Tg | Vstd | Vld | Vrd | Vfdd |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ksr | 146 | 109 | 2675060 | 192 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 191 | 125 | 100 | 100 | 119 | 100 |
| ksst | 100 | 450 | 2675060 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 191 | 125 | 100 | 100 | 100 | 100 |
| kstot | 125 | 100 | 658 | 121 | 100 | 100 | 11334 | 100 | 100 | 100 | 100 | 11334 | 100 | 143 | 114 | 100 | 100 | 109 | 100 |
| krs | 147 | 16069 | 100 | 203 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| krtot | 147 | 5478 | 100 | 174 | 100 | 100 | 100 | 100 | 2239 | 2239 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| kstl | 100 | 360141 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 120 | 100 | 100 | 100 |
| ksttot | 100 | 13194 | 100 | 100 | 100 | 100 | 100 | 100 | 13793 | 13793 | 100 | 100 | 100 | 100 | 100 | 115 | 100 | 100 | 100 |
| kla | 166601509 | 59740 | 100 | 181 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 131 | 122 | 100 | 120 | 100 | 100 |
| klst | 100 | 360141 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 120 | 100 | 100 |
| kltot | 1317 | 15836 | 100 | 140 | 100 | 100 | 100 | 100 | 8763 | 8763 | 100 | 100 | 100 | 123 | 116 | 100 | 116 | 100 | 100 |
| kal | 1324 | 968 | 100 | 181 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 251 | 100 | 100 | 100 | 100 | 100 |
| katot | 1216 | 891 | 100 | 166 | 100 | 7914 | 100 | 100 | 100 | 100 | 100 | 100 | 7914 | 251 | 100 | 100 | 100 | 100 | 100 |
| kfdl | 100 | 4265795188 | 100 | 100 | 18866 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 251 | 100 | 100 | 100 | 100 | 235 |
| kfdtot | 100 | 7991191 | 100 | 100 | 18812 | 100 | 100 | 300 | 100 | 100 | 300 | 100 | 100 | 249 | 100 | 100 | 100 | 100 | 233 |
| Mst | 8.7E+03 | 3.5E+02 | 4.7E+02 | 7.3E+02 | 1.5E+02 | 5.8E+03 | 3.6E+07 | 3.5E+02 | 2.6E+08 | 2.6E+08 | 3.5E+02 | 3.6E+07 | 5.8E+03 | 5.8E+04 | 1.4E+02 | 1.1E+02 | 1.2E+02 | 1.0E+02 | 1.2E+02 |

| max | Qxy | Qph | klai | Tlai | LAId | As | ls | lb | Ar | lro | rr | br | wr | lr | rst | bst | wst | lst | Va |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ksr | 101 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 119 | 149 | 110 | 100 | 45 | 100 | 100 | 100 | 100 | 100 | 100 |
| ksst | 106 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| kstot | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 109 | 126 | 105 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| krs | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 120 | 150 | 110 | 238 | 110 | 110 | 100 | 100 | 100 | 100 | 100 |
| krtot | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 119 | 150 | 110 | 200 | 110 | 108 | 100 | 100 | 100 | 100 | 100 |
| kstl | 106 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 294 | 150 | 110 | 100 |
| ksttot | 105 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 149 | 146 | 106 | 100 |
| kla | 100 | 100 | 100 | 135 | 119 | 109 | 144 | 150 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 294 | 150 | 110 | 100 |
| klst | 106 | 106 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 294 | 150 | 110 | 100 |
| kltot | 104 | 104 | 100 | 125 | 111 | 106 | 128 | 104 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 173 | 140 | 107 | 100 |
| kal | 100 | 100 | 100 | 135 | 119 | 109 | 144 | 150 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 150 |
| katot | 100 | 100 | 100 | 134 | 117 | 108 | 140 | 142 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 150 |
| kfdl | 100 | 100 | 109 | 124 | 119 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| kfdtot | 100 | 100 | 109 | 124 | 119 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Mst | 1.1E+02 | 1.1E+02 | 1.1E+02 | 5.2E+02 | 1.6E+02 | 1.7E+02 | 8.4E+02 | 1.3E+02 | 1.0E+02 | 1.0E+02 | 1.0E+02 | 1.0E+02 | 1.2E+02 | 1.0E+02 | 1.0E+02 | 2.5E+02 | 2.4E+02 | 1.1E+02 | 1.8E+03 |

| max | Dah2o | rsm | OC | spor | svolw | Vsb | Dwo2 | Pc | Gal | Kbw | Ds | TSCF | Kbm | Kba | k*0 | bfd | lfd | Gfdl | Kwxfd |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ksr | 157 | 150 | 150 | 120 | 136 | 150 | 295 | 100 | 100 | 2675064 | 177 | 109 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| ksst | 100 | 150 | 150 | 100 | 101 | 150 | 100 | 100 | 100 | 2675064 | 100 | 3910 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| kstot | 116 | 129 | 129 | 111 | 119 | 130 | 205 | 100 | 100 | 658 | 121 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| krs | 164 | 100 | 100 | 121 | 137 | 100 | 300 | 100 | 100 | 100 | 181 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| krtot | 155 | 100 | 100 | 121 | 137 | 100 | 299 | 100 | 100 | 100 | 174 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| kstl | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| ksttot | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| kla | 300 | 100 | 100 | 100 | 100 | 100 | 100 | 968 | 2275 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| klst | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| kltot | 228 | 100 | 100 | 100 | 100 | 100 | 100 | 580 | 1304 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| kal | 300 | 100 | 100 | 100 | 100 | 100 | 100 | 968 | 2275 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| katot | 279 | 100 | 100 | 100 | 100 | 100 | 100 | 891 | 2083 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| kfdl | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 300 | 190 | 150 | 18866 | 4265795188 |
| kfdtot | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 300 | 190 | 150 | 18812 | 7991191 |
| Mst | 1.1E+04 | 1.3E+02 | 1.3E+02 | 1.0E+02 | 1.0E+02 | 1.3E+02 | 1.0E+02 | 1.8E+02 | 4.6E+02 | 4.7E+02 | 1.0E+02 | 6.2E+02 | 1.0E+02 | 1.0E+02 | 1.3E+02 | 1.1E+02 | 1.1E+02 | 1.5E+02 | 4.1E+02 |

| max | Krw | Kstts | Klw | Kla | Kwc | ksr | ksst | kstot | krs | krtot | kstl | ksttot | kla | klst | kltot | kal | katot | kfdl | kfdtot |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ksr | 100 | 100 | 100 | 100 | 100 | 2348832 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| ksst | 100 | 100 | 100 | 100 | 100 | 100 | 89492091 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| kstot | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 11604 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| krs | 16069 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 22492 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| krtot | 5478 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 6794 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| kstl | 100 | 360141 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 386917 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| ksttot | 100 | 13194 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 20099 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| kla | 100 | 100 | 360141 | 597649009 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 47419683 | 100 | 100 | 100 | 100 | 100 | 100 |
| klst | 100 | 100 | 360141 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 386917 | 100 | 100 | 100 | 100 | 100 |
| kltot | 100 | 100 | 49868 | 31630 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 11228 | 100 | 100 | 100 | 100 |
| kal | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 2441 | 100 | 100 | 100 |
| katot | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 8441 | 100 | 100 |
| kfdl | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 41016670 | 100 |
| kfdtot | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 76936 |
| Mst | 1.0E+02 | 1.1E+03 | 3.6E+03 | 4.9E+02 | 1.0E+02 | 2.5E+02 | 2.0E+04 | 1.7E+08 | 1.2E+04 | 2.9E+12 | 3.8E+06 | 2.2E+21 | 7.4E+15 | 1.8E+07 | 3.3E+18 | 1.8E+41 | 6.0E+04 | 7.7E+05 | 5.5E+04 |

# F. Uncertainty analysis

Sensitivity analysis und uncertainty analysis of transfer rate as a function of main parameters of the model, for a set of substances used in wheat. Sensitivity for a change in input by 0.1%. Two levels of uncertainty: total confidence factor CF, partial confidence factor CF* excluding uncertainty due to half-life inputs.

| Parameters | CF | Diflufenican | | | Ioxynil | | | Isoproturon | | | Chlormequat | | | Ethephon | | | Trinexapac-ethyl | | | Cyproconazole | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* |
| CF Total | | | 9 | 6 | | 35 | 5 | | 87 | 3 | | 170 | 4 | | 8097 | 3 | | 70771 | 11649 | | 31 | 3 |
| Kaw | 2.5 | -0.1 | | | 1.1 | 1.1 | 1.1 | | | | | | | | | | 2.2 | 4.2 | 4.2 | | | |
| Kow | 2.5 | -0.7 | 0.4 | 0.4 | 0.1 | | | 0.1 | | | | | | | | | -1.4 | 1.6 | 1.6 | 0.1 | | |
| Koc | 2.5 | -0.1 | | | -0.1 | | | -0.5 | 0.3 | 0.3 | -0.7 | 0.4 | 0.4 | -0.1 | | | | | | -0.1 | | |
| MW | 1 | | | | 0.1 | | | | | | | | | | | | 3.2 | | | | | |
| MV | 1.1 | | | | -0.7 | | | | | | | | | | | | 0.2 | | | -0.3 | | |
| t0.5g | 3 | 0.2 | | | 1.0 | 1.1 | | | | | 0.1 | | | 0.1 | | | 4.1 | 19.8 | | 0.1 | | |
| t0.5s | 3 | | | | 0.1 | | | 3.5 | 14.7 | | 2.8 | 9.2 | | 0.5 | 0.3 | | | | | 0.2 | | |
| t0.5fd | 3 | | | | 0.3 | 0.1 | | | | | | | | 0.1 | | | 0.4 | 0.2 | | 0.1 | | |
| t0.5p | 3 | 1.1 | 1.4 | | 2.7 | 8.5 | | 1.9 | 4.2 | | 3.5 | 15.1 | | 8.1 | 79.2 | | 3.8 | 17.0 | | 3.0 | 11.0 | |
| klai | 1.1 | 0.6 | | | 0.2 | | | -0.2 | | | -0.3 | | | -0.1 | | | 0.3 | | | 0.4 | | |
| fspe | 1.1 | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | |
| fsps | 1.1 | -2.3 | | | -0.7 | | | 0.8 | | | 0.7 | | | 0.1 | | | -0.7 | | | -0.5 | | |
| fspa | 1.1 | 0.2 | | | 0.5 | | | -0.1 | | | 0.2 | | | 0.8 | | | 0.6 | | | | | |
| fsppl | 1.1 | 0.7 | | | 0.2 | | | | | | | | | | | | 0.4 | | | 0.7 | | |
| Mspray | 1 | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | |
| td | 1.1 | | | | -5.5 | 0.3 | 0.3 | -4.1 | 0.2 | 0.2 | -4.8 | 0.2 | 0.2 | -8.2 | 0.6 | 0.6 | -25.9 | 6.1 | 6.1 | -3.0 | 0.1 | 0.1 |
| Mpd | 1.1 | 0.9 | | | 0.1 | | | 0.4 | | | 0.6 | | | 0.1 | | | 0.5 | | | 0.1 | | |
| Tg | 1.1 | 0.4 | | | -2.4 | 0.1 | 0.1 | 1.4 | | | 1.6 | | | 0.3 | | | -3.9 | 0.1 | 0.1 | 0.4 | | |
| flpl | 1.1 | -0.8 | | | -1.8 | | | -0.4 | | | -0.7 | | | -0.8 | | | -2.6 | 0.1 | 0.1 | -0.7 | | |
| fstpl | 1.1 | 0.1 | | | 0.6 | | | 0.7 | | | 0.8 | | | 0.8 | | | 0.3 | | | 0.8 | | |
| ffpl | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| frpl | 1.1 | | | | | | | -0.1 | | | | | | | | | | | | | | |
| Vstd | 1.1 | 0.1 | | | 0.6 | | | 0.7 | | | 0.8 | | | 0.8 | | | 0.3 | | | 0.8 | | |
| Vld | 1.1 | -0.8 | | | -1.8 | | | -0.4 | | | -0.7 | | | -0.8 | | | -2.6 | 0.1 | 0.1 | -0.7 | | |
| Vrd | 1.1 | | | | | | | -0.1 | | | | | | | | | | | | | | |
| Vfdd | 1.5 | | | | -0.2 | | | | | | | | | | | | | | | -0.1 | | |

| Parameters | CF | Diflufenican | | | Ioxynil | | | Isoproturon | | | Chlormequat | | | Ethephon | | | Trinexapac-ethyl | | | Cyproconazole | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* |
| CF Total | | | 9 | 6 | | 35 | 5 | | 87 | 3 | | 170 | 4 | | 8097 | 3 | | 70771 | 11649 | | 31 | 3 |
| Qxy | 3 | 0.9 | 1.0 | 1.0 | 0.1 | | | 0.4 | 0.2 | 0.2 | 0.6 | 0.5 | 0.5 | 0.1 | | | 0.5 | 0.4 | 0.4 | 0.1 | | |
| Qph | 3 | 0.9 | 1.0 | 1.0 | 0.7 | 0.5 | 0.5 | 0.4 | 0.2 | 0.2 | 0.7 | 0.6 | 0.6 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.7 | 0.7 |
| Tlai | 1.1 | 0.7 | | | 0.1 | | | -0.2 | | | -0.2 | | | 0.2 | | | -19.8 | 3.6 | 3.6 | 1.0 | | |
| LAId | 1.1 | | | | | | | | | | 0.1 | | | 0.1 | | | -6.9 | 0.4 | 0.4 | 0.1 | | |
| As | 1.1 | | | | -0.2 | | | | | | | | | | | | -5.9 | 0.3 | 0.3 | | | |
| ls | 1.5 | | | | 0.2 | | | | | | | | | | | | 5.9 | 5.8 | 5.8 | | | |
| lb | 1.5 | | | | | | | | | | -0.1 | | | -0.1 | | | 0.5 | | | | | |
| Ar | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| lro | 1.5 | | | | | | | | | | | | | | | | | | | | | |
| rr | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| rw | 1.1 | 0.8 | | | 1.2 | | | 0.3 | | | 0.6 | | | 0.1 | | | 2.3 | 0.1 | 0.1 | | | |
| br | 1.1 | | | | | | | -0.1 | | | | | | | | | | | | | | |
| wr | 1.1 | | | | | | | -1.3 | | | -0.3 | | | | | | | | | | | |
| lr | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| rst | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| bst | 1.1 | -7.8 | 0.6 | 0.6 | -0.3 | | | 1.5 | | | | | | | | | -3.7 | 0.1 | 0.1 | 0.5 | | |
| wst | 1.1 | -2.9 | 0.1 | 0.1 | -5.8 | 0.3 | 0.3 | 1.4 | | | 0.5 | | | 0.1 | | | -10.6 | 1.0 | 1.0 | 0.3 | | |
| lst | 1.1 | -0.7 | | | -0.2 | | | 0.3 | | | | | | | | | -1.1 | | | 0.1 | | |
| Va | 1.5 | -0.2 | | | 1.4 | 0.3 | 0.3 | | | | -0.1 | | | -0.1 | | | 8.7 | 12.5 | 12.5 | -0.1 | | |
| Dah2o | 3 | | | | -0.2 | 0.1 | 0.1 | | | | 0.1 | | | 0.1 | | | -6.4 | 50.2 | 50.2 | | | |
| rsm | 1.5 | -0.1 | | | -0.1 | | | -0.5 | | | -0.7 | 0.1 | 0.1 | -0.1 | | | | | | -0.1 | | |
| OC | 1.5 | -0.1 | | | -0.1 | | | -0.5 | | | -0.7 | 0.1 | 0.1 | -0.1 | | | | | | -0.1 | | |
| spor | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| svolw | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| Vsb | 1.5 | -0.1 | | | -0.1 | | | -0.6 | 0.1 | 0.1 | -0.7 | 0.1 | 0.1 | -0.1 | | | | | | -0.1 | | |
| Dwo2 | 3 | | | | | | | | | | | | | | | | | | | | | |
| Pc | 3 | | | | | | | | | | | | | | | | -0.4 | 0.2 | 0.2 | | | |
| k*0 | 3 | | | | 0.2 | 0.1 | 0.1 | | | | | | | | | | | | | 0.1 | | |
| bfd | 1.1 | | | | -0.7 | | | | | | | | | | | | 0.2 | | | -0.3 | | |
| lfd | 1.5 | | | | 0.2 | | | | | | | | | | | | | | | 0.1 | | |

| Parameters | CF | Deltamethrine | | | Pirimicarb | | | Teflubenzuron | | | Azoxystrobin | | | Chlorothalonil | | | Prochloraz | | | Tebuconazole | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* |
| CF Total | | | 341 | 8 | | 6 | 4 | | 46 | 7 | | 142 | 3 | | 7 | 3 | | 110 | 5 | | 7 | 3 |
| Kaw | 2.5 | -0.1 | | | -0.4 | 0.1 | 0.1 | | | | | | | | | | -0.1 | | | | | |
| Kow | 2.5 | -0.9 | 0.6 | 0.6 | 0.5 | 0.2 | 0.2 | -0.9 | 0.6 | 0.6 | 0.1 | | | -0.2 | | | -0.7 | 0.4 | 0.4 | -0.4 | 0.1 | 0.1 |
| Koc | 2.5 | | | | -0.2 | | | | | | -0.5 | 0.2 | 0.2 | | | | | | | -0.1 | | |
| MW | 1 | | | | 0.2 | | | | | | | | | | | | | | | | | |
| MV | 1.1 | | | | -1.4 | | | | | | -0.3 | | | -0.1 | | | -0.1 | | | -0.1 | | |
| t0.5g | 3 | 0.1 | | | 0.1 | | | | | | | | | | | | 0.1 | | | 0.1 | | |
| t0.5s | 3 | | | | 0.1 | | | | | | 2.1 | 5.4 | | | | | | | | | | |
| t0.5fd | 3 | | | | 0.4 | 0.2 | | | | | 0.7 | 0.5 | | | | | | | | | | |
| t0.5p | 3 | 5.0 | 29.6 | | 0.7 | 0.6 | | 3.0 | 11.0 | | 3.8 | 17.5 | | 1.5 | 2.7 | | 4.0 | 19.3 | | 1.5 | 2.7 | |
| klai | 1.1 | 0.7 | | | 0.2 | | | 0.6 | | | -0.2 | | | 0.5 | | | 0.6 | | | 0.6 | | |
| fspe | 1.1 | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | |
| fsps | 1.1 | -1.0 | | | -0.3 | | | -0.9 | | | 0.3 | | | -0.6 | | | -0.7 | | | -1.2 | | |
| fspa | 1.1 | | | | | | | 0.1 | | | -0.1 | | | 0.1 | | | -0.1 | | | 0.1 | | |
| fsppl | 1.1 | 0.9 | | | 0.5 | | | 0.8 | | | 0.4 | | | 0.8 | | | 0.9 | | | 0.8 | | |
| Mspray | 1 | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | | 1.0 | | |
| td | 1.1 | -4.0 | 0.1 | 0.1 | -1.1 | | | -2.1 | | | -5.8 | 0.3 | 0.3 | -1.3 | | | -3.3 | 0.1 | 0.1 | -1.0 | | |
| Mpd | 1.1 | 1.0 | | | 0.1 | | | 0.9 | | | 0.3 | | | 0.2 | | | 0.8 | | | 0.4 | | |
| Tg | 1.1 | 0.2 | | | 2.0 | | | | | | 1.2 | | | | | | 0.3 | | | 0.1 | | |
| flpl | 1.1 | -0.9 | | | -0.2 | | | -1.0 | | | -0.5 | | | -0.9 | | | -0.8 | | | -0.8 | | |
| fstpl | 1.1 | | | | 1.0 | | | 0.1 | | | 0.7 | | | 0.7 | | | 0.2 | | | 0.5 | | |
| ffpl | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| frpl | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| Vstd | 1.1 | | | | 1.0 | | | 0.1 | | | 0.7 | | | 0.7 | | | 0.2 | | | 0.5 | | |
| Vld | 1.1 | -0.9 | | | -0.2 | | | -1.0 | | | -0.5 | | | -0.9 | | | -0.8 | | | -0.8 | | |
| Vrd | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| Vfdd | 1.5 | | | | -0.3 | | | | | | | | | | | | | | | | | |
| Qxy | 3 | 1.0 | 1.2 | 1.2 | 0.1 | | | 0.9 | 1.0 | 1.0 | 0.3 | 0.1 | 0.1 | 0.2 | | | 0.8 | 0.8 | 0.8 | 0.4 | 0.2 | 0.2 |
| Qph | 3 | 1.0 | 1.2 | 1.2 | 0.9 | 1.0 | 1.0 | 1.0 | 1.2 | 1.2 | 0.5 | 0.3 | 0.3 | 0.9 | 0.9 | 0.9 | 0.9 | 1.1 | 1.1 | 0.9 | 0.9 | 0.9 |
| Tlai | 1.1 | 1.2 | | | -0.6 | | | 1.2 | | | -0.3 | | | 1.2 | | | 1.1 | | | 1.0 | | |
| LAId | 1.1 | | | | -0.3 | | | | | | 0.1 | | | 0.1 | | | | | | 0.1 | | |
| As | 1.1 | | | | -0.1 | | | | | | | | | | | | | | | | | |

| Parameters | CF | Deltamethrine | | | Pirimicarb | | | Teflubenzuron | | | Azoxystrobin | | | Chlorothalonil | | | Prochloraz | | | Tebuconazole | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* | S | Cf | Cf* |
| CF Total | | | 341 | 8 | | 6 | 4 | | 46 | 7 | | 142 | 3 | | 7 | 3 | | 110 | 5 | | 7 | 3 |
| ls | 1.5 | | | | 0.1 | | | | | | | | | | | | | | | | | |
| lb | 1.5 | | | | 0.2 | | | | | | | | | | | | | | | | | |
| Ar | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| lro | 1.5 | | | | | | | | | | | | | | | | | | | | | |
| rr | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| rw | 1.1 | 0.9 | | | -0.6 | | | 0.9 | | | 0.3 | | | 0.2 | | | 0.7 | | | 0.4 | | |
| br | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| wr | 1.1 | | | | | | | | | | -0.3 | | | | | | | | | | | |
| lr | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| rst | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| bst | 1.1 | -10.7 | 1.0 | 1.0 | 1.5 | | | -9.0 | 0.7 | 0.7 | 1.1 | | | -1.2 | | | -6.0 | 0.3 | 0.3 | -2.8 | 0.1 | 0.1 |
| wst | 1.1 | -3.6 | 0.1 | 0.1 | 3.6 | 0.1 | 0.1 | -3.6 | 0.1 | 0.1 | 1.0 | | | -0.8 | | | -2.7 | 0.1 | 0.1 | -1.4 | | |
| lst | 1.1 | -0.9 | | | 0.4 | | | -0.9 | | | 0.2 | | | -0.2 | | | -0.7 | | | -0.4 | | |
| Va | 1.5 | -0.1 | | | -0.1 | | | | | | | | | | | | -0.1 | | | -0.1 | | |
| Dah2o | 3 | | | | -0.3 | 0.1 | 0.1 | | | | | | | | | | | | | | | |
| rsm | 1.5 | | | | -0.2 | | | | | | -0.5 | | | | | | | | | -0.1 | | |
| OC | 1.5 | | | | -0.2 | | | | | | -0.5 | | | | | | | | | -0.1 | | |
| spor | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| svolw | 1.1 | | | | | | | | | | | | | | | | | | | | | |
| Vsb | 1.5 | | | | -0.2 | | | | | | -0.5 | | | | | | | | | -0.1 | | |
| Dwo2 | 3 | | | | | | | | | | | | | | | | | | | | | |
| Pc | 3 | | | | -0.4 | 0.2 | 0.2 | | | | | | | | | | | | | | | |
| k*0 | 3 | | | | 0.3 | 0.1 | 0.1 | | | | | | | | | | | | | | | |
| bfd | 1.1 | | | | -1.4 | | | | | | -0.3 | | | -0.1 | | | -0.1 | | | -0.1 | | |
| lfd | 1.5 | | | | 0.3 | | | | | | | | | | | | | | | | | |

# G. Harvest fraction and human toxicity

## *G.1 Substances properties*

Physico-chemical and toxicological properties of substances used in field crops: CAS, partition coefficients $K_{aw}$, $K_{ow}$ and $K_{oc}$, molecular weight (MW), and molecular volume (MV, computed values), half-life in air ($t_{1/2}$ air, based on the degradation by OH radicals and deposition), half-life in soil, effect factors for cancer and non cancer (EF). Syntheses of data collected from different database (Agritox, SRC, Tomlin, Impact2002).

| Substances | CAS | log $K_{aw}$ | Log $K_{ow}$ | Log $K_{oc}$ | MW g/mol | MV mL/mol | $t_{1/2}$ air hours | $t_{1/2}$ soil hours | $EF_{non\ cancer}$ y/mg | $EF_{cancer}$ y/mg |
|---|---|---|---|---|---|---|---|---|---|---|
| 2,4-D | 94-75-7 | -8.3E+00 | 8.3E-01 | 1.3E+00 | 2.2E+02 | 1.4E+02 | 5.9E+01 | 2.2E+02 | 1.4E-07 | 2.5E-07 |
| Acibenzolar-S-methyl | 135158-54-2 | -5.3E+00 | 3.1E+00 | 3.1E+00 | 2.1E+02 | 1.5E+02 | 4.9E+01 | 3.4E+02 | n.a. | n.a. |
| Aclonifen | 74070-46-5 | -5.9E+00 | 4.4E+00 | 3.9E+00 | 2.6E+02 | 1.8E+02 | 3.3E+01 | 2.9E+03 | n.a. | n.a. |
| Alachlor | 15972-60-8 | -6.1E+00 | 4.5E-01 | 2.1E+00 | 2.7E+02 | 2.1E+02 | 2.Y1E+00 | 3.4E+02 | 3.7E-08 | 3.7E-07 |
| Aldicarb | 116-06-3 | -7.3E+00 | 1.4E+00 | 1.4E+00 | 1.9E+02 | 1.4E+02 | 4.2E+01 | 1.2E+03 | 2.4E-06 | 2.4E-05 |
| Amidosulfuron | 120923-37-7 | -6.5E+00 | 1.6E+00 | 0.0E+00 | 3.7E+02 | 2.4E+02 | 1.9E+00 | 2.2E+02 | 9.5E-11 | n.a. |
| Amitrole | 61-82-5 | -1.1E+01 | -8.6E-01 | 2.0E+00 | 8.4E+01 | 6.0E+01 | 7.3E+01 | 9.4E+02 | n.a. | 9.4E-07 |
| Asulam | 3337-71-1 | -1.0E+01 | -5.2E-01 | 2.1E+00 | 2.3E+02 | 1.6E+02 | 1.5E+01 | 2.6E+02 | 1.5E-08 | n.a. |
| Atrazin | 1912-24-9 | -7.0E+00 | 2.3E+00 | 1.9E+00 | 2.2E+02 | 1.6E+02 | 1.5E+01 | 1.6E+03 | 4.1E-08 | 3.0E-07 |
| Azoxystrobin | 131860-33-8 | -1.2E+01 | 2.5E+00 | 2.5E+00 | 4.0E+02 | 3.0E+02 | 6.6E+01 | 2.5E+02 | n.a. | n.a. |
| Benalaxyl | 71626-11-4 | -5.6E+00 | 3.4E+00 | 3.4E+00 | 3.3E+02 | 2.7E+02 | 1.4E+01 | 3.8E+03 | n.a. | n.a. |
| Benazolin | 3813-05-6 | -1.1E+01 | 1.3E+00 | 1.2E+00 | 2.4E+02 | 1.6E+02 | 9.4E+01 | 5.0E+02 | n.a. | n.a. |
| benoxacor | 98730-04-2 | -5.5E+00 | 2.7E+00 | 2.6E+00 | 2.6E+02 | 1.8E+02 | 8.4E+00 | 8.4E+02 | n.a. | n.a. |
| Bensultap | 17606-31-4 | -4.3E+00 | 3.4E+00 | 3.1E+00 | 4.3E+02 | 3.1E+02 | 1.1E+00 | 7.2E+01 | n.a. | n.a. |
| Bentazone | 25057-89-0 | -7.5E+00 | -4.6E-01 | 1.6E+00 | 2.4E+02 | 1.7E+02 | 6.2E+00 | 3.0E+02 | 1.2E-08 | 1.2E-07 |
| Bifenox | 42576-02-3 | -3.9E+00 | 4.5E+00 | 3.8E+00 | 3.4E+02 | 2.2E+02 | 3.6E+02 | 2.5E+02 | 9.4E-10 | 9.4E-09 |
| Bifenthrin | 82657-04-3 | -4.4E+00 | 6.0E+00 | 3.7E+00 | 4.2E+02 | 3.1E+02 | 1.5E+01 | 8.3E+02 | 2.5E-08 | 2.5E-07 |
| Bromacil | 314-40-9 | -8.3E+00 | 1.9E+00 | 1.8E+00 | 2.6E+02 | 1.6E+02 | 2.2E+01 | 3.5E+03 | 3.7E-08 | 3.7E-07 |
| Bromoxynil | 1689-84-5 | -8.3E+00 | 2.9E+00 | 2.2E+00 | 2.8E+02 | 1.3E+02 | 3.6E+02 | 6.8E+01 | 2.8E-08 | n.a. |
| Bromphenoxim | 13181-17-4 | -1.2E+01 | 3.2E+00 | 0.0E+00 | 4.6E+02 | 2.4E+02 | 1.2E+02 | 3.8E+01 | n.a. | n.a. |
| Carbendazime (L) | 10605-21-7 | -9.2E+00 | 1.6E+00 | 2.4E+00 | 1.9E+02 | 1.4E+02 | 2.4E+00 | 2.2E+03 | 8.3E-09 | 8.3E-08 |
| Carbendazime (S) | 10605-21-7 | -9.2E+00 | 1.6E+00 | 2.4E+00 | 1.9E+02 | 1.4E+02 | 2.4E+00 | 2.2E+03 | n.a. | n.a. |
| Carbetamide | 16118-49-3 | -8.4E+00 | -1.6E+00 | 1.9E+00 | 2.4E+02 | 1.9E+02 | 6.5E+00 | 5.6E+02 | n.a. | n.a. |
| Carbofuran | 1563-66-2 | -8.0E+00 | 1.5E+00 | 1.6E+00 | 2.2E+02 | 1.8E+02 | 1.5E+01 | 1.3E+03 | 7.5E-08 | 4.7E-07 |
| Carfentrazone-ethyl | 128639-02-1 | -7.0E+00 | 3.4E+00 | 1.2E+00 | 4.1E+02 | 2.3E+02 | 8.1E+01 | 3.6E+02 | n.a. | n.a. |

| Substances | CAS | log $K_{aw}$ | Log $K_{ow}$ | Log $K_{oc}$ | MW g/mol | MV mL/mol | $t_{1/2}$ air hours | $t_{1/2}$ soil hours | $EF_{non\ cancer}$ y/mg | $EF_{cancer}$ y/mg |
|---|---|---|---|---|---|---|---|---|---|---|
| Chloridazone | 1698-60-8 | -2.8E+00 | 2.2E+00 | 2.1E+00 | 2.2E+02 | 1.6E+02 | 9.6E+00 | 4.2E+02 | n.a. | n.a. |
| Chlormequat | 999-81-5 | -1.2E+01 | -1.6E+00 | 2.3E+00 | 1.2E+02 | 1.1E+02 | 5.8E+01 | 3.5E+02 | n.a. | n.a. |
| Chlorothalonil | 1897-45-6 | -5.1E+00 | 2.9E+00 | 3.1E+00 | 2.7E+02 | 1.5E+02 | 1.4E+04 | 8.5E+02 | 1.9E-08 | 3.7E-08 |
| Chlorpropham | 101-21-3 | -6.0E+00 | 3.5E+00 | 2.5E+00 | 2.3E+02 | 1.6E+02 | 8.6E+00 | 9.6E+02 | 2.8E-09 | n.a. |
| Chlorpyrifos | 2921-88-2 | -3.2E+00 | 4.7E+00 | 3.8E+00 | 3.5E+02 | 2.2E+02 | 4.2E+00 | 1.6E+03 | 7.9E-07 | 3.7E-06 |
| Chlorpyrifos-ethyl | 5598-13-0 | -3.8E+00 | 4.2E+00 | 3.5E+00 | 3.2E+02 | 2.2E+02 | 6.6E+00 | 7.0E+02 | n.a. | n.a. |
| Chlortoluron | 15545-48-9 | -7.7E+00 | 2.5E+00 | 2.3E+00 | 2.1E+02 | 1.6E+02 | 1.1E+01 | 7.9E+02 | 7.5E-10 | n.a. |
| cinidon-ethyl | 142891-20-1 | -4.6E+00 | 4.5E+00 | 3.3E+00 | 3.9E+02 | 2.8E+02 | 2.5E+00 | 5.8E+01 | n.a. | n.a. |
| Clodinafop-propargyl | 105512-06-9 | -6.9E+00 | 3.8E+00 | 2.8E+00 | 3.5E+02 | 2.4E+02 | 1.7E+01 | 2.4E+02 | n.a. | n.a. |
| Clomazone | 81777-89-1 | -5.8E+00 | 2.5E+00 | 2.4E+00 | 2.4E+02 | 1.8E+02 | 1.8E+01 | 7.2E+02 | n.a. | n.a. |
| Clopyralid | 1702-17-6 | -7.9E+00 | -2.6E+00 | 8.2E-01 | 1.9E+02 | 1.1E+02 | 6.0E+03 | 3.0E+02 | n.a. | n.a. |
| Cloquintocet | 99607-70-2 | -5.9E+00 | 5.2E+00 | 4.1E+00 | 3.4E+02 | 2.6E+02 | 1.6E+01 | 5.8E+01 | 2.7E-09 | n.a. |
| Cyanazin | 21725-46-2 | -9.9E+00 | 2.2E+00 | 2.4E+00 | 2.4E+02 | 1.8E+02 | 6.8E+01 | 3.2E+02 | n.a. | n.a. |
| cyhalothrin | 68085-85-8 | -4.2E+00 | 7.0E+00 | 5.3E+00 | 4.5E+02 | 3.2E+02 | 1.7E+01 | 1.0E+03 | 2.8E-07 | 2.8E-06 |
| Cymoxanil | 57966-95-7 | -8.5E+00 | 5.9E-01 | 1.9E+00 | 2.0E+02 | 1.4E+02 | 6.5E+01 | 1.8E+02 | n.a. | n.a. |
| Cypermethrin | 52315-07-8 | -4.8E+00 | 6.6E+00 | 4.8E+00 | 4.2E+02 | 3.1E+02 | 1.5E+01 | 6.5E+02 | 3.7E-08 | 2.5E-07 |
| Cyproconazole | 113096-99-4 | -7.6E+00 | 2.9E+00 | 2.5E+00 | 2.9E+02 | 2.3E+02 | 2.9E+01 | 6.4E+02 | n.a. | n.a. |
| Cyprodinil | 121552-61-2 | -5.5E+00 | 3.9E+00 | 3.4E+00 | 2.3E+02 | 1.9E+02 | 2.0E+00 | 3.1E+02 | n.a. | n.a. |
| Deltamethrine | 52918-63-5 | -4.9E+00 | 5.4E+00 | 6.4E+00 | 5.1E+02 | 3.2E+02 | 1.1E+01 | 5.0E+02 | 2.3E-08 | 2.3E-07 |
| Desmedipham | 13684-56-5 | -8.3E+00 | 3.4E+00 | 2.2E+00 | 3.0E+02 | 2.3E+02 | 7.3E+00 | 5.5E+02 | n.a. | n.a. |
| Diazinon | 333-41-5 | -5.3E+00 | 3.3E+00 | 2.9E+00 | 3.0E+02 | 2.3E+02 | 4.0E+00 | 3.4E+02 | 9.4E-07 | 9.4E-06 |
| Dicamba | 1918-00-9 | -1.3E+01 | 5.5E-01 | 8.4E-01 | 2.2E+02 | 1.4E+02 | 1.2E+02 | 2.1E+02 | 4.9E-08 | n.a. |
| Dichlobenil | 1194-65-6 | -3.6E+00 | 2.7E+00 | 2.6E+00 | 1.7E+02 | 1.1E+02 | 2.2E+03 | 1.4E+03 | n.a. | n.a. |
| Difenoconazole | 119446-68-3 | -9.4E+00 | 4.2E+00 | 3.2E+00 | 4.1E+02 | 2.9E+02 | 7.8E+01 | 8.7E+02 | n.a. | n.a. |
| Diflubenzuron | 35367-38-5 | -6.7E+00 | 3.9E+00 | 3.9E+00 | 3.1E+02 | 2.1E+02 | 3.3E+00 | 7.6E+02 | 1.9E-08 | n.a. |
| Diflufenican | 83164-33-4 | -4.9E+00 | 4.9E+00 | 3.3E+00 | 3.9E+02 | 2.6E+02 | 1.2E+02 | 3.7E+03 | n.a. | n.a. |
| Dimefuron | 34205-21-5 | -1.2E+01 | 2.5E+00 | 2.2E+00 | 3.4E+02 | 2.5E+02 | 9.4E+01 | 2.2E+03 | n.a. | n.a. |
| Dimethenamid | 87674-68-8 | -5.5E+00 | 2.2E+00 | 2.5E+00 | 2.8E+02 | 2.1E+02 | 7.4E+00 | 4.7E+02 | 4.7E-09 | n.a. |
| Dimethoate | 60-51-5 | -8.4E+00 | 7.0E-01 | 8.6E-01 | 2.3E+02 | 1.5E+02 | 5.0E+00 | 2.4E+02 | 2.8E-06 | 2.8E-05 |
| Dimethomorph | 110488-70-5 | -7.8E+00 | 2.7E+00 | 2.6E+00 | 3.9E+02 | 3.0E+02 | 4.2E+00 | 7.7E+02 | 9.6E-11 | n.a. |
| dinitrocresol | 534-52-1 | -4.2E+00 | 2.1E+00 | 2.5E+00 | 2.0E+02 | 1.3E+02 | 1.3E+03 | 2.0E+02 | n.a. | n.a. |
| Dinoseb | 88-85-7 | -6.6E+00 | 2.3E+00 | 1.5E+00 | 2.4E+02 | 1.7E+02 | 9.6E+01 | 7.2E+02 | 7.5E-07 | n.a. |
| Diquat | 2764-72-9 | -8.8E+00 | -4.6E+00 | 2.7E+00 | 1.8E+02 | 1.6E+02 | 1.1E+02 | 1.9E+02 | 2.4E-08 | n.a. |

| Substances | CAS | log $K_{aw}$ | Log $K_{ow}$ | Log $K_{oc}$ | MW g/mol | MV mL/mol | $t_{1/2}$ air hours | $t_{1/2}$ soil hours | $EF_{non\ cancer}$ y/mg | $EF_{cancer}$ y/mg |
|---|---|---|---|---|---|---|---|---|---|---|
| Dithianon | 3347-22-6 | -8.6E+00 | 3.2E+00 | 3.4E+00 | 3.0E+02 | 2.1E+02 | 3.2E+01 | 1.5E+03 | n.a. | n.a. |
| Epoxiconazole | 106325-08-0 | -7.8E+00 | 3.4E+00 | 3.2E+00 | 3.3E+02 | 2.4E+02 | 5.5E+01 | 1.8E+03 | n.a. | n.a. |
| Esfenvalerate | 66230-04-4 | -6.7E+00 | 6.2E+00 | 5.0E+00 | 4.2E+02 | 3.3E+02 | 3.8E+01 | 2.3E+03 | n.a. | n.a. |
| Ethephon | 16672-87-0 | -1.2E+01 | -2.2E+00 | 3.5E+00 | 1.4E+02 | 8.3E+01 | 3.1E+02 | 3.5E+02 | 8.2E-07 | n.a. |
| Ethiophencarb | 29973-13-5 | -7.3E+00 | 2.0E+00 | 2.0E+00 | 2.3E+02 | 1.8E+02 | 1.7E+01 | 2.3E+03 | n.a. | n.a. |
| Ethofumesate | 26225-79-6 | -6.6E+00 | 2.7E+00 | 2.2E+00 | 2.9E+02 | 2.1E+02 | 7.5E+00 | 3.2E+03 | n.a. | n.a. |
| Famoxadone | 131807-57-3 | -5.7E+00 | 4.7E+00 | 3.6E+00 | 3.7E+02 | 2.7E+02 | 7.8E+00 | 2.6E+02 | n.a. | n.a. |
| Fenpiclonil | 74738-17-3 | -7.7E+00 | 4.3E+00 | 3.4E+00 | 2.4E+02 | 1.7E+02 | 3.8E+01 | 6.0E+03 | n.a. | n.a. |
| Fenpropidin | 67306-00-7 | -4.5E+00 | 2.6E+00 | 3.0E+00 | 2.7E+02 | 2.6E+02 | 3.4E+00 | 1.2E+03 | n.a. | n.a. |
| Fenpropimorphe | 67564-91-4 | -4.2E+00 | 4.1E+00 | 3.6E+00 | 3.0E+02 | 2.8E+02 | 2.8E+00 | 9.2E+02 | n.a. | n.a. |
| Fenpyroximate | 111812-58-9 | -4.1E+00 | 5.0E+00 | 4.8E+00 | 4.2E+02 | 3.4E+02 | 8.2E+00 | 8.8E+02 | n.a. | n.a. |
| Fentin acetate | 900-95-8 | -3.9E+00 | 3.4E+00 | 3.3E+00 | 4.1E+02 | 2.7E+02 | 6.5E+01 | 1.7E+02 | n.a. | n.a. |
| Fentin hydroxide | 76-87-9 | -4.8E+00 | 3.4E+00 | 3.3E+00 | 3.7E+02 | 2.7E+02 | 6.5E+01 | 1.7E+02 | n.a. | n.a. |
| Fluazifop-P-Butyl | 79241-46-6 | -5.4E+00 | 4.5E+00 | 3.8E+00 | 3.8E+02 | 2.2E+02 | 1.4E+01 | 4.6E+02 | 2.6E-09 | n.a. |
| Fluaziname | 79622-59-6 | -1.2E+01 | 3.6E+00 | 3.7E+00 | 4.7E+02 | 2.4E+02 | 1.2E+02 | 1.1E+03 | n.a. | n.a. |
| Fludioxonil | 13141-86-1 | -7.7E+00 | 4.1E+00 | 4.8E+00 | 2.5E+02 | 1.7E+02 | 1.2E+01 | 3.8E+02 | n.a. | n.a. |
| Fluorochloridon | 61213-25-0 | -5.7E+00 | 3.4E+00 | 3.3E+00 | 3.1E+02 | 1.9E+02 | 5.2E+01 | 1.3E+03 | 2.3E-09 | n.a. |
| Fluroxypyr | 69377-81-7 | -1.1E+01 | 2.0E+00 | 1.8E+00 | 2.6E+02 | 1.5E+02 | 5.9E+01 | 1.2E+03 | 1.5E-10 | n.a. |
| Fluroxypyr - Ester | 81406-37-3 | -5.7E+00 | 4.5E+00 | 4.2E+00 | 3.7E+02 | 3.8E+02 | 1.2E+01 | 3.6E+01 | n.a. | n.a. |
| Flusilazole | 85509-19-9 | -4.5E+00 | 3.8E+00 | 3.1E+00 | 3.2E+02 | 2.6E+02 | 6.3E+01 | 3.0E+03 | 1.9E-07 | n.a. |
| Fonolos | 944-22-9 | -3.5E+00 | 3.9E+00 | 3.3E+00 | 2.5E+02 | 1.9E+02 | 4.4E+00 | 5.9E+02 | 1.9E-07 | n.a. |
| Furathiocarb | 65907-30-4 | -5.9E+00 | 4.8E+00 | 3.9E+00 | 3.8E+02 | 2.9E+02 | 1.2E+01 | 2.4E+01 | n.a. | n.a. |
| Glufosinate | 77182-82-2 | -1.2E+01 | 1.0E-01 | 1.6E+00 | 2.0E+02 | 1.2E+02 | 2.5E+01 | 3.5E+02 | 1.2E-06 | n.a. |
| Glyphosate | 1071-83-6 | -1.0E+01 | -3.2E+00 | 3.0E+00 | 1.7E+02 | 1.0E+02 | 4.9E+00 | 3.7E+02 | 3.7E-09 | n.a. |
| Haloxyfop | 072619-32-0 | -5.5E+00 | 4.3E+00 | 3.6E+00 | 3.8E+02 | 2.3E+02 | 2.0E+01 | 1.4E+03 | n.a. | n.a. |
| Hexaconazole | 79983-71-4 | -6.9E+00 | 3.9E+00 | 3.0E+00 | 3.1E+02 | 2.3E+02 | 3.7E+01 | 2.0E+03 | n.a. | n.a. |
| Hexaflumuron | 86479-06-3 | -3.4E+00 | 5.7E+00 | 4.6E+00 | 4.6E+02 | 2.6E+02 | 1.9E+01 | 2.6E+03 | n.a. | n.a. |
| Ioxynil | 1689-83-4 | -5.5E+00 | 8.9E-01 | 2.3E+00 | 3.7E+02 | 1.4E+02 | 1.8E+03 | 2.4E+02 | 4.7E-08 | 4.7E-07 |
| Iprodione | 36734-19-7 | -6.9E+00 | 3.1E+00 | 2.5E+00 | 3.3E+02 | 2.3E+02 | 2.3E+01 | 1.6E+03 | 9.0E-09 | n.a. |
| Isoproturon | 34123-59-6 | -8.3E+00 | 2.5E+00 | 1.9E+00 | 2.1E+02 | 1.8E+02 | 3.8E+01 | 4.8E+02 | n.a. | n.a. |
| Kresoxim | 143390-89-0 | -6.8E+00 | 3.4E+00 | 2.5E+00 | 3.1E+02 | 2.5E+02 | 1.1E+01 | 1.4E+02 | n.a. | n.a. |
| Lambda-cyhalothrin | 91465-08-6 | -5.1E+00 | 7.0E+00 | 5.0E+00 | 4.5E+02 | 3.2E+02 | 2.5E+01 | 5.2E+02 | 4.7E-08 | 4.7E-07 |
| Linuron | 330-55-2 | -6.6E+00 | 3.0E+00 | 2.7E+00 | 2.5E+02 | 1.7E+02 | 3.9E+01 | 1.1E+03 | 3.2E-07 | 3.2E-06 |

| Substances | CAS | log $K_{aw}$ | Log $K_{ow}$ | Log $K_{oc}$ | MW g/mol | MV mL/mol | $t_{1/2}$ air hours | $t_{1/2}$ soil hours | $EF_{non\ cancer}$ y/mg | $EF_{cancer}$ y/mg |
|---|---|---|---|---|---|---|---|---|---|---|
| Mancozeb | 8018-01-7 | -6.6E+00 | 1.3E+00 | 3.3E+00 | 5.4E+02 | 2.4E+02 | 1.8E+00 | 3.6E+01 | 5.3E-09 | 5.3E-08 |
| Maneb | 12427-38-2 | -4.6E+00 | 6.2E-01 | 2.4E+00 | 2.1E+02 | 1.3E+02 | 1.8E+00 | 1.0E+03 | 2.8E-08 | 2.8E-07 |
| MCPA | 94-74-6 | -7.7E+00 | 4.6E-01 | 8.2E-01 | 2.0E+02 | 1.1E+02 | 3.1E+01 | 1.7E+02 | 2.5E-07 | 1.9E-07 |
| MCPB | 94-81-5 | -6.9E+00 | 2.8E+00 | 2.7E+00 | 2.3E+02 | 1.7E+02 | 2.0E+01 | 2.4E+02 | 1.0E-08 | n.a. |
| MCPP | 7085-19-0 | -6.1E+00 | 1.0E-01 | 1.2E+00 | 2.1E+02 | 5.4E+01 | 2.2E+01 | 2.3E+02 | 2.9E-09 | n.a. |
| MCPP-P | 16484-77-8 | -7.6E+00 | 1.8E-01 | 1.1E+00 | 2.1E+02 | 1.5E+02 | 2.2E+01 | 2.6E+02 | n.a. | n.a. |
| Metalaxyl | 57837-19-1 | -8.3E+00 | 1.8E+00 | 1.7E+00 | 2.8E+02 | 2.2E+02 | 1.6E+01 | 1.0E+03 | 6.0E-09 | 6.0E-08 |
| Metamitron | 41394-05-2 | -6.3E+00 | 8.3E-01 | 2.3E+00 | 2.0E+02 | 1.6E+02 | 2.0E+01 | 9.2E+02 | n.a. | n.a. |
| Metazachlor | 67129-08-2 | -7.6E+00 | 2.1E+00 | 1.9E+00 | 2.8E+02 | 2.2E+02 | 7.0E+00 | 1.3E+02 | n.a. | n.a. |
| Metconazole | 125116-23-6 | -7.3E+00 | 3.9E+00 | 3.1E+00 | 3.2E+02 | 2.6E+02 | 3.1E+01 | 2.7E+03 | n.a. | n.a. |
| Methabenzthiazuron | 18691-97-9 | -5.7E+00 | 2.6E+00 | 2.7E+00 | 2.2E+02 | 1.7E+02 | 8.3E+00 | 3.1E+03 | n.a. | n.a. |
| Methidathion | 950-37-8 | -6.5E+00 | 2.2E+00 | 2.6E+00 | 3.0E+02 | 1.9E+02 | 2.6E+00 | 3.4E+02 | 3.7E-07 | 1.5E-06 |
| Methiocarbe | 2032-65-7 | -7.0E+00 | 3.3E+00 | 2.7E+00 | 2.3E+02 | 1.8E+02 | 3.1E+01 | 7.2E+01 | 1.6E-08 | 1.6E-07 |
| Methomyl | 16752-77-5 | -9.1E+00 | 9.3E-02 | 1.7E+00 | 1.6E+02 | 1.1E+02 | 5.9E+01 | 7.1E+02 | 1.5E-08 | 1.5E-07 |
| Metobromuron | 3060-89-7 | -6.9E+00 | 2.4E+00 | 2.3E+00 | 2.6E+02 | 1.6E+02 | 2.9E+01 | 7.2E+02 | n.a. | n.a. |
| Metolachlor | 51218-45-2 | -6.4E+00 | 2.9E+00 | 1.8E+00 | 2.8E+02 | 2.3E+02 | 5.7E+00 | 7.8E+02 | 9.4E-09 | 9.4E-08 |
| Metoxuron | 19937-59-8 | -6.2E+00 | 1.6E+00 | 2.1E+00 | 2.3E+02 | 1.7E+02 | 1.3E+01 | 7.2E+02 | n.a. | n.a. |
| Metribuzin | 21087-64-9 | -8.8E+00 | 1.6E+00 | 1.4E+00 | 2.1E+02 | 1.6E+02 | 1.2E+01 | 2.4E+03 | 1.5E-08 | 1.5E-07 |
| Metsulfuron | 74223-64-6 | -1.4E+01 | -1.7E+00 | 1.0E+00 | 3.8E+02 | 2.6E+02 | 3.0E+01 | 4.8E+02 | 5.6E-09 | n.a. |
| Mevinphos | 7786-34-7 | -8.6E+00 | 5.0E-01 | 8.5E-01 | 2.2E+02 | 1.5E+02 | 1.1E+01 | 4.8E+01 | n.a. | n.a. |
| Monolinuron | 1746-81-2 | -6.8E+00 | 2.2E+00 | 1.8E+00 | 2.1E+02 | 1.5E+02 | 2.8E+01 | 1.1E+03 | n.a. | n.a. |
| Napropamid | 15299-99-7 | -7.5E+00 | 3.4E+00 | 2.8E+00 | 2.7E+02 | 2.3E+02 | 2.1E+00 | 1.3E+03 | 4.9E-09 | n.a. |
| Nicosulfuron | 111991-09-4 | -1.9E+01 | -1.7E+00 | 9.9E-01 | 4.1E+02 | 2.8E+02 | 1.1E+02 | 2.4E+02 | 3.0E-12 | n.a. |
| Orbencarb | 34622-58-7 | -4.8E+00 | 4.7E+00 | 4.5E+00 | 2.6E+02 | 2.0E+02 | 1.6E+01 | 1.8E+03 | n.a. | n.a. |
| Oxadixyl | 77732-09-3 | -1.0E+01 | 7.3E-01 | 1.2E+00 | 2.8E+02 | 2.1E+02 | 1.3E+01 | 4.7E+03 | n.a. | n.a. |
| Parathion | 56-38-2 | -4.9E+00 | 3.8E+00 | 3.7E+00 | 2.9E+02 | 2.0E+02 | 4.3E+00 | 5.0E+02 | 7.5E-07 | 7.5E-06 |
| Pendimethaline | 40487-42-1 | -2.8E+00 | 5.2E+00 | 4.1E+00 | 2.8E+02 | 2.2E+02 | 1.3E+01 | 1.6E+03 | 3.0E-09 | 3.7E-08 |
| Permethrin | 52645-53-1 | -4.1E+00 | 6.1E+00 | 4.9E+00 | 3.9E+02 | 2.9E+02 | 1.1E+01 | 4.7E+02 | 2.8E-08 | 5.1E-08 |
| Phenmedipham | 13684-63-4 | -1.0E+01 | 3.6E+00 | 2.9E+00 | 3.0E+02 | 2.3E+02 | 2.7E+01 | 5.5E+02 | 5.6E-09 | n.a. |
| Phosalone | 2310-17-0 | -5.5E+00 | 4.1E+00 | 3.3E+00 | 3.7E+02 | 2.5E+02 | 1.7E+00 | 6.1E+02 | n.a. | n.a. |
| Phosmet | 732-11-6 | -6.5E+00 | 2.9E+00 | 2.6E+00 | 3.2E+02 | 2.2E+02 | 2.6E+00 | 2.9E+02 | 7.1E-08 | n.a. |
| Pirimicarb | 23103-98-2 | -7.5E+00 | 1.7E+00 | 2.6E+00 | 2.4E+02 | 1.9E+02 | 2.6E+00 | 2.9E+03 | n.a. | n.a. |
| Prochloraz | 67747-09-5 | -6.2E+00 | 4.1E+00 | 3.4E+00 | 3.8E+02 | 2.6E+02 | 5.6E+00 | 5.3E+02 | 4.1E-08 | 2.8E-07 |

| Substances | CAS | log $K_{aw}$ | Log $K_{ow}$ | Log $K_{oc}$ | MW g/mol | MV mL/mol | $t_{1/2}$ air hours | $t_{1/2}$ soil hours | $EF_{non\ cancer}$ y/mg | $EF_{cancer}$ y/mg |
|---|---|---|---|---|---|---|---|---|---|---|
| Propamocarb | 25606-41-1 | -1.0E+01 | -2.7E+00 | 2.5E+00 | 1.9E+02 | 1.6E+02 | 1.2E+01 | 4.8E+02 | n.a. | n.a. |
| Propaquizafop | 111479-05-1 | -8.9E+00 | 4.6E+00 | 2.6E+00 | 4.4E+02 | 3.3E+02 | 6.3E+01 | 4.8E+02 | n.a. | n.a. |
| Propham | 122-42-9 | -5.8E+00 | 4.1E-01 | 7.9E-01 | 1.8E+02 | 1.5E+02 | 7.4E+00 | 2.1E+02 | 9.4E-09 | n.a. |
| Propiconazole | 60207-90-1 | -6.8E+00 | 3.7E+00 | 2.9E+00 | 3.4E+02 | 2.5E+02 | 1.9E+01 | 2.0E+03 | 3.0E-08 | 3.0E-07 |
| Prosulfocarb | 52888-80-9 | -4.4E+00 | 4.7E+00 | 3.1E+00 | 2.5E+02 | 2.1E+02 | 1.2E+01 | 2.8E+02 | n.a. | n.a. |
| Pyridate | 55512-33-9 | -7.3E+00 | 5.0E-01 | 1.7E+00 | 3.8E+02 | 2.9E+02 | 2.3E+01 | 8.2E+01 | n.a. | n.a. |
| Quizalofop | 76578-14-8 | -6.4E+00 | 5.3E+00 | 4.3E+00 | 3.7E+02 | 2.5E+02 | 2.2E+01 | 2.4E+01 | 1.3E-07 | n.a. |
| Rhodamine | 143121-08-8 | -9.9E+00 | 3.0E+00 | 2.9E+00 | 2.8E+02 | 1.9E+02 | 5.9E+01 | 2.9E+03 | n.a. | n.a. |
| Rimsulfuron | 122931-48-0 | -6.5E+00 | 3.4E-02 | 1.7E+00 | 4.3E+02 | 2.9E+02 | 1.8E+00 | 2.2E+02 | n.a. | n.a. |
| Simazin | 122-34-9 | -7.4E+00 | 2.0E+00 | 2.5E+00 | 2.0E+02 | 1.5E+02 | 3.6E+01 | 1.9E+03 | 2.7E-07 | 2.7E-06 |
| S-Metolachlor | 87392-12-9 | -6.1E+00 | 3.1E+00 | 2.3E+00 | 2.8E+02 | 2.3E+02 | 7.1E+00 | 5.0E+02 | n.a. | n.a. |
| Spiroxamine | 118134-30-8 | -5.8E+00 | 2.9E+00 | 3.3E+00 | 3.0E+02 | 2.0E+02 | 3.1E+00 | 1.7E+02 | n.a. | n.a. |
| Sulcotrione | 99105-77-8 | -8.4E+00 | 2.3E+00 | 8.9E-01 | 3.3E+02 | 2.3E+02 | 5.7E+01 | 9.6E+01 | n.a. | n.a. |
| Sulfosulfuron | 141776-32-1 | -1.1E+01 | -7.7E-01 | 1.2E+00 | 4.7E+02 | 2.8E+02 | 2.0E+00 | 5.7E+02 | n.a. | n.a. |
| Tebuconazole | 107534-96-3 | -7.7E+00 | 3.7E+00 | 3.0E+00 | 3.1E+02 | 2.5E+02 | 4.5E+01 | 2.1E+03 | n.a. | n.a. |
| Tebutam | 35256-85-0 | -5.0E+00 | 3.0E+00 | 2.9E+00 | 2.3E+02 | 2.1E+02 | 1.2E+01 | 1.4E+03 | n.a. | n.a. |
| Teflubenzuron | 83121-18-0 | -9.3E+00 | 4.6E+00 | 3.8E+00 | 3.8E+02 | 2.2E+02 | 1.1E+02 | 8.2E+02 | n.a. | n.a. |
| Terbufos | 13071-79-9 | -3.4E+00 | 4.5E+00 | 2.7E+00 | 2.9E+02 | 2.1E+02 | 1.6E+00 | 4.2E+02 | 1.9E-05 | 3.7E-05 |
| Terbuthryn | 886-50-0 | -6.3E+00 | 3.7E+00 | 2.8E+00 | 2.4E+02 | 1.9E+02 | 3.8E+01 | 4.4E+03 | 1.4E-06 | n.a. |
| Terbuthylazine | 5915-41-3 | -5.8E+00 | 3.2E+00 | 2.4E+00 | 2.3E+02 | 1.8E+02 | 3.6E+01 | 1.0E+03 | 6.2E-08 | 6.2E-07 |
| Thiabendazole | 148-79-8 | -8.8E+00 | 2.4E+00 | 3.6E+00 | 2.0E+02 | 1.5E+02 | 8.3E+00 | 8.8E+03 | 2.7E-09 | 2.7E-08 |
| Thifensulfuron | 79277-27-3 | -1.5E+01 | -1.7E+00 | 1.4E+00 | 3.9E+02 | 2.5E+02 | 1.2E+02 | 1.9E+02 | 1.1E-07 | n.a. |
| Thiram | 137-26-8 | -5.4E+00 | 1.7E+00 | 3.8E+00 | 2.4E+02 | 1.7E+02 | 1.1E+00 | 1.1E+02 | 2.8E-08 | n.a. |
| Triasulfuron | 82097-50-5 | -7.5E+00 | -5.9E-01 | 1.1E+00 | 4.0E+02 | 2.7E+02 | 3.8E+01 | 2.9E+02 | 2.5E-07 | n.a. |
| triazamate | 112143-82-5 | -8.3E+00 | 3.0E+00 | 2.3E+00 | 3.1E+02 | 2.4E+02 | 2.6E+01 | 6.0E+00 | n.a. | n.a. |
| Tribenuron | 101200-48-0 | -1.1E+01 | -4.4E-01 | 1.7E+00 | 4.0E+02 | 2.6E+02 | 1.3E+02 | 1.3E+02 | 4.9E-08 | n.a. |
| Trichlorfon | 52-68-6 | -9.2E+00 | 4.3E-01 | 8.0E-01 | 2.6E+02 | 1.4E+02 | 6.2E+01 | 1.6E+02 | 2.3E-08 | 2.3E-07 |
| Triclopyr | 55335-06-3 | -1.2E+01 | -4.4E-01 | 1.7E+00 | 2.6E+02 | 1.5E+02 | 9.8E+01 | 6.4E+02 | n.a. | n.a. |
| Trifluralin | 1582-09-8 | -2.2E+00 | 4.8E+00 | 3.7E+00 | 3.4E+02 | 2.2E+02 | 1.6E+01 | 2.3E+03 | 4.9E-08 | 1.3E-08 |
| Triflusulfuron | 135990-29-3 | -6.3E+00 | 9.6E-01 | 1.9E+00 | 4.8E+02 | 3.0E+02 | 9.1E+01 | 7.2E+01 | 1.8E-09 | n.a. |
| Trinexapac | 95266-40-3 | -5.7E+00 | 1.6E+00 | 2.2E+00 | 2.5E+02 | 1.9E+02 | 4.1E+00 | 2.4E+01 | n.a. | n.a. |
| Vinclozolin | 50471-44-8 | -6.1E+00 | 4.9E-01 | 8.4E-01 | 2.9E+02 | 1.9E+02 | 1.2E+01 | 9.0E+02 | 1.5E-08 | 1.5E-07 |
| Zineb | 12122-67-7 | -7.0E+00 | 1.3E+00 | 2.8E+00 | 2.8E+02 | 1.3E+02 | 2.6E+00 | 2.4E+01 | 3.0E-08 | 3.7E-08 |

## *G.2 Phytosanitary data and harvest fraction*

Description of substances used in field crops and harvest fractions. Date of treatment according to data collected during three years (1998 – 2000) on 41 farms in Western Switzerland. Minimum and maximum application rate (kg/ha) according to the official list of plant protection products (OFAG, 2002), and average application per crop (kg/ha) according to collected data. Time (days) between treatment and harvest, harvest fraction according to the model (hF, kg substance in harvest / kg applied). Harvest fraction for single source ($hF_i$ kg substance in harvest / kg applied in source i) and parameters for simplified resolution for each source soil (s), formulation deposit (fd), air (a):, maximum harvest fraction ($hF_{i,max}$, kg in harvest /kg applied in source i), time to reach the $hF_{i,max}$ ($t_{i,max}$, days) and dissipation rate ($\mu_{i,2}$, 1/days).

| Substance | Crop | Application rate | | Dose | Date | Time | hF | Soil | | | | Formulation deposit | | | | Air | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | min | max | per crop | treat. | | | $hF_s$ | $hF_{s,max}$ | $t_{s,max}$ | $\mu_{s,2}$ | $hF_{fd}$ | $hF_{fd,max}$ | $t_{fd,max}$ | $\mu_{fd,2}$ | $hF_a$ | $hF_{a,max}$ | $t_{a,max}$ | $\mu_{a,2}$ |
| | | kg/ha | kg/ha | kg/ha | | | kg/ kg | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days |
| FUNGICIDES | | | | | | | | | | | | | | | | | | | |
| Acibenzolar-S-methyl | wheat winter | 0.030 | 0.030 | 0.021 | 16.3 | 121 | 1.0E-06 | 1.3E-06 | 2.9E-04 | 14 | -5.0E-02 | 3.5E-08 | 1.3E-02 | 8 | -9.9E-02 | 1.5E-08 | 6.5E-03 | 5 | -1.2E-01 |
| Azoxystrobin | wheat winter | 0.200 | 0.250 | 0.044 | 25.5 | 51 | 5.7E-05 | 5.7E-05 | 1.2E-03 | 10 | -6.8E-02 | 4.6E-05 | 1.8E-02 | 7 | -1.3E-01 | 5.8E-05 | 1.8E-02 | 5 | -1.3E-01 |
| Azoxystrobin | wheat spring | 0.200 | 0.250 | 0.067 | 9.6 | 36 | 2.8E-04 | 1.5E-04 | 1.5E-03 | 10 | -6.7E-02 | 3.0E-04 | 2.9E-02 | 7 | -1.3E-01 | 4.5E-04 | 2.6E-02 | 5 | -1.3E-01 |
| Azoxystrobin | Rape winter | 0.250 | 0.250 | 0.010 | 26.4 | 66 | 1.3E-05 | 2.9E-05 | 2.8E-03 | 10 | -6.8E-02 | 5.7E-06 | 2.6E-02 | 7 | -1.3E-01 | 6.3E-06 | 2.7E-02 | 5 | -1.3E-01 |
| Azoxystrobin | barley winter | 0.200 | 0.250 | 0.052 | 29.4 | 63 | 2.1E-05 | 3.0E-05 | 2.1E-03 | 10 | -6.8E-02 | 1.1E-05 | 3.3E-02 | 7 | -1.3E-01 | 1.2E-05 | 3.3E-02 | 5 | -1.3E-01 |
| Azoxystrobin | potato | 0.188 | 0.188 | 0.055 | 16.7 | 47 | 2.0E-04 | 2.0E-04 | 3.8E-03 | 10 | -6.8E-02 | 1.4E-04 | 4.9E-02 | 7 | -1.3E-01 | 1.9E-04 | 4.2E-02 | 5 | -1.3E-01 |
| Carbendazime | Rape winter | 0.240 | 0.240 | 0.046 | 25.4 | 67 | 7.9E-03 | 3.8E-03 | 3.9E-02 | 79 | -1.0E-02 | 8.9E-03 | 1.5E-01 | 13 | -1.5E-02 | 3.7E-03 | 7.9E-03 | 1 | -1.6E-02 |
| Chlorothalonil | wheat winter | 1.500 | 1.500 | 0.007 | 1.6 | 44 | 6.1E-03 | 3.4E-04 | 8.3E-04 | 35 | -2.0E-02 | 9.0E-03 | 1.9E-02 | 12 | -3.9E-02 | 1.1E-02 | 4.0E-02 | 33 | -6.5E-03 |
| Chlorothalonil | potato | 1.500 | 1.500 | 1.535 | 13.6 | 80 | 1.9E-03 | 4.7E-04 | 2.8E-03 | 35 | -2.0E-02 | 6.8E-03 | 5.2E-02 | 12 | -3.9E-02 | 9.1E-03 | 1.1E-01 | 33 | -6.5E-03 |
| Chlorothalonil | pea spring | 1.500 | 1.500 | 0.375 | 1.6 | 44 | 5.5E-03 | 3.5E-04 | 1.1E-03 | 35 | -2.0E-02 | 1.4E-02 | 4.1E-02 | 12 | -3.9E-02 | 1.7E-02 | 7.3E-02 | 29 | -6.2E-03 |
| Cymoxanil | potato | 1.200 | 1.200 | 0.227 | 24.6 | 69 | 4.8E-06 | 6.0E-06 | 7.2E-03 | 7 | -9.5E-02 | 1.0E-06 | 1.2E-01 | 5 | -1.8E-01 | 2.7E-07 | 1.7E-01 | 4 | -1.9E-01 |
| Cyproconazole | beet sugar | 0.060 | 0.080 | 0.011 | 17.8 | 59 | 1.7E-03 | 1.4E-03 | 6.1E-03 | 26 | -2.7E-02 | 2.6E-03 | 2.3E-02 | 11 | -5.2E-02 | 2.2E-03 | 8.2E-03 | 5 | -5.3E-02 |
| Cyproconazole | wheat winter | 0.060 | 0.080 | 0.024 | 22.5 | 54 | 1.9E-03 | 6.9E-04 | 2.3E-03 | 26 | -2.7E-02 | 2.8E-03 | 1.7E-02 | 11 | -5.2E-02 | 2.4E-03 | 6.0E-03 | 5 | -5.4E-02 |
| Cyproconazole | wheat spring | 0.060 | 0.080 | 0.027 | 18.4 | 88 | 2.9E-04 | 2.6E-04 | 2.9E-03 | 26 | -2.7E-02 | 4.7E-04 | 3.1E-02 | 11 | -5.2E-02 | 3.9E-04 | 1.1E-02 | 5 | -5.4E-02 |
| Cyproconazole | barley winter | 0.080 | 0.080 | 0.040 | 3.5 | 59 | 1.7E-03 | 7.4E-04 | 4.0E-03 | 26 | -2.7E-02 | 2.3E-03 | 3.0E-02 | 11 | -5.2E-02 | 2.0E-03 | 1.1E-02 | 5 | -5.4E-02 |
| Cyprodinil | wheat winter | 0.600 | 0.600 | 0.050 | 25.4 | 81 | 2.4E-06 | 1.9E-06 | 4.1E-05 | 13 | -5.3E-02 | 4.2E-06 | 1.9E-03 | 8 | -1.1E-01 | 1.6E-07 | 7.0E-05 | 1 | -1.1E-01 |
| Cyprodinil | barley winter | 0.600 | 0.600 | 0.081 | 26.4 | 66 | 1.5E-05 | 6.6E-06 | 7.2E-05 | 13 | -5.3E-02 | 2.7E-05 | 3.1E-03 | 8 | -1.1E-01 | 1.1E-06 | 1.2E-04 | 1 | -1.1E-01 |
| Difenoconazole | beet sugar | 0.125 | 0.125 | 0.026 | 16.8 | 60 | 6.3E-04 | 2.2E-04 | 2.9E-04 | 36 | -1.9E-02 | 1.9E-03 | 1.7E-03 | 13 | -3.8E-02 | 1.7E-03 | 1.2E-03 | 10 | -3.8E-02 |
| Difenoconazole | wheat winter | 0.125 | 0.125 | 0.004 | 2.6 | 43 | 1.3E-03 | 9.8E-05 | 1.1E-04 | 36 | -1.9E-02 | 1.9E-03 | 1.2E-03 | 13 | -3.8E-02 | 1.8E-03 | 8.7E-04 | 10 | -3.8E-02 |
| Difenoconazole | Rape winter | 0.125 | 0.125 | 0.019 | 25.4 | 67 | 1.2E-03 | 1.6E-04 | 2.5E-04 | 36 | -1.9E-02 | 1.6E-03 | 1.9E-03 | 13 | -3.8E-02 | 1.5E-03 | 1.4E-03 | 10 | -3.8E-02 |

| Substance | Crop | Application rate | | Dose | Date | Time | hF | Soil | | | | Formulation deposit | | | | Air | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | min | max | per crop | treat. | | | $hF_s$ | $hF_{s,max}$ | $t_{s,max}$ | $\mu_{s,2}$ | $hF_{fd}$ | $hF_{fd,max}$ | $t_{fd,max}$ | $\mu_{fd,2}$ | $hF_a$ | $hF_{a,max}$ | $t_{a,max}$ | $\mu_{a,2}$ |
| | | kg/ha | kg/ha | kg/ha | | | kg/ kg | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days |
| Dimethomorph | potato | 0.150 | 0.150 | 0.075 | 17.6 | 76 | 1.4E-03 | 1.2E-03 | 9.2E-03 | 31 | -2.2E-02 | 1.3E-03 | 7.0E-02 | 11 | -4.3E-02 | 7.6E-04 | 4.4E-03 | 1 | -4.5E-02 |
| Epoxiconazole | beet forage | 0.094 | 0.094 | 0.021 | 6.8 | 70 | 5.1E-02 | 2.0E-03 | 2.0E-03 | 75 | -9.3E-03 | 2.4E-01 | 9.8E-01 | 1 | -1.8E-02 | 2.2E-01 | 7.6E-01 | 3 | -1.9E-02 |
| Epoxiconazole | beet sugar | 0.094 | 0.094 | 0.032 | 8.8 | 68 | 4.1E-03 | 1.0E-03 | 2.1E-03 | 75 | -9.3E-03 | 1.5E-02 | 1.1E-02 | 17 | -1.8E-02 | 1.4E-02 | 5.5E-03 | 10 | -1.9E-02 |
| Epoxiconazole | wheat winter | 0.063 | 0.125 | 0.032 | 25.5 | 51 | 8.8E-03 | 4.6E-04 | 7.7E-04 | 75 | -9.3E-03 | 1.4E-02 | 7.5E-03 | 16 | -1.8E-02 | 1.3E-02 | 3.9E-03 | 10 | -1.9E-02 |
| Epoxiconazole | wheat spring | 0.063 | 0.125 | 0.042 | 27.5 | 49 | 6.1E-03 | 4.8E-04 | 9.6E-04 | 75 | -9.3E-03 | 1.8E-02 | 1.2E-02 | 16 | -1.8E-02 | 1.7E-02 | 6.1E-03 | 10 | -1.9E-02 |
| Epoxiconazole | barley winter | 0.125 | 0.125 | 0.041 | 1.5 | 61 | 9.7E-03 | 5.8E-04 | 1.4E-03 | 75 | -9.3E-03 | 1.6E-02 | 1.4E-02 | 16 | -1.8E-02 | 1.5E-02 | 7.4E-03 | 10 | -1.9E-02 |
| Epoxiconazole | rye winter | 0.063 | 0.125 | 0.060 | 4.5 | 58 | 8.7E-03 | 5.9E-04 | 1.3E-03 | 75 | -9.3E-03 | 1.7E-02 | 1.4E-02 | 16 | -1.8E-02 | 1.6E-02 | 7.3E-03 | 10 | -1.9E-02 |
| Famoxadone | wheat winter | 0.150 | 0.280 | 0.009 | 24.5 | 52 | 3.8E-06 | 7.1E-07 | 5.1E-06 | 11 | -6.3E-02 | 7.1E-06 | 2.9E-04 | 8 | -1.3E-01 | 2.1E-06 | 4.1E-05 | 1 | -1.3E-01 |
| Famoxadone | wheat spring | 0.150 | 0.280 | 0.150 | 7.6 | 38 | 1.7E-05 | 2.1E-06 | 6.5E-06 | 11 | -6.3E-02 | 4.5E-05 | 4.3E-04 | 8 | -1.3E-01 | 1.2E-05 | 6.1E-05 | 1 | -1.3E-01 |
| Fenpropimorphe | beet forage | 0.300 | 0.300 | 0.063 | 6.8 | 70 | 1.6E-03 | 1.1E-04 | 1.5E-04 | 38 | -1.8E-02 | 1.4E-02 | 9.8E-01 | 0 | -3.6E-02 | 2.8E-04 | 1.8E-02 | 1 | -6.1E-02 |
| Fenpropimorphe | beet sugar | 0.300 | 0.300 | 0.138 | 15.8 | 61 | 3.1E-04 | 1.1E-04 | 1.5E-04 | 38 | -1.8E-02 | 1.5E-03 | 2.3E-03 | 13 | -3.6E-02 | 2.9E-05 | 8.4E-05 | 1 | -4.1E-02 |
| Fenpropimorphe | wheat winter | 0.188 | 0.375 | 0.030 | 1.6 | 44 | 6.1E-04 | 5.0E-05 | 5.7E-05 | 38 | -1.8E-02 | 1.1E-03 | 1.6E-03 | 13 | -3.6E-02 | 2.8E-05 | 6.0E-05 | 1 | -4.1E-02 |
| Fenpropimorphe | wheat spring | 0.188 | 0.375 | 0.125 | 27.5 | 49 | 3.2E-04 | 5.7E-05 | 7.0E-05 | 38 | -1.8E-02 | 1.3E-03 | 2.6E-03 | 13 | -3.6E-02 | 2.6E-05 | 9.6E-05 | 1 | -4.4E-02 |
| Fentin acetate | potato | 0.230 | 0.288 | 0.024 | 23.6 | 70 | 3.8E-07 | 4.9E-07 | 1.7E-04 | 7 | -9.9E-02 | 1.3E-08 | 8.2E-03 | 6 | -1.4E-01 | 7.7E-09 | 5.6E-03 | 4 | -2.2E-01 |
| Fluaziname | potato | 0.250 | 0.250 | 0.300 | 30.5 | 94 | 1.0E-03 | 1.8E-04 | 4.8E-04 | 47 | -1.5E-02 | 5.8E-03 | 1.5E-02 | 14 | -2.9E-02 | 5.8E-03 | 1.5E-02 | 14 | -2.9E-02 |
| Fludioxonil | wheat winter | 0.009 | 0.009 | 0.001 | 5.10 | 136 | 1.5E-07 | 3.3E-07 | 3.7E-05 | 16 | -4.4E-02 | 1.5E-07 | 6.8E-04 | 9 | -8.8E-02 | 1.5E-07 | 1.2E-04 | 2 | -8.8E-02 |
| Flusilazole | beet sugar | 0.200 | 0.200 | 0.018 | 13.8 | 63 | 3.0E-03 | 1.3E-03 | 2.1E-03 | 123 | -5.7E-03 | 1.1E-02 | 4.8E-03 | 20 | -1.1E-02 | 3.7E-03 | 2.6E-03 | 11 | -1.8E-02 |
| Flusilazole | wheat winter | 0.250 | 0.300 | 0.033 | 4.5 | 72 | 2.2E-03 | 5.1E-04 | 7.9E-04 | 122 | -5.7E-03 | 5.1E-03 | 3.9E-03 | 20 | -1.1E-02 | 1.8E-03 | 2.0E-03 | 11 | -1.9E-02 |
| Flusilazole | wheat spring | 0.250 | 0.300 | 0.161 | 7.6 | 38 | 3.5E-03 | 4.9E-04 | 1.0E-03 | 123 | -5.7E-03 | 8.7E-03 | 5.2E-03 | 20 | -1.1E-02 | 3.1E-03 | 2.7E-03 | 10 | -2.2E-02 |
| Kresoxim-methyl | beet sugar | 0.095 | 0.126 | 0.015 | 1.8 | 75 | 3.0E-07 | 3.7E-07 | 9.2E-04 | 6 | -1.2E-01 | 1.6E-09 | 4.5E-03 | 5 | -1.4E-01 | 5.8E-10 | 1.1E-03 | 1 | -2.4E-01 |
| Kresoxim-methyl | wheat winter | 0.126 | 0.126 | 0.028 | 24.5 | 52 | 1.1E-06 | 2.3E-06 | 3.4E-04 | 6 | -1.2E-01 | 2.3E-07 | 3.1E-03 | 5 | -1.4E-01 | 9.6E-08 | 7.5E-04 | 1 | -2.4E-01 |
| Kresoxim-methyl | barley winter | 0.126 | 0.126 | 0.040 | 1.5 | 61 | 5.5E-07 | 1.2E-06 | 6.1E-04 | 6 | -1.2E-01 | 3.6E-08 | 5.9E-03 | 5 | -1.4E-01 | 1.5E-08 | 1.4E-03 | 1 | -2.4E-01 |
| Kresoxim-methyl | rye winter | 0.126 | 0.126 | 0.076 | 4.5 | 58 | 9.2E-07 | 1.7E-06 | 6.0E-04 | 6 | -1.2E-01 | 7.3E-08 | 5.8E-03 | 5 | -1.4E-01 | 2.9E-08 | 1.4E-03 | 1 | -2.4E-01 |
| Mancozeb | potato | 2.250 | 2.250 | 4.788 | 7.6 | 86 | 2.4E-13 | 8.6E-22 | 1.2E-04 | 1 | -4.6E-01 | 2.1E-09 | 4.3E-02 | 2 | -2.0E-01 | 1.4E-38 | 5.1E-03 | 0 | -9.4E-01 |
| Maneb | potato | 2.400 | 2.400 | 1.365 | 9.6 | 84 | 1.5E-04 | 1.8E-04 | 1.6E-02 | 41 | -1.8E-02 | 2.4E-09 | 3.2E-01 | 9 | -3.3E-02 | 1.5E-28 | 5.9E-03 | 0 | -8.6E-01 |
| Metalaxyl | potato | 0.100 | 0.100 | 0.058 | 3.6 | 90 | 6.1E-03 | 6.6E-03 | 1.1E-01 | 36 | -2.4E-02 | 1.2E-03 | 2.6E-01 | 10 | -3.2E-02 | 2.7E-03 | 6.5E-02 | 3 | -3.4E-02 |
| Metconazole | wheat winter | 0.090 | 0.090 | 0.010 | 26.5 | 50 | 6.7E-03 | 4.6E-04 | 7.2E-04 | 112 | -6.2E-03 | 1.1E-02 | 3.2E-03 | 19 | -1.2E-02 | 8.8E-03 | 9.7E-04 | 7 | -1.3E-02 |
| Metconazole | wheat spring | 0.090 | 0.090 | 0.034 | 7.6 | 38 | 6.3E-03 | 4.8E-04 | 9.2E-04 | 112 | -6.2E-03 | 1.4E-02 | 4.8E-03 | 19 | -1.2E-02 | 1.1E-02 | 1.4E-03 | 7 | -1.3E-02 |
| Metconazole | Rape winter | 0.072 | 0.090 | 0.010 | 29.4 | 63 | 9.8E-03 | 9.0E-04 | 1.6E-03 | 111 | -6.3E-03 | 1.4E-02 | 4.8E-03 | 19 | -1.2E-02 | 1.1E-02 | 1.5E-03 | 7 | -1.3E-02 |
| Metconazole | barley winter | 0.090 | 0.090 | 0.004 | 2.5 | 60 | 1.0E-02 | 7.3E-04 | 1.3E-03 | 112 | -6.2E-03 | 1.8E-02 | 6.0E-03 | 19 | -1.2E-02 | 1.4E-02 | 1.8E-03 | 7 | -1.3E-02 |
| Metconazole | rye winter | 0.090 | 0.090 | 0.023 | 7.5 | 55 | 8.9E-03 | 7.1E-04 | 1.3E-03 | 112 | -6.2E-03 | 1.8E-02 | 5.9E-03 | 19 | -1.2E-02 | 1.4E-02 | 1.8E-03 | 7 | -1.3E-02 |
| Oxadixyl | potato | 0.200 | 0.200 | 0.027 | 6.6 | 87 | 3.9E-02 | 4.2E-02 | 4.2E-01 | 89 | -7.1E-03 | 1.4E-03 | 2.0E-01 | 19 | -7.1E-03 | 2.8E-02 | 1.0E-01 | 4 | -7.2E-03 |

| Substance | Crop | Application rate | | Dose | Date | Time | hF | Soil | | | | Formulation deposit | | | | Air | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | min | max | per crop | treat. | | | $hF_s$ | $hF_{s,max}$ | $t_{s,max}$ | $\mu_{s,2}$ | $hF_{fd}$ | $hF_{fd,max}$ | $t_{fd,max}$ | $\mu_{fd,2}$ | $hF_a$ | $hF_{a,max}$ | $t_{a,max}$ | $\mu_{a,2}$ |
| | | kg/ha | kg/ha | kg/ha | | | kg/ kg | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days |
| Prochloraz | wheat winter | 0.464 | 0.464 | 0.079 | 1.5 | 75 | 6.7E-05 | 1.3E-05 | 4.6E-05 | 22 | -3.2E-02 | 1.7E-04 | 1.4E-03 | 10 | -6.3E-02 | 3.9E-05 | 1.1E-04 | 1 | -6.5E-02 |
| Prochloraz | barley winter | 0.464 | 0.464 | 0.018 | 24.4 | 68 | 1.8E-04 | 2.7E-05 | 8.1E-05 | 22 | -3.2E-02 | 3.9E-04 | 2.4E-03 | 10 | -6.3E-02 | 9.0E-05 | 2.0E-04 | 1 | -6.5E-02 |
| Propamocarb | potato | 0.938 | 0.938 | 0.372 | 25.5 | 99 | 2.0E-06 | 3.7E-08 | 2.5E-06 | 20 | -3.5E-02 | 6.4E-09 | 3.7E-04 | 10 | -6.9E-02 | 1.9E-05 | 6.7E-02 | 2 | -6.9E-02 |
| Propiconazole | wheat winter | 0.125 | 0.125 | 0.012 | 25.4 | 81 | 4.0E-03 | 7.7E-04 | 1.3E-03 | 83 | -8.4E-03 | 1.0E-02 | 5.7E-03 | 17 | -1.7E-02 | 5.9E-03 | 1.1E-03 | 4 | -1.9E-02 |
| Propiconazole | barley winter | 0.125 | 0.125 | 0.017 | 26.4 | 66 | 8.2E-03 | 1.1E-03 | 2.2E-03 | 83 | -8.4E-03 | 1.5E-02 | 9.5E-03 | 17 | -1.7E-02 | 9.2E-03 | 1.9E-03 | 4 | -1.9E-02 |
| Spiroxamine | wheat winter | 0.200 | 0.375 | 0.026 | 16.5 | 60 | 3.8E-07 | 6.5E-07 | 1.1E-04 | 7 | -1.0E-01 | 1.5E-07 | 1.0E-02 | 6 | -1.5E-01 | 5.5E-09 | 7.3E-04 | 1 | -2.2E-01 |
| Tebuconazole | wheat winter | 0.125 | 0.250 | 0.023 | 22.5 | 54 | 7.0E-03 | 6.3E-04 | 9.3E-04 | 85 | -8.2E-03 | 1.2E-02 | 4.5E-03 | 17 | -1.6E-02 | 1.0E-02 | 1.9E-03 | 9 | -1.7E-02 |
| Tebuconazole | Rape winter | 0.375 | 0.375 | 0.047 | 20.4 | 72 | 8.1E-03 | 1.1E-03 | 2.3E-03 | 85 | -8.3E-03 | 1.2E-02 | 7.0E-03 | 17 | -1.6E-02 | 1.0E-02 | 3.0E-03 | 9 | -1.6E-02 |
| Tebuconazole | rye winter | 0.250 | 0.250 | 0.250 | 21.5 | 41 | 1.1E-02 | 9.1E-04 | 1.6E-03 | 85 | -8.2E-03 | 1.8E-02 | 7.6E-03 | 17 | -1.6E-02 | 1.6E-02 | 3.3E-03 | 9 | -1.7E-02 |
| Vinclozolin | Rape winter | 0.375 | 0.375 | 0.052 | 23.4 | 69 | 4.5E-04 | 1.3E-03 | 1.1E-01 | 26 | -3.7E-02 | 9.4E-06 | 1.7E-02 | 13 | -3.7E-02 | 1.1E-05 | 2.3E-02 | 2 | -9.2E-02 |
| HERBICIDES | | | | | | | | | | | | | | | | | | | |
| 2,4-D | wheat winter | 0.900 | 1.200 | 0.036 | 22.4 | 84 | 4.1E-06 | 6.4E-06 | 1.2E-02 | 9 | -8.5E-02 | 2.3E-07 | 5.1E-02 | 6 | -1.5E-01 | 1.5E-07 | 7.2E-02 | 4 | -1.5E-01 |
| 2,4-D | wheat spring | 0.900 | 1.200 | 0.113 | 22.4 | 84 | 5.6E-06 | 6.6E-06 | 1.5E-02 | 9 | -8.3E-02 | 2.4E-07 | 1.4E-01 | 5 | -1.5E-01 | 1.5E-07 | 1.1E-01 | 4 | -1.5E-01 |
| 2,4-D | Maize grain | 0.600 | 0.700 | 0.019 | 25.5 | 129 | 1.5E-07 | 1.7E-07 | 2.3E-02 | 9 | -8.6E-02 | 4.8E-10 | 2.2E-01 | 4 | -1.5E-01 | 2.5E-10 | 1.5E-01 | 4 | -1.5E-01 |
| 2,4-D | barley winter | 0.900 | 1.200 | 0.063 | 10.4 | 82 | 4.8E-06 | 8.2E-06 | 2.1E-02 | 9 | -8.7E-02 | 3.2E-07 | 7.4E-02 | 6 | -1.5E-01 | 2.1E-07 | 1.2E-01 | 4 | -1.5E-01 |
| Aclonifen | potato | 2.400 | 3.000 | 0.149 | 6.5 | 118 | 1.1E-03 | 1.4E-04 | 1.8E-04 | 121 | -5.7E-03 | 1.3E-02 | 3.6E-03 | 20 | -1.1E-02 | 7.5E-03 | 1.1E-03 | 7 | -1.3E-02 |
| Aclonifen | pea spring | 2.400 | 3.000 | 1.510 | 16.3 | 121 | 7.8E-04 | 5.6E-05 | 7.5E-05 | 121 | -5.7E-03 | 1.1E-02 | 3.5E-03 | 20 | -1.1E-02 | 6.3E-03 | 1.1E-03 | 7 | -1.4E-02 |
| Aclonifen | sunflower | 2.400 | 3.000 | 2.853 | 22.4 | 146 | 3.2E-04 | 2.6E-05 | 3.9E-05 | 121 | -5.7E-03 | 4.6E-03 | 1.9E-03 | 20 | -1.1E-02 | 2.7E-03 | 6.0E-04 | 7 | -1.4E-02 |
| Alachlor | Maize plant | 1.920 | 4.800 | 0.035 | 5.5 | 149 | 7.7E-06 | 8.6E-06 | 9.4E-03 | 14 | -5.1E-02 | 9.6E-10 | 6.1E-01 | 4 | -9.9E-02 | 4.0E-12 | 1.2E-02 | 1 | -1.5E-01 |
| Alachlor | soybean | 1.920 | 4.800 | 0.891 | 10.5 | 128 | 5.0E-07 | 5.6E-07 | 2.1E-03 | 14 | -5.0E-02 | 1.1E-11 | 2.0E-01 | 6 | -9.9E-02 | 2.2E-24 | 5.6E-03 | 0 | -3.8E-01 |
| Amidosulfuron | wheat winter | 0.015 | 0.030 | 0.003 | 23.3 | 114 | 2.4E-08 | 3.1E-08 | 4.8E-02 | 7 | -1.2E-01 | 9.7E-10 | 5.1E-02 | 6 | -1.5E-01 | 3.0E-12 | 2.7E-03 | 0 | -1.8E-01 |
| Amidosulfuron | wheat spring | 0.015 | 0.030 | 0.014 | 29.4 | 77 | 5.3E-06 | 6.3E-06 | 5.7E-02 | 8 | -1.1E-01 | 2.5E-07 | 9.2E-02 | 6 | -1.5E-01 | 1.3E-09 | 3.8E-03 | 0 | -1.8E-01 |
| Amidosulfuron | barley winter | 0.015 | 0.030 | 0.002 | 15.3 | 108 | 2.9E-08 | 4.2E-08 | 8.5E-02 | 7 | -1.3E-01 | 2.3E-09 | 6.9E-02 | 6 | -1.5E-01 | 7.0E-12 | 4.7E-03 | 0 | -1.8E-01 |
| Amidosulfuron | barley spring | 0.015 | 0.030 | 0.011 | 10.6 | 35 | 4.9E-04 | 7.7E-04 | 5.6E-02 | 8 | -1.1E-01 | 1.2E-04 | 4.6E-02 | 6 | -1.5E-01 | 2.5E-06 | 3.6E-03 | 0 | -1.8E-01 |
| Asulam | ley int | 1.200 | 2.400 | 0.444 | 1.5 | 20 | 4.2E-02 | 3.1E-03 | 3.9E-03 | 11 | -6.4E-02 | 6.3E-02 | 3.5E-01 | 8 | -1.3E-01 | 5.2E-02 | 5.3E-01 | 1 | -1.3E-01 |
| Atrazin | Maize ear | 0.990 | 0.990 | 0.585 | 24.5 | 130 | 4.0E-03 | 4.4E-03 | 6.4E-02 | 58 | -1.5E-02 | 1.8E-03 | 1.4E-01 | 13 | -2.0E-02 | 6.9E-04 | 2.5E-02 | 3 | -3.2E-02 |
| Atrazin | Maize grain | 0.990 | 0.990 | 0.557 | 24.5 | 130 | 4.0E-03 | 4.4E-03 | 6.4E-02 | 58 | -1.5E-02 | 1.8E-03 | 1.4E-01 | 13 | -2.0E-02 | 6.9E-04 | 2.5E-02 | 3 | -3.2E-02 |
| Atrazin | Maize grain wet | 0.990 | 0.990 | 0.800 | 18.6 | 105 | 5.2E-03 | 5.7E-03 | 5.8E-02 | 59 | -1.4E-02 | 3.7E-03 | 1.3E-01 | 13 | -2.0E-02 | 1.4E-03 | 2.2E-02 | 3 | -3.2E-02 |
| Atrazin | Maize plant | 0.990 | 0.990 | 0.678 | 3.6 | 120 | 5.0E-02 | 5.4E-02 | 9.6E-02 | 58 | -1.5E-02 | 4.3E-02 | 9.9E-01 | 0 | -2.0E-02 | 1.6E-02 | 2.8E-01 | 3 | -2.4E-02 |
| Benoxacor | Maize ear | 0.050 | 0.050 | 0.042 | 15.5 | 139 | 1.8E-04 | 2.0E-04 | 7.1E-03 | 34 | -2.1E-02 | 1.2E-06 | 7.5E-02 | 11 | -3.9E-02 | 8.0E-08 | 6.9E-03 | 2 | -8.1E-02 |
| Benoxacor | Maize grain | 0.050 | 0.050 | 0.008 | 12.5 | 142 | 1.7E-04 | 1.9E-04 | 7.2E-03 | 34 | -2.1E-02 | 9.0E-07 | 7.6E-02 | 11 | -3.9E-02 | 6.3E-08 | 7.0E-03 | 2 | -8.1E-02 |
| Benoxacor | Maize plant | 0.050 | 0.050 | 0.004 | 15.5 | 139 | 1.2E-03 | 1.3E-03 | 1.1E-02 | 34 | -2.1E-02 | 1.7E-04 | 1.0E+00 | 0 | -3.9E-02 | 1.2E-05 | 5.6E-02 | 2 | -6.3E-02 |

| Substance | Crop | Application rate | | Dose | Date | Time | hF | Soil | | | | Formulation deposit | | | | Air | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | min | max | per crop | treat. | | | $hF_s$ | $hF_{s,max}$ | $t_{s,max}$ | $\mu_{s,2}$ | $hF_{fd}$ | $hF_{fd,max}$ | $t_{fd,max}$ | $\mu_{fd,2}$ | $hF_a$ | $hF_{a,max}$ | $t_{a,max}$ | $\mu_{a,2}$ |
| | | kg/ha | kg/ha | kg/ha | | | kg/ kg | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days |
| Bentazone | pea spring | 0.957 | 1.914 | 0.132 | 4.5 | 72 | 1.8E-05 | 2.1E-05 | 2.3E-03 | 12 | -5.6E-02 | 4.0E-07 | 1.3E-02 | 8 | -1.1E-01 | 9.3E-07 | 1.8E-02 | 1 | -1.2E-01 |
| Bentazone | ley int | 0.957 | 1.392 | 0.053 | 1.5 | 20 | 4.0E-02 | 1.2E-02 | 1.5E-02 | 12 | -5.9E-02 | 6.3E-02 | 3.3E-01 | 8 | -1.1E-01 | 5.7E-03 | 5.3E-02 | 1 | -1.2E-01 |
| Bifenox | wheat winter | 0.750 | 0.900 | 0.044 | 22.3 | 115 | 1.3E-08 | 7.3E-09 | 4.7E-06 | 10 | -6.8E-02 | 2.1E-08 | 5.5E-04 | 7 | -1.4E-01 | 4.2E-08 | 8.4E-04 | 12 | -4.7E-02 |
| Bifenox | wheat spring | 0.600 | 0.750 | 0.200 | 26.4 | 80 | 3.2E-07 | 8.7E-08 | 5.3E-06 | 10 | -6.8E-02 | 1.0E-06 | 7.0E-04 | 7 | -1.4E-01 | 1.9E-06 | 1.1E-03 | 12 | -4.7E-02 |
| Bromoxynil phenol | wheat winter | 0.240 | 0.480 | 0.041 | 23.3 | 114 | 5.3E-16 | 6.9E-16 | 5.7E-04 | 3 | -2.5E-01 | 3.5E-26 | 7.5E-03 | 3 | -1.6E-01 | 4.6E-26 | 9.4E-03 | 5 | -6.4E-02 |
| Bromoxynil phenol | Maize grain | 0.360 | 0.480 | 0.003 | 30.5 | 124 | 8.4E-17 | 9.4E-17 | 1.0E-03 | 3 | -2.5E-01 | 4.0E-28 | 1.4E-02 | 3 | -1.6E-01 | 5.5E-28 | 1.8E-02 | 5 | -6.4E-02 |
| Bromoxynil phenol | Maize plant | 0.360 | 0.480 | 0.009 | 11.6 | 112 | 3.6E-15 | 4.1E-15 | 1.5E-03 | 3 | -2.5E-01 | 1.6E-24 | 9.8E-01 | 0 | -4.9E-01 | 2.2E-24 | 5.4E-01 | 1 | -4.9E-01 |
| Bromoxynil phenol | barley winter | 0.240 | 0.480 | 0.019 | 15.3 | 108 | 3.1E-15 | 4.5E-15 | 1.0E-03 | 3 | -2.5E-01 | 6.9E-25 | 1.4E-02 | 3 | -1.6E-01 | 9.2E-25 | 1.7E-02 | 5 | -6.6E-02 |
| Carbetamide | Rape winter | 2.000 | 2.000 | 0.059 | 6.3 | 117 | 3.1E-06 | 5.3E-06 | 5.0E-04 | 23 | -3.0E-02 | 2.2E-08 | 2.0E-04 | 11 | -5.9E-02 | 2.6E-06 | 1.8E-02 | 1 | -5.9E-02 |
| Carbetamide | pea spring | 1.250 | 1.500 | 0.563 | 4.5 | 72 | 1.4E-05 | 9.6E-06 | 1.7E-04 | 23 | -3.0E-02 | 4.9E-07 | 1.1E-03 | 11 | -5.9E-02 | 6.0E-05 | 2.0E-02 | 1 | -6.0E-02 |
| Carfentrazone-ethyl | wheat spring | 0.020 | 0.020 | 0.007 | 2.5 | 74 | 3.4E-04 | 4.0E-04 | 1.4E-02 | 14 | -5.1E-02 | 5.9E-05 | 9.5E-03 | 9 | -9.2E-02 | 5.4E-05 | 7.4E-03 | 7 | -9.5E-02 |
| Carfentrazone-ethyl | potato | 0.060 | 0.060 | 0.022 | 19.8 | 13 | 1.3E-02 | 2.3E-02 | 3.4E-02 | 14 | -5.3E-02 | 1.1E-02 | 1.1E-02 | 9 | -9.2E-02 | 9.9E-03 | 8.8E-03 | 7 | -9.4E-02 |
| Chloridazone | beet forage | 1.300 | 1.300 | 0.528 | 8.5 | 160 | 6.8E-06 | 7.6E-06 | 2.2E-02 | 17 | -4.3E-02 | 2.2E-24 | 1.0E+00 | 0 | -7.9E-02 | 1.3E-26 | 3.3E-03 | 0 | -1.7E+00 |
| Chloridazone | beet sugar | 1.300 | 1.300 | 0.491 | 1.5 | 167 | 4.4E-06 | 4.9E-06 | 2.2E-02 | 17 | -4.3E-02 | 2.5E-24 | 1.0E-01 | 8 | -7.9E-02 | 5.5E-28 | 8.8E-03 | 1 | -5.1E-01 |
| Chlortoluron | wheat winter | 1.200 | 2.800 | 0.065 | 9.11 | 136 | 1.9E-04 | 2.8E-04 | 1.4E-01 | 16 | -4.2E-02 | 1.9E-04 | 2.2E-02 | 12 | -4.2E-02 | 1.9E-04 | 3.2E-03 | 2 | -5.6E-02 |
| Chlortoluron | barley winter | 1.200 | 2.800 | 0.240 | 21.10 | 122 | 3.5E-04 | 1.1E-03 | 9.9E-02 | 24 | -4.0E-02 | 3.5E-04 | 3.8E-02 | 12 | -4.2E-02 | 3.5E-04 | 5.5E-03 | 2 | -6.1E-02 |
| Chlortoluron | rye winter | 1.200 | 2.800 | 1.500 | 11.10 | 122 | 3.5E-04 | 5.1E-04 | 2.3E-01 | 16 | -4.2E-02 | 3.6E-04 | 3.9E-02 | 12 | -4.2E-02 | 3.5E-04 | 5.7E-03 | 2 | -5.7E-02 |
| Clodinafop-propargyl | wheat winter | 0.060 | 0.084 | 0.003 | 30.3 | 107 | 2.1E-07 | 2.7E-07 | 1.4E-04 | 10 | -6.9E-02 | 1.7E-08 | 2.3E-03 | 7 | -1.4E-01 | 9.7E-09 | 6.7E-04 | 2 | -1.4E-01 |
| Clodinafop-propargyl | rye winter | 0.060 | 0.084 | 0.015 | 2.4 | 90 | 1.0E-06 | 1.3E-06 | 2.5E-04 | 10 | -6.9E-02 | 2.0E-07 | 4.0E-03 | 7 | -1.4E-01 | 1.1E-07 | 1.1E-03 | 2 | -1.4E-01 |
| Clomazone | Rape winter | 0.090 | 0.120 | 0.090 | 29.8 | 122 | 2.9E-07 | 7.3E-05 | 2.6E-03 | 30 | -2.4E-02 | 1.6E-11 | 3.2E-02 | 11 | -4.6E-02 | 1.2E-11 | 5.8E-03 | 2 | -1.8E-01 |
| Clopyralid | beet sugar | 0.100 | 0.120 | 0.017 | 30.5 | 138 | 1.9E-08 | 4.0E-09 | 4.7E-05 | 12 | -5.5E-02 | 1.0E-11 | 7.0E-03 | 8 | -1.1E-01 | 1.6E-07 | 2.6E-01 | 12 | -6.2E-02 |
| Cloquintocet-mexyl | wheat winter | 0.012 | 0.021 | 0.001 | 30.3 | 107 | 1.0E-20 | 1.4E-20 | 8.1E-08 | 2 | -2.9E-01 | 8.3E-30 | 4.6E-05 | 3 | -1.4E-01 | 5.7E-30 | 2.0E-05 | 1 | -5.8E-01 |
| Cloquintocet-mexyl | rye winter | 0.012 | 0.021 | 0.004 | 2.4 | 90 | 2.0E-18 | 2.8E-18 | 1.4E-07 | 2 | -2.9E-01 | 1.6E-25 | 7.8E-05 | 3 | -1.4E-01 | 1.1E-25 | 3.3E-05 | 1 | -5.8E-01 |
| Desmedipham | beet forage | 0.068 | 0.136 | 0.013 | 18.5 | 150 | 2.5E-04 | 2.7E-04 | 7.9E-03 | 23 | -3.1E-02 | 1.1E-04 | 1.0E+00 | 0 | -6.0E-02 | 4.4E-05 | 3.3E-01 | 1 | -6.0E-02 |
| Desmedipham | beet sugar | 0.068 | 0.136 | 0.026 | 3.5 | 165 | 6.7E-05 | 7.4E-05 | 8.7E-03 | 23 | -3.1E-02 | 3.2E-06 | 1.2E-02 | 10 | -6.0E-02 | 1.2E-06 | 1.3E-03 | 2 | -6.0E-02 |
| Dicamba | wheat winter | 0.119 | 0.119 | 0.002 | 31.5 | 45 | 9.7E-05 | 1.7E-04 | 1.5E-02 | 8 | -9.2E-02 | 3.7E-05 | 2.2E-02 | 6 | -1.6E-01 | 4.9E-05 | 9.5E-02 | 5 | -1.6E-01 |
| Dicamba | Maize ear | 0.288 | 0.360 | 0.032 | 9.6 | 114 | 2.7E-07 | 3.1E-07 | 2.9E-02 | 8 | -9.3E-02 | 3.0E-09 | 1.8E-01 | 4 | -1.6E-01 | 1.5E-09 | 2.1E-01 | 4 | -1.6E-01 |
| Dicamba | Maize grain | 0.288 | 0.360 | 0.021 | 2.6 | 121 | 1.4E-07 | 1.5E-07 | 3.0E-02 | 8 | -9.3E-02 | 1.1E-09 | 1.9E-01 | 4 | -1.6E-01 | 5.0E-10 | 2.1E-01 | 4 | -1.6E-01 |
| Dicamba | Maize grain wet | 0.288 | 0.360 | 0.170 | 18.6 | 105 | 6.7E-07 | 7.7E-07 | 2.8E-02 | 8 | -9.2E-02 | 1.1E-08 | 1.6E-01 | 5 | -1.6E-01 | 6.1E-09 | 2.0E-01 | 4 | -1.6E-01 |
| Dicamba | Maize plant | 0.288 | 0.360 | 0.055 | 3.6 | 120 | 1.4E-06 | 1.5E-06 | 4.7E-02 | 8 | -9.4E-02 | 2.8E-08 | 7.0E-01 | 2 | -1.6E-01 | 6.7E-09 | 7.2E-01 | 2 | -1.6E-01 |
| Dicamba | meadow mid int | 0.014 | 0.027 | 0.003 | 1.5 | 20 | 5.4E-02 | 5.1E-02 | 1.2E-01 | 7 | -1.2E-01 | 5.9E-02 | 4.2E-01 | 6 | -1.6E-01 | 4.4E-02 | 7.7E-01 | 1 | -1.6E-01 |
| Dicamba | ley int | 0.014 | 0.027 | 0.002 | 1.5 | 20 | 5.4E-02 | 5.1E-02 | 1.2E-01 | 7 | -1.2E-01 | 5.9E-02 | 4.2E-01 | 6 | -1.6E-01 | 4.4E-02 | 7.7E-01 | 1 | -1.6E-01 |

| Substance | Crop | Application rate | | Dose | Date | Time | hF | Soil | | | | Formulation deposit | | | | Air | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | min | max | per crop | treat. | | | $hF_s$ | $hF_{s,max}$ | $t_{s,max}$ | $\mu_{s,2}$ | $hF_{fd}$ | $hF_{fd,max}$ | $t_{fd,max}$ | $\mu_{fd,2}$ | $hF_a$ | $hF_{a,max}$ | $t_{a,max}$ | $\mu_{a,2}$ |
| | | kg/ha | kg/ha | kg/ha | | | kg/ kg | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days |
| Diflufenican | oat spring | 0.038 | 0.063 | 0.043 | 5.5 | 88 | 5.0E-04 | 7.2E-05 | 9.0E-05 | 156 | -4.4E-03 | 3.4E-03 | 5.8E-04 | 21 | -8.9E-03 | 2.3E-03 | 5.7E-04 | 20 | -1.0E-02 |
| Diflufenican | wheat winter | 0.050 | 0.075 | 0.034 | 26.3 | 111 | 6.9E-04 | 7.0E-05 | 8.2E-05 | 156 | -4.5E-03 | 2.9E-03 | 5.0E-04 | 21 | -8.9E-03 | 2.0E-03 | 4.9E-04 | 21 | -9.9E-03 |
| Diflufenican | barley winter | 0.050 | 0.075 | 0.052 | 14.3 | 109 | 1.5E-03 | 1.2E-04 | 1.5E-04 | 156 | -4.5E-03 | 5.1E-03 | 9.3E-04 | 21 | -8.9E-03 | 3.6E-03 | 9.1E-04 | 20 | -1.0E-02 |
| Diflufenican | rye winter | 0.050 | 0.075 | 0.081 | 1.4 | 91 | 1.3E-03 | 1.1E-04 | 1.4E-04 | 156 | -4.5E-03 | 4.7E-03 | 8.2E-04 | 21 | -8.9E-03 | 3.2E-03 | 8.1E-04 | 20 | -1.0E-02 |
| Dimefuron | Rape winter | 1.000 | 1.000 | 0.029 | 6.3 | 117 | 5.9E-03 | 6.1E-03 | 6.6E-02 | 72 | -1.3E-02 | 3.6E-03 | 8.3E-02 | 15 | -1.5E-02 | 6.8E-03 | 7.6E-02 | 13 | -1.5E-02 |
| Dimefuron | pea spring | 0.625 | 0.750 | 0.281 | 4.5 | 72 | 8.4E-03 | 4.5E-03 | 2.5E-02 | 85 | -8.9E-03 | 1.3E-02 | 1.0E-01 | 15 | -1.5E-02 | 2.6E-02 | 8.8E-02 | 13 | -1.5E-02 |
| Dimethenamid | Maize ear | 1.080 | 1.440 | 0.543 | 17.5 | 137 | 1.2E-05 | 1.4E-05 | 6.0E-03 | 19 | -3.7E-02 | 3.4E-12 | 1.4E-01 | 8 | -7.1E-02 | 1.1E-13 | 1.1E-02 | 1 | -1.8E-01 |
| Dimethenamid | Maize grain | 1.080 | 1.440 | 0.155 | 14.5 | 140 | 1.1E-05 | 1.2E-05 | 6.1E-03 | 19 | -3.7E-02 | 1.9E-12 | 1.4E-01 | 8 | -7.1E-02 | 6.1E-14 | 1.1E-02 | 1 | -1.8E-01 |
| Dimethenamid | Maize plant | 1.080 | 1.440 | 0.154 | 18.6 | 105 | 2.5E-04 | 2.8E-04 | 8.2E-03 | 19 | -3.7E-02 | 1.2E-06 | 9.1E-01 | 1 | -7.1E-02 | 6.8E-08 | 4.0E-02 | 1 | -1.3E-01 |
| Dimethenamid | soybean | 1.080 | 1.440 | 0.113 | 5.5 | 133 | 4.6E-06 | 5.1E-06 | 2.4E-03 | 19 | -3.6E-02 | 4.6E-16 | 1.6E-01 | 7 | -7.1E-02 | 3.0E-24 | 1.1E-02 | 1 | -3.1E-01 |
| Diquat | potato | 1.600 | 1.600 | 0.067 | 19.8 | 13 | 1.1E-03 | 2.2E-11 | 1.4E-10 | 8 | -8.7E-02 | 1.5E-08 | 3.0E-07 | 6 | -1.4E-01 | 1.1E-02 | 1.5E-01 | 5 | -1.7E-01 |
| Ethofumesate | beet forage | 0.768 | 0.896 | 0.311 | 11.5 | 157 | 5.3E-02 | 5.8E-02 | 8.6E-02 | 114 | -7.3E-03 | 6.4E-02 | 1.0E+00 | 0 | -1.0E-02 | 1.2E-02 | 1.4E-01 | 2 | -1.6E-02 |
| Ethofumesate | beet sugar | 0.768 | 0.896 | 0.506 | 3.5 | 165 | 6.5E-03 | 7.1E-03 | 8.9E-02 | 113 | -7.4E-03 | 4.5E-03 | 7.2E-02 | 19 | -1.0E-02 | 8.6E-04 | 5.6E-03 | 2 | -1.6E-02 |
| Fluazifop-P-Butyl | beet forage | 0.188 | 0.375 | 0.042 | 3.6 | 134 | 2.4E-06 | 7.8E-07 | 2.5E-05 | 19 | -3.6E-02 | 5.2E-05 | 1.0E+00 | 0 | -7.2E-02 | 1.3E-05 | 2.1E-01 | 2 | -7.4E-02 |
| Fluazifop-P-Butyl | beet sugar | 0.188 | 0.375 | 0.022 | 20.5 | 148 | 4.2E-07 | 4.5E-07 | 2.6E-05 | 19 | -3.6E-02 | 6.4E-07 | 9.6E-04 | 10 | -7.2E-02 | 1.6E-07 | 1.9E-04 | 2 | -7.3E-02 |
| Fluazifop-P-Butyl | Rape winter | 0.188 | 0.375 | 0.011 | 18.3 | 105 | 5.7E-06 | 2.1E-06 | 2.8E-05 | 19 | -3.6E-02 | 1.0E-05 | 1.0E-03 | 10 | -7.2E-02 | 3.1E-06 | 2.0E-04 | 2 | -7.4E-02 |
| Fluazifop-P-Butyl | sunflower | 0.188 | 0.375 | 0.074 | 19.5 | 119 | 3.5E-07 | 2.7E-07 | 5.5E-06 | 19 | -3.6E-02 | 2.7E-06 | 7.6E-04 | 10 | -7.2E-02 | 6.8E-07 | 1.5E-04 | 2 | -7.5E-02 |
| Fluroxypyr | oat winter | 0.104 | 0.130 | 0.130 | 2.5 | 74 | 5.4E-03 | 4.6E-03 | 4.6E-02 | 42 | -2.0E-02 | 5.4E-03 | 1.3E-01 | 11 | -2.9E-02 | 6.1E-03 | 8.8E-02 | 8 | -2.9E-02 |
| Fluroxypyr | wheat winter | 0.104 | 0.130 | 0.034 | 19.4 | 87 | 3.8E-03 | 3.7E-03 | 3.0E-02 | 42 | -2.0E-02 | 3.4E-03 | 9.0E-02 | 11 | -2.9E-02 | 3.9E-03 | 5.9E-02 | 8 | -2.9E-02 |
| Fluroxypyr | barley winter | 0.104 | 0.130 | 0.023 | 17.3 | 106 | 3.1E-03 | 3.3E-03 | 5.7E-02 | 40 | -2.1E-02 | 2.1E-03 | 1.7E-01 | 10 | -2.9E-02 | 2.4E-03 | 1.2E-01 | 7 | -2.9E-02 |
| Haloxyfop-(R)-Methylester | beet sugar | 0.032 | 0.162 | 0.005 | 25.5 | 143 | 1.2E-04 | 8.6E-05 | 1.8E-04 | 60 | -1.2E-02 | 1.3E-03 | 2.1E-03 | 15 | -2.3E-02 | 4.1E-04 | 4.3E-04 | 4 | -2.5E-02 |
| Haloxyfop-(R)-Methylester | Rape winter | 0.032 | 0.162 | 0.001 | 23.9 | 122 | 4.7E-04 | 1.5E-05 | 2.4E-05 | 60 | -1.2E-02 | 4.7E-04 | 9.4E-04 | 15 | -2.3E-02 | 4.2E-04 | 2.0E-04 | 4 | -2.7E-02 |
| Ioxynil | oat spring | 0.213 | 0.355 | 0.328 | 5.5 | 88 | 8.2E-05 | 9.9E-06 | 1.9E-03 | 10 | -7.0E-02 | 7.4E-05 | 1.3E-01 | 5 | -1.4E-01 | 5.5E-04 | 6.5E-02 | 7 | -2.8E-02 |
| Ioxynil | wheat winter | 0.213 | 0.355 | 0.129 | 26.3 | 111 | 3.7E-05 | 5.2E-06 | 1.7E-03 | 10 | -7.1E-02 | 2.8E-05 | 6.9E-02 | 5 | -1.4E-01 | 2.0E-04 | 4.6E-02 | 7 | -3.0E-02 |
| Ioxynil | wheat spring | 0.213 | 0.284 | 0.061 | 26.4 | 80 | 1.1E-04 | 1.4E-05 | 2.0E-03 | 10 | -7.0E-02 | 1.0E-04 | 1.4E-01 | 5 | -1.4E-01 | 7.7E-04 | 6.4E-02 | 7 | -2.7E-02 |
| Ioxynil | Maize grain | 0.210 | 0.280 | 0.005 | 30.5 | 124 | 3.1E-05 | 5.6E-06 | 3.1E-03 | 10 | -7.1E-02 | 3.0E-05 | 2.1E-01 | 4 | -1.4E-01 | 2.3E-04 | 8.1E-02 | 7 | -2.9E-02 |
| Ioxynil | Maize plant | 0.210 | 0.280 | 0.004 | 2.6 | 121 | 1.7E-04 | 3.7E-05 | 4.9E-03 | 10 | -7.1E-02 | 1.5E-04 | 7.9E-01 | 2 | -1.4E-01 | 1.3E-03 | 1.9E-01 | 7 | -4.5E-02 |
| Ioxynil | barley winter | 0.213 | 0.355 | 0.101 | 9.3 | 114 | 4.3E-05 | 6.7E-06 | 3.3E-03 | 10 | -7.1E-02 | 3.1E-05 | 1.0E-01 | 6 | -1.4E-01 | 2.1E-04 | 7.3E-02 | 6 | -3.0E-02 |
| Ioxynil | rye winter | 0.212 | 0.276 | 0.282 | 29.3 | 94 | 8.1E-05 | 1.2E-05 | 3.0E-03 | 10 | -7.1E-02 | 6.0E-05 | 1.0E-01 | 6 | -1.4E-01 | 4.2E-04 | 7.2E-02 | 7 | -3.0E-02 |
| Isoproturon | wheat winter | 1.245 | 1.494 | 0.820 | 21.3 | 116 | 8.8E-05 | 1.1E-04 | 9.5E-03 | 19 | -3.9E-02 | 1.5E-05 | 4.3E-02 | 9 | -7.0E-02 | 1.4E-05 | 2.1E-02 | 5 | -7.1E-02 |
| Isoproturon | barley winter | 1.245 | 1.494 | 0.821 | 14.3 | 109 | 1.2E-04 | 1.7E-04 | 1.7E-02 | 19 | -3.9E-02 | 2.6E-05 | 7.6E-02 | 9 | -7.0E-02 | 2.4E-05 | 3.7E-02 | 5 | -7.1E-02 |
| Isoproturon | rye winter | 0.570 | 0.684 | 1.085 | 27.3 | 96 | 2.2E-04 | 2.7E-04 | 1.6E-02 | 19 | -3.9E-02 | 6.4E-05 | 7.0E-02 | 9 | -7.0E-02 | 5.9E-05 | 3.4E-02 | 5 | -7.1E-02 |

| Substance | Crop | Application rate | | Dose | Date | Time | hF | Soil | | | | Formulation deposit | | | | Air | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | min | max | per crop | treat. | | | $hF_s$ | $hF_{s,max}$ | $t_{s,max}$ | $\mu_{s,2}$ | $hF_{fd}$ | $hF_{fd,max}$ | $t_{fd,max}$ | $\mu_{fd,2}$ | $hF_a$ | $hF_{a,max}$ | $t_{a,max}$ | $\mu_{a,2}$ |
| | | kg/ha | kg/ha | kg/ha | | | kg/ kg | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days |
| Linuron | Maize ear | 0.330 | 0.440 | 0.043 | 1.2 | 243 | 1.5E-04 | 1.7E-04 | 1.3E-02 | 46 | -1.6E-02 | 3.0E-05 | 1.1E-01 | 12 | -2.9E-02 | 1.8E-05 | 4.5E-02 | 6 | -3.7E-02 |
| Linuron | Maize plant | 0.330 | 0.440 | 0.006 | 5.5 | 149 | 3.2E-03 | 2.9E-03 | 8.4E-03 | 47 | -1.5E-02 | 9.3E-03 | 1.0E+00 | 0 | -2.9E-02 | 5.6E-03 | 4.9E-01 | 4 | -3.1E-02 |
| Linuron | soybean | 0.330 | 0.440 | 0.241 | 6.5 | 132 | 1.9E-04 | 1.8E-04 | 2.0E-03 | 47 | -1.5E-02 | 4.8E-04 | 5.4E-02 | 13 | -2.9E-02 | 2.9E-04 | 2.0E-02 | 5 | -5.1E-02 |
| Linuron | sunflower | 0.330 | 0.440 | 0.171 | 21.4 | 147 | 1.3E-04 | 1.2E-04 | 1.8E-03 | 47 | -1.5E-02 | 2.6E-04 | 2.8E-02 | 13 | -2.9E-02 | 1.5E-04 | 1.1E-02 | 6 | -4.2E-02 |
| MCPA | oat winter | 0.660 | 1.485 | 0.800 | 2.5 | 74 | 1.0E-06 | 1.7E-06 | 1.8E-02 | 7 | -1.1E-01 | 2.1E-07 | 5.5E-02 | 5 | -1.9E-01 | 9.3E-09 | 5.9E-02 | 3 | -2.0E-01 |
| MCPA | wheat winter | 0.660 | 1.485 | 0.068 | 25.4 | 81 | 4.2E-07 | 6.7E-07 | 1.2E-02 | 7 | -1.1E-01 | 6.5E-08 | 3.8E-02 | 5 | -1.9E-01 | 2.2E-09 | 3.8E-02 | 3 | -2.0E-01 |
| MCPA | barley winter | 0.660 | 1.485 | 0.200 | 17.3 | 106 | 2.2E-08 | 3.2E-08 | 2.3E-02 | 7 | -1.2E-01 | 1.3E-09 | 7.3E-02 | 5 | -2.0E-01 | 1.4E-11 | 6.8E-02 | 3 | -2.0E-01 |
| MCPA | potato | 0.164 | 0.164 | 0.006 | 14.8 | 18 | 2.4E-03 | 2.6E-03 | 3.5E-02 | 7 | -1.1E-01 | 1.8E-03 | 6.5E-02 | 5 | -1.7E-01 | 1.4E-03 | 8.9E-02 | 3 | -2.0E-01 |
| MCPA | meadow mid int | 0.660 | 1.485 | 0.085 | 1.5 | 20 | 3.4E-02 | 2.5E-02 | 9.3E-02 | 6 | -1.4E-01 | 5.1E-02 | 4.7E-01 | 5 | -1.8E-01 | 8.3E-03 | 2.4E-01 | 2 | -2.0E-01 |
| MCPA | ley int | 0.660 | 1.485 | 0.015 | 1.5 | 20 | 3.4E-02 | 2.5E-02 | 9.3E-02 | 6 | -1.4E-01 | 5.1E-02 | 4.7E-01 | 5 | -1.8E-01 | 8.3E-03 | 2.4E-01 | 2 | -2.0E-01 |
| MCPB | meadow mid int | 2.000 | 2.399 | 0.572 | 1.5 | 20 | 3.5E-02 | 3.8E-03 | 5.4E-03 | 10 | -7.1E-02 | 5.4E-02 | 8.6E-01 | 1 | -1.4E-01 | 3.1E-02 | 4.1E-01 | 2 | -1.5E-01 |
| MCPB | ley int | 1.600 | 2.399 | 0.429 | 1.5 | 20 | 3.5E-02 | 3.8E-03 | 5.4E-03 | 10 | -7.1E-02 | 5.4E-02 | 8.6E-01 | 1 | -1.4E-01 | 3.1E-02 | 4.1E-01 | 2 | -1.5E-01 |
| MCPP | wheat winter | 1.400 | 1.600 | 0.075 | 22.3 | 115 | 2.0E-07 | 2.6E-07 | 6.7E-03 | 9 | -7.8E-02 | 1.3E-10 | 8.0E-02 | 5 | -1.5E-01 | 1.3E-13 | 2.2E-02 | 2 | -2.3E-01 |
| MCPP | barley winter | 1.400 | 1.600 | 0.068 | 17.3 | 106 | 3.9E-07 | 5.7E-07 | 1.2E-02 | 9 | -7.9E-02 | 5.0E-10 | 1.1E-01 | 5 | -1.5E-01 | 4.8E-13 | 3.6E-02 | 2 | -2.4E-01 |
| MCPP | rye winter | 1.400 | 1.600 | 0.228 | 27.3 | 96 | 9.7E-07 | 1.3E-06 | 1.1E-02 | 9 | -7.9E-02 | 3.0E-09 | 1.2E-01 | 5 | -1.5E-01 | 5.9E-12 | 3.5E-02 | 2 | -2.3E-01 |
| MCPP-P | oat spring | 0.520 | 0.650 | 0.410 | 5.5 | 88 | 9.8E-06 | 1.2E-05 | 1.2E-02 | 11 | -6.8E-02 | 1.3E-07 | 6.4E-02 | 7 | -1.3E-01 | 1.5E-07 | 4.4E-02 | 3 | -1.3E-01 |
| MCPP-P | wheat winter | 0.650 | 0.780 | 0.114 | 3.4 | 103 | 2.9E-06 | 4.0E-06 | 1.0E-02 | 10 | -7.0E-02 | 2.1E-08 | 2.0E-02 | 7 | -1.3E-01 | 2.2E-08 | 3.2E-02 | 3 | -1.3E-01 |
| MCPP-P | wheat spring | 0.520 | 0.650 | 0.222 | 22.4 | 84 | 1.3E-05 | 1.6E-05 | 1.2E-02 | 11 | -6.9E-02 | 2.1E-07 | 7.7E-02 | 6 | -1.3E-01 | 2.4E-07 | 4.7E-02 | 3 | -1.3E-01 |
| MCPP-P | barley winter | 0.650 | 0.780 | 0.067 | 9.3 | 114 | 1.3E-06 | 1.9E-06 | 2.0E-02 | 10 | -7.2E-02 | 5.5E-09 | 3.0E-02 | 7 | -1.3E-01 | 5.4E-09 | 5.6E-02 | 3 | -1.3E-01 |
| MCPP-P | rye winter | 0.650 | 0.780 | 0.527 | 1.4 | 91 | 7.7E-06 | 1.1E-05 | 1.8E-02 | 10 | -7.1E-02 | 9.7E-08 | 3.0E-02 | 7 | -1.3E-01 | 1.1E-07 | 5.3E-02 | 3 | -1.3E-01 |
| Metamitron | beet forage | 3.500 | 3.500 | 0.956 | 11.5 | 157 | 1.6E-03 | 1.8E-03 | 2.3E-02 | 37 | -2.0E-02 | 9.5E-06 | 9.5E-01 | 1 | -3.6E-02 | 7.7E-06 | 1.1E-01 | 3 | -6.5E-02 |
| Metamitron | beet sugar | 3.500 | 3.500 | 1.531 | 18.4 | 180 | 1.1E-04 | 1.2E-04 | 2.5E-02 | 37 | -2.0E-02 | 2.9E-07 | 3.5E-01 | 9 | -3.6E-02 | 2.5E-07 | 5.7E-02 | 3 | -6.2E-02 |
| Metazachlor | Rape winter | 0.500 | 1.500 | 0.080 | 4.9 | 122 | 7.0E-13 | 2.8E-10 | 1.6E-03 | 5 | -1.3E-01 | 2.6E-16 | 2.8E-02 | 5 | -1.7E-01 | 1.9E-16 | 5.0E-03 | 1 | -3.4E-01 |
| Metolachlor | Maize ear | 1.600 | 1.600 | 1.020 | 24.5 | 130 | 7.5E-04 | 8.4E-04 | 2.6E-02 | 30 | -2.5E-02 | 9.0E-05 | 4.9E-02 | 11 | -4.3E-02 | 1.3E-05 | 3.7E-03 | 1 | -5.3E-02 |
| Metolachlor | Maize grain | 1.600 | 1.600 | 0.254 | 12.5 | 142 | 5.6E-04 | 6.2E-04 | 2.7E-02 | 30 | -2.5E-02 | 4.8E-05 | 5.2E-02 | 11 | -4.3E-02 | 6.7E-06 | 4.0E-03 | 1 | -5.4E-02 |
| Metolachlor | Maize plant | 1.600 | 1.600 | 0.142 | 28.5 | 126 | 5.3E-03 | 5.9E-03 | 3.9E-02 | 30 | -2.5E-02 | 2.1E-03 | 9.9E-01 | 0 | -4.3E-02 | 2.9E-04 | 1.1E-01 | 1 | -4.8E-02 |
| Metribuzin | potato | 0.350 | 0.525 | 0.218 | 5.5 | 119 | 2.1E-02 | 2.3E-02 | 3.2E-01 | 57 | -1.4E-02 | 7.3E-03 | 4.0E-01 | 12 | -1.4E-02 | 9.9E-03 | 7.5E-02 | 3 | -1.5E-02 |
| Metribuzin | pea spring | 0.201 | 0.268 | 0.071 | 28.2 | 138 | 1.3E-02 | 1.4E-02 | 1.7E-01 | 65 | -1.4E-02 | 4.3E-03 | 3.5E-01 | 10 | -1.4E-02 | 5.8E-03 | 7.6E-02 | 3 | -1.6E-02 |
| Metribuzin | soybean | 0.268 | 0.268 | 0.033 | 5.5 | 133 | 9.3E-03 | 9.7E-03 | 1.0E-01 | 77 | -1.2E-02 | 4.1E-03 | 3.4E-01 | 10 | -1.4E-02 | 5.5E-03 | 7.3E-02 | 3 | -1.8E-02 |
| Metsulfuron-methyl | oat spring | 0.005 | 0.005 | 0.004 | 5.5 | 88 | 1.6E-05 | 7.8E-06 | 4.6E-04 | 20 | -3.5E-02 | 9.3E-09 | 1.6E-04 | 10 | -6.9E-02 | 9.4E-05 | 1.0E-01 | 4 | -6.9E-02 |
| Metsulfuron-methyl | wheat winter | 0.005 | 0.005 | 0.002 | 5.4 | 101 | 7.9E-06 | 5.9E-06 | 4.0E-04 | 20 | -3.5E-02 | 3.8E-09 | 3.7E-05 | 10 | -6.9E-02 | 3.7E-05 | 7.6E-02 | 3 | -6.9E-02 |
| Metsulfuron-methyl | wheat spring | 0.005 | 0.005 | 0.003 | 29.4 | 77 | 3.0E-05 | 1.2E-05 | 4.7E-04 | 20 | -3.5E-02 | 2.0E-08 | 1.6E-04 | 10 | -6.9E-02 | 2.0E-04 | 1.1E-01 | 4 | -6.9E-02 |

| Substance | Crop | Application rate | | Dose | Date | Time | hF | Soil | | | | Formulation deposit | | | | Air | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | min | max | per crop | treat. | | | $hF_s$ | $hF_{s,max}$ | $t_{s,max}$ | $\mu_{s,2}$ | $hF_{fd}$ | $hF_{fd,max}$ | $t_{fd,max}$ | $\mu_{fd,2}$ | $hF_a$ | $hF_{a,max}$ | $t_{a,max}$ | $\mu_{a,2}$ |
| | | kg/ha | kg/ha | kg/ha | | | kg/ kg | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days |
| Metsulfuron-methyl | barley winter | 0.005 | 0.005 | 0.000 | 22.3 | 101 | 8.7E-06 | 7.3E-06 | 7.5E-04 | 20 | -3.5E-02 | 4.1E-09 | 4.6E-05 | 10 | -6.9E-02 | 3.9E-05 | 1.3E-01 | 3 | -6.9E-02 |
| Metsulfuron-methyl | barley spring | 0.005 | 0.005 | 0.004 | 10.6 | 35 | 4.1E-04 | 4.4E-05 | 4.6E-04 | 20 | -3.5E-02 | 3.9E-07 | 3.3E-05 | 10 | -6.9E-02 | 3.9E-03 | 9.6E-02 | 4 | -6.9E-02 |
| Monolinuron | soybean | 0.190 | 0.285 | 0.041 | 5.5 | 133 | 6.7E-04 | 7.5E-04 | 2.5E-02 | 44 | -1.7E-02 | 4.2E-05 | 1.9E-01 | 10 | -2.9E-02 | 1.9E-05 | 5.3E-02 | 4 | -7.1E-02 |
| Monolinuron | sunflower | 0.190 | 0.285 | 0.114 | 21.4 | 147 | 4.4E-04 | 4.9E-04 | 2.3E-02 | 43 | -1.8E-02 | 5.0E-05 | 1.1E-01 | 11 | -2.9E-02 | 2.4E-05 | 3.1E-02 | 4 | -5.4E-02 |
| Napropamid | Rape winter | 1.350 | 1.350 | 0.584 | 27.8 | 122 | 1.1E-03 | 2.0E-04 | 7.6E-04 | 55 | -1.3E-02 | 1.1E-03 | 7.6E-03 | 15 | -2.5E-02 | 7.4E-04 | 1.9E-04 | 1 | -3.8E-02 |
| Nicosulfuron | Maize ear | 0.040 | 0.060 | 0.006 | 9.6 | 114 | 4.2E-08 | 4.2E-08 | 3.8E-04 | 10 | -6.9E-02 | 3.8E-12 | 2.3E-04 | 7 | -1.4E-01 | 1.2E-08 | 2.1E-01 | 4 | -1.4E-01 |
| Nicosulfuron | Maize grain | 0.040 | 0.060 | 0.007 | 28.5 | 126 | 1.8E-08 | 1.8E-08 | 4.0E-04 | 10 | -6.9E-02 | 7.9E-13 | 3.7E-04 | 7 | -1.4E-01 | 2.2E-09 | 2.2E-01 | 4 | -1.4E-01 |
| Nicosulfuron | Maize plant | 0.040 | 0.060 | 0.004 | 11.6 | 112 | 4.9E-07 | 4.9E-07 | 6.0E-04 | 10 | -6.9E-02 | 1.8E-07 | 3.7E-01 | 7 | -1.4E-01 | 1.8E-07 | 6.7E-01 | 2 | -1.4E-01 |
| Orbencarb | potato | 3.214 | 4.017 | 1.321 | 2.5 | 122 | 9.9E-05 | 1.0E-05 | 1.3E-05 | 75 | -9.2E-03 | 2.6E-03 | 1.6E-03 | 17 | -1.8E-02 | 4.9E-04 | 2.7E-04 | 4 | -2.0E-02 |
| Orbencarb | pea spring | 2.410 | 3.214 | 0.574 | 28.2 | 138 | 3.9E-05 | 4.2E-06 | 6.1E-06 | 75 | -9.2E-03 | 1.6E-03 | 1.8E-03 | 17 | -1.8E-02 | 2.9E-04 | 2.9E-04 | 4 | -2.1E-02 |
| Orbencarb | soybean | 3.214 | 3.214 | 0.269 | 5.5 | 133 | 2.8E-05 | 2.2E-06 | 3.1E-06 | 75 | -9.2E-03 | 1.1E-03 | 1.7E-03 | 17 | -1.8E-02 | 2.1E-04 | 2.8E-04 | 4 | -2.1E-02 |
| Pendimethaline | wheat winter | 1.200 | 1.600 | 0.043 | 9.11 | 136 | 7.5E-05 | 2.9E-05 | 9.6E-05 | 67 | -1.0E-02 | 7.5E-05 | 9.7E-05 | 16 | -2.1E-02 | 7.3E-05 | 1.3E-05 | 3 | -2.1E-02 |
| Pendimethaline | Maize ear | 1.200 | 2.000 | 0.369 | 1.2 | 243 | 2.8E-06 | 3.0E-06 | 1.2E-05 | 67 | -1.0E-02 | 1.0E-05 | 1.3E-03 | 16 | -2.1E-02 | 7.4E-07 | 1.8E-04 | 3 | -2.3E-02 |
| Pendimethaline | Maize plant | 1.200 | 2.000 | 0.077 | 11.6 | 112 | 3.4E-05 | 5.3E-06 | 6.5E-06 | 67 | -1.0E-02 | 9.3E-04 | 1.0E+00 | 0 | -2.1E-02 | 7.1E-05 | 6.3E-02 | 2 | -6.4E-02 |
| Pendimethaline | barley winter | 1.200 | 1.600 | 0.143 | 19.10 | 122 | 5.7E-05 | 2.5E-05 | 4.2E-05 | 67 | -1.0E-02 | 5.8E-05 | 1.7E-04 | 16 | -2.1E-02 | 5.3E-05 | 2.3E-05 | 3 | -2.1E-02 |
| Pendimethaline | pea spring | 0.400 | 0.400 | 0.272 | 20.4 | 86 | 7.5E-06 | 2.7E-06 | 2.9E-06 | 67 | -1.0E-02 | 1.0E-04 | 4.4E-04 | 16 | -2.1E-02 | 7.6E-06 | 6.2E-05 | 3 | -2.2E-02 |
| Pendimethaline | rye winter | 1.200 | 1.600 | 1.000 | 11.10 | 122 | 1.6E-04 | 5.6E-05 | 1.6E-04 | 67 | -1.0E-02 | 1.6E-04 | 1.7E-04 | 16 | -2.1E-02 | 1.6E-04 | 2.4E-05 | 3 | -2.1E-02 |
| Phenmedipham | beet forage | 0.242 | 0.484 | 0.273 | 11.5 | 157 | 4.2E-05 | 4.0E-05 | 1.2E-03 | 23 | -3.0E-02 | 7.7E-05 | 1.0E+00 | 0 | -6.0E-02 | 5.6E-05 | 6.0E-01 | 2 | -6.0E-02 |
| Phenmedipham | beet sugar | 0.242 | 0.484 | 0.344 | 18.4 | 180 | 1.0E-05 | 1.1E-05 | 1.3E-03 | 23 | -3.0E-02 | 1.3E-06 | 8.4E-03 | 11 | -6.0E-02 | 9.4E-07 | 2.8E-03 | 4 | -6.0E-02 |
| Propaquizafop | beet forage | 0.075 | 0.250 | 0.012 | 18.6 | 119 | 2.8E-05 | 1.4E-05 | 2.6E-04 | 20 | -3.5E-02 | 2.5E-04 | 1.0E+00 | 0 | -6.9E-02 | 1.2E-04 | 4.1E-01 | 2 | -6.9E-02 |
| Propaquizafop | beet sugar | 0.075 | 0.250 | 0.011 | 18.5 | 150 | 3.9E-06 | 4.3E-06 | 3.0E-04 | 20 | -3.5E-02 | 7.7E-07 | 7.9E-04 | 10 | -6.9E-02 | 3.7E-07 | 1.5E-04 | 2 | -6.9E-02 |
| Propaquizafop | Rape winter | 0.075 | 0.250 | 0.013 | 5.3 | 118 | 9.0E-06 | 1.2E-05 | 3.7E-04 | 20 | -3.5E-02 | 6.0E-06 | 9.1E-04 | 10 | -6.9E-02 | 3.2E-06 | 1.7E-04 | 2 | -6.9E-02 |
| Propaquizafop | soybean | 0.075 | 0.250 | 0.007 | 15.6 | 92 | 1.1E-05 | 8.5E-06 | 6.2E-05 | 20 | -3.5E-02 | 4.0E-05 | 1.1E-03 | 10 | -6.9E-02 | 2.0E-05 | 2.1E-04 | 2 | -6.9E-02 |
| Prosulfocarb | potato | 2.400 | 3.600 | 0.232 | 12.5 | 112 | 1.8E-07 | 2.1E-07 | 5.2E-05 | 11 | -6.0E-02 | 2.9E-08 | 9.3E-04 | 8 | -1.2E-01 | 3.2E-09 | 1.8E-04 | 2 | -1.2E-01 |
| Pyridate | wheat winter | 0.800 | 0.800 | 0.010 | 30.3 | 107 | 2.1E-11 | 2.7E-13 | 1.6E-03 | 3 | -2.1E-01 | 2.5E-11 | 1.2E-03 | 4 | -1.4E-01 | 1.5E-21 | 2.0E-02 | 2 | -4.1E-01 |
| Pyridate | Maize ear | 0.675 | 0.900 | 0.321 | 24.5 | 130 | 3.1E-14 | 2.9E-15 | 3.0E-03 | 3 | -2.1E-01 | 1.4E-12 | 2.5E-02 | 4 | -1.7E-01 | 1.3E-25 | 3.7E-02 | 2 | -4.1E-01 |
| Pyridate | Maize grain | 0.675 | 0.900 | 0.062 | 19.5 | 135 | 5.8E-15 | 1.0E-15 | 3.0E-03 | 3 | -2.1E-01 | 7.1E-13 | 2.9E-02 | 4 | -1.7E-01 | 1.6E-26 | 3.7E-02 | 2 | -4.1E-01 |
| Pyridate | Maize plant | 0.675 | 0.900 | 0.050 | 8.6 | 115 | 3.6E-10 | 4.8E-13 | 4.4E-03 | 3 | -2.1E-01 | 1.1E-07 | 5.7E-01 | 4 | -1.6E-01 | 9.6E-22 | 8.1E-02 | 2 | -4.1E-01 |
| Pyridate | barley winter | 0.800 | 0.800 | 0.020 | 4.11 | 122 | 1.1E-13 | 2.1E-18 | 3.1E-02 | 3 | -2.5E-01 | 2.5E-13 | 3.1E-02 | 4 | -1.8E-01 | 1.4E-23 | 3.5E-02 | 2 | -4.4E-01 |
| Quizalofop-P-Ethyle | beet sugar | 0.038 | 0.063 | 0.005 | 23.5 | 145 | 4.3E-51 | 4.8E-51 | 5.5E-08 | 1 | -6.9E-01 | 5.0E-70 | 2.7E-05 | 2 | -1.4E-01 | -7.0E-74 | 1.4E-05 | 1 | -1.2E+00 |
| Quizalofop-P-Ethyle | Rape winter | 0.038 | 0.063 | 0.003 | 17.3 | 106 | 1.4E-39 | 2.9E-39 | 6.0E-08 | 1 | -6.9E-01 | -2.8E-58 | 2.9E-05 | 2 | -1.4E-01 | 3.4E-61 | 1.5E-05 | 1 | -1.2E+00 |
| Rimsulfuron | Maize grain | 0.008 | 0.010 | 0.001 | 29.5 | 125 | 8.1E-08 | 9.2E-08 | 4.3E-03 | 9 | -7.9E-02 | 7.8E-12 | 1.6E-02 | 7 | -1.5E-01 | 7.7E-14 | 4.3E-03 | 0 | -1.9E-01 |

| Substance | Crop | Application rate | | Dose | Date | Time | hF | Soil | | | | Formulation deposit | | | | Air | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | min | max | per crop | treat. | | | $hF_s$ | $hF_{s,max}$ | $t_{s,max}$ | $\mu_{s,2}$ | $hF_{fd}$ | $hF_{fd,max}$ | $t_{fd,max}$ | $\mu_{fd,2}$ | $hF_a$ | $hF_{a,max}$ | $t_{a,max}$ | $\mu_{a,2}$ |
| | | kg/ha | kg/ha | kg/ha | | | kg/ kg | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days |
| Rimsulfuron | Maize grain wet | 0.008 | 0.010 | 0.008 | 18.6 | 105 | 3.8E-07 | 4.4E-07 | 3.9E-03 | 9 | -7.9E-02 | 1.3E-10 | 7.5E-03 | 7 | -1.4E-01 | 3.1E-12 | 4.2E-03 | 0 | -1.9E-01 |
| Rimsulfuron | Maize plant | 0.008 | 0.010 | 0.001 | 11.6 | 112 | 2.3E-06 | 2.6E-06 | 6.4E-03 | 9 | -7.9E-02 | 1.8E-07 | 3.9E-01 | 7 | -1.4E-01 | 5.1E-11 | 8.5E-03 | 0 | -1.7E-01 |
| Rimsulfuron | potato | 0.010 | 0.010 | 0.001 | 19.5 | 105 | 6.6E-07 | 7.6E-07 | 7.6E-03 | 9 | -7.9E-02 | 1.9E-10 | 1.1E-02 | 7 | -1.4E-01 | 1.1E-11 | 6.0E-03 | 0 | -1.8E-01 |
| S-Metolachlor | beet forage | 0.960 | 1.248 | 0.144 | 8.5 | 160 | 1.1E-04 | 1.2E-04 | 8.4E-03 | 21 | -3.4E-02 | 9.2E-06 | 1.0E+00 | 0 | -6.6E-02 | 1.1E-06 | 9.1E-02 | 1 | -7.2E-02 |
| S-Metolachlor | beet sugar | 0.960 | 1.248 | 0.277 | 15.5 | 153 | 4.9E-05 | 5.5E-05 | 8.3E-03 | 21 | -3.4E-02 | 1.3E-06 | 2.0E-02 | 10 | -6.6E-02 | 1.5E-07 | 2.0E-03 | 1 | -7.1E-02 |
| S-Metolachlor | Maize ear | 1.248 | 1.920 | 1.000 | 15.5 | 139 | 5.2E-05 | 5.8E-05 | 5.5E-03 | 21 | -3.4E-02 | 2.0E-06 | 3.0E-02 | 10 | -6.6E-02 | 2.3E-07 | 3.0E-03 | 1 | -7.8E-02 |
| S-Metolachlor | Maize grain | 1.248 | 1.920 | 0.104 | 12.5 | 142 | 4.7E-05 | 5.2E-05 | 5.6E-03 | 21 | -3.4E-02 | 1.6E-06 | 3.1E-02 | 10 | -6.6E-02 | 1.9E-07 | 3.1E-03 | 1 | -7.8E-02 |
| S-Metolachlor | Maize plant | 1.248 | 1.920 | 0.073 | 15.5 | 139 | 2.2E-04 | 2.5E-04 | 8.7E-03 | 21 | -3.4E-02 | 4.3E-05 | 9.9E-01 | 0 | -6.6E-02 | 4.9E-06 | 9.1E-02 | 1 | -7.2E-02 |
| S-Metolachlor | soybean | 0.960 | 1.920 | 0.193 | 5.5 | 133 | 2.5E-05 | 2.8E-05 | 2.2E-03 | 21 | -3.3E-02 | 2.8E-07 | 3.5E-02 | 10 | -6.6E-02 | 3.1E-08 | 3.5E-03 | 1 | -9.5E-02 |
| Sulcotrione | Maize ear | 0.450 | 0.750 | 0.188 | 24.5 | 130 | 3.1E-14 | 3.5E-14 | 2.3E-02 | 4 | -2.0E-01 | 1.3E-15 | 5.3E-02 | 4 | -2.0E-01 | 2.4E-21 | 3.7E-02 | 3 | -3.5E-01 |
| Sulcotrione | Maize grain | 0.450 | 0.750 | 0.164 | 24.5 | 130 | 3.1E-14 | 3.5E-14 | 2.3E-02 | 4 | -2.0E-01 | 1.3E-15 | 5.3E-02 | 4 | -2.0E-01 | 2.4E-21 | 3.7E-02 | 3 | -3.5E-01 |
| Sulcotrione | Maize plant | 0.450 | 0.750 | 0.141 | 2.6 | 121 | 8.5E-13 | 9.6E-13 | 3.3E-02 | 4 | -2.0E-01 | 3.3E-13 | 8.8E-01 | 0 | -3.5E-01 | 6.3E-19 | 5.0E-01 | 1 | -3.5E-01 |
| Sulfosulfuron | wheat winter | 0.010 | 0.020 | 0.001 | 4.4 | 102 | 7.2E-05 | 9.7E-05 | 3.9E-03 | 23 | -3.0E-02 | 5.9E-08 | 2.4E-04 | 11 | -5.8E-02 | 1.6E-05 | 7.5E-03 | 1 | -5.8E-02 |
| Terbuthryn | potato | 0.525 | 0.875 | 0.027 | 12.5 | 112 | 7.3E-03 | 4.8E-03 | 1.3E-02 | 178 | -4.0E-03 | 3.7E-02 | 1.7E-02 | 22 | -7.6E-03 | 2.3E-02 | 5.7E-03 | 8 | -1.1E-02 |
| Terbuthylazine | potato | 0.225 | 0.375 | 0.012 | 12.5 | 112 | 1.6E-03 | 1.7E-03 | 1.2E-02 | 42 | -1.7E-02 | 1.3E-03 | 3.4E-02 | 13 | -3.3E-02 | 4.8E-04 | 1.2E-02 | 6 | -4.2E-02 |
| Thifensulfuron-methyl | oat spring | 0.041 | 0.041 | 0.004 | 5.5 | 88 | 1.5E-08 | 1.7E-08 | 1.0E-04 | 8 | -9.0E-02 | 4.0E-11 | 1.2E-04 | 6 | -1.4E-01 | 9.0E-09 | 1.5E-01 | 4 | -1.8E-01 |
| Thifensulfuron-methyl | wheat winter | 0.061 | 0.061 | 0.002 | 4.4 | 102 | 3.8E-09 | 5.2E-09 | 9.0E-05 | 8 | -9.0E-02 | 5.9E-12 | 2.8E-05 | 6 | -1.4E-01 | 6.9E-10 | 1.1E-01 | 4 | -1.8E-01 |
| Thifensulfuron-methyl | wheat spring | 0.041 | 0.041 | 0.004 | 29.4 | 77 | 4.6E-08 | 4.7E-08 | 1.1E-04 | 8 | -9.0E-02 | 1.8E-10 | 1.2E-04 | 6 | -1.4E-01 | 6.4E-08 | 1.6E-01 | 4 | -1.8E-01 |
| Thifensulfuron-methyl | Maize plant | 0.008 | 0.008 | 0.001 | 11.6 | 112 | 2.9E-08 | 2.9E-08 | 2.5E-04 | 8 | -9.0E-02 | 1.8E-07 | 4.2E-01 | 6 | -1.4E-01 | 2.1E-09 | 6.5E-01 | 2 | -1.8E-01 |
| Thifensulfuron-methyl | barley spring | 0.041 | 0.041 | 0.004 | 10.6 | 35 | 1.3E-05 | 2.3E-06 | 1.0E-04 | 8 | -9.0E-02 | 5.7E-08 | 2.5E-05 | 6 | -1.4E-01 | 1.2E-04 | 1.4E-01 | 4 | -1.8E-01 |
| Thifensulfuron-methyl | meadow mid int | 0.023 | 0.023 | 0.250 | 1.5 | 20 | 3.9E-02 | 3.8E-04 | 7.6E-04 | 8 | -9.0E-02 | 6.2E-02 | 4.2E-01 | 6 | -1.4E-01 | 2.9E-02 | 7.1E-01 | 1 | -1.8E-01 |
| Trifluralin | Rape winter | 1.440 | 1.440 | 0.033 | 31.8 | 122 | 1.4E-06 | 8.8E-06 | 9.8E-06 | 96 | -7.2E-03 | 1.4E-06 | 3.5E-04 | 18 | -1.4E-02 | 7.6E-07 | 5.7E-05 | 4 | -1.6E-02 |
| Triflusulfuron | beet forage | 0.010 | 0.015 | 0.002 | 20.5 | 148 | 1.0E-17 | 1.1E-17 | 4.3E-03 | 3 | -2.4E-01 | 1.1E-09 | 6.1E-01 | 2 | -3.6E-01 | 6.1E-18 | 8.6E-02 | 3 | -2.6E-01 |
| Triflusulfuron | beet sugar | 0.010 | 0.015 | 0.004 | 25.5 | 143 | 5.2E-18 | 5.6E-18 | 4.2E-03 | 3 | -2.3E-01 | 3.2E-13 | 7.4E-02 | 3 | -2.0E-01 | 1.2E-18 | 5.0E-02 | 3 | -2.3E-01 |
| INSECTICIDE | | | | | | | | | | | | | | | | | | | |
| Bifenthrin | Rape winter | 0.015 | 0.015 | 0.001 | 2.4 | 90 | 1.2E-05 | 3.6E-07 | 7.2E-07 | 34 | -2.0E-02 | 2.3E-05 | 4.2E-05 | 13 | -4.0E-02 | 6.8E-06 | 6.8E-06 | 3 | -4.0E-02 |
| Carbofuran | Maize plant | 0.400 | 0.467 | 0.023 | 24.5 | 130 | 4.7E-02 | 5.1E-02 | 1.5E-01 | 43 | -2.2E-02 | 1.0E-02 | 9.5E-01 | 1 | -2.5E-02 | 1.4E-02 | 3.9E-01 | 2 | -2.6E-02 |
| Cyhalothrin | Rape winter | 0.008 | 0.010 | 0.001 | 7.4 | 85 | 3.1E-06 | 3.6E-10 | 4.8E-10 | 43 | -1.6E-02 | 5.7E-06 | 4.9E-06 | 14 | -3.2E-02 | 2.3E-06 | 7.1E-07 | 3 | -3.2E-02 |
| Cyhalothrin | Maize grain | 0.008 | 0.010 | 0.001 | 19.5 | 135 | 1.3E-07 | 1.4E-10 | 3.6E-10 | 43 | -1.6E-02 | 3.0E-06 | 8.1E-06 | 14 | -3.2E-02 | 1.0E-06 | 1.2E-06 | 3 | -3.2E-02 |
| Cypermethrin | Rape winter | 0.011 | 0.011 | 0.002 | 4.4 | 88 | 1.3E-06 | 1.8E-09 | 4.7E-09 | 27 | -2.6E-02 | 2.5E-06 | 1.0E-05 | 11 | -5.1E-02 | 1.0E-06 | 1.4E-06 | 2 | -5.1E-02 |
| Cypermethrin | Rape winter | 0.011 | 0.011 | 0.002 | 4.4 | 88 | 1.3E-06 | 1.8E-09 | 4.7E-09 | 27 | -2.6E-02 | 2.5E-06 | 1.0E-05 | 11 | -5.1E-02 | 1.0E-06 | 1.4E-06 | 2 | -5.1E-02 |
| Cypermethrin | pea spring | 0.050 | 0.050 | 0.008 | 1.6 | 44 | 4.2E-06 | 1.9E-09 | 2.2E-09 | 27 | -2.6E-02 | 1.4E-05 | 1.3E-05 | 11 | -5.1E-02 | 5.4E-06 | 1.8E-06 | 2 | -5.1E-02 |

| Substance | Crop | Application rate | | Dose | Date | Time | hF | Soil | | | | Formulation deposit | | | | Air | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | min | max | per crop | treat. | | | $hF_s$ | $hF_{s,max}$ | $t_{s,max}$ | $\mu_{s,2}$ | $hF_{fd}$ | $hF_{fd,max}$ | $t_{fd,max}$ | $\mu_{fd,2}$ | $hF_a$ | $hF_{a,max}$ | $t_{a,max}$ | $\mu_{a,2}$ |
| | | kg/ha | kg/ha | kg/ha | | | kg/ kg | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days | kg/ kg | kg/ kg | days | 1/days |
| Deltamethrine | beet forage | 0.008 | 0.013 | 0.001 | 18.5 | 150 | 1.1E-06 | 1.7E-10 | 6.0E-09 | 21 | -3.3E-02 | 4.4E-05 | 1.0E+00 | 0 | -6.6E-02 | 9.4E-06 | 1.8E-01 | 2 | -6.7E-02 |
| Deltamethrine | wheat winter | 0.008 | 0.008 | 0.000 | 15.5 | 61 | 8.8E-06 | 8.3E-10 | 1.8E-09 | 21 | -3.3E-02 | 2.0E-05 | 7.3E-05 | 10 | -6.6E-02 | 5.1E-06 | 1.1E-05 | 2 | -6.6E-02 |
| Deltamethrine | Rape winter | 0.008 | 0.010 | 0.001 | 18.3 | 105 | 1.6E-06 | 7.6E-10 | 6.4E-09 | 21 | -3.3E-02 | 3.5E-06 | 1.4E-04 | 10 | -6.6E-02 | 8.8E-07 | 1.9E-05 | 2 | -6.6E-02 |
| Deltamethrine | barley winter | 0.008 | 0.008 | 0.000 | 24.10 | 122 | 6.9E-07 | 2.6E-09 | 3.7E-08 | 21 | -3.3E-02 | 6.9E-07 | 6.8E-05 | 10 | -6.6E-02 | 6.7E-07 | 9.5E-06 | 2 | -6.6E-02 |
| Lambda-cyhalothrin | Maize plant | 0.008 | 0.010 | 0.000 | 19.5 | 135 | 8.6E-06 | 2.4E-11 | 4.8E-10 | 21 | -3.2E-02 | 1.7E-04 | 1.0E+00 | 0 | -6.4E-02 | 7.1E-05 | 3.8E-01 | 2 | -6.5E-02 |
| Lambda-Cyhalothrin | pea spring | 0.008 | 0.010 | 0.002 | 23.6 | 22 | 3.7E-06 | 2.0E-10 | 2.0E-10 | 21 | -3.2E-02 | 6.4E-06 | 4.4E-06 | 10 | -6.4E-02 | 3.2E-06 | 7.5E-07 | 2 | -6.4E-02 |
| Lambda-Cyhalothrin | ley int | 0.008 | 0.010 | 0.001 | 1.5 | 20 | 1.7E-01 | 1.3E-09 | 1.3E-09 | 21 | -3.2E-02 | 2.7E-01 | 1.0E+00 | 0 | -6.4E-02 | 1.4E-01 | 4.6E-01 | 1 | -6.5E-02 |
| Lambda-Cyhalothrin | soybean | 0.008 | 0.010 | 0.001 | 13.7 | 64 | 2.3E-07 | 3.8E-11 | 8.7E-11 | 21 | -3.2E-02 | 1.5E-06 | 5.3E-06 | 10 | -6.4E-02 | 6.4E-07 | 9.0E-07 | 2 | -6.4E-02 |
| Pirimicarb | wheat winter | 0.075 | 0.075 | 0.000 | 15.5 | 61 | 5.2E-03 | 1.9E-03 | 1.4E-02 | 112 | -6.7E-03 | 6.4E-03 | 9.5E-02 | 15 | -1.2E-02 | 1.6E-03 | 4.7E-03 | 1 | -2.1E-02 |
| Pirimicarb | Rape winter | 0.125 | 0.125 | 0.038 | 20.5 | 42 | 8.0E-03 | 1.9E-03 | 2.6E-02 | 110 | -7.1E-03 | 8.8E-03 | 1.2E-01 | 16 | -1.2E-02 | 2.3E-03 | 6.1E-03 | 1 | -2.0E-02 |
| Pirimicarb | pea spring | 0.075 | 0.075 | 0.072 | 26.5 | 50 | 5.6E-03 | 1.9E-03 | 1.9E-02 | 115 | -6.4E-03 | 9.7E-03 | 2.1E-01 | 14 | -1.2E-02 | 2.2E-03 | 9.1E-03 | 1 | -2.5E-02 |
| Teflubenzuron | wheat winter | 0.060 | 0.060 | 0.002 | 15.5 | 61 | 3.2E-04 | 9.4E-06 | 1.2E-05 | 34 | -2.0E-02 | 6.4E-04 | 5.8E-04 | 13 | -4.0E-02 | 5.5E-04 | 5.6E-04 | 12 | -4.0E-02 |
| Teflubenzuron | potato | 0.038 | 0.038 | 0.019 | 17.6 | 76 | 2.1E-04 | 2.5E-05 | 4.0E-05 | 34 | -2.0E-02 | 1.1E-03 | 1.5E-03 | 13 | -4.0E-02 | 8.9E-04 | 9.0E-04 | 8 | -4.0E-02 |
| Terbufos | beet forage | 0.300 | 0.300 | 0.142 | 30.3 | 199 | 2.6E-07 | 2.9E-07 | 3.0E-04 | 17 | -4.0E-02 | 5.5E-10 | 1.0E+00 | 0 | -7.9E-02 | 5.3E-12 | 8.9E-03 | 0 | -1.4E-01 |
| Terbufos | beet sugar | 0.480 | 0.600 | 0.069 | 21.3 | 208 | 1.6E-07 | 1.8E-07 | 3.2E-04 | 17 | -4.0E-02 | 2.2E-10 | 1.2E-03 | 9 | -7.9E-02 | 2.1E-12 | 3.1E-05 | 0 | -8.3E-02 |
| Triazamate | sunflower | 0.056 | 0.056 | 0.003 | 25.5 | 113 | 1.5E-108 | 6.9E-116 | 2.1E-05 | 0 | -2.8E+00 | 2.7E-28 | 9.3E-04 | 1 | -1.5E-01 | 1.5E-107 | 7.2E-04 | 0 | -9.0E-01 |
| GROWTH REG. | | | | | | | | | | | | | | | | | | | |
| Chlormequat chloride | wheat winter | 0.230 | 1.150 | 0.010 | 23.4 | 83 | 2.2E-06 | 4.4E-07 | 3.3E-05 | 14 | -4.8E-02 | 7.9E-08 | 7.5E-04 | 9 | -9.6E-02 | 1.8E-05 | 1.0E-01 | 4 | -9.6E-02 |
| Ethephon | oat spring | 0.136 | 0.226 | 0.146 | 28.5 | 65 | 1.2E-05 | 9.8E-09 | 4.4E-07 | 14 | -4.8E-02 | 2.0E-07 | 9.6E-04 | 9 | -9.6E-02 | 1.2E-04 | 2.3E-01 | 7 | -9.6E-02 |
| Ethephon | wheat winter | 0.360 | 0.720 | 0.056 | 2.5 | 74 | 4.9E-06 | 7.6E-09 | 3.7E-07 | 14 | -4.8E-02 | 9.1E-08 | 3.1E-04 | 9 | -9.6E-02 | 4.9E-05 | 1.6E-01 | 6 | -9.6E-02 |
| Ethephon | wheat spring | 0.136 | 0.226 | 0.081 | 6.5 | 70 | 8.1E-06 | 8.0E-09 | 4.5E-07 | 14 | -4.8E-02 | 1.3E-07 | 1.5E-03 | 9 | -9.6E-02 | 8.0E-05 | 2.5E-01 | 7 | -9.6E-02 |
| Ethephon | barley winter | 0.480 | 0.480 | 0.344 | 1.5 | 61 | 1.9E-05 | 1.7E-08 | 6.5E-07 | 14 | -4.8E-02 | 3.7E-07 | 3.7E-04 | 9 | -9.6E-02 | 1.9E-04 | 2.6E-01 | 6 | -9.6E-02 |
| Ethephon | rye winter | 0.480 | 0.480 | 0.135 | 26.4 | 66 | 1.2E-05 | 1.3E-08 | 6.4E-07 | 14 | -4.8E-02 | 2.1E-07 | 4.8E-04 | 9 | -9.6E-02 | 1.2E-04 | 2.6E-01 | 6 | -9.6E-02 |
| Trinexapac-ethyl | oat spring | 0.158 | 0.263 | 0.146 | 28.5 | 65 | 5.4E-16 | 1.2E-23 | 3.3E-04 | 1 | -6.9E-01 | 5.8E-09 | 2.1E-02 | 2 | -2.1E-01 | 2.3E-46 | 4.0E-03 | 0 | -1.5E+00 |
| Trinexapac-ethyl | wheat winter | 0.100 | 0.150 | 0.095 | 28.4 | 78 | 6.1E-14 | 1.3E-27 | 2.8E-04 | 1 | -7.0E-01 | 3.8E-10 | 1.3E-02 | 2 | -2.1E-01 | 1.9E-50 | 3.0E-03 | 0 | -1.5E+00 |
| Trinexapac-ethyl | wheat spring | 0.100 | 0.150 | 0.067 | 25.5 | 51 | 7.2E-12 | 2.2E-19 | 3.4E-04 | 1 | -6.9E-01 | 7.6E-08 | 2.1E-02 | 2 | -2.1E-01 | 2.2E-37 | 4.3E-03 | 0 | -1.5E+00 |
| Trinexapac-ethyl | barley winter | 0.200 | 0.250 | 0.046 | 26.4 | 66 | 4.5E-11 | 7.3E-24 | 4.9E-04 | 1 | -7.0E-01 | 4.1E-09 | 1.8E-02 | 2 | -2.0E-01 | 1.2E-46 | 5.1E-03 | 0 | -1.5E+00 |
| Trinexapac-ethyl | rye winter | 0.100 | 0.150 | 0.147 | 23.4 | 69 | 1.5E-12 | 8.8E-25 | 4.9E-04 | 1 | -7.0E-01 | 2.8E-09 | 2.1E-02 | 2 | -2.1E-01 | 1.5E-47 | 4.9E-03 | 0 | -1.5E+00 |

## *G.3 Human toxicity*

Toxicity evaluation for substances used in filed crops. Intake fraction (iF, kg substance ingested / kg applied)[1], Effect factor (DALY / kg substance absorbed) for cancer and non cancer, Human Damage Factor in DALY per unit quantity applied (DALY / kg substance applied); Human Damages per treatment (DALY / kg ha treated) and per unit crop area (DALY / ha crop cultivated), *in italic substances for which there is no Effect Factor for cancer effect.*

| Substances | Crop | Intake fraction | Effect Factor | | Human Damages | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | oral | non cancer | cancer | non cancer | cancer | per treat.min | per treat.max | per ha cult. crop |
| | | kg/kg | DALY/kg | DALY /kg | DALY /kg | DALY /kg | DALY /ha treat. | DALY /ha treat. | DALY /ha cult. |
| FUNGICIDES | | | | | | | | | |
| Carbendazime | Rape winter | 7.9E-03 | 8.3E-03 | 8.3E-02 | 6.6E-05 | 6.6E-04 | 1.7E-04 | 1.7E-04 | 3.3E-05 |
| Chlorothalonil | wheat winter | 6.1E-03 | 1.9E-02 | 3.7E-02 | 1.1E-04 | 2.3E-04 | 5.1E-04 | 5.1E-04 | 2.3E-06 |
| Chlorothalonil | potato | 1.9E-03 | 1.9E-02 | 3.7E-02 | 3.5E-05 | 7.1E-05 | 1.6E-04 | 1.6E-04 | 1.6E-04 |
| Chlorothalonil | pea spring | 5.5E-03 | 1.9E-02 | 3.7E-02 | 1.0E-04 | 2.1E-04 | 4.6E-04 | 4.6E-04 | 1.2E-04 |
| Dimethomorph | potato | 1.4E-03 | 9.6E-05 | - | 1.3E-07 | - | *2.0E-08* | *2.0E-08* | *9.8E-09* |
| Flusilazole | beet sugar | 3.0E-03 | 1.9E-01 | - | 5.5E-04 | - | *1.1E-04* | *1.1E-04* | *9.8E-06* |
| Flusilazole | wheat winter | 2.2E-03 | 1.9E-01 | - | 4.1E-04 | - | *1.0E-04* | *1.2E-04* | *1.4E-05* |
| Flusilazole | wheat spring | 3.5E-03 | 1.9E-01 | - | 6.6E-04 | - | *1.7E-04* | *2.0E-04* | *1.1E-04* |
| Mancozeb | potato | 2.4E-13 | 5.3E-03 | 5.3E-02 | 1.3E-15 | 1.3E-14 | 3.2E-14 | 3.2E-14 | 6.9E-14 |
| Maneb | potato | 1.5E-04 | 2.8E-02 | 2.8E-01 | 4.1E-06 | 4.1E-05 | 1.1E-04 | 1.1E-04 | 6.2E-05 |
| Metalaxyl | potato | 6.1E-03 | 6.0E-03 | 6.0E-02 | 3.7E-05 | 3.7E-04 | 4.0E-05 | 4.0E-05 | 2.4E-05 |
| Prochloraz | wheat winter | 6.7E-05 | 4.1E-02 | 2.8E-01 | 2.8E-06 | 1.9E-05 | 1.0E-05 | 1.0E-05 | 1.7E-06 |
| Prochloraz | barley winter | 1.8E-04 | 4.1E-02 | 2.8E-01 | 7.6E-06 | 5.2E-05 | 2.8E-05 | 2.8E-05 | 1.1E-06 |
| Propiconazole | wheat winter | 4.0E-03 | 3.0E-02 | 3.0E-01 | 1.2E-04 | 1.2E-03 | 1.7E-04 | 1.7E-04 | 1.6E-05 |
| Propiconazole | barley winter | 8.2E-03 | 3.0E-02 | 3.0E-01 | 2.5E-04 | 2.5E-03 | 3.4E-04 | 3.4E-04 | 4.6E-05 |
| Vinclozolin | Rape winter | 4.5E-04 | 1.5E-02 | 1.5E-01 | 6.7E-06 | 6.7E-05 | 2.8E-05 | 2.8E-05 | 3.8E-06 |
| HERBICIDES | | | | | | | | | |
| 2,4-D | wheat winter | 4.1E-06 | 1.4E-01 | 2.5E-01 | 5.9E-07 | 1.0E-06 | 1.5E-06 | 1.9E-06 | 5.8E-08 |
| 2,4-D | wheat spring | 5.6E-06 | 1.4E-01 | 2.5E-01 | 8.0E-07 | 1.4E-06 | 2.0E-06 | 2.6E-06 | 2.5E-07 |
| 2,4-D | Maize grain | 1.5E-07 | 1.4E-01 | 2.5E-01 | 2.2E-08 | 3.9E-08 | 3.6E-08 | 4.2E-08 | 1.2E-09 |
| 2,4-D | barley winter | 4.8E-06 | 1.4E-01 | 2.5E-01 | 6.8E-07 | 1.2E-06 | 1.7E-06 | 2.3E-06 | 1.2E-07 |
| Alachlor | Maize plant | 7.7E-06 | 3.7E-02 | 3.7E-01 | 2.9E-07 | 2.9E-06 | 6.1E-06 | 1.5E-05 | 1.1E-07 |
| Alachlor | soybean | 5.0E-07 | 3.7E-02 | 3.7E-01 | 1.9E-08 | 1.9E-07 | 3.9E-07 | 9.8E-07 | 1.8E-07 |
| Amidosulfuron | wheat winter | 2.4E-08 | 9.5E-05 | - | 2.3E-12 | - | *3.4E-14* | *6.9E-14* | *7.9E-15* |

| Substances | Crop | Intake fraction | Effect Factor | | Human Damages | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | oral | non cancer | cancer | non cancer | cancer | per treat.min | per treat.max | per ha cult. crop |
| | | kg/kg | DALY/kg | DALY /kg | DALY /kg | DALY /kg | DALY /ha treat. | DALY /ha treat. | DALY /ha cult. |
| Amidosulfuron | wheat spring | 5.3E-06 | 9.5E-05 | - | 5.1E-10 | - | *7.6E-12* | *1.5E-11* | *6.9E-12* |
| Amidosulfuron | barley winter | 2.9E-08 | 9.5E-05 | - | 2.8E-12 | - | *4.2E-14* | *8.4E-14* | *4.4E-15* |
| Amidosulfuron | barley spring | 4.9E-04 | 9.5E-05 | - | 4.6E-08 | - | *7.0E-10* | *1.4E-09* | *5.2E-10* |
| Asulam | ley int | 4.2E-02 | 1.5E-02 | - | 6.3E-04 | - | *7.5E-04* | *1.5E-03* | *2.8E-04* |
| Asulam | ley mid int | 4.2E-02 | 1.5E-02 | - | 6.3E-04 | - | *7.5E-04* | *1.5E-03* | *1.0E-03* |
| Atrazin | Maize ear | 4.0E-03 | 4.1E-02 | 3.0E-01 | 1.7E-04 | 1.2E-03 | 1.3E-03 | 1.3E-03 | 7.9E-04 |
| Atrazin | Maize grain | 4.0E-03 | 4.1E-02 | 3.0E-01 | 1.7E-04 | 1.2E-03 | 1.3E-03 | 1.3E-03 | 7.6E-04 |
| Atrazin | Maize grain wet | 5.2E-03 | 4.1E-02 | 3.0E-01 | 2.1E-04 | 1.5E-03 | 1.7E-03 | 1.7E-03 | 1.4E-03 |
| Atrazin | Maize plant | 5.0E-02 | 4.1E-02 | 3.0E-01 | 2.1E-03 | 1.5E-02 | 1.7E-02 | 1.7E-02 | 1.1E-02 |
| Bentazone | pea spring | 1.8E-05 | 1.2E-02 | 1.2E-01 | 2.0E-07 | 2.0E-06 | 2.2E-06 | 4.3E-06 | 3.0E-07 |
| Bentazone | ley int | 4.0E-02 | 1.2E-02 | 1.2E-01 | 4.7E-04 | 4.7E-03 | 4.9E-03 | 7.2E-03 | 2.7E-04 |
| Bifenox | wheat winter | 1.3E-08 | 9.4E-04 | 9.4E-03 | 1.2E-11 | 1.2E-10 | 9.8E-11 | 1.2E-10 | 5.8E-12 |
| Bifenox | wheat spring | 3.2E-07 | 9.4E-04 | 9.4E-03 | 3.0E-10 | 3.0E-09 | 2.0E-09 | 2.5E-09 | 6.5E-10 |
| Bromoxynil phenol | wheat winter | 5.3E-16 | 2.8E-02 | - | 1.5E-17 | - | *3.5E-18* | *7.1E-18* | *6.1E-19* |
| Bromoxynil phenol | Maize grain | 8.4E-17 | 2.8E-02 | - | 2.3E-18 | - | *8.4E-19* | *1.1E-18* | *6.9E-21* |
| Bromoxynil phenol | Maize plant | 3.6E-15 | 2.8E-02 | - | 1.0E-16 | - | *3.6E-17* | *4.8E-17* | *9.1E-19* |
| Bromoxynil phenol | barley winter | 3.1E-15 | 2.8E-02 | - | 8.7E-17 | - | *2.1E-17* | *4.2E-17* | *1.6E-18* |
| Chlortoluron | wheat winter | 1.9E-04 | 7.5E-04 | - | 1.4E-07 | - | *1.7E-07* | *3.9E-07* | *9.0E-09* |
| Chlortoluron | barley winter | 3.5E-04 | 7.5E-04 | - | 2.6E-07 | - | *3.1E-07* | *7.3E-07* | *6.3E-08* |
| Chlortoluron | rye winter | 3.5E-04 | 7.5E-04 | - | 2.7E-07 | - | *3.2E-07* | *7.4E-07* | *4.0E-07* |
| Cloquintocet-mexyl | wheat winter | 1.0E-20 | 2.7E-03 | - | 2.7E-23 | - | *3.3E-25* | *5.7E-25* | *2.1E-26* |
| Cloquintocet-mexyl | rye winter | 2.0E-18 | 2.7E-03 | - | 5.3E-21 | - | *6.3E-23* | *1.1E-22* | *2.0E-23* |
| Dicamba | wheat winter | 9.7E-05 | 4.9E-02 | - | 4.7E-06 | - | *5.6E-07* | *5.6E-07* | *7.5E-09* |
| Dicamba | Maize ear | 2.7E-07 | 4.9E-02 | - | 1.3E-08 | - | *3.8E-09* | *4.8E-09* | *4.3E-10* |
| Dicamba | Maize grain | 1.4E-07 | 4.9E-02 | - | 6.6E-09 | - | *1.9E-09* | *2.4E-09* | *1.4E-10* |
| Dicamba | Maize grain wet | 6.7E-07 | 4.9E-02 | - | 3.3E-08 | - | *9.4E-09* | *1.2E-08* | *5.6E-09* |
| Dicamba | Maize plant | 1.4E-06 | 4.9E-02 | - | 6.6E-08 | - | *1.9E-08* | *2.4E-08* | *3.6E-09* |
| Dicamba | meadow mid int | 5.4E-02 | 4.9E-02 | - | 2.6E-03 | - | *3.6E-05* | *7.2E-05* | *8.2E-06* |
| Dicamba | ley int | 5.4E-02 | 4.9E-02 | - | 2.6E-03 | - | *3.6E-05* | *7.2E-05* | *4.1E-06* |
| Dimethenamid | Maize ear | 1.2E-05 | 4.7E-03 | - | 5.9E-08 | - | *6.3E-08* | *8.4E-08* | *3.2E-08* |
| Dimethenamid | Maize grain | 1.1E-05 | 4.7E-03 | - | 5.3E-08 | - | *5.7E-08* | *7.6E-08* | *8.1E-09* |
| Dimethenamid | Maize plant | 2.5E-04 | 4.7E-03 | - | 1.2E-06 | - | *1.3E-06* | *1.7E-06* | *1.8E-07* |

| Substances | Crop | Intake fraction | Effect Factor | | Human Damages | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | oral | non cancer | cancer | non cancer | cancer | per treat.min | per treat.max | per ha cult. crop |
| | | kg/kg | DALY/kg | DALY /kg | DALY /kg | DALY /kg | DALY /ha treat. | DALY /ha treat. | DALY /ha cult. |
| Dimethenamid | soybean | 4.6E-06 | 4.7E-03 | - | 2.2E-08 | - | *2.4E-08* | *3.1E-08* | *2.5E-09* |
| Diquat | potato | 1.1E-03 | 2.4E-02 | - | 2.6E-05 | - | *4.2E-05* | *4.2E-05* | *1.7E-06* |
| Fluazifop-P-Butyl | beet forage | 2.4E-06 | 2.6E-03 | - | 6.2E-09 | - | *1.2E-09* | *2.3E-09* | *2.6E-10* |
| Fluazifop-P-Butyl | beet sugar | 4.2E-07 | 2.6E-03 | - | 1.1E-09 | - | *2.1E-10* | *4.2E-10* | *2.5E-11* |
| Fluazifop-P-Butyl | Rape winter | 5.7E-06 | 2.6E-03 | - | 1.5E-08 | - | *2.8E-09* | *5.6E-09* | *1.7E-10* |
| Fluazifop-P-Butyl | sunflower | 3.5E-07 | 2.6E-03 | - | 9.2E-10 | - | *1.7E-10* | *3.5E-10* | *6.8E-11* |
| Fluroxypyr | oat winter | 5.4E-03 | 1.5E-04 | - | 8.2E-07 | - | *8.5E-08* | *1.1E-07* | *1.1E-07* |
| Fluroxypyr | wheat winter | 3.8E-03 | 1.5E-04 | - | 5.9E-07 | - | *6.1E-08* | *7.6E-08* | *2.0E-08* |
| Fluroxypyr | barley winter | 3.1E-03 | 1.5E-04 | - | 4.7E-07 | - | *4.8E-08* | *6.1E-08* | *1.1E-08* |
| Ioxynil | oat spring | 8.2E-05 | 4.7E-02 | 4.7E-01 | 3.8E-06 | 3.8E-05 | 9.0E-06 | 1.5E-05 | 1.4E-05 |
| Ioxynil | wheat winter | 3.7E-05 | 4.7E-02 | 4.7E-01 | 1.8E-06 | 1.8E-05 | 4.1E-06 | 6.9E-06 | 2.5E-06 |
| Ioxynil | wheat spring | 1.1E-04 | 4.7E-02 | 4.7E-01 | 5.3E-06 | 5.3E-05 | 1.2E-05 | 1.7E-05 | 3.6E-06 |
| Ioxynil | Maize grain | 3.1E-05 | 4.7E-02 | 4.7E-01 | 1.4E-06 | 1.4E-05 | 3.3E-06 | 4.4E-06 | 7.9E-08 |
| Ioxynil | Maize plant | 1.7E-04 | 4.7E-02 | 4.7E-01 | 8.0E-06 | 8.0E-05 | 1.8E-05 | 2.5E-05 | 3.5E-07 |
| Ioxynil | barley winter | 4.3E-05 | 4.7E-02 | 4.7E-01 | 2.0E-06 | 2.0E-05 | 4.7E-06 | 7.8E-06 | 2.2E-06 |
| Ioxynil | rye winter | 8.1E-05 | 4.7E-02 | 4.7E-01 | 3.8E-06 | 3.8E-05 | 8.9E-06 | 1.2E-05 | 1.2E-05 |
| Linuron | Maize ear | 1.5E-04 | 3.2E-01 | 3.2E+00 | 4.8E-05 | 4.8E-04 | 1.8E-04 | 2.3E-04 | 2.3E-05 |
| Linuron | Maize plant | 3.2E-03 | 3.2E-01 | 3.2E+00 | 1.0E-03 | 1.0E-02 | 3.7E-03 | 5.0E-03 | 6.6E-05 |
| Linuron | soybean | 1.9E-04 | 3.2E-01 | 3.2E+00 | 6.1E-05 | 6.1E-04 | 2.2E-04 | 3.0E-04 | 1.6E-04 |
| Linuron | sunflower | 1.3E-04 | 3.2E-01 | 3.2E+00 | 4.1E-05 | 4.1E-04 | 1.5E-04 | 2.0E-04 | 7.7E-05 |
| MCPA | oat winter | 1.0E-06 | 2.5E-01 | 1.9E-01 | 2.5E-07 | 1.9E-07 | 2.9E-07 | 6.5E-07 | 3.5E-07 |
| MCPA | wheat winter | 4.2E-07 | 2.5E-01 | 1.9E-01 | 1.1E-07 | 7.9E-08 | 1.2E-07 | 2.7E-07 | 1.3E-08 |
| MCPA | barley winter | 2.2E-08 | 2.5E-01 | 1.9E-01 | 5.4E-09 | 4.1E-09 | 6.3E-09 | 1.4E-08 | 1.9E-09 |
| MCPA | potato | 2.4E-03 | 2.5E-01 | 1.9E-01 | 6.1E-04 | 4.5E-04 | 1.7E-04 | 1.7E-04 | 6.4E-06 |
| MCPA | meadow mid int | 3.4E-02 | 2.5E-01 | 1.9E-01 | 8.6E-03 | 6.4E-03 | 9.9E-03 | 2.2E-02 | 1.3E-03 |
| MCPA | ley int | 3.4E-02 | 2.5E-01 | 1.9E-01 | 8.6E-03 | 6.4E-03 | 9.9E-03 | 2.2E-02 | 2.2E-04 |
| MCPB | meadow mid int | 3.5E-02 | 1.0E-02 | - | 3.7E-04 | - | *7.3E-04* | *8.8E-04* | *2.1E-04* |
| MCPB | ley int | 3.5E-02 | 1.0E-02 | - | 3.7E-04 | - | *5.8E-04* | *8.8E-04* | *1.6E-04* |
| MCPP | wheat winter | 2.0E-07 | 2.9E-03 | - | 5.9E-10 | - | *8.2E-10* | *9.4E-10* | *4.4E-11* |
| MCPP | barley winter | 3.9E-07 | 2.9E-03 | - | 1.1E-09 | - | *1.6E-09* | *1.8E-09* | *7.7E-11* |
| MCPP | rye winter | 9.7E-07 | 2.9E-03 | - | 2.8E-09 | - | *4.0E-09* | *4.5E-09* | *6.4E-10* |
| Metolachlor | Maize ear | 7.5E-04 | 9.4E-03 | 9.4E-02 | 7.0E-06 | 7.0E-05 | 1.2E-04 | 1.2E-04 | 7.9E-05 |

| Substances | Crop | Intake fraction | Effect Factor | | Human Damages | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | oral | non cancer | cancer | non cancer | cancer | per treat.min | per treat.max | per ha cult. crop |
| | | kg/kg | DALY/kg | DALY /kg | DALY /kg | DALY /kg | DALY /ha treat. | DALY /ha treat. | DALY /ha cult. |
| Metolachlor | Maize grain | 5.6E-04 | 9.4E-03 | 9.4E-02 | 5.2E-06 | 5.2E-05 | 9.2E-05 | 9.2E-05 | 1.5E-05 |
| Metolachlor | Maize plant | 5.3E-03 | 9.4E-03 | 9.4E-02 | 4.9E-05 | 4.9E-04 | 8.7E-04 | 8.7E-04 | 7.7E-05 |
| Metribuzin | potato | 2.1E-02 | 1.5E-02 | 1.5E-01 | 3.2E-04 | 3.2E-03 | 1.2E-03 | 1.8E-03 | 7.7E-04 |
| Metribuzin | pea spring | 1.3E-02 | 1.5E-02 | 1.5E-01 | 1.9E-04 | 1.9E-03 | 4.2E-04 | 5.6E-04 | 1.5E-04 |
| Metribuzin | soybean | 9.3E-03 | 1.5E-02 | 1.5E-01 | 1.4E-04 | 1.4E-03 | 4.1E-04 | 4.1E-04 | 5.1E-05 |
| Metsulfuron-methyl | oat spring | 1.6E-05 | 5.6E-03 | - | 9.0E-08 | - | *4.5E-10* | *4.5E-10* | *3.7E-10* |
| Metsulfuron-methyl | wheat winter | 7.9E-06 | 5.6E-03 | - | 4.5E-08 | - | *2.2E-10* | *2.2E-10* | *7.8E-11* |
| Metsulfuron-methyl | wheat spring | 3.0E-05 | 5.6E-03 | - | 1.7E-07 | - | *8.4E-10* | *8.4E-10* | *5.2E-10* |
| Metsulfuron-methyl | barley winter | 8.7E-06 | 5.6E-03 | - | 4.9E-08 | - | *2.5E-10* | *2.5E-10* | *2.0E-11* |
| Metsulfuron-methyl | barley spring | 4.1E-04 | 5.6E-03 | - | 2.3E-06 | - | *1.2E-08* | *1.2E-08* | *9.4E-09* |
| Napropamid | Rape winter | 1.1E-03 | 4.9E-03 | - | 5.3E-06 | - | *7.1E-06* | *7.1E-06* | *3.1E-06* |
| Nicosulfuron | Maize ear | 4.2E-08 | 3.0E-06 | - | 1.3E-13 | - | *5.1E-15* | *7.6E-15* | *8.1E-16* |
| Nicosulfuron | Maize grain | 1.8E-08 | 3.0E-06 | - | 5.4E-14 | - | *2.2E-15* | *3.2E-15* | *3.8E-16* |
| Nicosulfuron | Maize plant | 4.9E-07 | 3.0E-06 | - | 1.5E-12 | - | *5.9E-14* | *8.8E-14* | *5.9E-15* |
| Pendimethaline | wheat winter | 7.5E-05 | 3.0E-03 | 3.7E-02 | 2.2E-07 | 2.8E-06 | 3.6E-06 | 4.9E-06 | 1.3E-07 |
| Pendimethaline | Maize ear | 2.8E-06 | 3.0E-03 | 3.7E-02 | 8.4E-09 | 1.0E-07 | 1.4E-07 | 2.3E-07 | 4.2E-08 |
| Pendimethaline | Maize plant | 3.4E-05 | 3.0E-03 | 3.7E-02 | 1.0E-07 | 1.3E-06 | 1.6E-06 | 2.7E-06 | 1.0E-07 |
| Pendimethaline | barley winter | 5.7E-05 | 3.0E-03 | 3.7E-02 | 1.7E-07 | 2.1E-06 | 2.8E-06 | 3.7E-06 | 3.3E-07 |
| Pendimethaline | pea spring | 7.5E-06 | 3.0E-03 | 3.7E-02 | 2.2E-08 | 2.8E-07 | 1.2E-07 | 1.2E-07 | 8.2E-08 |
| Pendimethaline | rye winter | 1.6E-04 | 3.0E-03 | 3.7E-02 | 4.8E-07 | 6.0E-06 | 7.8E-06 | 1.0E-05 | 6.5E-06 |
| Phenmedipham | beet forage | 4.2E-05 | 5.6E-03 | - | 2.3E-07 | - | *5.7E-08* | *1.1E-07* | *6.4E-08* |
| Phenmedipham | beet sugar | 1.0E-05 | 5.6E-03 | - | 5.7E-08 | - | *1.4E-08* | *2.8E-08* | *2.0E-08* |
| Quizalofop-P-Ethyle | beet sugar | 4.3E-51 | 1.3E-01 | - | 5.5E-52 | - | *2.0E-53* | *3.4E-53* | *3.0E-54* |
| Quizalofop-P-Ethyle | Rape winter | 1.4E-39 | 1.3E-01 | - | 1.8E-40 | - | *6.6E-42* | *1.1E-41* | *4.6E-43* |
| Terbuthryn | potato | 7.3E-03 | 1.4E+00 | - | 1.0E-02 | - | *5.5E-03* | *9.1E-03* | *2.8E-04* |
| Terbuthylazine | potato | 1.6E-03 | 6.2E-02 | 6.2E-01 | 1.0E-04 | 1.0E-03 | 2.5E-04 | 4.1E-04 | 1.3E-05 |
| Thifensulfuron-methyl | oat spring | 1.5E-08 | 1.1E-01 | - | 1.7E-09 | - | *6.8E-11* | *6.8E-11* | *6.8E-12* |
| Thifensulfuron-methyl | wheat winter | 3.8E-09 | 1.1E-01 | - | 4.3E-10 | - | *2.6E-11* | *2.6E-11* | *6.8E-13* |
| Thifensulfuron-methyl | wheat spring | 4.6E-08 | 1.1E-01 | - | 5.1E-09 | - | *2.1E-10* | *2.1E-10* | *1.8E-11* |
| Thifensulfuron-methyl | Maize plant | 2.9E-08 | 1.1E-01 | - | 3.3E-09 | - | *2.5E-11* | *2.5E-11* | *2.1E-12* |
| Thifensulfuron-methyl | barley spring | 1.3E-05 | 1.1E-01 | - | 1.5E-06 | - | *6.0E-08* | *6.0E-08* | *6.0E-09* |
| Thifensulfuron-methyl | meadow mid int | 3.9E-02 | 1.1E-01 | - | 4.3E-03 | - | *9.7E-05* | *9.7E-05* | *1.1E-03* |

| Substances | Crop | Intake fraction | Effect Factor | | Human Damages | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | oral | non cancer | cancer | non cancer | cancer | per treat.min | per treat.max | per ha cult. crop |
| | | kg/kg | DALY/kg | DALY /kg | DALY /kg | DALY /kg | DALY /ha treat. | DALY /ha treat. | DALY /ha cult. |
| Trifluralin | Rape winter | 1.4E-06 | 4.9E-02 | 1.3E-02 | 6.7E-08 | 1.7E-08 | 1.2E-07 | 1.2E-07 | 2.8E-09 |
| Triflusulfuron | beet forage | 1.0E-17 | 1.8E-03 | - | 1.8E-20 | - | *1.8E-22* | *2.7E-22* | *4.1E-23* |
| Triflusulfuron | beet sugar | 5.2E-18 | 1.8E-03 | - | 9.1E-21 | - | *9.1E-23* | *1.4E-22* | *4.0E-23* |
| INSECTICIDES | | | | | | | | | |
| Bifenthrin | Rape winter | 1.2E-05 | 2.5E-02 | 2.5E-01 | 3.0E-07 | 3.0E-06 | 4.9E-08 | 4.9E-08 | 2.2E-09 |
| Carbofuran | Maize plant | 4.7E-02 | 7.5E-02 | 4.7E-01 | 3.5E-03 | 2.2E-02 | 1.0E-02 | 1.2E-02 | 5.9E-04 |
| Cyhalothrin | Rape winter | 3.1E-06 | 2.8E-01 | 2.8E+00 | 8.7E-07 | 8.7E-06 | 7.2E-08 | 9.6E-08 | 1.1E-08 |
| Cyhalothrin | Maize grain | 1.3E-07 | 2.8E-01 | 2.8E+00 | 3.6E-08 | 3.6E-07 | 3.0E-09 | 4.0E-09 | 2.3E-10 |
| Cypermethrin | Rape winter | 1.3E-06 | 3.7E-02 | 2.5E-01 | 5.0E-08 | 3.3E-07 | 4.0E-09 | 4.0E-09 | 9.2E-10 |
| Cypermethrin | Rape winter | 1.3E-06 | 3.7E-02 | 2.5E-01 | 5.0E-08 | 3.3E-07 | 4.0E-09 | 4.0E-09 | 9.2E-10 |
| Cypermethrin | pea spring | 4.2E-06 | 3.7E-02 | 2.5E-01 | 1.6E-07 | 1.0E-06 | 6.0E-08 | 6.0E-08 | 9.0E-09 |
| Deltamethrine | beet forage | 1.1E-06 | 2.3E-02 | 2.3E-01 | 2.6E-08 | 2.6E-07 | 2.1E-09 | 3.5E-09 | 3.3E-10 |
| Deltamethrine | wheat winter | 8.8E-06 | 2.3E-02 | 2.3E-01 | 2.1E-07 | 2.1E-06 | 1.7E-08 | 1.7E-08 | 0.0E+00 |
| Deltamethrine | Rape winter | 1.6E-06 | 2.3E-02 | 2.3E-01 | 3.7E-08 | 3.7E-07 | 3.0E-09 | 4.0E-09 | 3.1E-10 |
| Deltamethrine | barley winter | 6.9E-07 | 2.3E-02 | 2.3E-01 | 1.6E-08 | 1.6E-07 | 1.3E-09 | 1.3E-09 | 8.3E-11 |
| Lambda-cyhalothrin | Maize plant | 8.6E-06 | 4.7E-02 | 4.7E-01 | 4.0E-07 | 4.0E-06 | 3.3E-08 | 4.5E-08 | 2.1E-09 |
| Lambda-Cyhalothrin | pea spring | 3.7E-06 | 4.7E-02 | 4.7E-01 | 1.8E-07 | 1.8E-06 | 1.4E-08 | 1.9E-08 | 3.3E-09 |
| Lambda-Cyhalothrin | ley int | 1.7E-01 | 4.7E-02 | 4.7E-01 | 8.0E-03 | 8.0E-02 | 6.6E-04 | 8.8E-04 | 1.1E-04 |
| Lambda-Cyhalothrin | soybean | 2.3E-07 | 4.7E-02 | 4.7E-01 | 1.1E-08 | 1.1E-07 | 9.0E-10 | 1.2E-09 | 8.0E-11 |
| Terbufos | beet forage | 2.6E-07 | 1.9E+01 | 3.7E+01 | 4.9E-06 | 9.8E-06 | 4.4E-06 | 4.4E-06 | 2.1E-06 |
| Terbufos | beet sugar | 1.6E-07 | 1.9E+01 | 3.7E+01 | 3.0E-06 | 6.1E-06 | 4.4E-06 | 5.5E-06 | 6.3E-07 |
| GROWTH REG. | | | | | | | | | |
| Ethephon | oat spring | 1.2E-05 | 8.2E-01 | - | 1.0E-05 | - | *1.4E-06* | *2.3E-06* | *1.5E-06* |
| Ethephon | wheat winter | 4.9E-06 | 8.2E-01 | - | 4.1E-06 | - | *1.5E-06* | *2.9E-06* | *2.3E-07* |
| Ethephon | wheat spring | 8.1E-06 | 8.2E-01 | - | 6.7E-06 | - | *9.0E-07* | *1.5E-06* | *5.4E-07* |
| Ethephon | barley winter | 1.9E-05 | 8.2E-01 | - | 1.6E-05 | - | *7.5E-06* | *7.5E-06* | *5.4E-06* |
| Ethephon | rye winter | 1.2E-05 | 8.2E-01 | - | 9.8E-06 | - | *4.7E-06* | *4.7E-06* | *1.3E-06* |

[1] The present intake fraction is assumed equal to the harvested fraction. Eilrich (1999) shows that Chlorothalonil, the intake fraction can be typically reduced by a factor 5 compared to the intake fraction, by the washing, peeling and cooking processes. By default, this factor 5 should be applied for all substances, further studies being required to study the reduction linked to these processes.