ORGANIC POLLUANTS IN SWISS COMPOST AND DIGESTATE

THÈSE N^{O} 3599 (2006)

PRÉSENTÉE LE 28 AOÛT 2006
À LA FACULTÉ DE L'ENVIRONNEMENT NATUREL, ARCHITECTURAL ET CONSTRUIT
Laboratoire des sciences et technologies de l'environnement
PROGRAMME DOCTORAL EN ENVIRONNEMENT

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

POUR L'OBTENTION DU GRADE DE DOCTEUR ÈS SCIENCES

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ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE
Suisse
2006

Abstract

Composting (aerobic treatment of organic wastes) and digestion (anaerobic treatment of organic wastes combined with biogas production) are important waste management strategies with increasing significance in the European Union and Switzerland. Most of the compost produced is applied to agricultural soils, which hereby recycles nutrients and influences soil properties beneficially. However, compost can contain pollutants that may be hazardous for the soil ecosystem. The problem related to heavy metals had been recognised and measures for reduction were taken. Regarding organic pollutants, the current knowledge is insufficient for quality control and risk assessment.

This thesis provides a comprehensive overview on organic contaminates in compost, digestate, and presswater and describes factors that may influence them. In the beginning an extensive literature review was carried out to summarize the current data. Compound classes to be analysed in Swiss composts and digestates were prioritized and analytical methods established. Polychlorinated biphenyl concentrations (Σ of PCB 28, 52, 101, 118, 138, 153, 180) were significantly higher in urban (median: 30 $\mu g/kg_{\text{dry weight (dw),}}$ n=52) than in rural samples (median: 14 $\mu g/kg_{dw}$, n=16), which points - together with low concentrations in general - to aerial deposition on feedstock material as major input pathway to compost. Median polycyclic aromatic hydrocarbon (PAH) concentration was 3010 $\mu g/kg_{dw}$ (Σ of 16 PAH defined by the US EPA except dibenzo[*a,h*]anthracene, n=69). PAH levels were influenced by the organic matter degradation process (higher levels in digestate than in compost), the season of input material collection (spring/summer>winter>autumn), the particle size (higher concentrations in unsieved or sieved >20mm than in sieved to ≤ 20mm products), and maturity (lower concentrations in more mature composts). One fourth of the samples exhibited PAH concentrations above the Swiss guide value for compost (Ordinance on the Reductions of Risks linked to Chemical Products). These elevated concentrations can lead to considerable input of PAH to soil by compost application. To assess the major contributors of PAH in compost, characteristic PAH ratios and some molecular markers were considered, which pointed mainly to combustion origin of these contaminants. Multifactor statistical analysis indicated traffic emission, straw combustion and some asphalt abrasion as potential additional sources. Concentrations of other organic pollutants determined (dibenzo-*p*-dioxins and –furans, dioxin-like PCB, brominated flame retardants (BFR), perfluorinated alkyl substances (PFAS), di(2-ethylhexyl)phthalate, nonylphenol and chlorinated paraffins) were mostly above levels found in background soil, except for nonylphenol, which was not detected. Out of 269 pesticides analysed, 30 fungicides, 14 herbicides, eight insecticides and one acaricide were detected.

For the first time, the fate of organic pollutants during full-scale composting and digestion was assessed. Concentrations of low chlorinated PCB increased during composting (about 30 %), whereas a slight decrease was observed for the higher chlorinated congeners (about 10%). Enantiomeric ratios of atropisomeric PCB were close to racemic and did not change. Levels of low molecular weight PAH were reduced during composting (50 to 90% reduction), whereas heavier compounds remained stable. However, as indicated above, conventional composting does not reduce PAH concentrations sufficiently to comply with Swiss guide values (see above).

Further research is needed to i) identify measures to reduce PAH concentrations in digestate and compost, ii) to monitor organic pollutants that are still increasing in other environmental matrices (e.g. BFR and PFAS) or identify new compounds which have not been detected in compost yet, iii) to evaluate potential risk of compost application to soil by assessing the bioavailable fractions of organic pollutants and iv) to examine possible new input materials and co-substrates for composting and digestion.

Keywords: compost, digestate, presswater, organic waste, organic pollutants, PAH, PCB, PCDD/F, brominated flame retardants, perfluorinated alkyl substances, phthalates, chlorinated paraffins, degradation

Résumé

Le compostage (le traitement aérobie de déchets organiques) et la méthanisation (le traitement anaérobie de déchets organiques combinée avec la production de biogaz) constituent des stratégies importantes pour la gestion des déchets dont l'importance augmente dans l'Union Européenne et en Suisse. La majeure partie du compost est appliquée sur les surfaces agricoles, ce qui permet de recycler les éléments nutritifs et d'améliorer les propriétés du sol. Cependant, le compost peut contenir des polluants, qui peuvent avoir des impacts sur l'écosystème du sol. Les problèmes dus aux métaux lourds ont été reconnus et des mesures de réduction ont été prises. Par contre, les connaissances actuelles relatives aux micro-polluants organiques sont insuffisantes pour permettre le contrôle de la qualité du compost et la gestion des risques liés à son utilisation.

Cette thèse donne une vue d'ensemble sur la présence des micro-polluants organiques dans les composts, les digestats et les jus de pressage. Elle caractérise les facteurs qui influencent l'occurrence de ces composés dans ces produits. Au début du présent travail, une importante étude bibliographique a été réalisée pour répertorier les données actuelles. Les classes de substances prévues pour l'analyse ont été priorisées et les méthodes analytiques ont été adaptées. Les concentrations des polychlorobiphényles, PCBs (somme des PCBs 28, 52, 101, 118, 138, 153, 180) dans les échantillons urbains (médiane : 30 µg/kg rapportés à la matière sèche (MS), n=52) sont supérieures à ceux d'origine rurale (médiane : 14 µg/kg$_{MS}$, n=16). Cette différence statistiquement significative, ainsi que les faibles concentrations mesurées indiquent que la déposition atmosphérique sur les matériaux de base représente la voie principale de contamination du compost. La concentration médiane des hydrocarbures polycycliques aromatiques (HAPs) est de 3010 µg/kg$_{MS}$ (somme des 16 HAPs définis par la US EPA à l'exception du dibenzo[*a,h*]anthracène, n=69). La teneur des HAPs est influencée par le processus de dégradation de la matière organique (les digestats montrent des concentrations plus élevées que le compost), la saison pendant laquelle les matériaux de base sont collectés (printemps/été>hiver>automne), le criblage (les concentrations sont plus élevées dans les produits non tamisés ou tamisés à >20 mm comparé à ceux tamisés à <20 mm) et la maturité (les concentrations sont plus faibles dans les composts plus mûrs). Un quart des échantillons dépasse la valeur indicative pour le compost d'après l'Ordonnance sur la réduction des risques liés aux produits chimiques. Ces concentrations élevées peuvent entraîner des apports considérables de HAPs dans les sols suite à l'application du compost. Afin d'évaluer les sources principales des HAPs dans le compost, les rapports caractéristiques des HAPs et des marqueurs moléculaires ont été pris en considération. Ils indiquent que la combustion est la source principale de contamination induite par ces composés. L'analyse statistique multifactorielle indique que les émissions provenant du trafic routier, de la combustion de la paille et de l'abrasion de l'asphalte représentent des sources supplémentaires potentielles. Les concentrations des autres polluants organiques recherchés (dibenzo-*p*-dioxines polychlorées et dibenzofuranes polychlorées, PCBs analogues des dioxines, les retardateurs de flamme polybromés, les substances alkylées perfluorées, le bis(2-ethylhexyl)phtalate (DEHP), le nonylphénol et les paraffines chlorées) sont plus élevées que le bruit de fond mesurés dans les sols sauf pour le nonylphénol qui n'a pas été détecté. Parmi les 269 pesticides analysés, 30 fongicides, 14 herbicides, huit insecticides et un acaricide ont été détectés. Pour la première fois, le devenir des micro-polluants organiques pendant le compostage et la méthanisation a été étudié en conditions réelles. Les concentrations des PCBs faiblement chlorés augmentent d'environ 30 % pendant le compostage et une diminution peu importante a été observée pour les congénères à degré de chloration plus élevé (environ 10 %). Les rapports enantiomériques des PCBs atropisomériques sont racémiques et restent inchangé. Les teneurs des HAPs à faible poids moléculaire diminuent (réduction de 50 à 90 %) mais les composés de poids moléculaire plus élevés restent inchangés. Cependant, les concentrations en HAPs ne sont pas suffisamment réduites pendant le compostage pour rendre les produits compatibles aux valeurs indicatives suisses (cf. plus haut).

Des recherches supplémentaires sont nécessaires pour i) identifier des mesures appropriées afin de réduire les concentrations en HAPs dans les digestats et les composts, ii) suivre les micro-polluants organiques qui augmentent dans d'autres matrices environnementales (p.ex. les retardateurs de flamme polybromés, les substances alkylées perfluorées) ou identifier de nouvelles substances qui n'ont pas été détectées jusqu'à ici et iv) étudier des nouveaux matériaux de départ potentiellement prévues pour le compostage et la digestion.

Mot clés : compost, digestats, jus de pressage, déchets organiques, micro-polluants organiques, HAPs, PCBs, PCDD/Fs, retardateurs de flamme polybromés, substances alkylées perfluorées, phthalates, paraffines chlorées, dégradation

Zusammenfassung

Kompostierung (aerobe Behandlung von organischen Abfällen) und Vergärung (anaerobe Behandlung kombiniert mit Erzeugung von Biogas) sind wichtige Abfallbehandlungsverfahren in der europäischen Union und der Schweiz, mit steigender Bedeutung. Kompost wird vorwiegend auf landwirtschaftliche Böden ausgebracht, wodurch der Nährstoffkreislauf geschlossen und die Bodeneigenschaften positiv beeinflusst werden. Er kann jedoch Schadstoffe enthalten, welche für die terrestrischen Ökosysteme schädlich sein können. Die Probleme im Zusammenhang mit Schwermetallen wurden erkannt und entsprechende Massnahmen zur Reduktion ergriffen. Die Kenntnisse über organische Schadstoffe in Kompost sind nicht ausreichend für eine Risikoabschätzung und die Anwendung eines Qualitätsmanagementsystems.

Die vorliegende Dissertation gibt einen detaillierten Überblick über organische Schadstoffe in Kompost, Gärgut und Presswasser und beschreibt Faktoren, welche die Konzentrationen beeinflussen können. Als Erstes wurde eine umfassende Literaturstudie durchgeführt und die Datenlage zusammengefasst. Die in Schweizer Kompost und Gärgut zu analysierenden organischen Schadstoffe wurden priorisiert und entsprechende Analysemethoden erarbeitet. Die Konzentrationen von polychlorierten Biphenylen (Σ von PCB 28, 52, 101, 118, 138, 153, 180) waren signifikant höher in städtischen Kompost- und Gärgutproben (Median: 30 $\mu g/kg_{Trockensubstanz\ (TS),}$ n=52) als in Proben von ländlichen Gebieten (Median: 14 $\mu g/kg_{TS}$, n=16). Dies deutet, zusammen mit generell tiefen Konzentrationen, auf atmosphärische Deposition auf Ausgangsmaterial als wichtigsten Eintragspfad von PCB in den Kompost hin. Die mittlere Konzentration von polyzyklischen aromatischen Kohlenwasserstoffen (PAK) lag bei 3010 $\mu g/kg_{TS}$ (Median der Σ von 16 PAK die durch die US-amerikanische Umweltbehörde (EPA) definiert wurden ohne Dibenzo[*a,h*]anthracen, n=69). Die PAK Gehalte wurden durch die Art des Abbauprozesses (höhere PAK Konzentrationen in Gärgut als in Kompost), durch die Saison, in welcher das Ausgangsmaterial gesammelt wurde (Frühling/Sommer > Winter > Herbst), durch die Siebweite (höhere Konzentrationen in ungesiebtem oder grob gesiebtem Kompost gegenüber gesiebtem (≤ 20mm) Material) und durch die Reife (tiefere PAK Gehalte in reiferem Kompost) beeinflusst. In einem Viertel der Proben wurde der Richtwert gemäss Chemikalien-Risikoreduktions-Verordnung überschritten. Diese erhöhten Konzentrationen können zu einem beachtlichen PAK-Eintrag in den Boden durch Kompostausbringung führen. Zwecks Identifizierung wichtiger Quellen von PAK in Kompost wurden charakteristische PAK Verhältnisse und molekulare Marker analysiert. Diese wiesen auf Verbrennungsprozesse als Hauptquelle hin. Ein multifaktorielles Modell identifizierte Verkehrsemissionen, Verbrennung von Stroh und Asphaltabrieb als weitere mögliche Quellen. Die Konzentrationen der weiteren analysierten Verbindungen (Dibenzo-*p*-dioxine und –furane, dioxin-ähnliche PCB, bromierte Flammschutzmittel (BFR), perfluorierte alkylierte Verbindungen (PFAS), Di(2-ethylhexyl)phthalat, Nonylphenol und chlorierte Paraffine) lagen vorwiegend über den Gehalten von Böden, welche eine übliche Hintergrundbelastung aufweisen. Von den 269 analysierten Pestiziden wurden 30 Fungizide, 14 Herbizide, acht Insektizide und ein Akarizid nachgewiesen.

Zum ersten Mal wurde das Verhalten von organischen Schadstoffen während der Kompostierung und der Vergärung im Rahmen von Feldstudien untersucht. Die Konzentrationen von niedrig chlorierten PCB nahmen während der Kompostierung zu (ungefähr 30%), wohingegen diejenigen von höher chlorierten leicht abnahmen (ungefähr 10%). Die Enantiomeren-Verhältnisse von chiralen PCB waren racemisch änderten sich nicht. Leichte PAK verschwanden im Laufe der Kompostierung, wohingegen schwerere Verbindungen stabil blieben. Diese Reduktion reicht jedoch nicht aus, um ausschliesslich Komposte zu produzieren, deren PAK Gehalte unter dem Richtwert liegen. (siehe oben).

Weitere Untersuchungen sind erforderlich um i) Massnahmen zur Reduktion der PAK Konzentrationen im Kompost und im Gärgut zu erarbeiten, ii) organische Schadstoffe zu überwachen, die in anderen Umweltkompartimenten ansteigende Konzentrationen zeigen (z.B. BFR und PFAS) oder neue Verbindungen zu identifizieren, iii) den biologisch verfügbaren Anteil der Schadstoffe im Boden nach der Kompostausbringung zwecks Risikoabschätzung zu bestimmen, und iv) mögliche neue Ausgangsmaterialien und Co-Substrate für die Kompostierung und Vergärung zu prüfen.

Schlagworte: Kompost, Gärgut, Presswasser, organische Schadstoffe, PAK, PCB, Polychlorierte Dibenzo-*p*-dioxine und -furane, bromierte Flammschutzmittel, perfluorierte alkylierte Verbindungen, Phthalate, chlorierte Paraffine, Abbaustudie

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1 Introduction

Composting (i.e. aerobic degradation) of organic waste represents an important and well established part of waste management in Europe and Switzerland. Digestion (i.e. anaerobic treatment with or without subsequent aerobic process) has been promoted in recent years due to increasing efforts to combine recycling of organic materials with the production of renewable energy. About 31.5×10^6 and 7.7×10^5 tonnes (t) of organic wastes are processed per year (y) in the 25 European Union member states (EU25) and Switzerland, respectively (Hügi and Kettler, 2004, European Communities, 2005b). Most of the resulting products, including the liquid fraction of the digestion process (presswater), are applied to agricultural land or are used in horticulture and landscaping. Utilization of compost and digestate follows the recycling principle and can have positive effects on physical, chemical and biological soil parameters. However, these products might contain significant amounts of pollutants that are introduced to the soil ecosystem by their application. The problem related to heavy metals had been recognized and statutory and voluntary quality standards were put in place. It was shown that reduction of the heavy metal contents can only be achieved by thorough separation of the input materials at the source (Hogg et al., 2002a), i.e., by excluding municipal solid waste, sewage sludge etc. The knowledge about organic pollutants in so-called source-separated compost (i.e. only containing green waste from private gardens and public green areas, and crude organic kitchen waste from private kitchens and industries) is limited. Information on respective digestate and presswater is completely lacking. From a (soil) risk assessment point of view, this gap of knowledge is problematic. The major goal of this thesis was therefore to inventory organic pollutant contents in Swiss source-separated compost, digestate and presswater (for more details on aims see below) and to determine factors influencing them.

For a thorough understanding of this thesis, the introduction gives an overview on organic pollutants and introduces the most important compound classes. It describes the composting and digestion process and covers strategies and regulations on waste management in Europe and Switzerland. A summary of the current knowledge on levels of organic pollutants in input material and compost and an overview on their fate during composting and after application to soil is provided. This outline results in aims that were pursued in this thesis. An overview of the strategies and methodologies employed follows, which also includes a list of the publications and submitted manuscripts generated during the thesis. A general conclusion is given after all the publications and manuscripts at the end of the thesis.

1.1 Organic Pollutants

Since 1962 when Rachel Carson brought in her book 'Silent Spring' (Carlson, 1962) adverse effects of organochlorine pesticides on the environment and non-target organisms to a general public, research activities on organic pollutants have been increasing continuously. Many other classes of organic pollutants were discovered in the environment (e.g. polychlorinated biphenyls (PCB) (Jensen et al., 1969), polycyclic aromatic hydrocarbons (PAH) (Blumer, 1961)) and still new compound classes are found to be persistent and hazardous (e.g. brominated flame retardants (BFR) (Jansson et al., 1987), polyfluorinated alkyl substances (PFAS) (Hansen et al., 2001)). More hazards than just acute toxicological effects as described by Carson (e.g. cancer, damage to the nervous system, reproductive disorders, and disruption of the immune system have been discovered (Environmental Protection Agency, 2006)). However, relating to organic pollutants, there are still many aspects which are poorly investigated such as mixture toxicity and the assignment of endocrine disrupting effects to specific compounds.

Even though organic pollutants can be emitted by natural processes (volcanic erosion, natural fires and biogenic processes) anthropogenic emissions by far outweigh natural releases (Gribble, 1994, Schauer et al., 2003, Gullett and Touati, 2003). About 100’000 chemicals are currently on the market in Europe and it was estimated that 4000 of them were introduced since 1981 (European Commission, 2006a). Worldwide production volumes have increased since 1930 from about 1×10^6 to about 400×10^6 t/y at present time (European Commission, 2006a). Even though for some organic pollutants regulatory and voluntary measures were taken (e.g. Stockholm convention on persistent organic pollutants (POPs), phase out of pentabrominated diphenyl ether (pentaBDE) and perfluorooctanesulfonate (PFOS)), release of potentially hazardous substances is likely to go in line with the increasing production volume. Three major primary emission pathways of organic pollutants can be distinguished: (incomplete) combustion (e.g. PAH, dibenzo-*p*-dioxins and –furans (PCDD/F)), leaching/volatilisation from products (PCB, BFR) or direct input into the environment (e.g. pesticide application, accidental releases). However, secondary sources e.g. evaporation of previously released and deposited chemicals from soil were also reported (Lee and Jones, 1999). After emission into the environment, organic pollutants undergo various processes such as phase distribution, transport, degradation, and accumulation in the food chain. Due to distribution and long-range transportation processes (mainly by air), many substances are ubiquitous (Jones and de Voogt P., 1999, Kalantzi et al., 2001, Berset et al., 2001) and were detected far from where they had been emitted, e.g. in the Arctic (Stern et al., 1997, Ikonomou et al., 2002, Lie et al., 2003, Smithwick et al., 2005) Via aerial deposition on input material and direct input (e.g., improper separation), organic pollutants can also enter compost. At least for persistent organic pollutants, concentrations are expected to increase during composting and digestion as a consequence of organic mass degradation. Below an outline of the most relevant organic pollutants from a compost point of view is provided, covering production volumes, applications, and effects.

1.1.1 PCB

PCB were used since 1930 as dielectric fluids in transformers, capacitors, heat exchangers, in hydraulic machinery, in lubricating and cutting oils, as plasticizer in sealants, adhesives, lacquers and paints (Borja et al., 2005). Although PCB production was phased out and use banned in the mid 80’s, significant amounts of these compounds remain in long-life equipments and products, which leads to a still important mass flow into the environment. In 2000, these emissions were estimated to be 14 kg/y (sum of PCB 28, 52, 101, 118, 138, 153, 180, Σ7PCB) in Switzerland and 1.5 t/y in EU25 (Breivik et al., 2002). Reemission from soil is considered as an additional secondary source (Lee and Jones, 1999). Emission data for dioxin-like PCB (DL-PCB, exhibiting close toxicological similarities to PCDD/F, see below) are scarce (Richter and Johnke, 2004). PCB are toxic and have potentially endocrine disrupting prosperities (World Health Organisation, 1993). They are listed in the Stockholm convention on POPs in Annex A (elimination) and C (unintentally produced chemicals) in order to reduce their presence in the environment.

1.1.2 PAH

PAH originate from (incomplete) combustion processes. Important sources are domestic heating, open fires, diesel and other combustion engines, combined heat and power plants, waste incineration plants, aluminium works, and abrasion from asphalt and tires (European Communities, 2001). Relative importance of the different sources varies considerably between countries (Mandalakis et al., 2005). Approximate emission in the EU25 and Switzerland was estimated to be 24’500 t/y and 240 t/y, respectively (sum of 16 PAH defined by the US EPA, Σ16PAH, basis 1990, (European Communities, 2001), assuming constant emissions over the last ten years (Convention on Long-Range Transboundary Air Pollution, 2006) and extrapolated to Σ16PAH with database used for source apportionment in (Brändli et al., 2006a)). PAH are carcino- and mutagenic and were detected in many environmental compartments (World Health Organisation, 1998).

1.1.3 PCDD/F

PCDD/F are possible by-products from the production of certain chemicals and are formed in combustion and incineration processes (World health organisation, 1989). In the EU25 yearly emissions were estimated at 43 μg I-TEQ/y/capita (cap) (sum of the 17 2,3,7,8-chlorosubstituted PCDD/F, Σ17PCDD/F (European Commission, 2005)). The main PCDD/F emission source in Switzerland was illegal combustion of household waste (50% of total emission), whereas industry and waste disposal accounted for 18% and 17%, respectively (Koch et al., 1999). Swiss emissions have significantly decreased over the last 25 years from 6.4 to 0.9 μg I-TEQ/y/cap (Koch et al., 1999). PCDD/F are toxic (appointed international toxicological equivalent factors (I-TEQ)), have endocrine disrupting effects and were classified as potential carcinogenic by the international agency for research on cancer (European Commission, 2005). They are listed in the Stockholm convention on POPs Annex C (unintentally produced chemicals), which calls for clear measures to reduce their emissions.

1.1.4 Brominated flame retardants

Brominated flame retardants (BFR) have been widely used in many products such as furniture, vehicles, textiles, material for construction and electronic equipment. They were estimated to have reduced fire death incidences by 20% in the EU in the last 10 years (BSEF, 2006). European market demand in 2001 was: decabrominated diphenyl ether (decaBDE): 7’600 t/y, pentaBDE: 610 t/y, octaBDE: 150 t/y, hexabromocyclododecan (HBCD): 9’500 t/y, tetrabromobisphenol A (TBBPA): 11’600 t/y (BSEF, 2006). PentaBDE and octaBDE production was phased out in 2002 in Europe. They have been detected in most environmental matrixes (de Wit, 2002) and even in top predators in remote areas (Muir et al., 2006). BFR were reported to bioaccumulate, to be toxic and to have endocrine disrupting effects (Rahman et al., 1998, de Wit, 2002).

1.1.5 Chlorinated paraffins

Chlorinated paraffins (CP) are utilized as additives in metal working fluids, as flame retardants, as plasticizers and as additives in paints, coatings and sealants (Alcock et al., 1999). In Europe, their production is lower than 15’000 t/y for short chain CP (C_{10-13}, SCCP) and between 45’000 and 160’000 t/y for medium chain CP (C_{14-17}, MCCP) (Barber et al., 2005). The use of SCCP is restricted to few applications in the EU and banned in Switzerland (Bolliger and Randegger-Vollrath A., 2003). They are persistent, bioaccumulative and toxic (Bolliger and Randegger-Vollrath A., 2003). CP were detected in many (environmental) matrixes such as sewage sludge (Stevens et al., 2003), sediments (Hüttig and Oehme, 2005), soils (Iozza et al., 2006) and even in human milk (Thomas et al., 2006).

1.1.6 Perfluorinated alkyl substances

Perfluorinated alkyl substances (PFAS) are employed as stain and water repellents for surface treatment of textiles, carpets, leather and paper products. Furthermore, these compounds are used in fire fighting foams, lubricants and insecticides. Even though most of the production volume of perfluorooctane sulfonate (PFOS) based chemicals has been voluntarily phased out, similar compounds with perfluorinated chains are still in use. Only rough estimations on the use of PFAS are available (Organisation for Economic Co-operation and Development OECD, 2005). These compounds have recently gained considerable attention due to their ubiquitous distribution in the environment (Kannan et al., 2002, Martin et al., 2004, Holmstrom et al., 2005). Top predator species from as remote locations as the Arctic often show PFOS and perfluorinated carboxylates concentrations exceeding the most prominent classical POPs (Verreault et al., 2005, Smithwick et al., 2005). PFAS are resistant to biological and chemical degradation and many of them have toxicological effects in laboratory animals (Higgins et al., 2005).

1.1.7 Pesticides

Pesticides (mainly herbicides, fungicides and insecticides) contribute to an increasingly efficient agricultural production and are also used on urban areas. Around 2'000 active substances are known worldwide and more than 600 are currently used (Tomlin, 1997). Worldwide use of herbicides, fungicides and insecticides in agricultural production was 132’000, 148’000, and 86’000 t/y, respectively in 2001 (Food and Agriculture Organisation of the United Nations, 2006). In Switzerland, the use of fungicides, herbicides and insecticides in 2000 was at 720, 650 and 190 t/y, respectively. Quantities of pesticides use decreased significantly between 1988 and 2000 from 2455 t/y to 1577 t/y (Swiss Federal Statistical Office, 2002). Together with the more and more thorough evaluation of these compounds before they are authorized to be used (Swiss Federal Office for Agriculture, 2006), these reduced quantities might point to decreasing hazards from pesticide application to the environment. Consumption numbers of individual pesticides are difficult to obtain, however some information is available from the Chemie Pharma Switzerland (Table 1, personal communication P. Vessel). Pesticides are used to exert controlling effects on specific organisms; however many of them have adverse effects on non-target organisms also. Pesticides and among them particularly the early organochlorine compounds can be very persistent. They were detected in many environmental compartments e.g., the atmosphere, rainwater and sediments (Bucheli et al., 1998, Unsworth et al., 1999, Warren et al., 2003, Quaghebeur et al., 2004)). It was also reported on long-range transport of pesticides, which lead to their detection in places far from where they were originally applied e.g., Arctic. (Hageman et al., 2006).

Table 1: Annual amounts of pesticides used in Swiss and American agriculture (source: personnel communication P. Vessel, SGCI

		US total 615'000 t			CH total 1800 t
1.	Atrazine	40‘000	1.	Folpet	95
2.	Metolachlor	32‘000	2.	Glyphosate	90
3.	Metam Natrium	28‘000	3.	Mancozeb	80
4.	Methylbromid	20‘000	4.	Isoproturon	65
5.	Glyphosate	18‘000	5.	Captan	45
6.	Dichlorpropen	17‘000	6.	Atrazine	35
7.	Acetochlor	16‘000	7.	Metamitron	30
8.	2,4-D	15‘000	8.	Phosethyl Aluminium.	30
9.	Pendimethalin	13‘000	9.	Dinoseb	30
10.	Trifluralin	12‘000	10.	Mecoprop	30
11.	Cyanazin	10‘000	11.	Tebutam	20
12.	Alachlor	7‘000	12.	Orbencarb	20
13.	Copper hydroxide	6‘000	13.	Chlorothalonil	20
14.	Chlorpyrifos	6‘000	14.	Prosulfocarb	20

1.1.8 Other compound classes

The above-mentioned list is by far not complete. There are many other compounds such as plasticizers (e.g. di(2-ethylhexyl)phthalate (DEHP), produced at 250’000 t/y in Germany (Fromme et al., 2002)), or surfactants (e.g. nonylphenolpolyethoxylate (NPnEO), production rate in Western Europe: 77’600 t/y in 1997, use restricted in Switzerland in 2005 (Wettstein, 2004)) which find their way to the environment and might have adverse effects to the ecosystems. Other currently widely investigated compounds such as personal care products or pharmaceuticals are not covered in this study, because they are considered of minor importance for compost due to their major input pathways to the environment via urban drainage systems.

1.2 Waste management, legislation and quality assurance with regard to organic pollutants and compost/digestate

In industrialised countries, waste production has been constantly increasing over the last years. In Europe, 534 kg/y/cap municipal waste was produced (European Communities, 2005a). Swiss municipal solid waste production amounted to 359 kg/y/cap (Federal Office for the Environment, 2005). Waste management has therefore become a major task. Composting and digestion is a sustainable waste reduction strategy that recycles nutrients and generates energy. Here, an overview on statutory and voluntary aspects on waste management and quality assurance regarding organic pollutants in compost is provided.

1.2.1 Composting process

Composting is the process employed for the controlled aerobic treatment of organic material. There are a variety of systems such as triangle and table windrow composting, shed composting, aerated boxes and trenches, vermicomposting etc. In Switzerland 73% of the organic wastes composted was treated in open windrows systems, 8% in halls and 6% in aerated boxes (status 2003). The remaining material (12%) was digested (Hügi and Kettler, 2004).

Input material for composting is first chopped and a feasible mixture of organic wastes and structuring material is prepared to ensure sufficient porosity for aerobic conditions. Composting is a dynamic and complicated ecological process in which temperature, pH and nutrient availability are constantly changing (Figure 1a). It passes through four microbiological phases identified by different temperature levels (Chen et al., 1997, Potter et al., 1999). In the initial mesophilic (30-45 °C) phase, which lasts about 1-3 days, microorganisms (Figure 1b) decompose the readily degradable compounds, enhancing temperature. The pH decreases slightly due to organic acids production. At a temperature above 40 ºC the thermophilic strains take over. If the temperature rises above 60 ºC, the fungi are deactivated and the reaction is continued by thermophilic bacteria. This thermophilic stage (45-75 °C) lasts for about one to six weeks and substances such as sugars, fats, starch and proteins are metabolized. During this stage, most of the human and plant pathogens are destroyed. The pH changes to alkaline as ammonia is released due to degradation of proteins. The reaction rate decreases as the more resistant materials are attacked and the compost enters the cooling-down stage. As the temperature decreases, the thermophilic fungi whose spores withstood the high temperature or which survived in the cooler outer zones (re-)invade the compost material. They start to attack the cellulose, hemicellulose and other polymers. In the fourth stage, the maturation stage, little heat is generated since the most degradable organic matter has been metabolized already. The final pH is normally slightly alkaline and mesophilic microorganisms and macrofauna (Figure 1b) colonise the compost. The material is considered stable as no further biodegradation occurs.

Since microbial activities are crucial during the composting process, it is essential to achieve appropriate water and oxygen supply by irrigating, covering the windrow with a air-permeable membrane and turning it on a regular basis. As a consequence of organic matter degradation, composting reduces the initial mass of input material by about 40% (Hügi and Kettler, 2004).

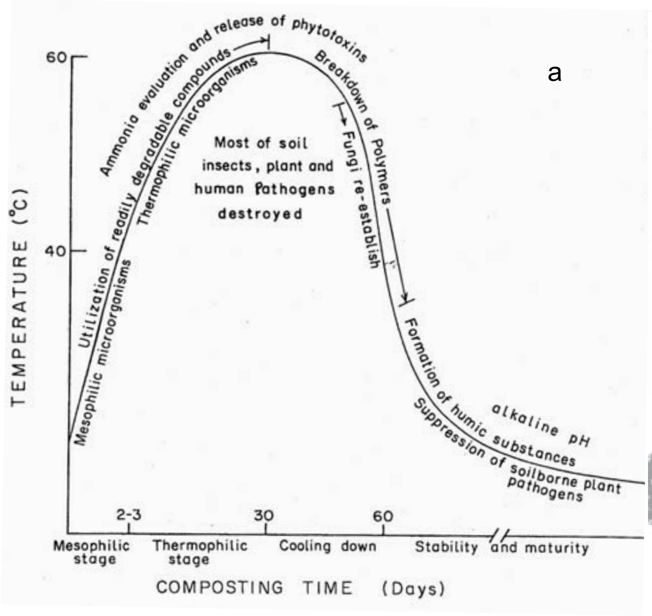

Figure 1a: Temperature and processes versus time of composting (Chen et al., 1997)

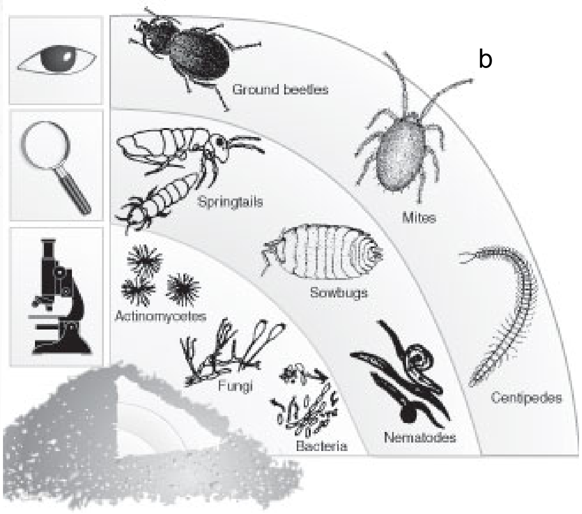

Figure 1b: Compost organisms (Starbuck, 2006)

1.2.2 Digestion

Digestion is the anaerobic treatment of organic wastes mostly coupled with biogas production. Different systems are employed, such as mesophilic (34-45 °C) and thermophilic (50-58 °C) digestion and liquid (input material is liquid) and solid (input material is more solid) fermentation. The latter two processes are also called wet and dry digestion. Thermophilic digestion complies mostly with the hygienic standards of the Swiss Association of Swiss Compost Plants (Fuchs et al., 2001), whereas in mesophilic processes a separate hygienisation step might be necessary. Wet digestion is commonly applied to farmland manure. Even though other organic wastes are worked up as co-substrates by such agricultural digestion processes, the amount of green and kitchen waste treated with this set-up is limited in Switzerland. However, the trend is increasing, since biogas plants are more and more popular amongst farmers. For green and organic kitchen waste thermophilic dry digestion is probably the most significant process in Switzerland. There is one important operator (Kompogas, Glattbrugg, Switzerland) running nine solid-fuel fermentation plants, which treat about 93’000 t organic waste per year (status 2005, with increasing perspective). In this process, the input material undergoes a mechanical pre-treatment where it is chopped up and ferrous metal is removed. The material is passed to the feeder, where a homogeneous pumpable mixture is produced by adding press- and tapwater. In order to initiate the digestion process the substrate is inoculated with digestate. Passing through a heat exchanger, the material is pumped to a fermenter. The residence time in the tank is about 12 days at a temperature of 55 ºC. The characteristic stages of the digestion process are briefly summarized here (Vorkamp, 2000): after the establishment of anaerobic conditions macromolecules such as proteins, sugars and fats are degraded to amino acids, monosaccharide and fatty acids. These hydrolytic reactions are the speed limiting step of the fermentation process. In the following acidic phase, organic acids (e.g. acidic acid, butyric acid, lactic acid) and other compounds such as alcohol, carbon dioxide (CO_2) and water are produced. It is possible that in this stage the pH decreases due to a potential low buffer capacity of the input material. In the following methanogenic phase these acids, water and carbon dioxide are degraded by microorganisms to CO_2 and methane (CH_4). Optimal growing conditions for methanogenic microorganisms are at pH 6.5 to 8 and therefore it might be possible that the pH has to be raised. CH_4 produced during fermentation is used as biogas for energy production or as fuel for cars. The fermentation residues are dewatered and the presswater is either recycled into the fermentation process or applied to agricultural land as liquid fertilizer. The solid fraction is submitted to subsequent aerobic stabilization applying similar techniques as in compositing. The total mass reduction during fermentation is about 13% (personal communication, R. Leisner, Kogas AG, Uzwil, Switzerland).

1.2.3 The Situation in Europe regarding composting and digestion

1.2.3.1 Waste management and corresponding regulations

European waste management is based on three principles: waste prevention, recycling and reuse and improving final disposal and monitoring (European commission, 2006b). Composting and digestion belongs to the second principle –reuse and recycling- of organic matter.

In the EU25 $31.5x10^6$ t wet weight (ww) of organic municipal waste is composted per year (European Communities, 2005b). The ten new European member states contribute little to this amount, whereas in other countries (e.g. Austria, Germany) nearly 60% of the potential material is recycled (Hogg et al., 2002a). The EC Council Directive on the Landfill of Waste (1999/31/EC) has implemented strict limits on the amount of biodegradable municipal waste that can be disposed of via landfill. These amounts must be reduced to:

- 75% of the amount produced in 1995, by 2006
- 50% of the amount produced in 1995, by 2009
- 35% of the amount produced in 1995, by 2016.

The most straightforward strategy to reach these targets is composting or digestion. Additionally, the European directive on the promotion of electricity produced from renewable energy sources (2001/77/EC) targets at doubling the proportion of renewable energy to 12% of the gross energy consumption by 2010. Digestion of organic wastes is one strategy to pursue this target. Based on the above directives, it can be expected that the amount of compost and digestate produced in Europe will increase in the next years.

1.2.3.2 Legislation and voluntary quality assurance systems relating to organic pollutants in compost

Generally, the legal framework for compost with regard to organic pollutants levels is largely lacking and differs widely between the few European countries where they are implemented. Organic pollutants in compost are regulated in Austria, Denmark and Luxemburg (Hogg et al., 2002a) (Table 2). In Austria, limit values refer to municipal solid waste compost. Values are comprised in the “Düngemittelverordnung” and apply for organochlorine pesticides, PCB, PCDD/F, PAH and some pesticides (cypermethrin, deltamethrin, fenvalerate) (Zethner et al., 2000). The Danish environmental agency has implemented limit values within the ‘Statutory Order Regarding the Application of Waste Products for Agricultural Purposes’ for linear alkylbenzene sulphonates (LAS), PAH, nonylphenol (NP) and NPnEO and DEHP (Hogg et al., 2002b). Luxemburg applies guide values for PCB, PCDD/F and PAH.

Table 2: Limit and guide values respectively for organic pollutants in compost in different European countries (adapted from (Hogg et al., 2002a))

	Austria	Denmark	Luxemburg	Switzerland
PCB [a]	1 mg/kg$_{dw}$		0.1 mg/kg$_{dw}$	
PCCD/F [b]	50 ng I-TEQ/kg$_{dw}$		20 ng/kg$_{dw}$	20 ng I-TEQ/kg$_{dw}$
PAH [c]	6 mg/kg$_{dw}$	3 mg/kg$_{dw}$	10 mg/kg$_{dw}$	4 mg/ kg$_{dw}$
AOX [d]	500 mg/kg$_{dw}$			
Hydrocarbons	3000 mg/ kg$_{dw}$			
LAS [e]		1300 mg/kg$_{dw}$		
NPE [f]		30 mg/kg$_{dw}$		
DEHP [g]		50 mg/kg$_{dw}$		
Remarks	Limit values for mixed MSW[h] compost	Limit values for biowaste compost	Guide values	Guide values

[a]PCB: polychlorinated biphenyls; [b]PCCD/F: polychlorinated dibenzo-*p*-dioxins/furans, *sum of the 17 2,3,7,8-chlorosubstituted PCDD/F*; [c]PAH: polycyclic aromatic hydrocarbons, sum of 16 PAH defined by US EPA; [d]AOX: absorbable organic halogens; [e]LAS: linear alkylbenzene sulphonates; [f]NPE: nonylphenol and -ethoxylates; [g]DEHP: di (2-ethylhexyl) phthalate [h]MSW: municipal solid waste, dw: dry weight.

In some countries such as Austria, Germany, the Netherlands, Sweden and Belgium, voluntary quality assurance systems have been established (Hogg et al., 2002a). Important points apply to separate collection, plant engineering, compost production, marketing, public relations work, definition of product range, policy/regulation and certification. A main objective of quality assurance is environmental protection and soil conservation. For further information also including heavy metals it is referred to (Hogg et al., 2002a, Amlinger et al., 2004).

1.2.4 Situation in Switzerland

1.2.4.1 Waste management

In contrast to the EU, the Swiss waste management system is prioritised: first priority is prevention of waste production. Only if waste production cannot be reduced, the second measure –reuse and recycling- is applied. And as an ultimate measure, waste is, as environmental friendly as possible, disposed of (Federal Act on Environmental Protection, USG (Swiss Confederation, 1983)). Composting and digestion belongs to the second priority –reuse and recycling- of organic matter. Compost is defined in the Regulation on Commercialisation of Fertilisers (own translation DüBV, (Swiss Confederation, 2001)) as ‘professionally aerobically rotted material originating from plants or animal material used as fertilizer, soil improver, growing substrate, erosion protection agent, in land reclamation or as artificial substrate’. Digestate is ‘professionally anaerobically rotted and subsequently aerated material originating form plants or animal wastes’ used for the same purposes as compost. The legislation related to fertilisers is currently under change.

Approximately 770'000 t ww of green wastes, crude organic kitchen waste and organic waste of industrial origin (e.g. paper sludge, residues from food processing etc.) are processed to compost and digestate in Switzerland every year. This amount has doubled in the last ten years (Baier et al., 2005) and accounted in 2005 for 100 kg/y/cap (Federal Office for the Environment, 2005). It was estimated that almost 80% of the potential compostable wastes are recycled nowadays (Hügi and Kettler, 2004), and a further increase is expected due to improved recycling and stimulation of the production of renewable energy. About 70% of compost, digestate and presswater is applied to agricultural land, the rest is used in horticulture or landscaping (Hügi and Kettler, 2004). For production and application of compost and digestate, four domains within the Swiss legislation are important: The Technical

Ordinance on Waste (TVA), the Ordinance on the Reductions of Risks linked to Chemical Products (ORRChem), the Regulation on the Commercialisation of Fertilisers (DüBV, own translation) and the Ordinance relating to Impacts on the Soil (OIS).

1.2.4.2 Technical Ordinance on Waste (TVA)

The legal framework for composting is given in TVA (Swiss Confederation, 1990). It is based on the Federal Act on Environmental Protection (USG, (Swiss Confederation, 1983)) and the Federal Act on the Protection of Waters against Pollution (GSchG, (Swiss Confederation, 1991)). The TVA sets rules for location und operation of composting facilities. According to this ordinance, once a year heavy metals and nutrients analyses have to be carried out by every composting and digestion plant processing more than 100 t/y and respective results as well as amounts of organic wastes processed have to be reported on behalf of the authorities.

1.2.4.3 Ordinance on the Reductions of Risks linked to Chemical Products (ORRChem)

The ORRChem (Swiss Confederation, 2005) is based on the Federal Act on Protection against Dangerous Substances and Preparations (ChemG, (Swiss Confederation, 2000)), the Federal Act on Environmental Protection (USG, (Swiss Confederation, 1983)), the Federal Act on the Protection of Waters against Pollution (GSchG, (Swiss Confederation, 1991)) and Federal Act on Foodstuffs and Utility Articles (LMG, (Swiss Confederation, 1992)). The ORRChem prohibits or regulates the handling of dangerous substances. Compost falls into the category ‘fertilizer’ and limit values for heavy metals (Pb, Cd, Cu, Ni, Hg, Zn) as well as guide values for PAH (Σ16PAH: 4 mg/kg dry weight (dw)) and Σ17PCDD/F: 20 ng I-TEQ/kg$_{dw}$) for compost are implemented (Table 2). Additionally, it lists duties and responsibilities for operators of composting and digestion plants and provides (maximum) application rates for compost and presswater used as fertilizer (25 t$_{dw}$/ha/3y, and 200 m^3/ha/3y, respectively) and as soil conditioner (100 t$_{dw}$/ha/10y).

1.2.4.4 Regulation on the Commercialisation of Fertilisers (DüBV)

Compost and digestate must be registered at the Swiss Federal Office for Agriculture, according to the Regulation on the Commercialisation of Fertilisers (DüBV, own translation, (Swiss Confederation, 2001)). For environmental relevant exigencies on the quality, it is referred to ORRChem.

1.2.4.5 Ordinance relating to Impacts on the Soil (OIS)

The purpose of OIS (Swiss Confederation, 1998) is to maintain soil fertility. Its appendix gives guide values for PAH (Σ16PAH: 1 mg/kg$_{dw}$) and PCDD/F (Σ17PCDD/F: 5 ng I-TEQ/kg$_{dw}$) and trigger values for PCB (Σ7PCB: 0.2 mg/kg$_{dw}$ for plant production. In contrast to other European countries, these limit values are not related to application of fertilizers. However, this ordinance is of relevance, since it defines substances which are considered as relevant with respect to soil fertility in Switzerland.

1.2.4.6 Voluntary quality assurance

The Association of Swiss Compost Plants (ASCP) has implemented additional voluntary quality standards for its members (Fuchs et al., 2001). Recently, these quality standards were adapted by the two other composting associations (Biogas-Forum and Interessensgemeinschaft Anlagen des Kompostforums) and a common office commissioned with the quality control was set up. However, these guidelines do not refer to organic pollutants.

1.3 Organic pollutants in compost

1.3.1 Data in input material

Plausible input pathways of organic pollutants to compost and digestate are aerial deposition on green waste, accidental (i.e., improper separation of input materials, e.g., plastic debris) and/or deliberate input (e.g., pesticide application to fruits and vegetables). Data on organic pollutants in compost input material is very limited. Green waste, kitchen waste with and without paper, shrub clippings, grass, leaves and/or bark were analysed for PCB, PAH, PCDD/F (Krauss, 1994, Sihler et al., 1996, Wilke, 1997), for organochlorines (Harrad et al., 1991, Epstein, 1997, Buyuksonmez et al., 2000) and CP (Nilsson, 2000). Swiss data could only be found for some organochlorines in grass (Kuhn et al., 1990) and for PAH in foliage (Kuhn and Arnet, 2003). Concentrations were in general compared to finished compost. Aerial deposition data as well as reports from laboratories monitoring pesticides residues in fruits and vegetables might give further indications on organic pollutants levels in input materials. It has to be considered that the analysis of input material is particularly challenging due to its heterogeneous structure.

1.3.2 Fate during composting and digestion

Mineralization and/or evaporation of some organic pollutants (e.g. some PAH, DEHP (Martens, 1982, Joyce et al., 1998, Hund et al., 1999, Vergé-Leviel, 2001, Hartlieb et al., 2003) during composting was observed. Other compounds (e.g. PCB, benzo[*a*]anthracene (Joyce et al., 1998, Vergé-Leviel, 2001)) were found to be stable during aerobic treatment. Based on dw this results in an increase of concentrations during composting as a consequence of organic mass degradation, which accounts for roughly 40% (Hügi and Kettler, 2004).

Little data on the fate of organic pollutants during thermophilic digestion of green and organic kitchen waste is available. Vorkamp (2000) found some pesticides (chlorothalonil, thiabendazole, methidation, endosulfan) to be reduced during digestion or the subsequent maturation phase whereas others were stable (O-phenyl-phenol, dodemorph). It has to be considered, that in both, composting and digestion, formation of stable metabolites and non-extractable residues might mimic mineralization or transformation processes (van Raaij et al., 1996, Vergé-Leviel, 2001, Hartlieb et al., 2003). Composting and also amendment of compost has been applied as soil remediation strategy. For review see (Semple et al., 2001).

1.3.3 Current knowledge on contamination level

The occurrence of PAH, PCB, and PCDD/F in source-separated compost is well documented. However, most of the data relevant to this subject have been published in form of government reports, master or diploma theses, or dissertations. Other compounds, such as BFR, pesticides, phthalates, LAS, CP, NP, chlorobenzenes and chlorophenols have been detected in source-separated composts as well, but the number of samples is very limited (Kummer, 1990, Harrad et al., 1991, Krauss, 1994, Aldag and Bischoff, 1995, Tørsløv et al., 1997, Hund et al., 1999, Paulsrud et al., 2000, Nilsson, 2000, Paulsrud et al., 2000, Zethner et al., 2000, Buyuksonmez et al., 2000, Vanni et al., 2000a, Vanni et al., 2000b). Some data on organic contaminants in Swiss source-separated compost are available for PAH (Kuhn et al., 1990, Berset and Holzer, 1995, Schleiss, 2002, Kuhn and Arnet, 2003), PCB (Kuhn et al., 1990, Berset and Holzer, 1995) and some organochlorine pesticides (Kuhn et al., 1990). However, the number of samples analyzed and the substance classes included are very narrow and the results do not provide a representative overview on the contamination of Swiss compost. Data on digestate and presswater is completely lacking.

Even though the occurrence of organic pollutants in compost may not be directly linked to impacts for the soil ecosystem (e.g. because the amounts of pollutants extracted from compost do not reflect the biological available fraction), investigation of the contamination level in compost is necessary for an integrated assessment of this matrix, long term soil quality assurance, and legislative requirements (OIS).

1.3.4 Fate in compost-amended soil

Studies on long term fate of organic pollutants in agricultural soils are limited and influencing factors multiple. The knowledge about the fate of organic pollutants applied via compost to soils is even sparser. Vergé-Leviel (2001) studied the fate of labelled PAH (phenanthrene, fluoranthene, benzo[*a*]anthracene), pesticides (dicamba and carbendazime) and PCB 52 (concentrations 20-60 $\mu g/kg_{dw}$) in a compost soil mixture (1:20) in the lab. Mineralization of PAH and pesticides was reduced or enhanced after compost amendment to soil, depending on the degradation capacities of the soil and the composts. For PCB no difference was observed in mineralization if compost was incubated separately or in combination with soil. However, in this study labelled substances were applied to finished compost (28 days before soil amendment) and not to input material, which might possibly have influenced their behaviour (i.e. not ‘bound’ originally to compost). Hund et al. (1999) studied the fate of ^{14}C-labelled pyrene, di(2-ethylhexyl)phthalate (DEHP) and pentachlorophenol (PCP) applied to input material (1.5-4 mg/kg_{dw}), which was then composted and amended to soil in a reactor and a lysimeter (both 4.8 kg_{dw}/m^2) set-up. In both studies concentrations of organic pollutants decreased considerably over 500 days and the ratio of non-extractable residues increased continuously. In the leachates and in plants grown in the lysimeter only traces of labelled substances were detected. There was no effect on the soil organisms by contaminated compost. The data discussed here is based on laboratory studies and no corresponding field studies were found. Extrapolation of (simplified, small scale) laboratory derived findings to (complex, large scale) environmental systems always bears the risk of failure. In a long-term study on the fate of PCB and PAH in an agricultural soil, it was for instance found that persistency of these contaminants might have been underestimated by a factor of ten or more (Doick et al., 2005). It is important that in such studies organic pollutants are applied to soil via compost (no direct spiking), since compost might influence the behaviour of organic pollutants as was found before for farmland manure (Burkhardt et al., 2005).

1.4 Aim of this thesis

Composting and digestion is an important, already well established, and further increasing waste management strategy in the European Union and Switzerland. However, current data on organic pollutants in Swiss compost and digestate is insufficient for quality control and risk assessment. Due to the lack of knowledge, emotional messages in relation to the risk of organic pollutants in compost and digestate distributed by media might turn public opinion towards non-acceptance. Therefore, scientifically established information to this topic is needed.

The overarching goal of this thesis is to provide a comprehensive and state-of-the-art overview on the current levels of organic pollutants in Swiss compost, digestate and presswater, and to determine factors influencing them. This was pursued by:

- compiling existing data on organic pollutants in compost and its input material and evaluating parameters that might affect their concentrations.

- selecting and prioritizing representative organic compounds to be analysed in Swiss compost, and generating a representative sampling plan.
- establishing optimized analytical methods (incl. sample preparation) to determine first priority organic pollutants in compost, digestate and presswater.
- analysing organic pollutants in these matrices.
- identifying the factors that influence organic pollutant concentration in compost and digestate and appointing relevant sources.
- comparing the data with literature and legislative values and with concentrations in recipient soil.
- relating organic pollutant input to soil by compost application to other input pathways such as aerial deposition.
- studying possible degradation of first priority organic pollutants during composting and digestion on full-scale plants.

1.5 Strategy and Methodology

The aims listed above were followed by the strategies and methodologies outlined here. Since methods are described in details in the respective publications and manuscripts, a short overview is provided only.

1.5.1 Literature review

All reports and publications on organic pollutants in compost and digestate available were collected (n > 60) and an extensive database established. Data were grouped in different input materials (kitchen waste, organic household waste, green waste, foliage, shrub clippings, bark and grass) and in two classes of compost (organic household waste compost, green waste compost). Organic pollutant concentrations in these groups were compared by applying statistical tests. Possible factors (e.g. characteristic of the area of input material collection, urban/rural) influencing the concentrations in compost were hypothesized and tested on the dataset. Median values in compost were related to data from soil, its main recipient matrix. For results see the first paper (Brändli et al., 2005). This overview provided the basis for the selection of compound classes to be analysed in Swiss compost and digestate.

1.5.2 Selected compound classes and corresponding concentrations in compost literature

PAH and PCDD/F were selected as representative pollutants that are produced unintentionally from various, mainly anthropogenic combustion processes. Median value of PAH in compost from the literature was 1870 $\mu g/kg_{dw}$ (Σ16 EPA PAH, n=101), which is roughly ten times higher than values in soil (Brändli et al., 2005). Based on their high emission rates (see above), their anthropogenic origin, their toxicity and the existing guide value for compost in the ORRChem, PAH were selected as first priority compounds in this study. Levels of PCDD/F in compost from the literature were 9.3 ng I-TEQ/kg_{dw} (n=185), which is, as for PAH in the upper range of values measured in soil (Schmid et al., 2005). Due to decreasing emissions (see above), PCDD/F were considered as second priority pollutants, even though there is a guide value in the ORRChem for compost.

PCB are a representative of POPs that are banned for use but still present in the environment. Median PCB concentration in compost in the literature was 38 $\mu g/kg_{dw}$ (sum of PCB 28, 52, 101, 138, 153, 180, n=179), which is as for the above mentioned compounds higher than background soil levels (Meijer et al., 2003). PCB were selected as first priority compounds due to their ability to serve as an indicator for POPs of anthropogenic origin and the existing trigger value for soil (OIS (Swiss Confederation, 1998)).

BFR and CP were considered as appropriate indicators for persistent, high volume and ubiquitous chemicals still under production. PBDE were analysed in German compost before. Median concentration was 12 $\mu g/kg_{dw}$ (sum of tri to heptaBDE). SCCP and MCCP were analysed qualitatively in source separated organic household waste from Sweden (Nilsson, 2000). BFR and CP were both considered as second priority pollutants in this inventory due to analytical limitations and particular analytical challenges, respectively. PFAS, which have recently received considerable attention, have never been analysed in compost before. To get a first overview, they were included as second priority pollutants in this study.

Pesticides are mostly high production chemicals applied on agricultural crops. Median concentrations of (organochlorine) pesticides in compost from the literature were below 20 $\mu g/kg_{dw}$ (Brändli et al., 2005). There is a number of additional studies that analysed specific pesticides in compost ((Kummer, 1990, Harrad et al., 1991, Krauss, 1994, Aldag and Bischoff, 1995, Tørsløv et al., 1997, Hund et al., 1999, Paulsrud et al., 2000, Nilsson, 2000, Paulsrud et al., 2000, Zethner et al., 2000, Buyuksonmez et al., 2000, Vanni et al., 2000a, Vanni et al., 2000b) and a review on (mostly) organochlorine pesticides in compost from mainly the US (Harrad et al., 1991, Epstein, 1997, Buyuksonmez et al., 2000). Pesticides were analysed in this study as second priority pollutants since their presence in compost is considered as less problematic compared to other organic contaminants (except for organochlorines), due to low concentrations found in the literature and their limited significance in compost compared to direct application on agricultural crops.

Phthalates were taken into account as ubiquitous chemicals with high production volumes. The median value for DEHP in the literature for compost was 300 $\mu g/kg_{dw}$ (n=79, (Brändli et al., 2005)). Phthalates were appointed second priority due to their well documented degradability in the environment, particularly in the soil compartment (e.g. (Petersen et al., 2003)) and due to analytical limitations. NP is one of the breakdown products of NPnEO, which is mainly used as surfactant. However, it is also employed as emulsifiers in pesticide formulations (Guenther et al., 2002). In a Swedish study, NP was determined in both biowaste and biowaste compost from two communities at similar concentrations (approx. 200 $\mu g/kg_{dw}$ (Ulen, 1997)) which indicates no degradation during composting. Value in Danish compost sample were 780 $\mu g/kg_{dw}$ (Tørsløv et al., 1997), whereas Paulsrud et al. (2000) and Marb et al. (2003) did not detect NP and NPnEO in their samples. NP was included as second priority pollutant in this study.

1.5.3 Experimental Design

Compounds appointed first priority (PAH, PCB) were inventoried in a broad study including over 80 compost, digestate and presswater samples from 39 commercial plants all over Switzerland. To describe these samples thoroughly heavy metal and nutrient contents as well as pH, electrical conductivity (as a measure for salt content) and the amount of impurities were determined as well. All samples were also analysed for various other parameters by the partner project ‘Effects of Composts and Digestate on the Environment, Soil Fertility and Plant Health’ carried out by the Research Institute of Organic Agriculture (FiBL) and the Agroscope Reckenholz-Tänikon Research Station (ART). Second priority pollutants (PCDD/F, BFR, PFAS, pesticides, CP, phthalates, NP) were analysed by several partner laboratories in a subset of samples (n=3-18). Ecotoxicological tests of compost was carried out in another subset of samples (n=18) to study effects of compost application to the soil ecosystem (Pohl et al., in preparation). These studies give an integrated assessment on properties of

Swiss compost and digestate and provide a basis for balancing beneficial and hazardous effects of compost application to soil.

1.5.4 Sampling strategy

In a first step, factors that might influence organic pollutant concentrations in compost were hypothesised (Brändli et al., 2005). These were: type of treatment process (anaerobic/aerobic), origin of input material (urban/rural), composition of the input material (green waste with/without organic kitchen waste) and season of input material collection (spring/summer (unified due to sampling limitations), autumn, winter). Sampling accounted for the above listed factors, included all regions in Switzerland (see Supporting information Figure 1 (Brändli et al., 2006a) and accounted for the most important composting and digestion technologies (windrow and table composting, aerated boxes and trenches, field-edge composting, etc.). Samples were described as thoroughly as possible, i.e. in addition to the above listed factors information such as contractors of input material delivery, auxiliary substances added during composting, times of windrows turning and irrigation, temperature evolution during composting, miscellaneous data such as odour, structure etc. was recorded.

1.5.5 Sampling, sample preparation and analytical method

Sampling is a crucial step in general. Errors can arise from the relation of particle size of the matrix to the size of sample taken, from the sampling frequency, from grouping and segregation effects as well as from instruments used for sampling. For a thorough description of possible sampling (and analytical errors) see (Desaules, 2005). Special challenges arise from the particularly heterogeneous structure of compost, which consists of very fine (soil) particles to 0.5 m long and 5 cm diameter branches, and the presumably uneven distribution of target analytes in the input material. It was reported before that relative standard deviation between twenty single samples of compost (taken from 20 spots along the windrow) can easily account for 20% (for heavy metals, nutrients, PCB and PAH) and that the median of these twenty single measurements and the concentration measured in the mixed sample can differ by more than 30% for PAH and PCB (Breuer et al., 1997). Variations might even be higher in other composting systems (e.g., box composting). Even though sampling error was tried to be minimised by best possible sampling strategy (see sampling description see (Brändli et al., 2006a), it cannot really be quantified.

Sampling and sample preparation is further challenged if ubiquitous and semivolatile compounds are analysed. Contamination and volatilisation during sampling, sample preparation and analysis have been reported (Alcock et al., 1994, Ferrario et al., 1997, Cousins et al., 1997, Berset et al., 1999). To minimize these effects, special care was taken during sampling (e.g. cleaning all equipments with acetone/hexane before use), samples were dried chemically (which in turn made size reduction more difficult) and method blanks were run with every batch of analyses. For further details on sample preparation see (Brändli et al., 2006a). In this study, it was abstained from using a field blank due to several reasons: i) ideal field blanks would be an uncontaminated compost sample that does not exist, ii) the most similar matrix to compost would be soil. However, uncontaminated soil is hardly available, iii) an artificial field blank such as sand or an infinite sink (e.g. XAD) would have different sorption properties than compost, would need to be pre-cleaned and is expensive in comparable quantities (60 litres).

Analytical methods for the extraction of the first priority compound classes were optimised for compost since application of methods for soil was considered not appropriate, due to considerably higher organic matter content (up to 60 % in compost, (Brändli et al., 2005)), which can influence sorption behaviour of organic compounds. Analyses of second priority compound classes were carried out by contracting laboratories. For references see (Brändli et al., 2006).

1.5.6 Evaluation of organic pollutant concentrations in Swiss composts

After outliers had been removed (e.g due to non-compliance with the definition of source-separated compost) a through evaluation of the dataset was carried out. Factors possibly influencing organic pollutant concentrations in compost and digestate were evaluated applying a linear model (Brändli et al., 2006a) or a non-parametric test (Mann-Whitney-U Test, (Brändli et al., 2006)). Samples with different compound patterns were identified by employing principal component analysis.

For the apportionment of possible sources of PAH in compost and digestate characteristic PAH ratios and molecular marker substances were used, which can be easily integrated in conventional PAH analysis (Brändli et al., 2006a). However, such ratios were often determined close to emission and it is unclear if they are appropriate for processed (composted or digested) recipient matrixes such as compost (Brändli et al., accepted). Additionally, a linear unmixing model was applied to the compost data that identified entire (i.e. including all 15 compounds analysed) characteristic PAH source profiles, which were then matched with emission profiles from the literature. Enantiomeric shifts of chiral compounds identify biological transformation processes. Since compost is a biological very active matrix, atropisomeric PCB were included in the analysis to identify possible microbial degradation during composting.

1.5.7 Degradation during composting and digestion

It is important to investigate possible degradation of organic pollutants during composting to see whether the composting process itself can help to minimize contamination. Degradation of organic pollutants during composting has mainly been studied on a laboratory scale and rarely pure kitchen- and/or green waste were used as input material. Therefore, we followed organic pollutant concentrations on two composting (one processing green waste, the other treating green waste and organic kitchen waste) and one digestion plant. Input and processed material was sampled on all plants whereas for composting and stabilisation of the digestate several samples were taken during the process. For methodology and results it is referred to (Brändli et al., 2006b).

1.5.8 List of publications and manuscripts generated by this thesis

This thesis resulted in the following peer-reviewed papers and submitted manuscripts, which are included in the following.

Paper 1:

Brändli, R.C., Bucheli, T.D., Kupper, T., Furrer, R., Stadelmann, F.X., Tarradellas, J. 2005. Persistent Organic Pollutants in Source-Separated Compost and Its Feedstock Materials - a Review of Field Studies. J. Environ. Qual. 34, 735-760.

Paper 2:

Brändli, R.C., Bucheli, T.D., Kupper, T., Stadelmann, F.X., Tarradellas, J. 2006a. Optimised accelerated solvent extraction of PCBs and PAHs from compost. Intern, J. Environ. Anal. Chem. 86, 505-525.

Paper 3:

Bucheli, T.D., Brändli, R.C. 2006a. Two-dimensional gas chromatography coupled to triple quadrupole mass spectrometry for the unambiguous determination of atropisomeric polychlorinated biphenyls in environmental samples. J. Chromatogr. A .156-164.

Paper 4:

Brändli, R.C., Bucheli, T.D., Kupper, T., Furrer, R., Stahel, W.A., Stadelmann, F.X., Tarradellas, J. 2006b. Organic pollutants in Swiss compost and digestate. 1. Polychlorinated biphenyls, polycyclic aromatic hydrocarbons and molecular markers, determinant processes, and source apportionment. Environ. Sci. Technol. submitted.

Paper 5:

Brändli, R.C., Kupper, T., Bucheli, T.D., Zennegg, M., Huber, S., Ortelli, D., Müller, J., Schaffner, C., Iozza, S., Schmid, P., Berger, U., Edder, P., Oehme, M., Stadelmann, F.X., Tarradellas, J. 2006c. Organic pollutants in Swiss compost and digestate; 2. Polychlorinated Dibenzo-p-dioxins, and -furans, dioxin-like polychlorinated biphenyls, brominated flame retardants, perfluorinated alkyl substances, pesticides, and other compounds. Environ. Sci. Technol. submitted.

Paper 6:

Brändli, R.C., Bucheli, T.D., Kupper, T., Mayer, J., Stadelmann, F.X., Tarradellas, J. 2006d. Fate of PCBs, PAHs and their source characteristic ratios during composting and digestion of source-separated organic waste in full-scale plants. Environ. Pollut. submitted.

Short Paper 1

Brändli, R.C., Bucheli, T.D., Kupper, T., Stadelmann, F.X., Tarradellas, J., 2006e. Can sources of environmental contamination with PAHs be identified in recipient matrices by concomitant analysis of molecular markers? Organohalogen Comp. accepted.

Short Paper 2

Brändli, R.C., Bucheli, T.D., Kupper, T., Zennegg, M., Berger, U., Edder, P., Oehme, M., Müller, J., Schaffner, C., Furrer, R., Schmid, P., Huber, S., Ortelli, D., Iozza, S., Stadelmann, F.X., Tarradellas, J. 2006f. Organic pollutants in source-separated compost. Organohalogen Comp. accepted.

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Brändli, R.C., Kupper, T., Bucheli, T.D., Zennegg, M., Huber, S., Ortelli, D., Müller, J., Schaffner, C., Iozza, S., Schmid, P., Berger, U., Edder, P., Oehme, M., Stadelmann, F.X., Tarradellas, J. 2006c. Organic pollutants in Swiss compost and digestate; 2. Polychlorinated dibenzo-p-dioxins, and -furans, dioxin-like polychlorinated biphenyls, brominated flame retardants, perfluorinated alkyl substances, pesticides, and other compounds. Environ. Sci. Technol. submitted.

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2 Paper 1

Persistent organic pollutants in source-separated compost and its feedstock materials - a review of field studies

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Journal of Environmental Quality, 2005, 34, 735-760.

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Journal of
Environmental Quality

VOLUME 34 • MAY–JUNE 2005 • NUMBER 3

Persistent Organic Pollutants in Source-Separated Compost and Its Feedstock Materials—A Review of Field Studies

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ABSTRACT

Composting and the application of compost to the soil follow the principle of recycling and sustainability. Compost can also have a positive effect on physical, chemical, and biological soil parameters. However, little is known about the origin, concentration, and transformation of persistent organic pollutants (POPs) in compost. We therefore compiled literature data on some priority POPs in compost and its main feedstock materials from more than 60 reports. Our data evaluation suggests the following findings. First, median concentrations of Σ 16 polycyclic aromatic hydrocarbons (PAHs), Σ 6 polychlorinated biphenyls (PCBs), and Σ 17 polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs) were higher in green waste (1803, 15.6 μg/kg dry wt., and 2.5 ng international toxicity equivalent [I-TEQ]/kg dry wt.) than in organic household waste (635, 14.6 μg/kg dry wt., and 2.2 ng I-TEQ/kg dry wt.) and kitchen waste (not available [NA], 14.9 μg/kg dry wt., 0.4 ng I-TEQ/kg dry wt.). The POP concentrations in foliage were up to 12 times higher than in other feedstock materials. Second, in contrast, compost from organic household waste and green waste contained similar amounts of Σ 16 PAHs, Σ 6 PCBs, and Σ 17 PCDD/Fs (1915, 39.8 μg/kg dry wt., and 9.5 ng I-TEQ/kg dry wt., and 1715, 30.6 μg/kg dry wt., and 8.5 ng I-TEQ/kg dry wt., respectively). Third, concentrations of three-ring PAHs were reduced during the composting process, whereas five- to six-ring PAHs and Σ 6 PCBs increased by roughly a factor of two due to mass reduction during composting. Σ 17 PCDD/Fs had accumulated by up to a factor of 14. Fourth, urban feedstock and compost had higher POP concentrations than rural material. Fifth, the highest concentrations of POPs were usually observed in summer samples. Finally, median compost concentrations of POPs were greater by up to one order of magnitude than in arable soils, as the primary recipients of compost, but were well within the range of many urban soils. In conclusion, this work provides a basis for the further improvement of composting and for future risk assessments of compost application.

Modern societies produce considerable amounts of waste. Some 40 million Mg of municipal solid waste (MSW) are collected annually for recycling in the 15 member states of the European Union (before 2004). This corresponds to approximately 18% of the total municipal waste produced (European Commission, 2003). In Switzerland, the annual production of MSW is about 660 kg per capita, of which 45% is recycled and 55% is incinerated or disposed of (Kettler, 2002). To save incineration costs and landfill capacities, recycling of MSW is essential. Policies aiming at reducing volumes

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Published in J. Environ. Qual. 34:735–760 (2005).
doi:10.2134/jeq2004.0333

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Abbreviations: ACY, acenapththylene; ANT, anthracene; ASE, accelerated solvent extraction; B*a*A, benzo[*a*]anthracene; B*a*P, benzo[*a*]pyrene; B*b*F, benzo[*b*]fluoranthene; BBP, butylbenzylphthalate; B*k*F, benzo[*k*]fluoranthene; BPE, benzo[*ghj*]perylene; CBz, chlorobenzene; CHR, chrysene; CP, chlorophenol; CPA, chlorinated paraffin; DAD, diode array detector; DBA, dibenzo[*a,h*]anthracene; DBP, dibutylphthalate; DCP, dichlorophenol; DEHP, di(2-ethylhexyl)phthalate; ECD, electron captor detector; FD, fluorescence detector; FLT, fluoranthene; GC, gas chromatography; GPC, gel permeation chromatography; HCB, hexachlorobenzene; HCH, hexachlorohexane; HPLC, high performance liquid chromatography; IPY, indeno[1,2,3-*cd*]pyrene; I-TEQ, international toxicity equivalent; LAS, linear alkylbenzene sulfonate; MS, mass spectrometry; MSW, municipal solid waste; NA, not available; NER, non-extractable residue; PAH, polycyclic aromatic hydrocarbon; PBDE, polybrominated diphenylether; PCB, polychlorinated biphenyl; PCBz, pentachlorobenzene; PCDD/F, polychlorinated dibenzo-*p*-dioxin and -furan; PCP, pentachlorophenol; PHE, phenanthrene; POP, persistent organic pollutant; PYR, pyrene; TCBz, tetrachlorobenzene; TCP, tetrachlorophenol; T-OCDD/F; tetra- to octachloro dibenzo-*p*-dioxin and -furan; TrCP, trichlorophenol.

of MSW have resulted in the collection and composting (i.e., the controlled conversion of organic material into humus by composting plants) of nonseparated or partly separated (both non-organic and organic) refuse from households. The problems arising in connection with such mixed waste compost have been recognized since the beginning of the 1980s: it contains higher percentages of impurities and contaminants such as heavy metals and organic pollutants than compost from source-separated organic waste (Lisk et al., 1992a; Grossi et al., 1998; Hogg et al., 2002). In consequence, the production of mixed-waste composts is currently being phased out in most European countries. This is also due to the implementation of statutory quality standards or voluntary quality assurance programs by compost plant operators, which demand composting of source-separated biodegradable wastes from gardens or kitchens.

A plethora of different terms are in use within the disciplines of waste management and compost science and utilization to describe different types of wastes and compost feedstock materials. Even more confusingly, the vocabulary varies considerably between national and international directives and guidelines (German Ordinance on Biowastes, 1998; European Union, 1999; Hogg et al., 2002; United States Composting Council, 2002; Pain and Menzi, 2003; Amlinger et al., 2004; European Compost Network, 2004; USEPA, 2004). In this review, we largely use the following terms: "kitchen waste" (crude organic waste originating from private kitchens), "organic household waste" (a mixture of kitchen waste, garden waste, and small amounts of paper), "green waste" (organic waste from private gardens and public green areas), "green waste compost," and "organic household waste compost." Note that organic household waste always contains kitchen waste and needs to be mixed with green waste to achieve sufficiently aerated composting. The resulting compost, known as organic household waste compost, cannot therefore be directly compared with either organic household waste or with kitchen waste.

About 17×10^6 Mg of organic household and green waste are collected per annum in the 15 European Union member states (before 2004), which is about 35% of the total estimated recoverable potential. This results in about 9×10^6 Mg of compost (Hogg et al., 2002). The amount of separately collected organic household and green waste differs considerably between the countries. Thus more than 60% of the organic waste is separately collected in Germany, Austria, and Denmark, whereas this fraction hardly reaches 1% in Greece, Portugal, Spain, and Ireland (Hogg et al., 2002).

The risk of compost pollution by organic pollutants remains even if separately collected organic waste is composted, because of aerial deposition or accidental [e.g., via the increasingly ubiquitous plastic debris (Thompson et al., 2004)] and deliberate input (e.g., pesticide application) of such chemicals to organic materials. Organic pollutants may also accumulate during composting because of a mass reduction of about 40 to 60% due to mineralization (Gronauer et al., 1997; Schleiss, 2003). Consequently, a large number of compounds such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs), brominated flame retardants, phthalates, linear alkylbenzene sulfonates (LAS), pesticides, and nonylphenols have been detected in compost derived from source-separated organic residues (Berset and Holzer, 1995; Ulén, 1997; Tørsløv et al., 1997; Hund et al., 1999; Büyüksönmez et al., 2000; Vanni et al., 2000; Zethner et al., 2000; Vergé-Leviel, 2001; Marb et al., 2003). Note that heavy metals are frequently found in compost (Lisk et al., 1992a; Tørsløv et al., 1997; Grossi et al., 1998; Krogmann, 1999; Zethner et al., 2000; Marb et al., 2001, 2003; Hogg et al., 2002; Herter et al., 2003; Amlinger et al., 2004) but are not covered by this report.

Although the concentrations of organic pollutants measured in compost may be regarded as rather low, the total input to its main recipient, namely the soil, cannot be neglected. Since the nutrient content of compost is relatively low, considerable quantities (8–10 Mg dry wt./ha/yr) are required to obtain a sufficient fertilizing effect (Herter et al., 2003; Timmermann et al., 2003). Even higher amounts are applied if the compost is used as a soil conditioner. Consequently, the input of PAHs, PCBs, and PCDD/Fs to the soil via compost application may be equal to or even higher than that introduced by aerial deposition or the application of other organic fertilizers such as sewage sludge or manure (Herter et al., 2003). To assure a sustainable soil quality, the input of organic pollutants to the soil has to be minimized. Conversely, the risk of soil pollution due to compost application has to be balanced with the soil-improving qualities of the compost, such as the stability of the soil particles, its pore volume, water capacity, organic matter content, and the related carbon and nitrogen content (Timmermann et al., 2003).

In view of this ambivalent role of compost in soil protection and improvement, it seems essential to increase our knowledge on the actual contamination level of compost and to evaluate whether the concentrations of pollutants in compost derived from source-separated organic residues can be reduced. This requires a knowledge of the sources of the pollutants and of potentially contaminated feedstock materials. Although there is an extensive review of the literature on pesticide concentrations in compost, mostly from the United States (Büyüksönmez et al., 1999, 2000), persistent organic pollutants (POPs) relevant to the environment such as PAHs, PCBs, PCDD/Fs, and other organochlorines have not yet been thoroughly reviewed. Moreover, most of the data and publications relevant to this subject have been published in the form of government reports, theses, or dissertations. This prevents the efficient dissemination of this knowledge among scientists and decision-makers. We have reviewed and analyzed more than 60 such studies to make these results more accessible. Only some 25 of them proved to be of sufficiently high scientific and information quality to be entered into a quantitative database which served as a basis for statistical evaluation (see below for details). Most of the data included originate from European studies. However, it should be noted that the present compilation by no means claims to be complete. There may well be more (non-European) reports of interest to our study, but since not officially published, this "gray literature" is difficult to access.

In summary, this review aims to contribute to the following aspects of compost research:

- characterization of actual POP concentration levels in relevant compost feedstock materials,
- evaluation of contamination levels in compost derived from different source-separated feedstock materials,
- investigation of the potential for POP degradation during the composting process,
- assessment of regional and temporal contamination variations,
- identification of the main sources contributing to POPs in compost, and
- comparison of the POP content in compost and recipient soils.

DATA SELECTION

This review focuses on reports on POP data in composts and their feedstock materials gathered from field studies. These data were collected in a database and statistically analyzed as specified below. The database did not include the extensive data originating from studies dealing with the composting of soil with other organic wastes for remediation purposes, laboratory composting experiments, experiments with artificially spiked (isotope-labeled) compounds, and compost containing sewage sludge. However, such results were occasionally used for comparison with the results obtained from the database analysis.

The criteria for including data in the database were a clear definition of the feedstock to exclude mixed-waste composts and MSW composts, composting or anaerobic digestion as a treatment process, field data, and reporting of single-compound concentration on a dry-weight basis. These rigorous demands reduced the more than 60 studies originally reviewed to about 25. Table 1 shows the 25 studies integrated into the database and subjected to detailed data analysis and Table 2 lists the remaining reports. Although they are not suitable for further evaluation (for the reasons given in Table 2), they are added here to (i) illustrate the vast amount of information available on this topic, (ii) allow this often gray literature to be tracked in future, and (iii) save the time and effort of other researchers seeking similar information.

Very little data were found on the fate of POPs during anaerobic digestion and its concentrations in related products (Nilsson et al., 2000; Vorkamp et al., 2002). Our investigations were consequently focused on composting and the compost itself.

DATA PROCESSING

Information about the type of feedstock, catchment areas, collection time (season), sample preparation, and analysis as well as the original pollutant concentrations was extracted from the original references. The grouping of the data into subclasses of organic wastes and respective composts for subsequent comparison was based on the following criteria/restrictions: (i) the presence of sufficient data per category, (ii) consideration of common practices and peculiarities in the composting process, and (iii) initial hypotheses relating to processes potentially relevant for the occurrence of POPs in compost.

The feedstocks kitchen waste, organic household waste, and green waste were separated on the basis of the hypothesis of different POP exposures: accidentally discharged nonbiodegradable waste (e.g., plastics, electrical equipment, insulation material, hydraulic liquids, etc., known as "impurities") is thought to have a considerable influence on kitchen and organic household waste, whereas aerial deposition is suspected to be the main input pathway for green waste. The direct application of pesticides could play a role in both types of feedstocks. After the initial screening of the literature, the number of individual samples (>10) allowed four more feedstocks to be identified, namely grass, shrub clippings, bark, and foliage. Compost containing organic household waste and kitchen waste (organic household waste compost) and compost derived from green waste were compared to assess the influence of kitchen waste on POP concentrations in the compost. The evolution of organic pollutants during composting was evaluated by comparing their concentrations in green waste with those in the corresponding compost. Note that the comparison of organic household waste and its compost is difficult, since the former feedstock is often mixed with considerable amounts of green waste or other structuring material to achieve a balanced mix and thus a sufficiently aerated composting process. The composting process was further compared with relevant laboratory studies.

Persistent organic pollutant concentrations are expected to be higher in urban compost and feedstock materials due to higher emissions (Buehler et al., 2001; Meijer et al., 2003a; Krauss and Wilcke, 2003; Jaward et al., 2004). To account for these different emission patterns, the collecting areas were grouped as urban, semiurban, and rural according to information given in the original reports. Moreover, POP emissions vary according to the seasons (Halsall et al., 1995; Rahman et al., 1998; Schauer et al., 2003). The volatilization and recondensation processes of these semivolatile compounds depend on the temperature (Lee and Jones, 1999; Meijer et al., 2003a). Seasonally varying concentrations of POPs in both feedstock and compost can therefore be expected and were evaluated by comparing the data gathered during the different seasons (spring, summer, autumn, winter). Unfortunately, seasonal information was included in only few datasets and in those cases it was rarely specified whether the reporting time referred to the time of sampling or of feedstock collection. The catchment area and seasonal data were cross-checked to exclude possible process interference.

Both the concentrations of individual compounds and their sums were evaluated for all samples in the database. The summation was performed as follows: (i) sum of 16 USEPA priority PAHs (Σ 16 PAHs); (ii) sums of three-ring PAHs (acenaphthylene [ACY], acenaphthene, fluorene, phenanthrene [PHE], anthracene [ANT]), four-ring PAHs (fluoranthene [FLT], pyrene [PYR], benzo[*a*]anthracene [B*a*A], chrysene [CHR]), five-ring PAHs (benzo[*b*]fluoranthene [B*b*F], benzo[*k*]fluoranthene [B*k*F], benzo[*a*]pyrene [B*a*P], dibenzo [*a,h*]anthracene) [DBA]), and six-ring PAHs (indeno[1,2,3-*cd*]pyrene [IPY], benzo[*ghj*]perylene [BPE]); (iii) sum of the PCBs #28, #52, #101, #138, #153, and #180 (Σ 6 PCBs); and (iv) sum of 17 polychlorinated dibenzo-*p*-dioxins and -furans (Σ 17 PCDD/Fs). Since data on Σ 17 PCDD/F concentrations in the feedstock were scarce and some publications reported the sum of all tetra- to octa-chlorinated dibenzo-

Table 1. Field studies on the occurrence of organic pollutants in compost and its feedstock. These data were compiled in the database for statistical analysis.

Sample specifications					Concentrations†								
Type	Category‡	Country of origin	Catchment areas	Season of sampling	PAH§	PCB¶	PCDD/F#	Other organochlorines	Others	Sample preparation††	Analysis‡‡	Outliers	Reference
					μg/kg dry wt.; 10th, 50th, 90th percentile (no. of samples/no. quantified)								
Feedstock	grass	Switzerland	not available (NA)	NA	–	–	–	heptachlor 28.5 (2/1); Σ DDT§§ 12.9 (2/1); hexachlorobenzene (HCB) 0.6 (2/1)	–	NA, air-drying (40°C, 48 h), milling, NA	Soxhlet (hexane, acetone, toluene), SiO_2, gas chromatography (GC), mass spectrometry (MS)	none	Kuhn et al. (1990)
Compost	organic household waste	Switzerland	NA	NA	–	–	–	heptachlor 1.7, 4.6, 42.5 (5/4); Σ DDT§§ 11.2, 24.1, 34.1 (5/5); HCB 0.6, 1.6, 1.7 (5/4)	–	ditto	ditto	none	Kuhn et al. (1990)
Compost	organic household waste	Germany	rural, semi-rural, urban	NA	–	–	6.1, 10.6, 23.3 (8/8); 1164, 2000, 3353 (8/8)	–	–	NA, air-drying (under vacuum), mortar, 1 mm	Soxhlet (toluene), Alumina B Super 1, mixed column, gel permeation chromatography (GPC), GC, MS	none	Kummer (1990)
Compost	green waste	Germany	rural, semi-rural, urban	NA	–	–	7.3, 12.5, 33.4 (9/9); 1659, 2500, 3569 (9/9)	–	–	ditto	ditto	none	Kummer (1990)
Feedstock	green waste	USA	urban	spring	–	–	–; 180, 220, 1164 (3/3)	HCB 2.1, 2.3, 16.6 (3/3); pentachlorobenzene (PCBz) 0.7, 0.7, 1.0 (3/3); pentachlorophenol (PCP) 18, 23, 173 (3/3); tetrachlorobenzene (TCBz) 0.1, 0.7, 0.7 (3/2); tetrachlorophenol (TCP) (3/0); trichlorophenol (TrCP) (3/0)	–	NA, air-drying (room temperature), grinding, NA	Soxhlet (hexane, acetone), $Na_2SO_4/H_2SO_4/NaHCO_3/SiO_2$, Florisil, GC, MS	none	Harrad et al. (1991)
Compost	green waste	USA	rural, semi-rural	spring, autumn, winter	–	–	–; 10492, 21423, 25793 (13/13)	HCB 2.0, 3.9, 16.6 (13/13); PCBz 0.6, 0.7, 1.6 (13/13); PCP 8, 20, 35 (13/13); TCBz 0.0, 0.4, 0.5 (13/5); TCP 0.0, 0.0, 6.9 (13/5); TrCP 0.0, 1.2, 5.5 (13/8)	–	ditto	ditto	PCDD/F# –; 30564	Harrad et al. (1991)
Compost	green waste	USA	semirural	winter, spring, autumn	–	–	–; 10571, 21427, 32950 (7/7)	HCB 1.1, 2.0, 8.2 (6/6); PCBz 0.0, 0.2, 1.3 (6/3); PCP 7.8, 18.0, 31.8 (7/7)	–	NA, air-drying (room temperature), grinding, NA	Soxhlet (hexane, acetone), $Na_2SO_4/H_2SO_4/NaHCO_3/$ SiO_2, Florisil, GC, MS	none	Malloy et al. (1993)
Feedstock	organic household waste	Germany	NA	spring, autumn	–	10.8, 21.9, 47.3 (7/7)	2.2, 3.9, 20.6 (7/7); 297, 775, 3237 (7/7)	–	–	NA, freeze-drying or air-drying, milling, <0.5 mm	Soxhlet (toluene), Na_2SO_4, SiO_2, $Al_2O_3/AgNO_3$, GPC, Alumina B Super I, GC, MS	none	Krauss (1994)
Feedstock	green waste	Germany	NA	spring	–	3.6, 6.7, 16.0 (6/6)	0.8, 1.7, 2.9 (6/6); 102, 220, 721 (6/6)	–	–	ditto	ditto	PCDD/F# 20.2, 21.3; 4147, 2631	Krauss (1994)
Feedstock	grass	Germany	NA	NA	–	4.8, 7.1, 9.2 (4/4)	0.7, 2.0, 4.0 (4/4); 480, 959, 2145 (4/4)	–	–	ditto	ditto	none	Krauss (1994)
Feedstock	foliage	Germany	NA	NA	–	17.0, 27.0, 55.3 (3/3)	1.4, 2.7, 4.1 (3/3); 189, 356, 485 (3/3)	–	–	ditto	ditto	none	Krauss (1994)
Compost	organic household waste	Germany	NA	spring, summer, autumn, winter	1597, 2175, 4067 (26/26)¶¶	18.8, 32.4, 98.9 (33/33)	4.6, 9.9, 16.0 (33/33); 759, 2147, 3781 (33/33)	aldrin 0.2, 1.1 (17/2); chlordane 0.0, 0.0, <0.1 (17/3); dieldrin 0.3, 0.9, 2.6 (17/15); endrin 0.0, 0.0, 0.3 (17/3); heptachlor 7.4 (17/1); heptachloroepoxid (17/0); Σ DDT 1.2, 7.5, 54.1 (17/16); Σ hexachlorohexane (HCH) 0.4, 1.2, 9.4 (17/17); HCB 0.8, 1.3, 3.8 (18/18); PCBz 0.4, 1.0, 4.7 (16/16); TCBz 0.3, 0.5, 2.1 (16/16)	–	ditto	PAH: Soxhlet (toluene), SiO_2, high performance liquid chromatography (HPLC), NA; PCB, PCDD/F, chlorobenzene (CBz): Soxhlet (toluene), Na_2SO_4, SiO_2, $Al_2O_3/AgNO_3$, GPC, Alumina B Super I, GC, MS; other organochlorines: Soxhlet (hexane, acetone), $Al_2O_3/$ $AgNO_3$, SiO_2, GC, electron captor detector (ECD)	none	Krauss (1994)
Compost	green waste	Germany	NA	spring, summer, autumn, winter	1744, 2655, 5836 (4/4)¶¶	12.8, 28.0, 51.8 (20/20)	2.3, 5.2, 13.0 (20/20); 547, 1620, 3784 (20/20)	aldrin (13/0); chlordane 0.0, 0.0, 0.5 (13/3); dieldrin 0.4, 0.8, 6.3 (13/13); endrin 2.1 (13/1); heptachlor (13/0); heptachloroepoxid 0.5, 1.1 (13/2); Σ DDT 0.0, 8.0, 55.9 (13/10); Σ HCH 0.0, 0.0, 0.4 (13/5); HCB 0.7, 1.0, 3.3 (12/12); PCBz 0.8, 0.9, 1.2 (4/4); TCBz 0.1, 0.4, 0.9 (4/3)	–	ditto	ditto	PCB 540; DDT 253	Krauss (1994)

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Table 1. Continued.

Sample specifications					Concentrations†								
Type	Category‡	Country of origin	Catchment areas	Season of sampling	PAH§	PCB¶	PCDD/F#	Other organochlorines	Others	Sample preparation††	Analysis‡‡	Outliers	Reference
					µg/kg dry wt.; 10th, 50th, 90th percentile (no. of samples/no. quantified)								
Compost	organic household waste	Germany	semirural, urban	summer, winter	–	28.9, 52.5, 74.1 (8/8)	0.0, 5.5, 19.4 (8/4); –	aldrin 0.0, 3.5, 15.8 (8/4); chlordane 0.0, 1.0, 5.8 (8/4); dieldrin 0.0, 1.0, 8.3 (8/4); endrin 0.0, 2.5, 6.9 (8/4); heptachlor 0.0, 1.0, 8.3 (8/6); heptachloroepoxid 0.0, 2.0, 6.5 (8/5); Σ DDT 0.0, 25.0, 60.3 (8/5); Σ HCH 0.0, 5.5, 41.9 (8/6); HCB 1.4, 3.0, 10.6 (8/7); PCP 6.6, 14.0, 39.4 (8/8)	di(2-ethylhexyl) phthalate (DEHP)## 16.9, 32.4, 60.8 (8/8)	NA	NA	PCDD/F# 86; –; dieldrin 41.9	Aldag and Bischoff, (1995)
Compost	green waste	Germany	urban	summer, winter	–	48.5, 61.0, 82.0 (6/6)	10.2, 12.0, 14.0 (5/5); –	aldrin 7.0 (6/1); chlordane (6/0); dieldrin 13.0 (6/1); endrin (6/0); heptachlor (6/0); heptachloroepoxid 42.0 (6/1); Σ DDT 5.0, 10.0, (6/2); Σ HCH 18 (6/1); HCB 1.0, 2.0, 6.5 (6/6); PCP 3.0, 6.0, 33.5 (6/6)	DEHP## 0.0, 10.0, 23.7 (6/4)	NA	NA	none	Aldag and Bischoff, (1995)
Compost	organic household waste	Germany	NA	NA	–	41.9, 75.9, 126.1 (27/27)	3.7, 11.4, 22.7 (28/28); 666, 2698, 6987 (28/28)	–	–	NA, freeze-drying or air-drying (105°C), NA, NA	Soxhlet (toluene), Alumina B Super 1, H_2SO_4–SiO_2/NaOH-SiO_2, GC, MS	none	Bayerisches Landesamt für Umweltschutz (1995)
Compost	green waste	Germany	NA	NA	–	46.4, 65.8, 85.6 (8/8)	7.4, 11.4, 26.2 (8/8); 1020, 2347, 10757 (8/8)	–	–	ditto	ditto	none	Bayerisches Landesamt für Umweltschutz (1995)
Compost	organic household waste	Switzerland	rural, urban	NA	827, 2698 (2/2)	25.9, 69.8 (2/2)	–	–	–	−20°C, freeze-drying, grinding, <0.63 mm	saponification/liquid–liquid extraction, SiO_2, Al_2O_3; PAH: GC, MS; PCB: GC, ECD	none	Berset and Holzer (1995)
Compost	green waste	Switzerland	urban	NA	2492 (1/1)	30.6 (1/1)	–	–	–	ditto	ditto	none	Berset and Holzer (1995)
Compost	organic household waste	Germany	NA	NA	–	–	14.8 (1/1); –	γ-HCH 1.0 (1/1)	–	NA	NA	none	Kummer (1996)
Compost	green waste	Germany	NA	NA	–	–	11.0 (1/1); –	γ-HCH 0.50 (1/1)	–	NA	NA	none	Kummer (1996)
Feedstock	green waste	USA	NA	NA	–	–	–	chlordane 190 (1/1); dieldrin 130 (1/1); endosulfan 70 (1/1); Σ DDT††† 850 (1/1), α-HCH 30 (1/1), γ-HCH 6 (1/1)	methoxychlor 130 (1/1)	NA	NA	none	Epstein (1997)
Compost	green waste	USA	NA	NA	–	–	–	aldrin (2/0); chlordane 20.6, 23.7, 156.7 (3/3); dieldrin 19.0, 19.0, 171.8 (3/3); endosulfan (2/0); endrin (2/0); heptachlor (2/0); heptachloroepoxid (2/0); Σ DDT††† 102, 192, 470 (3/3); Σ HCH 6.3, 9.4, 9.9 (3/3); HCB (2/0); PCP (2/0)	chlorpyrifos (2/0); dibutylphthalate (DBP) (2/0); DEHP## 0, 1, 5 (4/2); diazinon (2/0); dichlorprop (2/0); dimethoate (2/0), malathion (2/0); MCPA (2/0); simazine (2/0)	NA	NA	none	Epstein (1997)
Compost	organic household waste	Denmark	NA	NA	–	–	–	dieldrin 16.0 (1/1)	nonylphenol (+ethoxylates) 14000 (1/1); butylbenzylphthalate (BBP) 98 (1/1); DEHP 15## (1/1); dioctylphthalate 34 (1/1); isophorone 59 (1/1)	4°C, none, NA, NA	extraction (dichloromethane), sulfur removal using copper, derivatization (diazomethane), Florisil, GC, MS	none	Tørsløv et al. (1997)
Feedstock	organic household waste	Germany	NA	autumn	–	6.5, 9.1, 29.1 (5/5)	0.2, 0.6, 1.4 (13/13); 42, 132, 254 (13/13)	–	–	NA, air-drying, milling, <0.1 mm	Soxhlet (toluene), SiO_2/H_2SO_4, GPC, Micro Alumina B Super I, GC, MS	none	Wilke (1997)
Feedstock	kitchen waste	Germany	NA	NA	–	4.4, 14.9, 27.8 (8/8)	0.1, 0.4, 0.8 (9/9); 34, 71, 194 (9/9)	–	–	ditto	ditto	none	Wilke (1997)

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Table 1. Continued.

Sample specifications					Concentrations†								
Type	Category‡	Country of origin	Catchment areas	Season of sampling	PAH§	PCB¶	PCDD/F#	Other organochlorines	Others	Sample preparation††	Analysis‡‡	Outliers	Reference
					µg/kg dry wt.; 10th, 50th, 90th percentile (no. of samples/no. quantified)								
Feedstock	green waste	Germany	NA	NA	–	6.2, 11.3, 62.1 (3/3)	2.9, 4.1, 5.7 (3/3); 212, 558, 961 (3/3)	–	–	ditto	ditto	none	Wilke (1997)
Feedstock	shrub clippings	Germany	NA	NA	–	4.3, 9.8, 29.1 (12/11)	0.2, 0.5, 2.4 (12/12); 30, 64, 238 (12/12)	–	–	ditto	ditto	none	Wilke (1997)
Feedstock	grass	Germany	NA	NA	–	4.7, 10.1, 22.2 (33/33)	0.3, 0.8, 3.9 (33/33); 39, 97, 463 (33/33)	–	–	ditto	ditto	none	Wilke (1997)
Feedstock	foliage	Germany	NA	NA	–	22.3, 36.7, 52.0 (26/26)	2.3, 3.8, 5.8 (26/26); 158, 236, 401 (26/26)	–	–	ditto	ditto	PCDD/F# 27.8; 4046	Wilke (1997)
Feedstock	bark	Germany	NA	NA	–	3.2, 4.2 (2/2)‡‡‡	0.6, 0.7, 1.0 (4/4); 49.6, 56.8, 72.2 (4/4)	–	–	ditto	ditto	none	Wilke (1997)
Feedstock	green waste	Germany	rural	NA	12792 (1/1)	22.9 (1/1)	–	Σ DDT 10.5 (1/1); Σ HCH 6.9 (1/1); HCB (1/0); PCBz (1/0); TCBz§§§ (1/0)	BBP (1/0); biphenyl 13 (1/1); DBP 53 (1/1); DEHP 41 (1/1); *o*-phenylphenol 0.0 (1/1); thiabendazole 5.4 (1/1)	NA	PAH, PCB, DDT: Soxhlet (toluene), GPC, SiO$_2$/AgNO$_3$, GC, MS; phthalates: Soxhlet (methanol), SiO$_2$, HPLC, ECD	none	Hund et al. (1999)
Compost	organic household waste	Germany	rural, semirural, urban	spring, winter	1708, 2786, 3872 (7/7)	38.8, 41.8, 86.8 (7/7)	–	Σ DDT 5.1, 7.0, 9.4 (7/7); Σ HCH 1.6, 4.9, 16.6 (7/7); HCB (7/0); PCBz (7/0); TCBz§§§ (7/0)	BBP 0, 25, 140 (7/4); biphenyl 4, 7, 30 (7/7); DBP 37, 154, 523 (7/6); DEHP 66, 258, 1286 (7/7); *o*-phenylphenol 5.8 (7/1); thiabendazole 12.3, 26.7, 47.1 (7/7)	NA	ditto	none	Hund et al. (1999)
Compost	green waste	Germany	urban	spring	3309 (1/1)	41.7 (1/1)	–	Σ DDT 9.1 (1/1); Σ HCH 1.9 (1/1); TCBz§§§ (1/0)	BBP (1/0); biphenyl 10 (1/1); DBP 56 (1/0); DEHP 67 (1/0); *o*-phenylphenol (1/0); thiabendazole 16.6 (1/1)	NA	ditto	none	Hund et al. (1999)
Feedstock	organic household waste	Germany	urban, rural	spring, summer, autumn, winter	198, 659, 4284 (71/71)	5.0, 14.7, 81.7 (71/71)	–; 83, 192, 756 (71/71)	–	–	NA	NA	none	Sihler et al. (1999)
Feedstock	green waste	Germany	urban, rural	spring, summer, autumn, winter	661, 1922, 8202 (32/32)	8.1, 17.1, 42.0 (32/32)	–; 76, 273, 1741 (31/31)	–	–	NA	NA	PAH 28641, 22937; PCB 513; PCDD/F# –; 18788	Sihler et al. (1999)
Feedstock	bark	Germany	urban, rural	spring, summer, winter	129, 365, 1559 (18/18)	2.7, 6.8, 11.0 (18/18)	21, 60, 170 (18/18); –	–	–	NA	NA	PAH 60935, 51939; PCB 195	Sihler et al. (1999)
Feedstock	grass	Germany	NA	NA	–	12.4, 7.3 (2/2)	–; 42, 42 (2/2)	–	–	NA	NA	none	Sihler et al. (1999)
Compost	organic household waste	Sweden	NA	NA	–	–	–	chlordane 0.1, 0.2, 0.2 (3/3); dieldrin 1.0, 1.3, 3.5 (3/3); heptachlor (3/0); heptachloroepoxid 0.1, 0.1, 0.2 (3/3); HCB 1.0, 2.1, 4.7 (3/3); PCP 0.7, 1.0, 6.3 (3/3), Σ DDT 4.1, 5.9, 6.5 (3/3)	MC5 0.03, 0.05, 0.06 (3/3); nanochlor 0.03, 0.03, 0.06 (3/3)	NA, air-drying (2 d), homogenization, NA	Soxhlet (toluene), dialysis through polyethene film into cyclopentane, Florisil, GPC, GC, MS	none	Wågman et al. (1999)
Feedstock	green waste	USA	NA	NA	–	–	–	aldrin (1/0); chlordane 13.6 (1/1); dieldrin 9.3 (1/1); endosulfan 5.2 (1/1); endrin (1/0); heptachlor (1/0); heptachloroepoxid (1/0); Σ DDT††† 60.9 (1/1); Σ HCH 5.8 (1/1)	2,4,5-T (1/0); 2,4-D (1/0); 2,4-DB (1/0); methoxychlor 9.3 (1/1); dicamba (1/0)	NA	NA	none	Büyüksönmez et al. (2000)

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Table 1. Continued.

Sample specifications					Concentrations†								
Type	Category‡	Country of origin	Catchment areas	Season of sampling	PAH§	PCB¶	PCDD/F#	Other organochlorines	Others	Sample preparation††	Analysis‡‡	Outliers	Reference
					µg/kg dry wt.; 10th, 50th, 90th percentile (no. of samples/no. quantified)								
Compost	green waste	USA	NA	NA	–	–	–	aldrin (1/0); chlordane 0.8 (1/1); dieldrin (1/0); endosulfan (1/0); endrin (1/0); heptachlor (1/0); heptachloroepoxid (1/0); Σ DDT††† 31.9 (1/1); Σ HCH 0.68 (1/1)	2,4,5-T (1/0); 2,4-D (1/0); 2,4-DB (1/0); methoxychlor 6.2 1/1); dicamba (1/0)	NA	NA	none	Büyüksönmez et al. (2000)
Feedstock	organic household waste	Norway	NA	NA	–	–	–	–	short- and medium-chained chlorinated paraffins (CPA)## 1.2 13.5 44.3 (14/14)	−24°C, none, grinding, NA	accelerated solvent extraction (ASE) (cyclohexane), XAD, H_2SO_4, GC, ECD	none	Nilsson (2000)
Compost	organic household waste	Norway	NA	NA	–	–	–	–	DBP## 0, 3, 6 (9/7); DEHP## 0, 1, 16 (9/6); linear alkylbenzene sulfonate (LAS)## 18, 41, 142 (9/8)	NA	various analytical methods referenced in (Paulsrud et al., 2000)	none	Paulsrud et al. (2000)
Compost	foliage	USA	NA	NA	–	12/0	–	chlordane 0.3, 0.7, 2.0 (12/12)	–	NA	NA	none	Strom (2000)
Compost	green waste	USA	NA	NA	–	–	–	chlordane 0.3, 0.6, 1.8 (6/6)	–	NA	NA	none	Strom (2000)
Compost	green waste	Italy	NA	NA	–	–	–	–	3,5-DCA 18.0 (1/1); chlozolinate 200.0 (1/1)	NA, frozen, grinding, NA	sonication (acetonitrile), filtered, HPLC, diode array detector (DAD)	none	Vanni et al. (2000)
Compost	organic household waste	Italy	NA	NA	–	–	–	–	iprodione 403.0 (1/1)	ditto	ditto	none	Vanni et al. (2000)
Compost	organic household waste	Austria	rural, semirural, urban	spring, summer, autumn, winter	457, 965, 3027 (29/29)¶¶¶	1.8, 11.6, 24.9 (29/26)	2.1, 6.9, 13.2 (29/29); –	aldrin (29/0); chlordane (29/0); dieldrin (29/0); endosulfan 0.0, 0.0, 0.2 (29/3); endrin 0.0, 1.5, 3.0 (29/22); Σ DDT 9.2, 11.5, 17.1 (8/8); Σ HCH 0.0, 0.0, 0.9 (29/5); HCB 0.0, 0.0, 1.4 (28/7); PCP 6.0, 20.9, 47.1 (29/29); TCP### 0.6, 3.1, 4.1 (3/3); TrCP†††† 0.4, 2.0, 9.0 (3/3); dichlorophenol (DCP)‡‡‡‡ 0.0, 0.0, 1,6 (3/3); 3-chlorophenol (CP) (3/0); 4-CP 35.2, 38.9, 66.3 (3/3)	cyflutrin 56.2, 38.3 (8/2); cypermethrin (8/0); deltamethrin 0.0, 0.0, 55.4 (8/3); fenpropathrin 0.0, 4.1, 31.5 (8/4); fenvalerate (8/0); λ-cyhalothrin (8/0); permethrin (8/0); phenothrin (8/0); thiabendazole 0.0, 4.1, 31.5 (8/4)	4°C, freeze-drying, milling, <2 mm	PAH: Soxhlet (hexane), PAH SOIL, HPLC, DAD; PCDD/F: Soxhlet (toluene), celite/ H_2SO_4, Al_2O_3, GC–MS; PCB and other organochlorines: Soxhlet (hexane), sulfur removal using copper, Florisil, $SiO_2/AgNO_3$, GC, ECD; pyrethroides: Soxhlet (ethyl acetate), Florisil, GC, MS; thiabendazole: ultrasonication (ethyl acetate), liquid–liquid extraction (1 N NaOH, 0.1 N HCl, ethyl acetate), GC, N and P detector	none	Zethner et al. (2000)
Compost	green waste	Austria	rural, semirural, urban	spring, summer, autumn, winter	210, 774, 2175 (13/13)¶¶¶	2.5, 7.2, 27.9 (13/13)	2.4, 5.1, 24.2 (13/13); –	aldrin (13/0); chlordane (13/0); dieldrin (13/0); endosulfan 0.0, 0.0, 0.2 (13/2); endrin 0.0, 1.2, 2.8 (13/8); Σ DDT 4.1, 7.8, 14.3 (13/13); Σ HCH 0.0, 0.0, 2.4 (13/5); HCB 0.0, 0.0, 1.9 (13/4); PCP 3.8, 11.4, 57.0 (12/12); TCP### 233 (1/1); TrCP†††† 59.6 (1/1); DCP‡‡‡‡ 8.6 (1/1); 3-CP 4.0 (1/1); 4-CP 63.5 (1/1)	cyflutrin 75.9 (7/1); cypermethrin (7/0); deltamethrin 61.6 (7/1); fenpropathrin (7/0); fenvalerate (7/0); λ-cyhalothrin (7/0); permethrin (7/0); phenothrin (7/0); thiabendazole 7.1 (7/1)	ditto	ditto	none	Zethner et al. (2000)

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Table 1. Continued.

Sample specifications					Concentrations†								
Type	Category‡	Country of origin	Catchment areas	Season of sampling	PAH§	PCB¶	PCDD/F#	Other organochlorines	Others	Sample preparation††	Analysis‡‡	Outliers	Reference
					μg/kg dry wt.; 10th, 50th, 90th percentile (no. of samples/no. quantified)								
Compost	organic household waste	Germany	NA	NA	–	28.0, 43.0, 150.4 (15/15)	8.3, 10.7, 16.2 (15/15); –	HCB 0.4, 4.0, 9.8 (15/13); PCP 6.4, 9.0, 29.8 (15/15)	biphenyl 42, 79, 134 (15/15); DEHP## 0, 2, 18 (15/11); pendimethalin 14, 30, 66 (15/15)	NA, freeze-drying, NA, NA	PAH: ASE (toluene), SiO_2, GC, MS; PCB and PCDD/F: ASE (toluene), NaOH-SiO_2/H_2SO_4–SiO_2, Alumina B Super 1, GC, MS; phthalates: extraction (hexane), none, GC, MS; phenols: ASE (toluene, acid), SiO_2, derivatization (methylsilyltrifluoracetamide), GC, MS	none	Marb et al. (2001)
Compost	green waste	Germany	NA	NA	–	19.8, 29.0, 47.2 (5/5)	4.9, 9.3, 11.5 (5/5); –	HCB 2.0, 2.0, 4.8 (5/5); PCP 1.8, 6.0, 8.6 (5/5)	biphenyl 26, 45, 83 (5/5); DEHP## 0, 2, 5 (5/3); pendimethalin 20, 20, 40 (5/5)	ditto	ditto	none	Marb et al. (2001)
Feedstock	organic household waste	Norway	NA	NA	–	–	–	–	CPA## 5.3, 5.4, 5.5 (3/3)	−24°C, none, grinding, NA	ASE (cyclohexane), XAD, H_2SO_4, GC, ECD	none	Nilsson et al. (2001)
Compost	organic household waste	France	NA	NA	1760, 3200, 3592 (3/3)¶¶	59.4, 85.0, 94.6 (3/3)	–	–	–	NA, freeze-drying, milling, <0.32 mm	PAH: ASE (acetone, dichloromethane), Al_2O_3, filtration, LC, fluorescence detector (FD); PCB: ASE (acetone, dichloromethane), liquid–liquid extraction, H_2SO_4, sulfur removal using copper, GC, ECD	none	Vergé-Leviel (2001)
Compost	green waste	France	NA	NA	1670 (1/1)¶¶	59.0 (1/1)	–	–	–	–	ditto	ditto	Vergé-Leviel (2001)
Compost	organic household waste	France	NA	NA	2779 (1/1)¶¶	27.3 (1/1)	–	–	–	NA, air-drying, grinding, <0.25 mm	PAH: ASE (acetone, dichloromethane), Al_2O_3, filtration, HPLC, FD; PCB: ASE (acetone, hexane), H_2SO_4, sulfur removal using copper, GC, ECD	none	Houot et al. (2002)
Compost	organic household waste	Switzerland	NA	NA	1320, 2442, 4981 (6/6)	–	–	–	–	NA, freeze-drying, NA, NA	Soxhlet (cyclohexane), Hg, dimethylformamide, SiO_2, GC, MS	none	Schleiss (unpublished data, 2002)
Compost	green waste	Switzerland	NA	NA	2260, 2602, 2674 (3/3)	–	–	–	–	ditto	ditto	none	Schleiss (unpublished data, 2002)
Compost	organic household waste	Germany	NA	NA	–	–	9.4, 9.6, 10.1 (3/3); 799, 894, 1040 (3/3)	–	–	NA	NA	none	Weiss (2002)
Compost	green waste	Germany	NA	NA	–	–	4.5, 13.2 (2/2); 581, 829 (2/2)	–	–	NA	NA	none	Weiss (2002)
Feedstock	foliage	Switzerland	rural, semi-rural	NA	1729, 5010, 26362 (14/14)	–	–	–	–	−20°C, none or at 40°C overnight, manually mixed, NA	method A: Soxhlet (hexane, acetone, toluene), Florisil, GC, MS; method B: Soxhlet (acetone), SiO_2, GC, MS	none	Kuhn and Arnet (2003)
Compost	organic household waste	Switzerland	rural, semi rural	NA	3487, 4119, 5131 (4/4)	–	–	–	–	ditto	ditto	PAH 174008, 68450	Kuhn and Arnet (2003)
Compost	foliage	USA	NA	NA	–	–	–	chlordane 22.8, 73.9, 261.9 (33/33)	–	room temperature, none, homogenization, NA	liquid–liquid extraction (water, propanol, petroleum), Na_2SO_4, Florisil, GC, MS	none	Lee et al. (2003)

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Table 1. Continued.

Sample specifications					Concentrations†								
Type	Category‡	Country of origin	Catchment areas	Season of sampling	PAH§	PCB¶	PCDD/F#	Other organochlorines	Others	Sample preparation††	Analysis‡‡	Outliers	Reference
					µg/kg dry wt.; 10th, 50th, 90th percentile (no. of samples/no. quantified)								
Compost	organic household waste	Germany	NA	summer	–	–	–	–	DEHP## 49, 145 1130 (11/11); C9-LAS 5.9, 16.4, 57.3; C10-LAS 0.0, 0.0, 129.6 (11/3); C11-LAS 0.0, 0.0, 161.6 (11/3); C12-LAS 0.0, 0.0, 165.2; C13-LAS 166.3, 190.5 (11/2); C14-LAS 0.0, 0.0, 194.2 (11/3); C15-LAS 0.0, 0.0, 188.0 (11/3), mono- 1.2, 2.8, 5.2 (11/9); di- 1.2, 1.4 (11/2); tri- (11/0); tetra- (11/0)- butyltin§§§§; mono- 0.0, 0.0, 3.3 (11/5); di- 1.5 (11/1)-octyltin§§§§; tricyclohexyltin (11/0); triphenyltin (11/0); bisphenol A 0, 105, 393 (11/8); musk xylol (11/0); 4-nonylphenol 299, 680, 2110 (11/11)	NA, freeze-drying or none, milling	DEHP, musk xylol: ultrasonication (methanol), none; GC, MS; LAS: ultrasonication (methanol), none, LC, MSMS; bisphenol A, 4-nonylphenol: extraction (butyl-methyl-ether), none, GC, MS	none	Marb et al. (2003)
Compost	green waste	Germany	NA	summer	–	–	–	–	DEHP## 51, 88, 235 (11/11); C9-LAS 6.7, 11.8, 17.3 (5/5); C10-LAS (11/0); C11-LAS (11/0); C12-LAS (11/0); C13-LAS (11/0); C14-LAS (11/0); C15-LAS (11/0); Mono- 0.0, 0.0, 1.7 (11/5); di- 0.0, 0., 1.1 (11/3); tri- (11/0); tetra- (11/0)-butyltin§§§§; mono- (11/0); di- (11/0)-octyltin; tricyclohexyltin (11/0); triphenyltin (11/0); bisphenol A (11/0); musk xylol (11/0); 4-nonylphenol 64, 147, 359 (11/11)	ditto	ditto	none	Marb et al. (2003)

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† Concentrations are listed individually if number quantified = 1 or 2.

‡ Green waste: organic waste from gardens and public green areas; organic household waste: a mixture of kitchen waste, garden waste, and small amounts of paper; kitchen waste: crude organic waste originating from private kitchens; compost containing organic household waste: usually contains green waste as a structuring material.

§ Sum of 16 USEPA polycyclic aromatic hydrocarbons (PAHs) if not otherwise stated.

¶ Sum of six polychlorinated biphenyls (PCB) #28, #52, #101, #138, #153, and #180 if not otherwise stated.

Sum of 17 polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/F) in ng international toxicity equivalent [I-TEQ]/kg dry wt.; sum of tetra- to octa-PCDD/F in ng/kg dry wt.

†† Includes storage temperature, drying technique, homogenization, and fraction analyzed.

‡‡ Includes extraction, cleanup, separation, and detection.

§§ Sum of *p,p′*-DDT and *p,p′*-DDE only.

¶¶ Sum of 15 USEPA PAHs without acenaphthylene (ACY).

In mg/kg dry wt.

††† Sum of *p,p′*-DDT, *p,p′*-DDE, and *p,p′*-DDD only.

‡‡‡ Concentration for PCB #28 not available for two out of four samples.

§§§ Sum of 1,2,3,4-TCBz, 1,2,3,5-TCBz, 1,2,4,5-TCBz.

¶¶¶ Sum of 15 USEPA PAHs without naphthalene.

Sum of 2,3,4,5-TCP, 2,3,4,6/2,3,5,6-TCP.

†††† Sum of 2,3,4-TrCP, 2,3,5-TrCP, 2,3,6-TrCP, 2,4,6-TrCP, 3,4,5-TrCP, 2,4,5-TrCP.

‡‡‡‡ Sum of 2,6-DCP, 2,4/2,5-DCP, 3,4-DCP, 2,3-DCP, 3,5-DCP.

§§§§ In µg organotin cations/kg dry wt.

Table 2. Field studies on the occurrence of organic pollutants in compost and its feedstock. For the reasons indicated, these data were not included in the database.

Sample specifications				Organic pollutants analyzed							
Type	Category†	Country of origin	Catchment areas	PAH	PCB	PCDD/F	Other organochlorines	Others	Reason of exclusion from database	Remarks	Reference
Compost	organic household waste	Germany	not available (NA)	Σ 6 PAH‡	Σ PCB§	–	Σ hexachlorohexane (HCH), Σ DDT, aldrin, endrin, heptachlor, dieldrin	–	mean concentrations reported only	–	Fricke (1988)
Feedstock and compost	organic household waste	Germany	semirural	Σ 6 PAH‡	Σ PCB	–	Σ HCH, Σ DDT, aldrin, endrin, heptachlor, dieldrin	–	six mean concentrations reported over a year, Σ PCB not specified	analytical details given	Fricke et al. (1989)
Compost	organic household waste, green waste	Germany	NA	–	PCB	PCDD/F	chlorobenzene (CBz), chlorophenol (CP)	–	individual congeners not specified, mean of three samples reported	–	Hagenmeier et al. (1990)
Compost	foliage	USA	NA	–	–	–	chlordane, γ-HCH,	2,4-D, captan	mean concentrations reported only	–	Richard and Chadsey (1990)
Compost	green waste	USA	NA	–	PCB	–	chlordane, DDE, DDT, *o,p′*-DDT, *p,p′*-DDT, aldrin, endrin, γ-HCH, dieldrin, pentachlorophenol (PCP)	2,4-D, 2,4-DB, 2,4,5-T, silvex, MCPA, MCPP, dichloroprop, dicamba, malathion, parathion, diazinon, dursban, trifluralin, dalapon, dinoseb, casoron	mean concentrations and ranges reported only	–	Hegberg et al. (1991)
Compost	organic household waste, green waste	Germany	NA	PAH	PCB	PCDD/F	–	–	PAH, PCB, PCDD/F not specified, mean and median concentrations reported only	–	Fricke et al. (1992)
Compost	green waste	USA	NA	–	PCB	–	–	–	PCB measured as Aroclor 1254	–	Lisk et al. (1992a)
Compost	green waste	USA	NA	–	PCB	–	–	–	PCB reported as Aroclor 1254	other compost analyzed than in (Lisk et al., 1992a)	Lisk et al. (1992b)
Feedstock and compost	green waste	USA	NA	–	PCB	–	DDD, DDE, dieldrin, heptachlor, hetachlorepoxide, γ-HCH	alachlor, atrazine, carbaryl, chlordane, chlorpyrifos, 2,4-D, diazinon, dichlobenil, fonofos, malathion, methoxychlor, metalachlor, parathion, 2,4,5-T, trifluralin	mean concentrations and ranges reported only, PCB not specified	analytical details given	Miller et al. (1992)
Compost	green waste	USA	NA	–	PCB	PCDD/F	PCP, pentachlorobenzene (PCBz), hexachlorobenzene (HCB)	–	PCB not specified, PCDD/F, PCP, PCBz and HCB included in database	analytical details given	Malloy et al. (1993)
Compost	normal and highway organic waste	Switzerland	NA	Σ PAH	Σ PCB	–	–	–	poor sample description, sum not specified, qualitative description only	–	Kuhn et al. (1994)
Compost	green waste, organic household waste	Germany	NA	PAH	PCB	PCDD/F	γ-HCH, CBz, CP	–	PAH, PCB, PCDD/F, CBz, CP not specified	–	Kummer (1996)
Feedstock	various feedstock, organic household waste, green waste	Germany	NA	Σ 6PAH‡	Σ PCB§	PCDD/F	–	–	mean, median, min., max., concentrations reported only, PCDD/F not specified	–	Sihler et al. (1996)
Compost	organic household waste	Germany	–	Σ 6PAH‡	Σ PCB§	–	γ-HCH, HCB, DDT	2,4-D, 2,4,5-T	range reported only	–	van Raaij et al. (1996)
Feedstock and compost	foliage	Germany	NA	Σ 12PAH¶	Σ PCB§	–	–	–	graphical data reporting only	analytical details given	van Raaij et al. (1996)
Compost	organic household waste, green waste	Germany	NA	16 USEPA PAH and triphenylene, benzo[*e*]pyrene, perylene, anthanthrene	PCB #28, #52, #101, #138, #153, #180		HCB, α-HCH, β-HCH, γ-HCH, δ-HCH, *p,p′*-DDD, *p,p′*-DDT, *p,p′*-DDE	–	mean, median, min, max 25th and 75th percentile reported	analytical details given	Breuer et al. (1997)

Continued next page.

Table 2. Continued.

Sample specifications				Organic pollutants analyzed							
Type	Category†	Country of origin	Catchment areas	PAH	PCB	PCDD/F	Other organochlorines	Others	Reason of exclusion from database	Remarks	Reference
Feedstock and compost	green waste	USA	NA	–	–	17 PCDD/F single congeners	–	–	range reported only	analytical details given	Eitzer et al. (1997)
Feedstock and compost	organic household waste	USA	NA	PAH	PCB	PCDD/F	α-HCH, γ-HCH, DDE, DDT, dieldrin, endrin, heptachlor, PCPs, CBz	aldrin, chlordane, cyanide, methoxychlor, mirex, toxaphene, diazinon, malathion, methylparathion, 2,4-D, 2,4,5-T, 2,4,5-TP	ranges or mean concentrations reported only, PCB and PAH not specified	some data included in database	Epstein (1997)
Feedstock and compost	organic household waste	Sweden	NA	fluoranthene (FLT)	PCB #28, #52, #101, #138, #153, #180	–	–	nonylphenols	median and maximum concentrations reported only	–	Ulén (1997)
Compost	organic household waste	Brazil	NA	Σ 15 PAH	Σ 6 PCB§	Σ 17 PCDD/F	–	–	mean concentrations normalized to 30% loss on ignition reported, PAH not specified	analytical details given	Grossi et al. (1998)
Compost	organic household waste	Germany	NA	PAH	PCB	PCDD/F	–	–	PAH, PCB, PCDD/F not specified, range reported only	–	Hackenberg et al. (1998)
Feedstock	southern fruit peel, flowers, fruits and grass	–	NA	–	–	–	–	captan, chlorthalonil, dicofol, dodemorph, endosulfan, methiathione, *o*-phenyl-phenol, thiabendazole	mean concentrations reported	analytical details given	Vorkamp et al. (1999)
Feedstock and compost	green waste	USA	NA	–	–	–	aldrin, α-HCH, β-HCH. γ-HCH, δ-HCH, α-chlordane, χ-chlordane, *p,p′*-DDT, *p,p′*-DDD, *p,p′*-DDE, dieldrin, α-endosulfan, β-endosulfan, endosulfan sulfate, endrin, endrin ketone, heptachlor, heptachloroepoxide, methoxychlor, toxapane	2,4-D, 2,4-DB, 2,4,5-T, dalapon, dicamba, dinosep, silvex	unit ppm (not specified if dry wt. or wet wt.)	–	Büyüksönmez et al. (2000)
Compost digestate, feedstock	organic household waste	Sweden	NA	–	–	–	–	di(2-ethylhexyl)phthalate (DEHP)	qualitative results only	analytical details given	Nilsson et al. (2000)
Compost	green waste	USA	NA	–	–	–	aldrin, chlordane, DDE, DDT, *o,p′*-DDT, *p,p′*-DDT, dieldrin, endrin, γ-HCH, PCP	2,4-D, 2,4-DB, 2,4,5-T, casoron, dalapon, diazinon, dicamba, dichlorprop, dinoseb, dursban, malathion, MCPA, MCPP, parathion, silvex, triflualin	mean concentrations reported only	–	Strom (2000)
Compost	green waste	USA	NA	12 PAH¶	–		–	–	mean concentrations reported only	analytical details given	McGowin et al. (2001)
Feedstock	various fruit and vegetables, ornamentals	–	NA	–	–	–	DDD, DDE, *p,p′*-DDE, endosulfan	atrazine, captan, chlorthalonil, dichlorvos, dicofol, dimethoat, dodemorph, iprodione, malathion, metalaxyl, methidathion, methiocarb, *o*-phenyl-phenol, pendimethalin, phosalon, procymidon, propamocarb, pyrazophos, thiabendazole, vinclozolin	mean concentrations reported only	analytical details given	Taube (2001)
Compost	green waste, organic household waste	Denmark	NA	PAH	–	–	–	DEHP, linear alkylbenzene sulfonate (LAS), nonylphenolethoxylate	mean concentrations reported only, PAH not specified	–	Petersen and Hansen (2002)
Feedstock	vegetables, fruits, ornamental flowers, tropic fruit peels	Germany	NA	–	–	–	DDE, endosulfan, *p,p′*-DDE	biphenyl, captan, chlorthalonile, diazinon, cichlorovos, dicofol, cimethaot, dodemorph, iprodione, malathion, metalaxyl, methidathion, methiocarb, *o*-phenyl-phenol, pendimethalin, phosalon, procymidon, propamocarb, pyrazophos, thiabendalole, vinclozolin	concentrations reported in kg wet wt.	analytical details given	Taube et al. (2002)
Compost	organic household waste	France	NA	16 USEPA PAH except acenaphthylene (ACY)	PCB #8, #18, #28, #44, #52, #66, #77, #101, #105, #118, #128, #126, #138, #153, #170, #180, #187, #195, #206, #209	–	–	–	mean concentrations reported only ($n = 3$)	analytical details given	Houot et al. (2002)

Continued next page.

Table 2. Continued.

Sample specifications				Organic pollutants analyzed							
Type	Category†	Country of origin	Catchment areas	PAH	PCB	PCDD/F	Other organochlorines	Others	Reason of exclusion from database	Remarks	Reference
Feedstock and compost	organic household waste and green waste, grass	Germany	winter	–	PCB #28, #52, #77, #81, #101, #105, #114, #123, #126, #138, #153, #156, #157, #167, #169, #180, #189	–	–	–	median values reported only	analytical details given, indicator PCB the same as in Marb et al. (2003)	Kerst et al. (2003)
Compost	organic household waste and green waste	Germany	summer, winter	Σ 16 USEPA PAH	Σ 6 PCB§	Σ 17 PCDD/F		polybrominated diphenylethers (PBDE)#	sums reported only	–	Marb et al. (2003)
Compost	organic household waste	Germany	NA	Σ 16 USEPA PAH				DEHP, LAS, nonylphenol mono- and diethoxylates	sums and mean values reported only	analytical details given	Petersen et al. (2003)
Feedstock	green waste	USA	NA	–	–	–	4,4′-DDE, α-chlordane, γ-chlordane, endosulfan I	atrazin, 2,4,5-T, 2,4-DB, 2,4-D, alachlor, ametryn, atraton, bormacil, butachlor, butylate, chlorpropham, chlorpyrifos, cyanazine, cycloate, dalapon, dicamba, dichlorprop, dichlorvos, dinoseb, diphenamid, EPTC, ethoprop, fenarimol, fluridone, hexazinone, MCPA, MCPP, methyl metolachlor, metribuzin, mevinphos, molinate, napropamide, norflurazon, paraoxon, pebulate, prometon, pronamide, propachlor, propazine, silvex, simetryn, stirofos, tebuthiuron, terbacil, terbutryn, triademefon, tricyclazole, trifluralin, vernolate	not clear if per dry wt. or wet wt.	analytical details given	Wilson et al. (2003)

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† Green waste: organic waste from gardens and public green areas; organic household waste: a mixture of kitchen waste, garden waste and small amounts of paper; kitchen waste: crude organic waste originating from private kitchens; compost containing organic household waste: usually contains green waste as a structuring material.

‡ Sum of FLT, benzo[*k*]fluoranthene (B*k*F), benzo[*b*]fluoranthene (B*b*F), benzo[*a*]pyrene (B*a*P), indeno[1,2,3-*cd*]pyrene (IPY), benzo[*ghj*]perylene (BPE).

§ Sum of PCB #28, #52, #101, #138, #153, and #180.

¶ Phenanthrene (PHE), anthracene (ANT), FLT, pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), B*k*F, B*b*F, B*a*P, IPY, BPE, dibenzo[*a,h*]anthracene (DBA).

Sum of IUPAC congeners #17, #28, #47, #66, #71, #85, #99, #100, #138, #153, #154, #183, and #190.

p-dioxins and -furans (T-OCDD/Fs), these data were also taken into account.

Certain PAH ratios are representative for specific PAH emission sources and could contain information on the origin of PAHs (Yunker et al., 2002; Bucheli et al., 2004). The following ratios were calculated from the individual PAH of the original references: ANT/(ANT and PHE), B*a*A/(B*a*A and CHR), FLT/(FLT and PYR), and IPY/(IPY and BPE). The first two ratios differentiate between petrogenic and pyrogenic sources, with numbers below 0.1 and 0.2 respectively being indicative of the former, and numbers above 0.1 and 0.35 respectively pointing to the latter source. The last two ratios separate petrogenic (<0.4 and 0.2, respectively) from liquid fossil-fuel combustion (0.4 to 0.5 and 0.2 to 0.5 respectively), and biomass and coal burning (> 0.5 in both cases). For further details on PAH ratios and other molecular markers as well as typical numbers in specific emission sources, see Yunker et al. (2002) and Bucheli et al. (2004). Generally, PAH ratios have to be judged carefully and evaluated in concert. They may be biased in the present case, especially for lower-weight PAHs and particularly in composted samples due to possible preferential biodegradation or volatilization. Moreover, the borderline ratio between liquid fossil-fuel combustion and biomass or coal-burning derived from pure emission-source analysis is suspected to somewhat overestimate the latter source when applied to soils (Bucheli et al., 2004) and possibly to composts.

STATISTICS

The datasets were depicted as box-plots, and mean concentrations were included to better visualize the data distribution. Some datasets contained extremely high pollutant levels. They were considered as outliers (Table 1) and were not taken into account in the data analysis. All subsequently given concentrations represent median numbers unless otherwise stated. The Wilcoxon–Mann–Whitney test (Wilcoxon, 1945) was chosen to compare the means of two datasets (level of significance 0.025). This test does not require the samples to be normally distributed. The test is also robust to outliers.

CRITICAL ASSESSMENT OF SAMPLE PREPARATION AND ANALYTICAL METHODS

Reliable sample preparation and analytical methods are preconditions for the reliable interpretation of pollutant concentrations. So we will start this review by looking at the analytical methodologies used. To the best of our knowledge, no standardized analytical method, guideline, or best laboratory practice has acquired international acceptance for the analysis of POPs in compost and/or its feedstocks. The treatment of compost samples was often similar to or adopted from soil or sewage-sludge analysis. A few national attempts to harmonize and standardize methods have been made by the research and education foundation of the United States Composting Council (2002), the Austrian legislator (Bundesminister für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2001; Österreichisches Normungsinstitut, 2002), and the German association of agricultural research and analysis stations (Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten, 1995). These rather recent guidelines have clearly not yet made any significant impact on the majority of the scientific or analytical community. As apparent from Table 1, compost samples were prepared and analyzed very differently by various investigators. Sample preparation mostly included drying, homogenization and/or grinding, and milling as well as storage. However, detailed method validations, mostly for soil analysis, have shown that most sample preparation steps are prone to artifacts. Thus the analysis of semivolatile compounds often involves drying at elevated temperatures, which may lead to some volatilization of the analyte (Auer and Malissa, 1990; Chiarenzelli et al., 1996; Berset et al., 1999; Desaules and Dahinden, 2000). Water removal at room temperature may also contaminate samples with pollutants ubiquitously present in ambient air (Alcock et al., 1994; Cousins et al., 1997). Drying and freezing may alter the interaction of the analyte with the sample matrix (Northcott and Jones, 2001). Even though freeze-drying is faster and minimizes contamination by ambient air, the risk of losses due to volatilization (Berset et al., 1999), cross-contamination (own results, unpublished), and the alteration of analyte–solid interaction remains. In most cases, the samples were homogenized by mixing, milling, or grinding. Very few studies took countermeasures against sample heating, which often takes place in this step. The size fraction selected for analysis varied considerably (0.1 to 2 mm). Many studies did not even bother to provide information on the homogenization step and their final size fraction. The same was true for storage conditions such as the storage containers used, the temperature, light conditions, and storage time. In conclusion, it seems that no artifact-free sample preparation technique exists, although some measures may be more suitable than others. In our own current work (Brändli et al., unpublished data, 2004), we attempt to reduce analyte losses, contamination, and matrix alterations by performing chemical drying instead of air-drying and homogenizing the samples while at the same time cooling them with ice.

The most commonly used technique for extracting hydrophobic organic contaminants from compost was Soxhlet extraction (Table 1). However, use was also made of alternative techniques such as sonication, saponification with liquid–liquid extraction, solid–liquid extraction, and accelerated solvent extraction (ASE). A wide range of solvents was applied: hexane, toluene, dichloromethane, methanol, acetone, and some mixtures of these. Numerous studies have been performed to evaluate and compare the different extraction techniques (Popp et al., 1997; Schantz et al., 1997; Berset et al., 1999; Dupeyron et al., 1999; Hubert et al., 2000; Martens et al., 2002; Song et al., 2002; Hollender et al., 2003). Unfortunately, none of these concerned compost samples. Few general conclusions can be drawn from the various comparative studies. Some of them found significant differences in extraction potencies of individual techniques (at least for certain sample types and compound classes) (Popp et al., 1997; Schantz et al., 1997; Dupeyron et al., 1999; Hubert et al., 2000; Martens et al., 2002; Hollender et al., 2003). But others did not (Heemken et al., 1997; Berset et al., 1999), or did so only at high levels of contamination (Song et al., 2002).

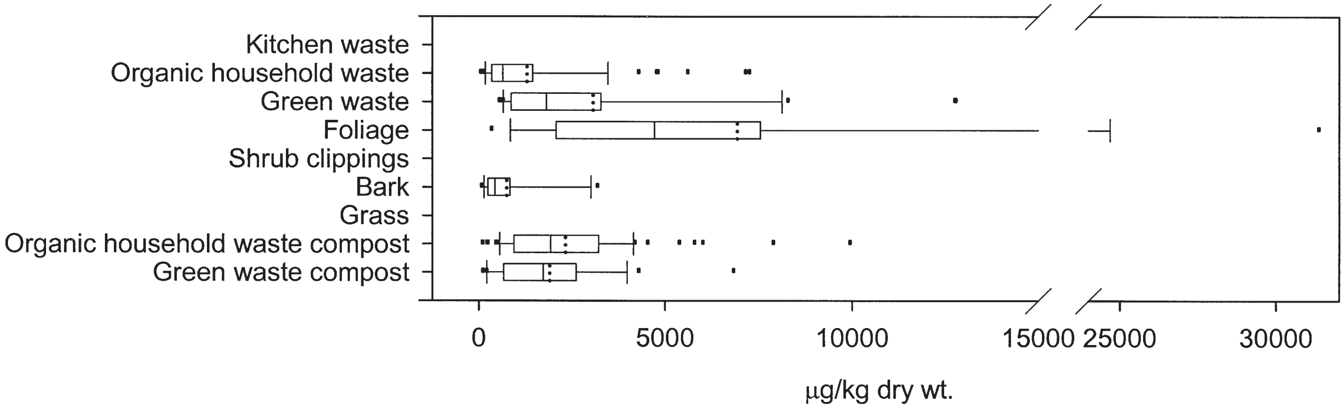

Fig. 1. Sum of 16 USEPA polycyclic aromatic hydrocarbons (Σ 16 PAHs; µg/kg dry wt.) in kitchen waste (not available [NA]), organic household waste ($n = 69$, one study only), green waste ($n = 31$), foliage ($n = 13$, one study only), shrub clippings (NA), bark ($n = 18$, one study only), grass (NA), compost containing organic household waste ($n = 78$), and compost originating from green waste ($n = 23$). Line: median; dotted line: mean; box: 25th and 75th percentile; lines with whiskers: 10th and 90th percentile; dots: outside values.

Overall, the studies are difficult to compare, as they used different samples and chose different apparatus conditions and solvents.

Given the high content of organic matter in compost samples of up to 60%, a rigorous cleanup is crucial. Various silica gels, Al_2O_3, and/or Florisil columns were often used. Gas chromatography (GC)–mass spectrometry (MS) was the most frequently selected technique for detecting semivolatiles such as PAHs, PCBs, PCDD/Fs, and organochlorines, but other techniques were also used, such as GC–electron captor detector (ECD) and high performance liquid chromatography (HPLC)–fluorescence detection. In view of the different sample-preparation methods and the wide range of analytical methods used, it is likely that some of the data variability and statistical uncertainty observed in the compost literature compiled here originates from analytical differences.

DATA EVALUATION

Polycyclic Aromatic Hydrocarbons

Feedstock

Median concentrations of Σ 16 PAHs were 421 µg/kg dry wt. ($n = 18$) in bark, 635 µg/kg dry wt. ($n = 69$) in organic household waste, 1803 µg/kg dry wt. ($n = 31$) in green waste, and 4710 µg/kg dry wt. ($n = 13$) in foliage (Fig. 1). The significantly elevated PAH concentrations for all individual compounds as well as for Σ 16 PAHs (Table 3) in foliage and green waste may be explained by an increased exposure time and the filtering effects of these feedstock materials for semivolatile organic compounds (Wania and McLachlan, 2001; Horstmann and McLachlan, 1998). Alternatively, green waste could have contained some fractions of highway clippings exposed to vehicle exhaust emissions.

Median ranges of the diagnostic PAH ratios for emission sources ANT/(ANT and PHE) (0.11–0.19), FLT/(FLT and PYR) (0.55–0.59), B*a*A/(B*a*A and CHR) (0.34–0.57), and IPY/(IPY and BPE) (0.44–0.52) reveal that the PAHs in all feedstock types originated overwhelmingly from pyrogenic sources (i.e., liquid fossil fuel combustion or biomass burning). Potential contamination of feedstocks with crude oil or unburned fossil fuels can largely be excluded. Based on typical numbers from PAH emission sources (Yunker et al., 2002; Bucheli et al., 2004), about 90% of all FLT/(FLT and PYR) and roughly 50% of all IPY/(IPY and BPE) figures indicate that, besides liquid fossil fuel combustion, biomass burning and coal combustion might have contributed to the presence of PAHs in the feedstocks. The PAHs might not have originated solely from atmospheric deposition, but could also stem from other minor contributions such as charcoal ash. However, no such indications were given in the original literature.

Table 3. *P* values of the comparison of Σ 16 polycyclic aromatic hydrocarbon (PAH) concentrations in different feedstocks and composts.

	Kitchen waste	Organic household waste	Green waste	Foliage	Shrub clippings	Bark	Grass	Organic household waste compost	Green waste compost
Number of samples	**0**	**69**	**31**	**13**	**0**	**18**	**0**	**78**	**23**
Kitchen waste		**not available (NA)**	**NA**	**NA**	**NA**	**NA**	**NA**	**–†**	**–**
Organic household waste			***<0.0001*‡**	***<0.0001***	**NA**	**0.0667**	**NA**	**–**	**–**
Green waste				**0.0252**	**NA**	***<0.0001***	**NA**	**–**	**0.2704**
Foliage					**NA**	***0.0001***	**NA**	**–**	**–**
Shrub clippings						**NA**	**NA**	**–**	**–**
Bark							**NA**	**–**	**–**
Grass								**–**	**–**
Organic household waste compost									**0.2355**

† The – indicates that the comparison is not meaningful.
‡ Levels of significance < 0.025 are marked italic type.

Compost

The PAH concentration in compost containing organic household waste was slightly higher than in green waste compost for all 16 compounds except for naphthalene. However, on a 95% level the difference is significant only for ANT, PYR, and CHR. The median Σ 16 PAH concentration for green waste compost was 1715 μg/kg dry wt. ($n = 23$), whereas compost containing organic household waste had a median of 1915 μg/kg dry wt. ($n = 78$) (Fig. 1). The difference for the Σ 16 PAHs is not statistically significant (Table 3). This is not surprising since organic household waste is often blended with considerable amounts of green waste as a structuring material to achieve a sufficiently aerated composting process. Median source diagnostic PAH ratios in organic household waste [ANT/(ANT and PHE): 0.16, FLT/(FLT and PYR): 0.57, B*a*A/(B*a*A and CHR): 0.41, and IPY/(IPY and BPE): 0.48] and green waste compost [ANT/(ANT and PHE): 0.14, FLT/(FLT and PYR): 0.59, B*a*A/(B*a*A and CHR): 0.40, and IPY/(IPY and BPE): 0.53)] are not significantly different from the respective numbers in the feedstocks, except for B*a*A/(B*a*A and CHR), which decreased from about 0.55 to about 0.40. These numbers lead to a qualitative apportionment of PAH sources similar to that stated above for the feedstocks (i.e., predominantly pyrogenic sources with some contribution from biomass burning).

The median concentration of Σ 16 PAHs is not significantly different in green waste and its respective compost (1803 and 1715 μg/kg dry wt.; Fig. 1). However, a more detailed inspection of the PAH data revealed that the median concentrations of three- and four-ring PAHs were higher in green waste (379 and 869 μg/kg dry wt. respectively) than in its corresponding compost (127 μg/kg dry wt., $p = 0.001$, and 773 μg/kg dry wt., $p = 0.257$). In contrast, higher concentrations of five- and six-ring PAHs were measured in compost (380 and 232 μg/kg dry wt.) than in feedstock (328 and 119 μg/kg dry wt.), the difference being significant for the six-ring PAHs on a 90% level ($p = 0.0449$). We therefore hypothesize the degradation/and or volatilization of the lower-fused PAHs, whereas the accumulation of the higher-fused rings may be due to mass reduction (40–60%) during composting. This hypothesis is supported by laboratory composting studies using ^{14}C-labeled PAHs (van Raaij et al., 1996; Vergé-Leviel, 2001; Carlstrom and Tuovinen, 2003). Phenanthrene (a three-ring PAH) was mineralized to CO_2 more efficiently than fluoranthene (four rings). Benzo[*a*]pyrene (five rings) was not mineralized at all. However, the formation of non-extractable residues (NER) was observed in all studies. Hund et al. (1999) observed a degradation of PYR (four rings) to about 50% during composting and 36% NER formation. Similar results were reported by Hartlieb and Klein (2001). Decreasing biodegradation with an increasing number of fused rings in a mixture of soil and mixed-waste compost and a lower degradation of higher-fused rings during mixed waste composting or soil remediation was reported by several authors (Martens, 1982; Wischmann and Steinhart, 1997; Dahosch, 1998; Loser et al., 1999). Delayed mineralization of PAHs was reported to occur after the thermophilic phase (Vergé-Leviel, 2001; Ertunc et al., 2002; Hartlieb et al., 2003). However, losses may be considerable in this phase due to volatilization (Joyce et al., 1998; Hund et al., 1999). It is generally impossible to distinguish between the formation of NER and degradation when working with nonlabeled substances, so a possible degradation is difficult to quantify.

Catchment Areas

Higher median PAH concentrations (Σ 16 PAHs = 1390 μg/kg dry wt., $n = 12$, and 4149 μg/kg dry wt., $n = 7$) were measured in urban organic household waste and green waste than in rural material (Σ 16 PAHs = 584 μg/kg dry wt., $n = 45$, and 1693 μg/kg dry wt., $n = 20$). Semirural concentrations (1060 μg/kg dry wt., $n = 12$) of organic household waste were recorded between urban and rural concentrations, whereas semirural levels (994 μg/kg dry wt., $n = 4$) of green waste were even lower than rural ones. Urban compost containing organic household waste had higher median PAH concentrations (Σ 16 PAHs = 2698 μg/kg dry wt., $n = 17$) than rural compost (Σ 16 PAHs = 827 μg/kg dry wt., $n = 15$). Semirural levels laid between the two extremes. The dataset of green waste compost was too small to be evaluated for different catchment areas. In summary, these findings correspond well with the higher emissions of PAHs found in urban areas than rural ones (Buehler et al., 2001; Schauer et al., 2003).

Inspection of PAH ratios for source diagnosis revealed no significant differences in the major PAH contributors to composts or feedstocks separated in urban or rural areas. In particular, the data did not point to elevated contributions of liquid fossil-fuel combustion compared to biomass burning in the urban areas with their heavier traffic concentrations, as might have been suspected.

Seasonality

The seasonal PAH concentration pattern in organic household waste conflicted with the usual temporal succession in the environment: higher concentrations were measured in summer (952 μg/kg dry wt., $n = 17$) and spring (938 μg/kg dry wt., $n = 15$) than in autumn (557 μg/kg dry wt., $n = 18$) and winter (494 μg/kg dry wt., $n = 18$). In general, PAH concentrations in the environment are higher in winter than in summer as observed in air and plant material (Smith et al., 2001), rainwater (Gans et al., 1999), roof runoffs (Shu and Hirner, 1997; Gans et al., 1999), and sewage plant effluents (Pham et al., 1999). These higher concentrations are attributed to higher emissions from heating systems (Schauer et al., 2003) and combustion (Lee and Jones, 1999). In contrast, concentrations of green waste were higher in spring (3169 μg/kg dry wt., $n = 9$) and winter (2846 μg/kg dry wt., $n = 4$) than in summer (2435 μg/kg dry wt., $n = 8$) and autumn (1037 μg/kg dry wt., $n = 10$). Even though the number of measurements is rather low ($4 < n < 10$), these findings correspond with the seasonal pattern in the environment. The difference be-

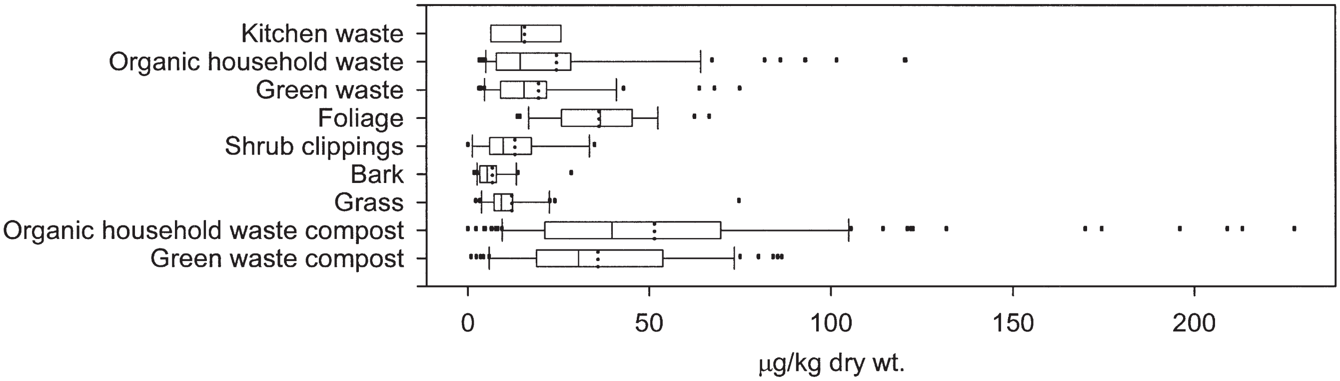

Fig. 2. Sum of six polychlorinated biphenyls (Σ 6 PCBs; μg/kg dry wt.) in kitchen waste (*n* = 8, one study only), organic household waste (*n* = 82), green waste (*n* = 41), foliage (*n* = 29), shrub clippings (*n* = 12, one study only), bark (*n* = 20), grass (*n* = 39), compost containing organic household waste (*n* = 124), and compost originating from green waste (*n* = 55). Line: median; dotted line: mean; box: 25th and 75th percentile; lines with whiskers: 10th and 90th percentile; dots: outside values.

tween organic household waste and green waste may be explained by their varying origins (e.g., imported kitchen waste such as tropical or citrus fruits vs. more local green waste), the shorter exposure time of kitchen waste to air, its possible lower affinity to semivolatile and hydrophobic compounds (e.g., root and tuber vegetable residues as compared to grass and leaves), and the small number of measurements.

The picture of inversed seasonal PAH concentration was even more pronounced in compost: the highest concentrations in compost containing organic household waste and green waste compost were reported in summer (3186 μg/kg dry wt., *n* = 7, NA) and autumn (2576 μg/kg dry wt., *n* = 13, and 3498 μg/kg dry wt., *n* = 3). In contrast, the levels in spring (1869 μg/kg dry wt., *n* = 15, and 774 μg/kg dry wt., *n* = 7) and winter (1165 μg/kg dry wt., *n* = 26, and 1715 μg/kg dry wt., *n* = 7) were lower. These findings correspond to those of another study on seasonal patterns of PAHs in compost (Breuer et al., 1997).

It still remains largely unclear why the PAH concentrations in compost were highest in seasons with lower emissions: in view of the varying residence time of green and organic household waste in the composting process (a few weeks to more than a year), a defined lag of about half a year is implausible. A possible higher mass reduction during composting in summer compared to winter due to a change of prevailing feedstocks [more easily degradable material such as grass in summer compared to more ligneous material in winter (Krogmann, 1994; Krauss et al., 1996; Krogmann, 1999; Taube, 2001)] cannot fully account for this discrepancy. The effects of elevated ambient temperatures in summer that may influence the composting, the PAH-degradation kinetics, and thus the total mass reduction are considered minimal.

Soil Concentration

A thorough overview of the literature on the PAH content in temperate topsoils was provided by Wilcke (2000). Median levels of Σ 16 PAHs were as follows: arable soil: 216 μg/kg, grassland: 194 μg/kg, forest soils: 410 μg/kg, and urban soils: 1103 μg/kg. The median concentration (Σ 16 PAHs) in the compost literature compiled here was 1870 μg/kg (*n* = 101). This suggests that the PAH concentrations in compost are up to one order of magnitude higher than in the recipient soils. As a complement to the concentrations, however, the actual input loads need to be assessed and compared to inputs from other sources such as fertilizers (e.g., sewage sludge, manure) or atmospheric deposition (Herter et al., 2003).

Polychlorinated Biphenyls

Feedstock

Median concentrations of Σ 6 PCBs were 5.4 μg/kg dry wt. (*n* = 20) in bark, 9.3 μg/kg dry wt. (*n* = 39) in grass, 9.8 μg/kg dry wt. (*n* = 12) in shrub clippings, 14.6 μg/kg dry wt. (*n* = 82) in organic household waste, 14.9 μg/kg dry wt. (*n* = 8) in kitchen waste, 15.6 μg/kg dry wt. (*n* = 41) in green waste and 36.6 μg/kg dry wt. (*n* = 29) in foliage (Fig. 2). The differences were significant for Σ 6 PCBs between bark and foliage and the other feedstock materials, grass and green waste, and organic household waste (Table 4). This picture was identical for most individual PCBs. The fact that the highest concentrations were found in foliage may, as for PAHs, be explained by its filtering effect on semivolatile organic compounds (Horstmann and McLachlan, 1998; Wania and McLachlan, 2001). In contrast to PAHs, whose concentrations in green waste outweighed those in organic household waste, PCB concentrations were similar in organic household and green waste. This fact, as well as the higher 90th percentile and outside concentrations (Fig. 2), might be explained by fractions of accidentally discharged impurities (e.g., plastics) in organic household waste.

Compost

Higher PCB concentrations were measured in compost containing organic household waste (Σ 6 PCBs = 39.8 μg/kg dry wt., *n* = 124) than that containing green waste (Σ 6 PCBs = 30.6 μg/kg dry wt., *n* = 55) (Fig. 2). Except for PCB #52, and as for the PAHs (see above),

Table 4. *P* values of the comparison of Σ 6 polychlorinated biphenyl (PCB) concentrations in different feedstocks and composts.

	Kitchen waste	Organic household waste	Green waste	Foliage	Shrub clippings	Bark	Grass	Organic household waste compost	Green waste compost
Number of samples	**8**	**82**	**41**	**29**	**12**	**20**	**39**	**124**	**55**
Kitchen waste		**0.7071**	**0.3710**	***0.0007*†**	**0.5120**	***0.018***	**0.1698**	**–‡**	**–**
Organic household waste			**0.9444**	***<0.0001***	**0.1669**	***<0.0001***	***0.0069***	**–**	**–**
Green waste				***<0.0001***	**0.1454**	***<0.0001***	***0.0032***	**–**	***0.0002***
Foliage					***<0.0001***	***<0.0001***	***<0.0001***	**–**	**–**
Shrub clippings						***0.0127***	**0.6893**	**–**	**–**
Bark							***0.0007***	**–**	**–**
Grass								**–**	**–**
Organic household waste compost									**0.0932**

† Levels of significance < 0.025 are marked italic type.
‡ The – indicates that the comparison is not meaningful.

this difference is not significant (Table 4). This similarity in median concentration may be at least partially due to the large portions of green waste often mixed into organic household waste (compost). However, some studies showed that organic household waste contained significantly more PCBs than green waste (e.g., Krauss, 1994). This is also indicated by the elevated 90th percentile and outside values in Fig. 2 for organic household waste compost and may again be explained on the basis of improperly separated organic waste and the presence of impurities such as plastics in organic household waste.

A possible accumulation of PCBs is hypothesized during green waste composting. The median concentration in green waste was 15.6 μg/kg dry wt. (Σ 6 PCBs, $n = 41$) whereas the corresponding compost contained 30.6 μg/kg dry wt. (Σ 6 PCBs, $n = 55$) (Fig. 2). The difference of roughly a factor of two is significant on a 95% level for PCBs #101, #138, #153, and #180, but not for Σ 6 PCBs ($p = 0.093$; Table 4), and corresponds to the respective mass reduction during composting. The increase of PCB #28 by a factor of 1.3 and of PCB #52 by a factor of 1.6 is less pronounced and not significant. It may be due to some volatilization or degradation of these less stable congeners. This hypothesis is supported by laboratory composting studies: Vergé-Leviel (2001) found only small mineralization rates of ^{14}C-labeled PCB #52, although 38% of the compound was volatilized during composting. Van Raaij et al. (1996) found that ^{14}C-labeled PCB #77 remained stable during composting and reported 10% of NER after composting. Dahosch (1998) found that PCB levels did not decrease during the composting of mixed waste and Lazzari et al. (1999) even observed an increase in PCBs during the composting of sewage sludge and crushed ligneous waste. This was explained by the degradation of organic matter. Block (1998) reported PCB degradation of up to 40% in heavily contaminated soil composted with yard trimmings. However, remediation of heavily contaminated soil may be successful whereas degradation is probably much slower or does not occur at all at lower concentrations. Furthermore, since nonlabeled substances were used, the reduction could also be due to the formation of NER. In conclusion, it seems that PCBs are unlikely to degrade during composting and accumulate instead (due to mass reduction). Some volatilization of the lower chlorinated compounds such as PCBs #28 and #52 appears possible.

Catchment Areas

In organic household waste and green waste, no significant concentration differences were found between rural (Σ 6 PCBs = 12.0 μg/kg dry wt., $n = 46$, and 15.3 μg/kg dry wt., $n = 19$) and urban (Σ 6 PCBs = 29.0 μg/kg dry wt., $n = 12$, and 21.9 μg/kg dry wt., $n = 9$) catchment areas. But the difference of over a factor of two between urban and rural organic household waste is still considerable. Semirural concentrations of organic household waste (18.1 μg/kg dry wt., $n = 12$) laid between the rural and urban values, whereas concentrations of green waste were in the same range as rural concentrations (13.2 μg/kg dry wt., $n = 4$). In compost containing organic household waste, the differences between rural and urban regions were significant on a 90% confidence level for all congeners except for PCBs #28 and #52 and for Σ 6 PCBs ($p = 0.0359$). Semirural concentrations of organic household waste compost laid between rural and urban levels. Due to a lack of data, green waste compost could not be evaluated according to catchment area. These findings may be attributed to the generally higher PCB burden in urban areas, such as was reported in air (Harner et al., 2004; Jaward et al., 2004) and soil (Langenkamp and Part, 2001; Krauss and Wilcke, 2003; Schmid et al., 2005).

Seasonality

Higher concentrations of organic household waste, although not significantly so, were measured in spring and summer (Σ 6 PCBs = 19.0 μg/kg dry wt., $n = 18$, and 14.9 μg/kg dry wt., $n = 18$) than in autumn and winter samples (Σ 6 PCBs = 11.8 μg/kg dry wt. $n = 27$, and 8.8 μg/kg dry wt., $n = 18$). The PCB concentrations in green waste differed little and ranged from 13.2 μg/kg dry wt. (Σ 6 PCBs, $n = 15$) in spring to 20.9 μg/kg dry wt. (Σ 6 PCBs, $n = 4$) in winter. However, a distinct seasonal change in PCB concentrations of compost containing organic household waste and green waste compost was observed. In both composts the highest concentrations were measured in summer (Σ 6 PCBs = 60 μg/kg dry wt., $n = 45$, and 49.8 μg/kg dry wt., $n = 22$) and autumn (Σ 6 PCBs = 39.3 μg/kg dry wt., $n = 12$, and 60 μg/kg dry wt., $n = 6$). Lower levels were reported in spring (Σ 6 PCBs = 27.5 μg/kg dry wt., $n = 15$, and 10.0 μg/kg dry wt., $n = 10$) and winter (Σ 6 PCBs = 22.9 μg/kg dry wt., $n = 30$, and 23.7 μg/kg dry wt., $n =$

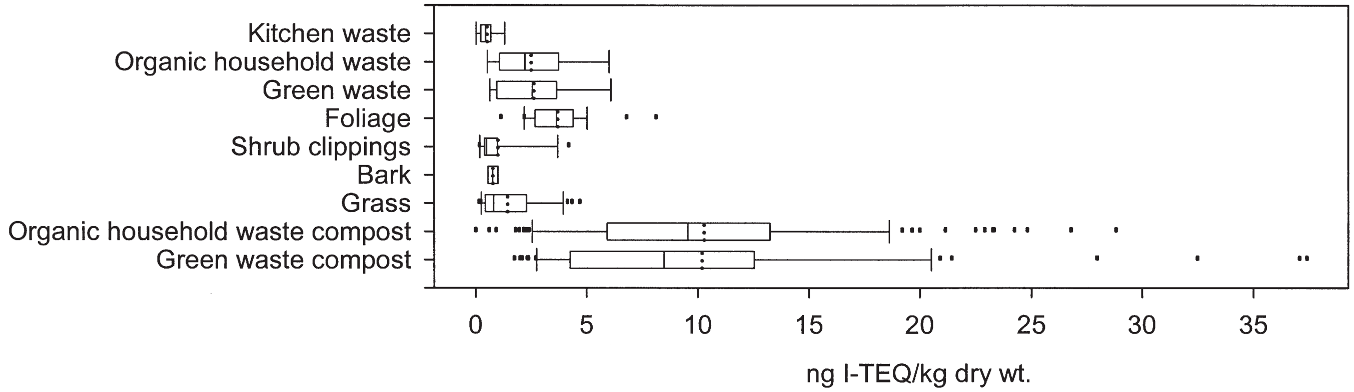

Fig. 3. Sum of 17 polychlorinated dibenzo-*p*-dioxins and -furans (Σ 17 PCDD/Fs; ng international toxicity equivalent [I-TEQ]/kg dry wt.) in kitchen waste (*n* = 9, one study only), organic household waste (*n* = 9), green waste (*n* = 9), foliage (*n* = 28), shrub clippings (*n* = 12, one study only), bark (*n* = 4), grass (*n* = 36), compost containing biowaste (*n* = 124), and compost originating from green waste (*n* = 61). Line: median; dotted line: mean; box: 25th and 75th percentile; lines with whiskers: 10th and 90th percentile; dots: outside values.

9). In contrast to the PAHs, the concentration gradient over time in compost follows that found in other environmental compartments (Halsall et al., 1995; Lohmann et al., 2000). It is therefore suspected to be governed by the annual temperature regime, thus leading to increased release and volatilization of PCBs at higher temperatures in summer and autumn (Lee and Jones, 1999; Lohmann et al., 2000) and may, as for the PAHs, also reflect a possible variation in the degradation efficiency of organic waste.

Soil Concentration

In background soil samples from 191 global surface (0–5 cm) soils, the Σ 6 PCBs of the mean concentrations of individual congeners was 2.5 μg/kg (Meijer et al., 2003b). German soil samples from private gardens, urban parks, and industrial/traffic sites exhibited higher Σ 6 PCBs concentrations (30, 80, and 48 μg/kg, respectively) than samples from arable land, grassland, and forest (10 to 18 μg/kg) (Langenkamp and Part, 2001). The median compost concentration found in the present literature review is 38 μg/kg (*n* = 179). As with PAHs, this concentration is roughly higher by a factor of 15 than the background soil concentrations, but well within the range of many soils in urban areas. The PCB soil input loads from other recycling fertilizers lay within the same range as the compost. The input by atmospheric deposition varies greatly and can exceed that due to recycling fertilizers (Herter et al., 2003).

Polychlorinated Dibenzo-*p*-Dioxins and -Furans

Feedstock

Few measurements were reported for PCDD/Fs in organic waste (Table 1). Median concentrations of Σ 17 PCDD/Fs were 0.44 ng I-TEQ/kg dry wt. (*n* = 9) in kitchen waste, 0.48 ng I-TEQ/kg dry wt. (*n* = 12) in shrub clippings, 0.76 ng I-TEQ/kg dry wt. (*n* = 4) in bark, 0.81 ng I-TEQ/kg dry wt. (*n* = 36) in grass, 2.22 ng I-TEQ/kg dry wt. (*n* = 9) in organic household waste, 2.54 ng I-TEQ/kg dry wt. (*n* = 9) in green waste, and 3.64 ng I-TEQ/kg dry wt. (*n* = 28) in foliage (Fig. 3). The elevated concentrations in foliage correspond to similar findings for PAHs and PCBs (see above). However, on a concentration basis (ng/kg dry wt.), which might be the more relevant unit for evaluating environmental distribution processes, the median concentration in foliage Σ 17 PCDD/Fs was lower (82.1 ng/kg dry wt.) than, for instance, in green waste (216.6 ng/kg dry wt.). Due to a lack of data, Σ T-OCDD/Fs (in ng/kg dry wt.) was also taken into account. The Σ T-OCDD/F concentrations were 58 ng/kg dry wt. (*n* = 22) in bark, 64 ng/kg dry wt. (*n* = 12) in shrub clippings, 70 ng/kg dry wt. (*n* = 9) in kitchen waste, 98 ng/kg dry wt. (*n* = 38) in grass, 197 ng/kg dry wt. (*n* = 79) in organic household waste, 235 ng/kg dry wt. (*n* = 28) in foliage, and 292 ng/kg dry wt. (*n* = 42) in green waste. Significant differences were observed between bark and organic household waste, green waste, and foliage; shrub clippings and the former three feedstocks; kitchen waste and organic household waste, green waste, and foliage; as well as between grass and green waste (Table 5).

Compost

Except for octachloro dibenzo-*p*-dioxin and octachloro dibenzofuran, all single congeners followed the same pattern: concentrations of organic household waste compost were in general higher than those of green waste compost. However, Σ 17 PCDD/F concentrations varied little between compost containing organic household waste (9.6 ng I-TEQ/kg dry wt., *n* = 124; Fig. 3) and that containing green waste (8.5 ng I-TEQ/kg dry wt., *n* = 61) and the differences are far from significant (Table 5). This finding contrasts with the significant differences found between the respective feedstocks and may, as with PAHs and PCBs, be caused by the blending of organic household waste and kitchen waste with green waste for facilitated composting.

During the composting process, an increase of PCDD/Fs (Σ 17 PCDD/Fs and Σ T-OCDD/Fs) concentrations was observed (Fig. 3). This increase is much more pronounced than with PAHs and PCBs and higher than the usual mass reduction of about 40 to 60%. To explain this, the formation of PCDD/Fs during composting has

Table 5. ***P*** **values of the comparison of polychlorinated dibenzo-*p*-dioxin and -furan (PCDD/F) and tetra- to octachloro dibenzo-*p*-dioxin and -furan (T-OCDD/F) concentrations in different feedstocks and composts.**

	Kitchen waste	Organic household waste	Green waste	Foliage	Shrub clippings	Bark	Grass	Organic household waste compost	Green waste compost
				Σ 17 PCDD/F					
Number of samples	9	9	9	28	12	4	36	124	61
Kitchen waste		*0.0027*†	*0.002*	<*0.0001*	0.4138	0.1897	0.0631	–‡	–
Organic household waste			0.6588	0.0295	*0.0173*	0.0538	0.0555	–	–
Green waste				0.0537	*0.0095*	0.0538	0.0300	–	*0.0002*
Foliage					<*0.0001*	*0.0016*	<*0.0001*	–	–
Shrub clippings						0.3026	0.2386	–	–
Bark							0.8392	–	–
Grass								–	–
Organic household waste compost									0.3463
				Σ T-OCDD/F					
Number of samples	9	78	42	28	12	22	38	72	59
Kitchen waste		*0.0024*	*0.0016*	*0.0004*	0.8036	0.4208	0.2735	–	–
Organic household waste			0.0996	0.2553	*0.0007*	<*0.0001*	*0.0230*	–	–
Green waste				0.4323	*0.0003*	<*0.0001*	*0.0015*	–	<*0.0001*
Foliage					*0.0006*	<*0.0001*	0.0361	–	–
Shrub clippings						0.6013	0.2330	–	–
Bark							0.0300	–	–
Grass								–	–
Organic household waste compost									*0.0090*

† Levels of significance < 0.025 are marked italic type.

‡ The – indicates that the comparison is not meaningful.

been hypothesized. Dahosch (1998) found PCDD/Fs persistent during MSW composting and even observed the formation of octachloro dibenzo-*p*-dioxins. Similar results were found by Krauss et al. (1994), Öberg et al. (1994), and Fiedler et al. (1994). The possibility of PCDD/F-formation during composting is still controversially discussed and has also been stated as being unlikely to occur (Öberg et al., 1994).

Catchment Areas

For both organic household waste and green waste, higher concentrations of Σ T-OCDD/Fs were reported in urban (229 ng/kg dry wt., $n = 12$, and 1343 ng/kg dry wt., $n = 11$) than in rural material (175 ng/kg dry wt., $n = 47$, $p = 0.2950$, and 236 ng/kg dry wt., $n = 19$, $p = 0.0569$). In both feedstocks, semirural concentrations (148 ng/kg dry wt., $n = 12$, and 119 ng/kg dry wt., $n = 4$) were even lower than rural ones. This may be due to the fact that all PCDD/F data in organic household waste and green waste data originated from the same source (Sihler et al., 1999). The elevated concentrations of PCDD/Fs in urban feedstocks correspond well with the findings for PCBs and PAHs (see above). No difference was found between rural and urban composts containing organic household waste (Σ 17 PCDD/Fs = 8.4 ng I-TEQ/kg dry wt., $n = 14$, and Σ 17 PCDD/Fs = 7.9 ng I-TEQ/kg dry wt., $n = 24$). Semirural levels (Σ 17 PCDD/Fs = 9.3 ng I-TEQ/kg dry wt., $n = 13$) were even slightly higher than rural concentrations in this type of compost. In green waste compost, the difference between rural (Σ 17 PCDD/Fs = 5.23 ng I-TEQ/kg dry wt., $n = 8$) and urban (Σ 17 PCDD/Fs = 10.58 ng I-TEQ/kg dry wt., $n = 16$) samples is significant for the Σ 17 PCDD/Fs ($p = 0.011$), but not for most single compounds.

Seasonality

In organic household waste, higher PCDD/F concentrations (Σ T-OCDD/Fs) were measured in spring (293 ng/kg dry wt., $n = 17$) and summer (249 ng/kg dry wt., $n = 18$) than in winter (148 ng/kg dry wt., $n = 18$) and autumn (180 ng/kg dry wt., $n = 26$). The difference between the spring concentration and that of autumn and winter is significant. In green waste, the highest concentrations were reported in spring (694 ng/kg dry wt., $n = 17$) and winter (611 ng/kg dry wt., $n = 4$). Summer (191 ng/kg dry wt., $n = 9$) and autumn (170 ng/kg dry wt., $n = 9$) concentrations were lower. Even though median concentrations varied considerably, the differences were not significant. The high levels in spring might be explained by higher emissions of PCDD/Fs during the heating period due to domestic burning of wood/coal (Lohmann et al., 2000). In compost containing organic household waste, however, the highest concentrations were observed in summer (17 PCDD/Fs = 11.3 ng I-TEQ/kg dry wt., $n = 46$) and autumn (8.1 ng I-TEQ/kg dry wt., $n = 13$), which conflicts with the expected emission pattern dominated by waste incineration which is largely independent of the season (Dettwiler et al., 1997). In green waste compost, PCDD/F concentrations were similar in summer (Σ 17 PCDD/Fs 8.4 ng I-TEQ/kg dry wt., $n = 22$), autumn (7.7 ng I-TEQ/kg dry wt., $n = 6$), and winter (9.0 ng I-TEQ/kg dry wt., $n = 9$), but lower in spring (4.2 ng I-TEQ/kg dry wt., $n = 8$). In view of the small numbers of measurements, we will not interpret these results further.

Soil Concentration

The Σ 17 PCDD/F concentrations in soil were observed in the range of 2 to 5 ng I-TEQ/kg (Dettwiler et al., 1997; Langenkamp and Part, 2001). Schmid et al.

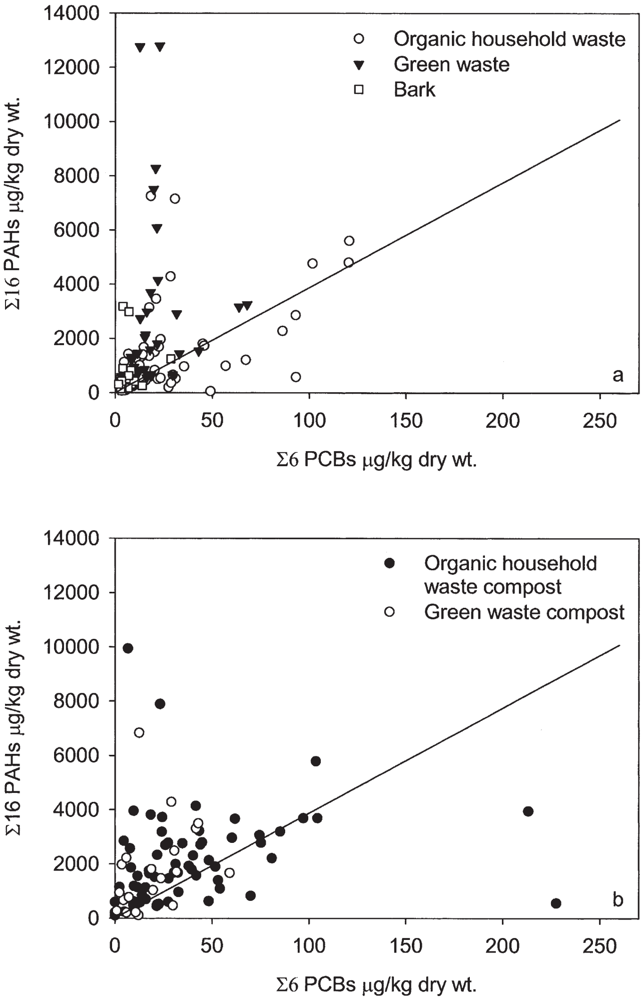

Fig. 4. Sum of 16 polycyclic aromatic hydrocarbons (Σ 16 PAHs; µg/kg dry wt.) versus sum of six polychlorinated biphenyls (Σ 6 PCBs; µg/kg dry wt.) measured in the same samples of (a) organic household waste (*n* = 68), green waste (*n* = 29), and bark (*n* = 18), and (b) compost containing organic household waste (*n* = 67) and compost originating from green waste (*n* = 20). No concomitant PCB and PAH analysis is available for kitchen waste, foliage, shrub clippings, and grass. For illustration, the regression line (forced through zero) from all available data is added.

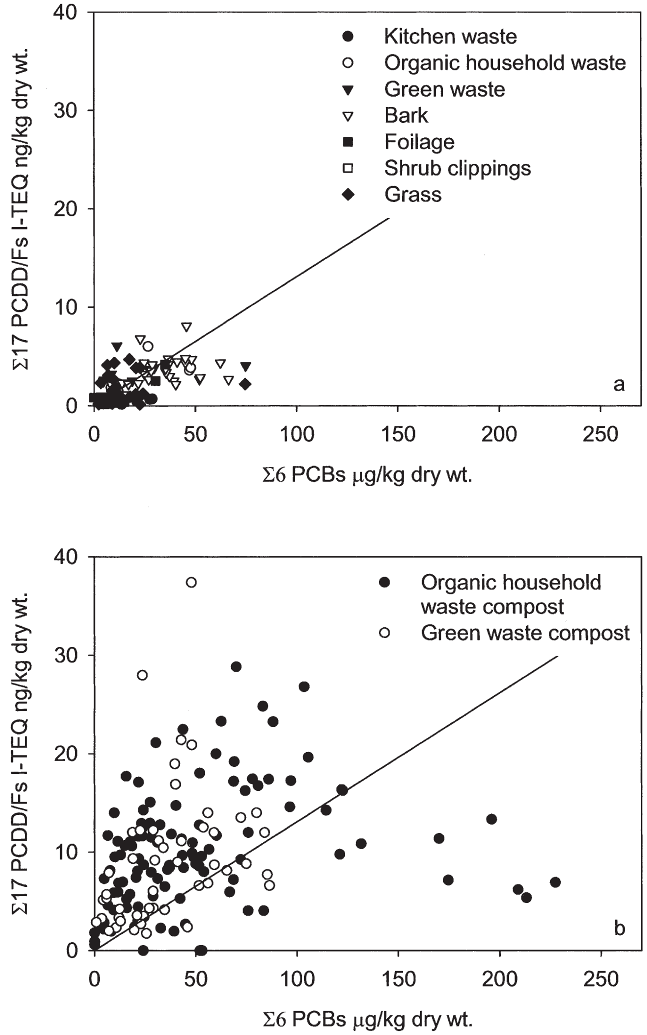

Fig. 5. Sum of 17 polychlorinated dibenzo-*p*-dioxins and -furans (Σ 17 PCDD/Fs; ng international toxicity equivalent [I-TEQ]/kg dry wt.) versus sum of six polychlorinated biphenyls (Σ 6 PCBs; µg/kg dry wt.) measured in the same samples of (a) kitchen waste (*n* = 7), organic household waste (*n* = 9), green waste (*n* = 9), foliage (*n* = 28), shrub clippings (*n* = 12), bark (*n* = 2), and grass (*n* = 36), and (b) compost containing organic household waste (*n* = 111) and compost originating from green waste (*n* = 50). For illustration, the regression line (forced through zero) from all available data is added.

(2005) reported Σ 17 PCDD/F numbers between 1.1 and 11.4 ng I-TEQ/kg dry wt. with a median of 2.4 ng I-TEQ/kg dry wt. (*n* = 23). The median concentration for Σ 17 PCDD/Fs in compost was 9.25 ng I-TEQ/kg dry wt. (*n* = 185). As with PAHs and PCBs, this number is in the upper range of the measured concentrations in soils.

PERSISTENT ORGANIC POLLUTANTS COMPARISON

The comparison of PCB and PAH concentrations in feedstock and compost (Fig. 4) shows that these two compound classes corresponded in most samples: the higher the PCB the higher the PAH concentration. This points to similar environmental behavior and the same input pathway, probably aerial deposition. However, there is a group of mostly green waste samples which had considerably high PAHs (Σ 16 PAHs = 6000–14 000 µg/kg dry wt.) but relatively low PCB concentrations (Fig. 4: data points clearly above the regression line, which was derived from the total of all data). These samples may originate from road clippings or contain ashes. High PCB concentrations with concomitantly lower PAH levels, as mostly observed in some organic household waste and organic household waste compost samples, may be explained by higher fractions of impurities in organic household waste.

Higher PCDD/F levels were reported for most samples with increasing PCB concentrations (Fig. 5), again pointing to similar behavior and input pathways. However, certain samples of the foliage and the organic household waste compost groups exhibited elevated PCB concentrations (Σ 6 PCBs = 40–70 and 120–250 µg/kg dry wt.)

Table 6. Further organic compounds analyzed in compost.

	Median concentration†	Number of samples analyzed	Number of detections	Number of reports‡
	μg/kg dry wt.			
		Organochlorines		
Aldrin	0	88	6	5
Chlordane	0	97	22	7
Dieldrin	0	91	37	6
Endosulfan	0	45	5	3
Endrin	0	87	36	5
Heptachlor	0	53	9	6
Heptachlorepoxid	0	49	11	5
Σ DDT§	8.1	66	55	4
Σ hexachlorohexane (HCH)¶	0	45	13	3
Hexachlorobenzene (HCB)	1.2	142	98	10
Pentachlorbenzene	0.7	47	36	4
Pentachlorophenol	14	100	98	7
Tetrachlorbenzene	0.4	33	26	2
		Other compounds		
Biphenyl	48.5	28	28	2
Cyfluthrin	0	15	3	1
Deltamethrin	0	15	4	1
Fenpropathrin	0	15	5	1
***O*-phenylphenol**	20	28	21	2
Thiabendazole	7.1	23	13	3
Di(2-ethylhexyl)phthalate (DEHP)	300	79	64	7
Polybrominated diphenylethers (PBDE)#	12.2	12	12	1

† Median is zero if more than 50% could not be quantified.

‡ For detailed references see Table 1.

§ Sum of *o,p′*-DDD, *o,p′*-DDE, *o,p′*-DDT, *p,p′*-DDD, *p,p′*-DDE, and *p,p′*-DDT.

¶ Sum of α-, β-, γ-, and δ-HCH.

Sum of IUPAC congeners #17, #28, #47, #66, #71, #85, #99, #100, #138, #153, #154, #183, and #190.

but relatively low PCDD/F levels (Fig. 5). As for the PCB–PAH concentration, these higher PCB concentrations can probably be attributed to impurities.

OTHER ORGANOCHLORINES

No organochlorine data could be found in the literature on compost feedstock. However, a considerable number of these compounds were analyzed in compost (Table 6). Most of the organochlorine pesticides have rarely been detected and median concentrations were very low or zero. Therefore no evaluation according to feedstock, catchment areas, and seasonality was performed.

The ubiquitous pesticide Σ DDT (sum of *o,p′*-DDD, *o,p′*-DDE, *o,p′*-DDT, *p,p′*-DDD, *p,p′*-DDE, and *p,p′*-DDT) was also detected in compost (8.1 μg/kg dry wt., $n = 45$). For comparison, Meijer et al. (2001) measured 1.36 μg/kg dry wt. (sum of *p,p′*-DDE, *o,p′*-DDT, and *p,p′*-DDT) in a UK soil sample and Webber and Wang (1995) detected DDT (sum of *p,p′*-DDE, *o,p′*-DDT, and *p,p′*-DDT) in 10 out of 30 Canadian soil samples, with concentrations ranging from 1 to 70260 μg/kg dry wt. Hexachlorobenzene (HCB), a precursor in the production of various organochlorine compounds, was used as a fungicide for the treatment of seeds and is linked to combustion processes and to the metallurgical industry. Applications of HCB are believed to have been phased out in North America and Western Europe (Bailey, 2001). It is listed in Annex C of the Stockholm convention on POPs that requires measures to reduce or eliminate releases from unintentional production. The median HCB concentration in compost was 1.2 μg/kg dry wt. ($n = 142$). Hexachlorobenzene was detected in agricultural soils at a concentration of 1 to 6 μg/kg dry wt. (Marb et al., 2003). Pentachlorobenzene (PCBz) and tetrachlorobenzene (TCBz) are precursors of pesticides. They were measured at 0.74 μg/kg dry wt. ($n = 74$) and 0.44 μg/kg dry wt. ($n = 43$) in compost. Target values for PCBz in Dutch soil are 2.5 and 10 μg/kg dry wt., respectively (Netherlands Ministry of Housing, Spatial Planning and Environment, 1994). Pentachlorophenol (PCP) is used as a wood-protection product with fungicide and bactericide properties. Its usage at a concentration of 1% or higher is prohibited within the EU (European Union, 1991). The median PCP concentration in compost was 14 μg/kg dry wt. ($n = 100$).

OTHER COMPOUNDS

Biphenyl, a fungicide predominately used in citrus fruits, was detected in all the samples analyzed (Table 6). Marb et al. (2003) argued that this compound is used by the chemical industry and suspected that its major input pathway to compost was via organic household waste. However, the dataset was too small to check this hypothesis. Other citrus fungicides, namely *o*-phenylphenol and thiabendazole, were detected in compost at 20 μg/kg dry wt. ($n = 28$) and 7.1 μg/kg dry wt. ($n = 23$), respectively. Other pesticides, such as cyfluthrin, deltamethrin, and fenpropathrin, were rarely measured and reported.

The median concentration of di(2-ethylhexyl)phthalate (DEHP) in compost was 300 μg/kg dry wt. The DEHP concentration was significantly higher in compost containing organic household waste (1300 μg/kg dry wt., $n = 51$) than in green waste compost (84 μg/kg dry wt., $n = 28$) ($p = 0.0036$). This can be explained by the higher plastic content of organic household waste compared to green waste. It supports the hypothesis derived from the above findings for PCBs that organic household waste might contain more such impurities than green waste. In a German study, the DEHP concentration in agricultural soils ranged from 300 to 700 μg/kg (Langenkamp and Part, 2001). In Denmark, DEHP concentrations of 12 to 40 μg/kg dry wt. were measured in uncultivated and arable soils (Vikelsøe et al., 2002).

A recent study showed that the median concentration of polybrominated diphenylethers (PBDE) (expressed as the sum of IUPAC congeners #17, #28, #47, #66, #71, #85, #99, #100, #138, #153, #154, #183, and #190) in compost was 12.2 μg/kg dry wt. ($n = 10$) (Marb et al., 2003). Polybrominated diphenylethers, used as a flame retardant, are detected at increasing concentrations in the environment (Rahman et al., 1998; De Boer et al., 2000; de Wit, 2002; Hites, 2004). Its soil concentrations ranged from 0.065 to 12 μg/kg dry wt. (sum of all congeners) in remote areas (Hassanin et al., 2004).

Chlorinated paraffins (sum of short- and medium-chained compounds) are used as secondary plasticizers as well as in paints and adhesives: they were detected in organic household waste at a concentration of 16041 μg/kg dry wt. ($n = 17$) (Nilsson, 2000). No quantitative compost and soil data could be found, but concentrations of between 5 and 200 μg/kg dry wt. were reported in sediments (Bolliger and Randegger-Vollrath, 2003).

CONCLUSIONS

This review compiles environmentally relevant POP data from some 25 individual studies in compost and its feedstocks. The sample preparation and analytical procedures reported varied widely. Of the seven types of feedstocks differentiated here, foliage contained the highest concentrations of PAHs, PCBs, and PCDD/Fs. Bark, shrub clippings, and grass exhibited the lowest levels of POPs, followed by kitchen waste, organic household waste, and green waste. The elevated concentrations of these semivolatile compounds in green waste and foliage may be explained by the efficient filter characteristics of these materials. Organic household waste and green waste composts contained similar amounts of POPs, because the former is often blended with significant amounts of green waste to achieve an aerobic composting process. Whereas the PAH concentration in compost was between the levels observed for the different feedstock materials, PCB concentrations in compost were at the higher end of feedstock concentrations. This suggests degradation/volatilization of the lower-fused PAHs, but no such indications were observed for the heavier PAHs and PCBs. Most strikingly, PCDD/F compost concentrations were elevated by a factor of 2 to 14 compared with feedstock levels. This is more than can be expected from the organic mass reduction occurring during composting. Comparison of the main POP compound classes investigated suggests that atmospheric deposition may be a relevant input source for most of these semivolatile pollutants. The PAH or PCB concentrations can sometimes be relatively elevated, probably due to inputs from traffic emissions, ashes, or impurities. Specific contamination might also occur due to pesticide application. Urban feedstock and compost was generally elevated in PAH, PCB, and PCDD/F levels in comparison with rural samples. This corresponds to the pattern observed in other environmental compartments. Seasonal differences were observed for PAHs, PCBs, and PCDD/Fs, the concentrations generally being highest during summer. This is in accordance with the seasonal variation observed in the environment for PCBs, but not for PAHs and PCDD/Fs. The POP level in compost was compared with representative data from soils (i.e., its primary recipient). Concentrations of PAHs, PCBs, and PCDD/Fs were up to one order of magnitude higher than those reported for arable soils, but of the same order of magnitude as for many urban soils. Overall, these findings may provide a best-possible current-state basis for future measures to reduce the POP content in compost as well as to assess the risks of compost application.

ACKNOWLEDGMENTS

Our thanks are due to Hans Jörg Bachmann (FAL) and Martin Kohler (EMPA) for their useful comments on the manuscript. We would also like to acknowledge the Swiss Agency for the Environment, Forest and Landscape (SAEFL), the Swiss Federal Office of Energy (SFOE), and the Office for Waste, Water, Energy and Air (AWEL), Zürich, for their financial support.

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3 Paper 2

Optimised accelerated solvent extraction of PCBs and PAHs from compost

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International Journal of Environmental Analytical Chemistry, 2006, 86, 505-525.

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Intern. J. Environ. Anal. Chem.
Vol. 86, No. 7, 15 June 2006, 505–525

Optimised accelerated solvent extraction of PCBs and PAHs from compost

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(*Received 2 March 2005; in final form 5 November 2005*)

This study is the first thorough method optimisation for accelerated solvent extraction (ASE) of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) from chemically dried compost. For PCBs, optimised solvent composition, temperature, pressure, number of static cycles, duration, and flush volume were as follows: toluene/acetone 1 : 3 (v/v), 120°C, 2000 psi, 3 × 5 min, and 50%, respectively. Limits of quantification and method precision were between 0.16 and 2.46 $\mu g\,kg^{-1}$ dw and 6–17% respectively for individual PCBs. Absolute recoveries of isotope-labelled extraction standards used for each of the analytes ranged from 65 to 105% and relative recoveries were between 85 and 99%. The method proofed to be robust and was successfully applied to different compost samples.

The optimisation of PAHs extraction was performed and resulted in the following conditions: solvent: hexane/acetone 1/3 (v:v), temperature: 140°C, pressure: 1500 psi, extraction time: 3 × 5 min, and 50% flush volume. Limits of detection and method precision for individual PAHs were between 1.1 and 37.2 $\mu g\,kg^{-1}$ dw and 12–34% respectively. Absolute and relative recoveries ranged from 24 to 68% and from 85 to 99%, respectively. Optimal extraction conditions for PAHs were more difficult to determine due to the inhomogeneous distribution of PAHs in samples. However, the method appeared to be feasible and suggestions for further improvements are presented.

Keywords: ASE; Polychlorinated biphenyls; Polycyclic aromatic hydrocarbons; Sample preparation

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International Journal of Environmental Analytical Chemistry
ISSN 0306-7319 print/ISSN 1029-0397 online © 2006 Taylor & Francis
DOI: 10.1080/03067310500410839

1. Introduction

Persistent organic pollutants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are nowadays ubiquitously present in a variety of solid samples, such as sediment, soil, sewage sludge and compost (i.e., solid residues from the aerobic decomposition process of crude kitchen waste from private households and green waste from garden and public green areas). Among these, the latter is neglected from an analytical point of view. Although there is an increasing awareness among environmental analytical chemists that each matrix requires individual analytical treatment (see, e.g., the EU project Horizontal [1]), compost and digestate (i.e., the product of the anaerobic digestion process of the above mentioned feedstock materials with subsequent aerobic treatment), are, in practice, often implicitly or intentionally regarded as equal to other solids and treated accordingly [2–4]. This equalisation bears the risk of inaccurate quantification of important organic pollutants such as PCBs and PAHs due to varying extraction efficiency of a given analytical technique for different solid matter composition.

One of the most important characteristics of solid samples is organic matter (OM), into which organic pollutants are predominately partitioned. OM content and composition vary widely between different matrices. Typical mass fractions are 0.1 to 5% (median value around 0.5%) in global coastal sediments [5] and <12% in Western European topsoils [6] (assuming 50% organic carbon). In contrast, OM content in compost usually is around 40% (median value, $n = 170$, compost database of [7]) and can sometimes be as high as 70% [8]. This high OM content makes it a very challenging matrix for organic pollutant analysis, since a high number of interfering substances and matrix constituents are co-extracted.

Besides the sheer amount of OM, the affinity of analytes to such solid matrices and consequently their extractability are highly dependent on the OM composition [9], which varies in different solid materials and probably also within different compost samples themselves. Moreover, a recent review on organic pollutants in compost and its feedstock illustrated that the analytical protocols used for compost analysis differed widely at all steps of the analytical chain from sampling, sample preparation, extraction and clean-up to analysis [7].

Taking into account the ubiquitous distribution of PCBs and PAHs and their semivolatility, special care is required during sample and extract manipulations to avoid analyte losses and/or (cross-)contamination. In the light of the ongoing discussion about the quality of recycling fertilisers and soil improvers with regard to soil protection, accurate and robust quantification of organic pollutants in compost and digestate is mandated for a proper risk assessment of these products. Here, we report a method that has been specifically adapted and optimised for these analytically challenging matrices.

Accelerated solvent extraction (ASE^{TM}, Dionex Corporation, Sunnyvale, CA, USA), also termed pressurised fluid extraction (PFE, see EPA 3545a method), pressurised liquid extraction (PLE, Elsevier Science), enhanced solvent extraction (ESE) or high pressure solvent extraction (HSPE) [10], is a low solvent consuming, fast, effective, and automated extraction technique. It employs high temperature and pressure to increase the contact of the solvent with the matrix and the analyte. Consequently, extraction time and solvent consumption are reduced compared to other extraction techniques such as Soxhlet. (For details on the ASE principles, see [10–14].) ASE has been chosen for the extraction of a wide range of compounds from various matrices [10, 12, 13, 15, 16]. In particular, it has been used for extraction of PCBs and PAHs from soil [11, 17–22], sediment [23–28] and sewage sludge samples [14, 17, 24, 29]. In comparison with other extraction techniques, such as Soxhlet, supercritical fluid, ultrasonic and microwave-assisted extraction, ASE proved to perform generally equally well or better [17, 18, 20–22, 26, 29].

PCBs and PAHs were previously extracted from compost samples using ASE [30, 31]. However, in these studies samples were lyophilised and extracted with the solvents required by local ordinances and guidelines for lyophilised sludge extraction, i.e., toluene or acetone/hexane 1 : 1 (v/v) and acetone/dichloromethane 1 : 1 (v/v). The remaining extraction conditions were set as suggested by Dionex (Application notes 313 and 316). This study presents the first-time optimisation of ASE conditions for the extraction of PCBs from compost including method validation and quality assurance. An optimised and validated method is also presented for PAHs, although it was more difficult to establish due to enhanced sample inhomogeneity compared to PCBs.

2. Experimental section

2.1 *Chemicals and materials*

Mixtures containing each of the seven Institute of Reference Materials and Measurements (IRMM) PCBs (i.e., PCB #28, #52, #101, #118, #138, #153, #180) at $10\,\mu g\,mL^{-1}$ in isooctane and each of the respective $^{13}C_{12}$-labeled congeners at $40 \pm 2\,\mu g\,mL^{-1}$ in nonane were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). The recovery standard 1,2,3,4-tetrachloronaphthalene (TCN) in nonane was obtained from the same supplier at a concentration of $100\,\mu g\,mL^{-1}$.

The 16 EPA PAHs (i.e., naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IPY), dibenz[*a,h*]anthracene (DBA), and benzo[*ghi*]perylene (BPE)), their deuterated analoques (i.e., D_8-NAP, D_8-ANY, D_{10}-ANA, D_{10}-FLU, D_{10}-PHE, D_{10}-ANT, D_{10}-FLT, D_{10}-PYR, D_{12}-BaA, D_{12}-CHR, D_{12}-BbF, D_{12}-BkF, D_{12}-BaP, D_{12}-IPY, D_{14}-DBA, and D_{12}-BPE) and the recovery standard indeno[1,2,3-*cd*]fluoranthene were purchased from LGC Promochem (Wesel, Germany). Concentrations are specified in [32].

Acetone, toluene, isooctane, methanol, N-N-dimethylformamide (DMF) and cyclohexane (all suprasolv, for gas chromatography), potassium hydroxide pellets, sodium sulphate, and sulphuric acid (all for analysis) were purchased from Merck (Darmstadt, Germany). Hexane (96%, for pesticide residue analysis) was obtained from Scharlau (Barcelona, Spain). Deionised water was further treated with a Milli-Q Gradient A10 water purification system (Millipore, Billerica, MS, USA). Silanised glass wool was purchased from Macherey & Nagel (Düren, Germany). Hydromatrix (diatomaceous earth) was procured from Varian, Inc. (Walnut Creek, CA, USA). Silica gel 60 (0.063 – 0.200 mm) for column chromatography was obtained from Merck. Helium and nitrogen gas (both 5.0) were purchased from Pangas (Dagmarsellen, Switzerland).

2.2 *Precleaning and conditioning*

Nitrogen was cleaned by a Big Moisture Trap and a Big Supelcarb^{TM} HC (Model 23991 and 24564, both Supelco, Bellefonte, PA) in series. Silica gel, sodium sulphate and hydromatrix were baked at 500°C overnight. The activated silica gel was washed with dichloromethane in a separatory funnel and dried applying nitrogen. This silica gel was conditioned acid (60 g silica gel and 40 g sulphuric acid were mixed over night in a TURBULA shaker-mixer (Willy A. Bachofen AG, Maschinenfabrik, Basel, Switzerland)) and neutral (90 g silica gel and 10 g Milli-Q water, same mixing procedure as above). For basic conditioning 168 g potassium hydroxide were dissolved in 700 mL methanol. Activated silica gel (300 g, not washed with dichloromethane) were added and mixed for 90 min at 55°C by the Rotavap without applying vacuum. The silica gel was transferred to a separatory funnel, washed with dichloromethane and dried by applying nitrogen. All glassware was washed in a laboratory washing machine (WA Combi, CE 0044) using the reagents Labopur Assa and Des 1000 (all from Renggli, Rotkreuz, Switzerland) and further cleaned by heat exposure (at least 4 h at 500°C).

2.3 *Sample collection and preparation*

It is important that environmental and non-spiked samples are used in optimisation studies, since real samples represent the aging process better [33]. Additionally, spiked samples cannot account for the strongly bound residues and thus might exhibit different extraction efficiencies with varying extraction conditions than real world samples. Compost and digestate were collected from commercial composting and digestion plants in Switzerland. Sample preparation took place within 24 h. For each sample, three to six full profiles of a windrow were collected with a stainless steel rake and shovel. Samples (60 L) were filled in alumina containers (pre-cleaned with acetone and hexane), hermetically closed and transported to the laboratory. The compost and digestate samples were homogenised in a commercial concrete mixer, which was rinsed thoroughly with tap water before use. Subsamples were taken for subsequent analysis, and stones and other discernable debris were removed manually by tweezers.

Cutting and milling of fresh and thus wet compost samples is difficult. Additionally, ASE extraction requires free flowing samples (Dionex application note 313 and 316). Hence, compost containing up to 65% of water had to be dried prior to milling/cutting and extraction. During sample drying, losses and (cross-)contamination need to be prevented. Such artefacts were reported for the ubiquitous and semivolatile PCBs and PAHs when applying common drying techniques such as air drying at ambient [34–36] or elevated temperatures [20, 37], and lyophilisation [20, 38]. Additionally, it was found that the extractability of heavier PAHs and PCBs was lower in dried compared to fresh soil samples [39]. For these reasons, chemical drying was chosen in this study. Since some samples dried with hydromatrix (2 : 1, w/w) could not be extracted by ASE due to a blocked system possibly caused by insufficient drying capacity, sodium sulphate (1 : 2, w/w) was selected as drying agent in this study. To compensate for hydration and friction energy, samples were kept on ice before and after mixing by the TURBULA shaker-mixer (7 min). Complying with [4] and [40], samples were milled by a cutting mill (Model SM 2000 Retsch GmbH & Co. KG, Haan, Germany) to <2 mm, and stored in amber glass jars at 4°C until analysis.

For method optimisation and validation, compost samples of three individual compost plants were blended to a representative ‘average’ compost.

2.4 *ASE method optimisation*

Extraction was carried out using an ASE 200 Accelerated Solvent Extractor (Dionex, Sunnyvale, CA, USA). A cellulose filter (Dionex) was placed at the bottom of a 33 mL extraction cell, which had been completely disassembled and rinsed with acetone and hexane prior to use. Frits were cleaned in acetone (10 min) and hexane (10 min) in an ultrasonicator. The cell was filled half way with chemically dried compost or digestate and extraction standard (50 ng of each of the seven $^{13}C_{12}$-labelled IRMM PCBs in nonane (5 $\mu g\,mL^{-1}$) or 200 ng of each of the 16 deuterated EPA-PAHs in isooctane (10 $\mu g\,mL^{-1}$)) was added. Thereafter, the cell was filled with the remaining sample and another filter was placed on top. The cell was closed to finger tightness. Typically, a 33 mL extraction cell contained some 4–7 g (dw) of net compost/digestate.

There is a vast literature dealing with the optimisation of ASE parameters (e.g., reviewed in [12, 16]), including some experimental design approaches [18]. Since parameters are interdependent and thought to act differently on different matrices a systematic evaluation of the literature is impossible. However, the solvent type seems to influence the extraction more selectively [13] than pressure and temperature. Consequently, in this study the solvent composition was optimised first. Extractions were conducted using hexane, toluene and dichloromethane with 0%, 25%, 50%, 75% (v/v) of acetone and 100% acetone using the remaining ASE conditions as suggested by Dionex (Application notes 313 and 316 for solid samples: 100°C, 2000 psi (13.79 MPa), prefill mode and purge time 60 s). Several authors found extraction efficiencies increasing with longer extraction time (from 5 to 10 or 15 min [17, 41] or more cycles (two instead of one [17, 24, 42]) Because extraction time was not a limiting factor in this study, three static cycles of 5 min were chosen to assure maximal possible extraction yield. Flush volume was set to 50% because collection vials could not receive a higher volume of extracts especially if toluene was used as a solvent.

After the ideal solvent mixture had been selected, the effect of different extraction temperatures was evaluated in new batches of compost material. The temperatures evaluated were: 80, 100, 120, and 140°C for PCBs and 80, 100, 120, 140, 160, and 180°C for PAHs. The time required to heat up the cell filled with solvent to the extraction temperature depends on the temperature chosen and is set by the system. It varied between five (80°C) and nine (180°C) minutes. The remaining parameters (pressure, number of cycles, extraction and purge time) were kept as mentioned above. The last parameter optimised was pressure. It was varied from 1000 to 2500 psi in steps of 500 psi applying optimised solvent mixtures and temperatures as explained above. The remaining parameters were kept as described above.

2.5 *Clean-up*

ASE extracts usually had an intense dark green to brown color and consisted of two or even three different phases, depending on the extraction solvent. Moreover, precipitates and coagulants were frequently present. Extracts were passed through a funnel filled with sodium sulfate to remove the water phase, which was probably re-extracted from the drying agent under the strong ASE conditions, as well as the solid fractions.

Then they were concentrated in a twelve position Syncore Analyst (Büchi Labortechnik AG, Flawil, Switzerland) using isooctane as a keeper (1 mL) unless toluene was used for extraction. Although there are sophisticated treatments that would allow for fractionation and concomitant clean-up of PCBs and PAH [43], we preferred to stay with traditional, but very robust clean-up techniques. Unfortunately, neither of the two clean-up techniques can handle the respective other compound class: PAHs are destroyed on acid silica gel and PCB recoveries were reduced in the liquid–liquid clean-up [44 and own preliminary experiments].

PCB: The clean-up procedure for PCBs was adapted from [45]. The concentrated extracts were applied to open glass columns (0.45 m, 1 cm i.d.) filled with (from bottom to top) glass wool, water free sodium sulphate (2 cm), deactivated silica gel (10% Milli-Q water, 10 cm), potassium hydroxide impregnated silica gel (10 cm), sulphuric acid impregnated silica gel (10 cm), water free sodium sulphate (2 cm), and prewashed with 50 mL hexane. The extracts were eluted with 150 mL hexane at a flow rate of 2–3 drops s^{-1} applying nitrogen pressure. Concentration of the eluates to a volume of 4–5 mL was performed with a six position Syncore Analyst (Büchi Labortechnik AG) apparatus. The extracts were transferred into a 10 mL conical reaction vessel (Supelco, Bellefonte, PA, USA), and further concentrated to a final volume of approximately 200 µL under a gentle nitrogen stream. The concentrated extracts were spiked with 10 µL of the recovery standard (50 ng of TCN in isooctane) and transferred to 200 µL GC-vials.

PAH: Filtration of the ASE extracts over sodium sulphate was not sufficient to remove the co-extracted water for certain combinations (e.g., hexane/acetone 1 : 3 (v/v)) of extraction solvents. In such cases, after evaporating solvents at 50°C and 40000 Pa in a twelve position Syncore Analyst, the aqueous phases were liquid–liquid extracted three times with 3 mL cyclohexane each. The extracts were combined and reduced to 1.5 mL in the Syncore Analyst. If no water was present, the extract was reduced directly to 1.5 mL. Clean-up steps by DMF:MilliQ water 9 : 1 (v/v) liquid–liquid partitioning and over water-deactivated silica gel were performed as described in [32].

2.6 *GC-MS*

PCBs were separated on an Agilent GC 6890 by on-column injection of 1 µL of extract on a SGE HT-8 capillary column (50 m, 0.22 mm i.d., 0.25 µm film thickness). As a retention gap, a 2 m fused silica capillary column (Agilent, 0.53 mm i.d.) was mounted prior to the separation column. Helium was used as a carrier gas at a constant flow of 1 mL min^{-1}. The injector temperature was set to oven track mode (3°C above oven temperature at all times) and the oven temperature was programmed as follows: 1 min at 90°C, to 200°C at 20°C min^{-1}, 10 min at 200°C, to 285°C at 3°C min^{-1}, to 310°C at 10°C min^{-1} and 20 min at 310°C. Detection was performed with an Agilent mass spectrometer 5973 in the electron impact mode with a 70 eV ionisation energy and single ion monitoring. Identification of a given analyte was assured by using two compound-specific ions with a mass ratio similar to the one determined by internal calibration. For all (labelled and unlabelled) PCBs, except for PCB #52, $^{13}C_{12}$-PCB #52, and TCN, the quantifier ion was $[M]^{+\cdot}$. The qualifier ion was $[M+2]^{+\bullet}$ for all corresponding PCBs. For PCB #52, $^{13}C_{12}$-PCB #52 and TCN, the quantifier ion corresponded to $[M+2]^{+\cdot}$, and the qualifying ion to $[M]^{+\cdot}$, respectively.

Quantification was carried out using the internal standard method. Isooctane mixtures containing different amounts of analytes (5–250 $\mathrm{pg\,\mu L^{-1}}$) and constant amounts of extraction (and recovery) standards (50 $\mathrm{pg\,\mu L^{-1}}$) were used for calibration. Occasionally, PCB #118 had to be quantified via the qualifier ion $[M+2]^{+\bullet}$ of the internal standard due to disturbances at the mass of the quantifier ion. In some compost samples, both qualifier and quantifier ion of $^{13}C_{12}$-PCB #138 were interfered and consequently quantification was carried out in reference to $^{13}C_{12}$-PCB #153. These deviations from the normal quantification procedure did not cause any significantly altered results as evidenced for instance with standard addition experiments and inter-laboratory comparison (section 3.1.2). PAH quantification was performed as described in [32], using the internal standard method and deuterated extraction standards for each of the 16 EPA PAHs.

2.7 *Method validation*

The optimised methods were validated thoroughly, i.e., by determination of limits of quantification, linearity and absolute as well as relative recoveries, verification of precision, completeness of the extraction and sample stability. Robustness was tested by triplicate analysis of five different samples that covered the whole range of organic pollutant concentrations and OM content. Additionally, these five samples were also extracted under EPA conditions, to verify the higher extraction efficiencies of the optimised methods. Optimised PAH extraction conditions were tested against the optimised PCB method as well, to check whether PAHs could be extracted concomitantly with PCBs.

2.8 *Statistics*

Every analysis for method optimisation was carried out at least three times and mean and standard variations were determined. If relative standard deviation was unusually high compared to method precision, additional measurements were carried out and outliers were identified by the Grubbs outlier test [46]. To compare different extraction conditions the student's *t*-test or, if there were more than two treatments, the analysis of variance was applied.

3. Results and discussion

3.1 *PCBs*

3.1.1 ASE parameter optimisation

3.1.1.1 Solvents Extraction efficiency of PCBs from compost was affected by the solvent composition (figure 1). Standard deviations were small (max 13%, $n=3$). However, an outlier (hexane 100%: Σ7PCBs = 32.4 $\mathrm{\mu g\,kg^{-1}}$ dw) had to be removed from the dataset. Toluene/acetone 1 : 3 (v/v) extracted the significantly highest amounts of PCBs (Σ7PCBs = 29.2 $\mathrm{\mu g\,kg^{-1}}$ dw, $n=3$) and was consequently selected as solvent composition for extraction.

Theoretical principles on interactions between analytes and extraction solvents, such as the Hildebrand solubility parameters [47, 48], or octanol–water partitioning

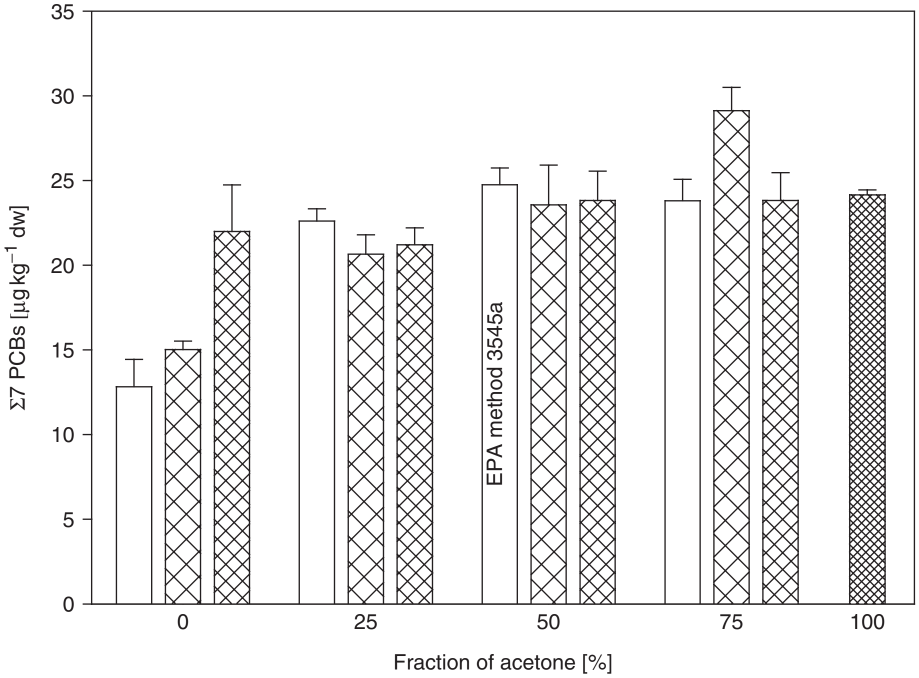

Figure 1. PCB concentrations (Σ7PCBs, μg kg^{-1} dw) in compost obtained by ASE using hexane □, toluene ▨, dichloromethane ▩ with 0% ($n=3$; $n=3$; $n=3$), 25% ($n=3$; $n=3$; $n=3$), 50% ($n=3$; $n=3$; $n=3$), 75% ($n=3$; $n=3$; $n=3$) and 100% ($n=3$) acetone ▩ at 100°C, 2000 psi and 3 × 5 min.

coefficients (log K_{ow}) are of limited use in practice, because they do not consider the influence of the matrix constituents on analyte extractability. This is nicely illustrated here: among the pure solvents dichloromethane, toluene and hexane, the former exhibits the highest extraction efficiency for PCBs, which is in accordance with their close vicinity on the Teas plot [48]. Also, dichloromethane is the most polar of these three solvents and may have an advantageous extracting capacity regarding matrices with high organic matter content [49]. However, acetone seemed to play an overwhelming role as a solvent mediator and results in maximum extractability of PCBs from compost in combination with toluene.

3.1.1.2 Temperature Temperature did not show a significant effect on PCB extraction efficiencies (figure 2a). Apparently, already at the lowest temperature applied (80°C), the resulting diffusion rates and solubilities of the analytes, and activation energies of desorption, viscosities and surface tensions of the solvents allowed for efficient extraction. An outlier (80°C, Σ7PCBs = 49.3 μg kg^{-1} dw) had to be eliminated from the PCB dataset. Since 120°C extracted slightly higher PCB concentrations, this temperature was chosen for subsequent operations. In general, higher recoveries at higher temperatures have been reported [14, 21, 23, 27, 33, 50] levelling off or decreasing once a specific temperature (mostly over 100°C) is exceeded.

3.1.1.3 Pressure The effect of pressure on the extraction efficiency was assessed with the optimal solvent combination and temperature (see above). It was found to

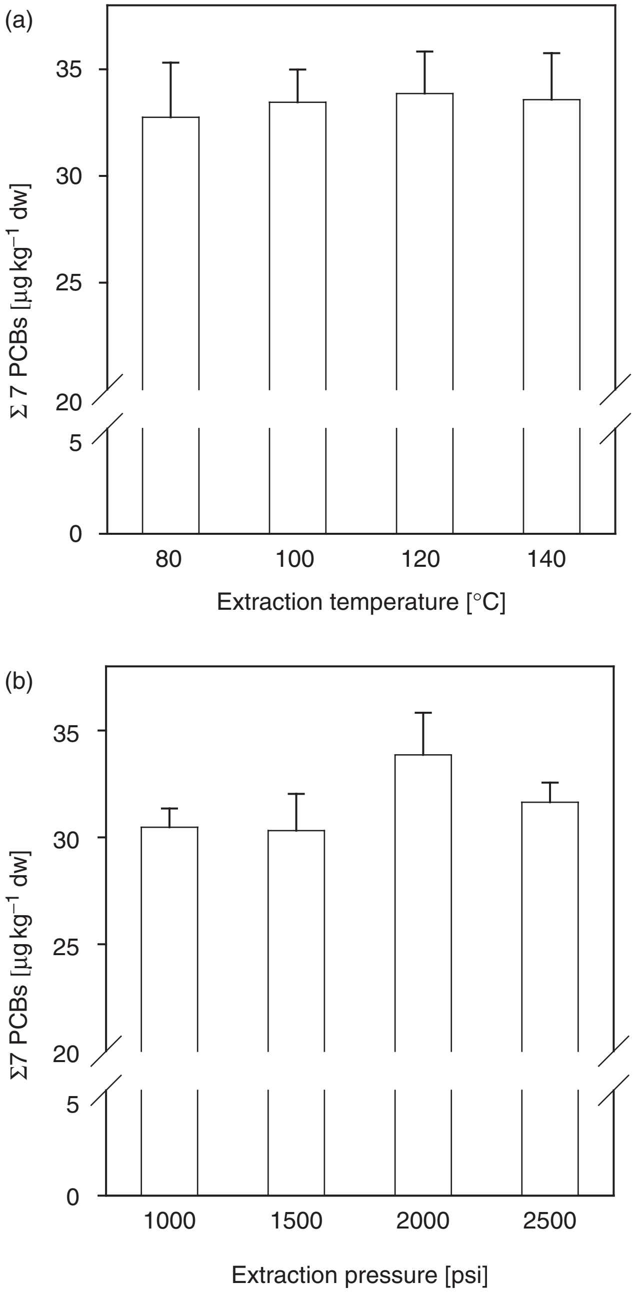

Figure 2. (a) PCB concentrations (Σ7PCBs, μg kg^{-1} dw) in chemically dried compost obtained by ASE using toluene/acetone 1 : 3 (v/v) at 80 ($n = 4$), 100 ($n = 4$), 120 ($n = 6$), 140°C ($n = 3$), 2000 psi and 3 × 5 min; (b) PCB concentrations (Σ7PCBs, μg kg^{-1} dw) in chemically dried compost obtained by ASE using toluene/acetone 1 : 3 (v/v) at 120°C and at 1000 ($n = 3$), 1500 ($n = 3$), 2000 ($n = 6$) and 2500 psi ($n = 3$) and 3 × 5 min.

be marginal (figure 2b) and 2000 psi was selected corresponding to Dionex Application note 316. In general, pressure is reported to influence extraction efficiency little [23, 41] but can be of importance, if wet samples are extracted [50].

3.1.2 Method validation. The above described optimised ASE method (solvent: acetone/toluene 3 : 1 (v/v), temperature: 120°C, pressure: 2000 psi, time: 3 × 5 min, flush volume: 50%) combined with the subsequent clean-up steps was validated with a series of analytical quality control experiments. Specifically, limits of quantification, linearity, precision, absolute and relative recoveries, completeness of extraction, sample stability and robustness, are presented.

3.1.2.1 Limits of quantification and linearity Limits of quantification (LOQ, table 1) as determined by a signal to noise ratio of 10 in compost extract chromatograms were between 0.16 and 2.46 μg kg^{-1} dw for individual PCBs. Average blank levels were < LOQ. The method proved to be linear from LOQ up to 46 μg kg^{-1} dw for individual PCBs.

Table 1. Analytical figures of merit for quantification of PCBs and PAHs in compost.

	Precision (%)^a	Limit of quantification (μg kg^{-1} dw)^b	Blank levels (μg kg^{-1} dw)^c	Absolute recoveries (%)^d	Relative recoveries (%)^e
PCBs	$n = 10$		$n = 5$	$n = 18$	$n = 4$
PCB #28	nd	2.46^f	nd	105 (89–125)	96 (90–97)
PCB #52	8 (2.48)	0.44	0 (0.0–0.2)	65 (57–70)	97 (95–98)
PCB #101	6 (5.95)	0.27	0.18 (0.1–0.5)	93 (82–100)	98 (97–100)
PCB #118	8 (4.74)	0.16	0.13 (0.1–0.3)	97 (88–104)	97 (94–102)
PCB #138	8 (6.68)	0.38	0.15 (0.0–0.7)	na	98 (92–101)
PCB #153	11 (8.59)	0.21	0.18 (0.0–0.8)	90 (78–99)	98 (97–99)
PCB #180	17 (4.03)	0.48	0.05 (0.0–0.4)	87 (79–92)	100 (94–102)
PAHs	$n = 8$		$n = 5$	$n = 18$	$n = 4$
Naphthalene	22 (22.8)	0.14	3.72 (2.59–3.99)	27 (22–32)	99 (97–103)
Acenaphthylene	12 (3.9)	0.05	0.17 (0.13–1.31)	36 (29–42)	89 (89–90)
Acenaphthene	19 (18.4)	0.16	0.39 (0.26–1.90)	24 (20–29)	89 (89–91)
Fluorene	34 (23.0)	0.08	0.38 (0.22–1.35)	34 (28–39)	89 (88–91)
Phenanthrene	27 (252.5)	0.07	1.61 (0.84–2.13)	43 (36–52)	91 (88–109)
Anthracene	20 (36.3)	0.16	0.11 (0.08–0.42)	43 (35–53)	88 (88–95)
Fluoranthene	16 (576.0)	0.21	0.88 (0.43–1.31)	50 (41–60)	87 (85–104)
Pyrene	17 (426.5)	0.22	0.85 (0.31–1.38)	49 (40–59)	86 (84–103)
Benzo[*a*]anthracene	26 (250.0)	0.08	0.35 (0.10–0.38)	54 (44–65)	85 (83–98)
Chrysene	33 (444.9)	0.27	0.48 (0.05–0.53)	54 (42–76)	88 (83–99)
Benzo[*b*]fluoranthene	21 (369.1)	0.13	0.45 (0.05–1.02)	60 (37–72)	87 (83–92)
Benzo[*k*]fluoranthene	24 (168.9)	0.12	0.19 (0.09–0.67)	65 (51–78)	91 (84–98)
Benzo[*a*]pyrene	31 (209.0)	0.32	0.34 (0.06–0.84)	65 (53–75)	86 (81–96)
Indeno[1,2,3-*cd*]pyrene	17 (184.3)	0.17	0.45 (0.00–1.22)	68 (55–76)	95 (90–99)
Benzo[*ghi*]perylene	11 (201.5)	0.36	0.44 (0.25–1.61)	63 (51–71)	95 (91–100)

[a] Relative standard deviation of repeated analysis of an 'average' compost and respective mean concentrations (μg kg^{-1} dw) in brackets. [b] Derived from compost sample extract chromatograms (ten times noise). [c] Blank levels extrapolated to compost, median (min, max). [d] Recoveries of the isotope-labelled extraction standards added before extraction, determined by means of a recovery standard added before injection. Spike level was 7–10 μg kg^{-1} dw for each PCB and 30–40 μg kg^{-1} dw for each PAH, median (min, max). [e] Recoveries of spiked analytes. Fortification levels were as follows: individual PCB: 3.4, 6.7, 10.1 and 13.2 μg kg dw; individual PAH: 63, 127, 190 and 244 μg kg^{-1} dw, median (min, max). [f] Derived from fortified (3.4 μg kg^{-1} dw) sample, 0.39 μg kg^{-1} dw if derived from the lowest calibration standard (5 ng mL^{-1}). nd: Not detectable. na: Not available due to interferences.

3.1.2.2 Precision Precision (relative standard deviations of ten replicates) was between 6 and 17% for individual PCBs (table 1), which corresponds well with overall method uncertainties as calculated from error propagation at these concentration levels [51].

3.1.2.3 Recoveries Recoveries of isotope-labelled extraction standards (absolute recoveries) from compost samples increased with increasing molecular weight and ranged from 65 to 105% (table 1). Interfering substances may have caused relatively high recoveries of PCB #28. However this compound was never detected in real samples. Losses of analytes were compensated by the use of each of their respective $^{13}C_{12}$-analogues as extraction standards, as evident by the relative recoveries (96–100% for all analytes at four different spike levels, table 1).

3.1.2.4 Extraction completeness Three sample replicates were re-extracted with the optimised conditions to assess the completeness of the extraction. This secondary extraction accounted for 0% (PCB #52) to 4.5% (PCB #101, #153) of the first one, with a method blank holding between 0% (PCB #28, #52, #118) and 3% (PCB #101). These findings indicate that the extraction is complete under the conditions applied. However, it cannot be excluded that there are non-extractable fractions of PCBs. This could only be verified by adding isotope-labelled compounds to feedstock material and following their fate during a real world composting process.

3.1.2.5 Sample stability Samples were stored up to 17 months at 4°C in amber glass jars. Digestate and compost were mixed with sodium sulphate as described above. PCB contents were analysed at the beginning of the experiment ($n = 2$), after three ($n = 1$), eight ($n = 1$) and 17 months ($n = 2$). Extraction was performed according to the EPA Method 3545a. Overall, PCB contents were observed to be stable over a period of 17 months. All our samples were analysed within five months.

3.1.2.6 Robustness Unfortunately, accuracy of the applied method could not be verified since no certified compost material exists. Application to other types of reference materials such as soils or sediments is not feasible for reasons given above. However, in addition to the multiple extractions performed with compost samples for method optimisation, a selection of samples covering a wide range of properties (sample A–E, table 2) was analysed three times to assess the robustness of the method. The relative standard deviations observed in triplicate analysis were lower than method precision in three samples (sample A–C) and not considerably higher in the remaining two samples (sample D–E). Consequently, the method can be considered as sufficiently robust.

The optimal extraction condition (toluene/acetone 1 : 3 (v/v), 120°C) is not in accordance with the EPA Method 3545a and the Dionex application note 316 recommending hexane/acetone 1 : 1 (v/v) and 100°C for the extraction of PCBs from soils, clays, sediments, sludges, and solid wastes. Therefore, the optimised method was tested against the 'second best' (figure 1) EPA Method by parallel analysis of the same samples (sample A–E, table 2). It was found that the optimised conditions extracted PCBs more efficiently from all five samples (figure 3). For all compost samples with a low PCB content (sample A–C) the difference was significant on a 95% level. One outlier (EPA Method, sample C: Σ7 PCBs 19.68 $\mu g\,kg^{-1}$ dw) had to be removed from the dataset. This value was confirmed with three additional measurements.

Table 2. PCB and PAH contents of selected compost and digestate samples in Switzerland (all data in μg kg^{-1} dw).[a]

	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G	Sample H	Sample I
PCBs									
Product	Compost	Compost	Compost	Compost	Compost	Compost	Compost	Compost	Digestate
Feedstock	Green waste	Green waste	Green waste[b]	Green waste	Green waste	Green waste	Green waste	Kitchen waste	Kitchen waste
Catchment area	Rural	Rural	Rural	Urban	Rural	Urban	Urban	Urban	Urban
Water content [% w/w]	57	42	34	53	65	47	41	43	51
OM content [% w/w]	25	53	79	40	27	62	43	52	45
No. of analyses/ No. of outliers	3/0	3/0	3/0	3/0	3/0	1/0	1/0	1/0	1/0
PCB #28	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB #52	0.41 (4%)	1.96 (2%)	1.03 (4%)	5.41 (**27%**)	4.63 (1%)	0.49	0.73	2.16	1.93
PCB #101	0.83 (4%)	2.57 (1%)	1.92 (3%)	9.38 (**10%**)	14.38 (**9%**)	1.26	2.35	5.65	4.42
PCB #118	0.58 (3%)	3.13 (4%)	1.64 (5%)	6.80 (5%)	6.18 (8%)	0.91	1.83	3.87	3.56
PCB #138	1.26 (7%)	2.80 (3%)	2.54 (6%)	10.72 (**19%**)	25.99 (**12%**)	1.76	3.85	5.07	7.80
PCB #153	1.80 (6%)	3.46 (3%)	3.02 (4%)	14.32 (11%)	25.77 (**14%**)	2.26	4.32	8.99	5.25
PCB #180	1.24 (6%)	1.92 (3%)	2.76 (1%)	9.22 (**37%**)	20.30 (**23%**)	1.39	2.34	3.27	2.46
Σ7 PCBs	6.12 (4%)	15.84 (2%)	12.91 (3%)	55.86 (**18%**)	97.24 (**13%**)	8.06	15.42	29.01	25.42
PAHs									
No. of analyses/ No. of outliers	2/0	2/0	3/0	4/0	2/0	3/0	6/1	3/0	3/0
Naphthalene	14.3[c] (10%)	90.5 (5%)	11.3[c] (13%)	16.3[c] (15%)	27.6[c] (16%)	5.8[c] (15%)	8.8[c] (15%)	72.3 (**54%**)	148.2 (10%)
Acenaphthylene	1.3[c] (3%)	2.1 (5%)	2.3 (2%)	2.4 (**24%**)	3.6 (2%)	0.8[c] (11%)	1.0[c] (12%)	18.3 (**40%**)	14.7 (10%)
Acenaphthene	2.2[c] (11%)	1.1[c] (2%)	1.3[c] (5%)	2.4[c] (**23%**)	8.6 (12%)	1.0[c] (9%)	1.6[c] (12%)	6.8 (**47%**)	926.6 (5%)
Fluorene	2.7[c] (12%)	4.2 (1%)	1.9[c] (6%)	4.9 (20%)	14.6 (8%)	1.9[c] (7%)	3.3[c] (8%)	24.9 (**38%**)	1215.0 (7%)
Phenanthrene	38.4 (1%)	68.5 (3%)	103.1 (1%)	80.0 (16%)	159.0 (12%)	49.3 (5%)	42.3 (6%)	552.0 (15%)	5776.3 (15%)
Anthracene	5.3 (1%)	5.9 (**22%**)	3.9 (6%)	10.2 (**20%**)	24.4 (8%)	3.3 (16%)	3.0 (10%)	108.1 (**38%**)	984.1 (16%)
Fluoranthene	89.6 (3%)	165.3 (3%)	182.9 (3%)	349.9 (**22%**)	497.4 (12%)	102.2 (8%)	137.4 (6%)	1160.3 (6%)	3401.7 (**19%**)
Pyrene	53.0 (6%)	54.4 (9%)	130.8 (3%)	151.4 (**45%**)	249.2 (15%)	73.1 (11%)	54.6 (8%)	611.1 (13%)	2044.6 (**18%**)
Benzo[*a*]anthracene	52.2 (4%)	54.3 (2%)	57.8 (2%)	156.7 (**56%**)	265.2 (6%)	46.1 (14%)	31.1 (20%)	517.5 (7%)	516.4 (15%)
Chrysene	87.6 (5%)	115.0 (16%)	103.3 (3%)	317.8 (24%)	432.6 (9%)	67.4 (6%)	83.5 (10%)	593.0 (1%)	508.2 (8%)
Benzo[*b*]fluoranthene	75.5 (5%)	117.1 (18%)	98.2 (6%)	300.4 (19%)	499.8 (13%)	78.8 (14%)	80.9 (13%)	590.6 (10%)	304.7 (4%)
Benzo[*k*]fluoranthene	30.8 (5%)	64.2 (**51%**)	49.6 (5%)	123.0 (**31%**)	225.5 (2%)	35.8 (12%)	26.4 (18%)	337.6 (12%)	160.6 (2%)
Benzo[*a*]pyrene	51.2 (1%)	70.5 (20%)	57.0 (11%)	155.6 (**39%**)	263.1 (14%)	54.0 (15%)	31.4 (**22%**)	413.1 (11%)	252.2 (5%)
Indeno[1,2,3-*cd*]pyrene	59.0 (5%)	106.0 (14%)	80.0 (5%)	217.3 (16%)	322.6 (14%)	61.4 (17%)	50.8 (13%)	455.3 (7%)	200.9 (12%)
Benzo[*ghi*]perylene	61.6 (3%)	99.7 (9%)	105.0 (5%)	223.0 (**15%**)	294.9 (**15%**)	73.9 (**12%**)	59.2 (10%)	461.6 (7%)	197.5 (8%)
Σ15 PAHs	624.5 (0.3%)	1018.9 (12%)	988.3 (1%)	2111.2 (**25%**)	3288.1 (**11%**)	654.8 (10%)	615.3 (10%)	5922.4 (9%)	16651.7 (**13%**)

[a] In brackets relative standard deviations, bold if higher than method precision. [b] Including road clippings. [c] Less than 10 times blank level. nd: not detectable.

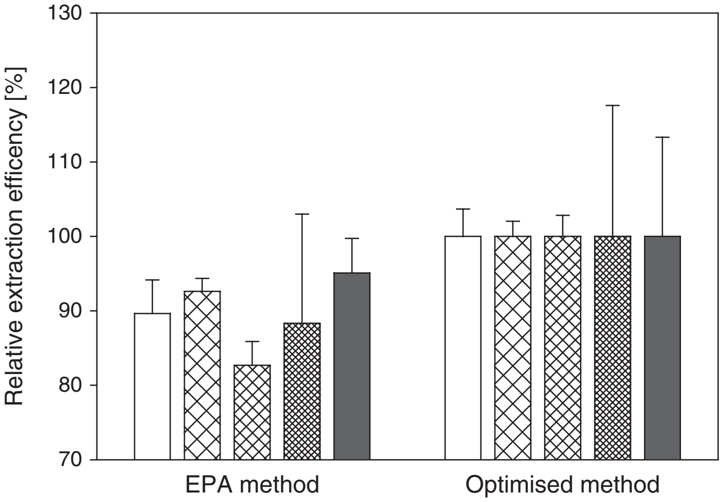

Figure 3. Relative extraction efficiencies and standard deviations of PCBs in different compost samples (☐ low PCB concentration, low OM content; ⊠ low PCB concentration, medium OM content; ▩ low PCB concentration, high OM content; ▒ medium PCB concentration, medium OM content; ■ high PCB concentration, low OM content) determined with the EPA method ($n = 3$; $n = 3$; $n = 5$; $n = 3$; $n = 3$) and the optimised method of this study ($n = 3$; $n = 3$; $n = 3$; $n = 3$; $n = 3$).

No correlation was found between relative extraction efficiencies and OM content. However, in line with this study, it was reported before that the amount of PCBs might be underestimated using hexane/acetone 1 : 1 (v/v) [25] for sediments rich in organic carbon.

3.1.2.7 Inter-laboratory comparison To further test our method for PCB analysis, an inter-laboratory comparison was carried out in collaboration with the Laboratory of Organic Chemistry at the Swiss Federal Laboratories for Materials Testing and Research (EMPA) in Dübendorf, Switzerland. For this purpose, six samples were analysed in both laboratories. Two sub-samples were taken of the initial compost or digestate sample (60 L), the first being air-dried for seven days and delivered to EMPA, the second being chemically dried and analysed in our laboratory (FAL) as described above. Results of this inter-laboratory study are compiled in table 3. Overall results are in good agreement and correlations highly significant. The 95% confidence intervals of slopes and intercepts included the value one and zero, respectively, indicating no significant difference between the laboratories for all compounds except PCB #52. At low concentrations (positive intercept), PCB #52 contents in EMPA samples were higher than in samples analysed at FAL. This may be due to deposition or (cross-) contamination during air-drying before sample deliverance to EMPA. In the chemically dried samples analysed in our laboratory, the risk for such artefacts was probably lower. However, slopes were <1 for all PCBs except PCB #138, which might indicate that the optimised ASE conditions exhibit a somewhat higher extraction efficiency than Soxhlet extraction using toluene, which was used by the EMPA laboratory. In our laboratory, quantification of PCB #138 had to be carried out in relation to $^{13}C_{12}$-PCB #153 due to interferences in the $^{13}C_{12}$-PCB #138 mass

Table 3. Correspondence of PCB concentrations in compost samples ($n = 6$) determined independently at EMPA[a] and our laboratory (FAL).

$PCB_{EMPA} = a * PCB_{FAL} + b$

	Slope	Confidence interval (95%) of the slope	Intercept	Confidence interval (95%) of the intercept	R^2 of regression
PCB #28[b]	–	–	–	–	–
PCB #52	0.74	0.52–0.97	0.62	0.05–1.18	0.9541
PCB #101	0.84	0.58–1.11	0.85	−0.76–2.47	0.9506
PCB #118[c]	–	–	–	–	–
PCB #138	1.26	0.91–1.61	0.64	−3.37–2.10	0.9610
PCB #153	0.80	0.38–1.22	2.08	−0.92–5.01	0.8746
PCB #180[d]	0.82	0.46–1.20	0.81	−0.66–2.25	0.9547

[a]PCB measurements (unpublished) carried out at Laboratory of Organic Chemistry at the Swiss Federal Laboratories for Material Testing and Research (EMPA). [b]nd at FAL. [c]na at EMPA. [d]One outlier removed.

traces, which may explain the exceptionally high slope of >1. PCB #28 was quantified by EMPA and ranged from 0.3–1.1 $\mu g\,kg^{-1}$ dw, whereas at FAL, it was below LOQ. The more sophisticated clean-up procedure (multiple adsorption chromatography) and detection devices (HRMS vs MS) at EMPA and perhaps some deposition during air drying may account for these differences. However, the PCB #28 contribution to the total sum of the six PCBs analysed at EMPA (#28, #52, #101, #138, #153, #180) was marginal (1–4%).

3.2 *PAHs*

For a given sample, results of repeated PAH analysis varied considerably more than those of PCBs. Even though several outliers were identified and removed from the dataset, relative standard deviations remained high. These observations correspond with reports in the literature: PAH concentrations analysed in ten samples taken from different profiles along a compost windrow were more heterogeneous than respective numbers for PCBs [52]. Measures to counteract this observed PAH inhomogeneity are reduction of particle size, larger sample volumes, or increased numbers of replicate analyses. However, the first is difficult to achieve with chemically dried materials and the second would require ASE hardware not available at our laboratory. Moreover, the particle size <2 mm used in this study is in accordance with recommendations for soil, sludge and compost analysis [4, 40]. In the literature, particle size is apparently largely neglected or at least not reported upon (for compilation, see [7]). However, recent studies within the EU Project Horizontal addressed this problem systematically and suggested smaller particle size for compost and waste [1]. Despite these adversities, we decided to carry out a full method optimisation with increased numbers of replicate analyses where necessary, knowing that certain analytical figures of merit might suffer.

3.2.1 ASE parameter optimisation

3.2.1.1 Solvents Repeated analysis of PAH contents using different solvent composition varied considerably and three outliers (hexane: $\Sigma 15PAHs = 2048\,\mu g\,kg^{-1}$ dw; hexane/acetone 3 : 1 (v/v): $\Sigma 15PAHs = 4759\,\mu g\,kg^{-1}$, and toluene/acetone 3 : 1 (v/v): $\Sigma 15PAHs = 5530\,\mu g\,kg^{-1}$) were eliminated from the dataset by the Grubbs outlier test.

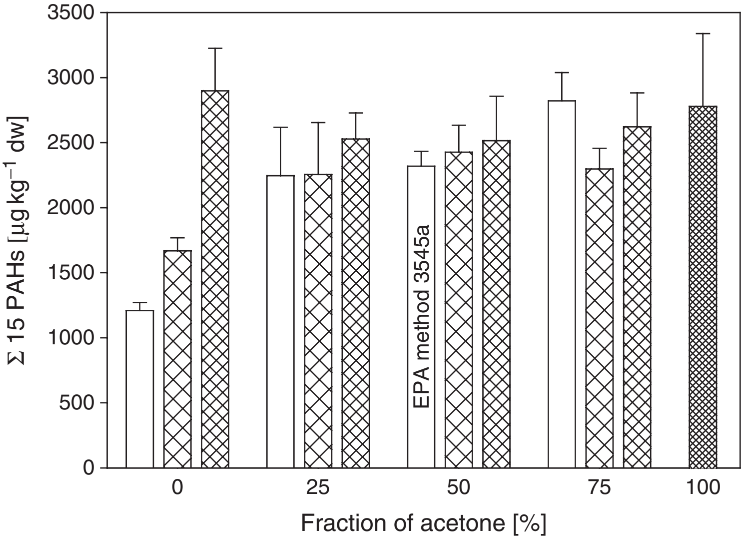

Figure 4. PAH concentrations (Σ15PAHs, $\mu g\,kg^{-1}$ dw) in compost obtained by ASE using hexane □, toluene ▩, dichloromethane ▦ with 0% (*n* = 3; *n* = 3; *n* = 3), 25% (*n* = 4; *n* = 4; *n* = 3), 50% (*n* = 3; *n* = 3; *n* = 3), 75% (*n* = 3; *n* = 3; *n* = 3) and 100% (*n* = 3) acetone ▦ at 100°C, 2000 psi and 3 × 5 min.

The corresponding concentrations were confirmed by one (100% hexane) or two (hexane/acetone 3 : 1 (v/v) and toluene/acetone 3 : 1 (v/v)) additional analyses. Still, relative standard deviations remained high (*n* = 3–4, max 20%). Highest PAH concentrations were obtained using 100% dichloromethane (figure 4). However, hexane/acetone 1 : 3 (v/v) was chosen as an alternative and equally powerful solvent combination, since it poses fewer hazards to the environment and might be more versatile towards different composts and digestates. Moreover, various authors found a combination of polar and non-polar solvents to be more effective for organic pollutant extraction, especially if wet samples were extracted [13, 22, 33, 42, 50].

If toluene was used for PAH extraction absolute recoveries were found to be very low (max 30%), which may be due to π-electron interactions of residual toluene with PAHs competing with DMF during the extract clean-up. To overcome this problem, the clean-up succession was changed: deactivated silica column followed by the DMF clean-up. In this case, the final extract was again dried over sodium sulphate in order to ensure removal of water prior to GC-injection.

3.2.1.2 Temperature Increasing amounts of PAHs were extracted with increasing temperature up to 140°C (figure 5a). One data point (100°C, Σ15PAHs = 5143 $\mu g\,kg^{-1}$ dw) was identified as an outlier and removed from the dataset. At 160°C the total concentration detected decreased, but at 180°C it was roughly at the 140°C level again. Similar results were observed in another study [21] for PAH concentrations in soil but interpretation of this phenomenon remains unclear. Standard deviations were much higher and selectivity lower at 180°C than at lower temperatures as observed by others [21, 42]. Therefore, 140°C was chosen as an optimal extraction temperature.

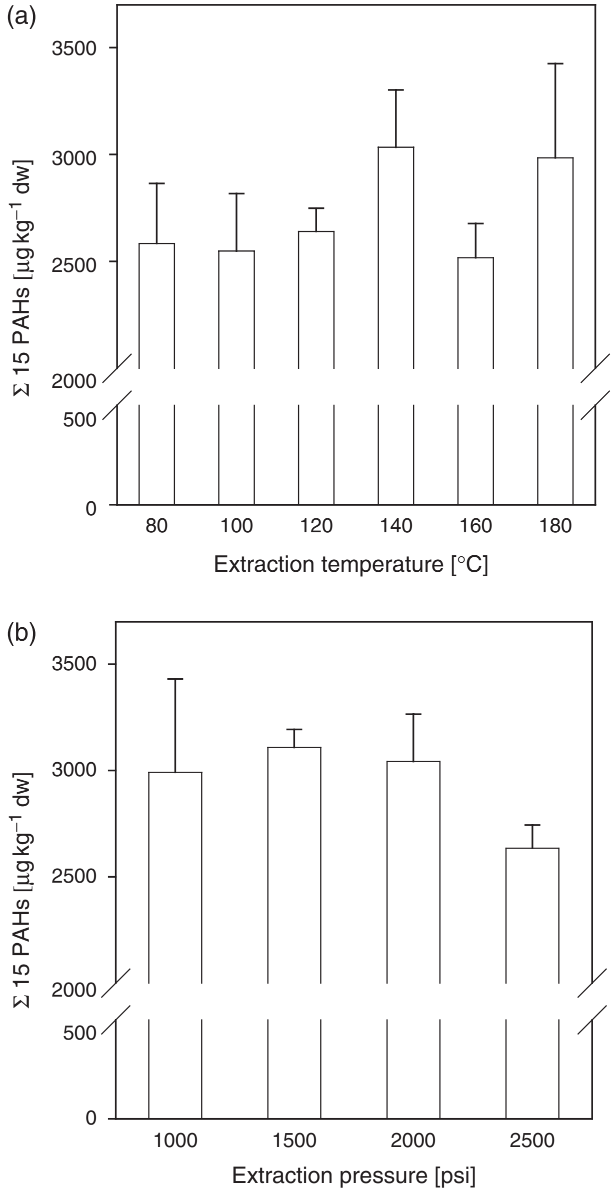

Figure 5. (a) PAH concentrations (Σ15PAHs, µg kg^{-1} dw) in chemically dried compost obtained by ASE using hexane/acetone 1 : 3 (v/v) at 80 ($n = 4$), 100 ($n = 4$), 120 ($n = 4$), 140 ($n = 4$), 160 ($n = 4$) and 180°C ($n = 4$), 2000 psi and 3 × 5 min; (b) PAH concentrations (Σ15PAHs, µg kg^{-1} dw) in chemically dried compost obtained by ASE using hexane/acetone 1 : 3 (v/v) at 140°C at 1000 ($n = 4$), 1500 ($n = 5$), 2000 ($n = 6$) and 2500 psi ($n = 3$) and 3 × 5 min.

3.2.1.3 Pressure A lower pressure (1500 psi) than in the EPA Method 3545a was selected for PAH extraction (figure 5b) to reduce co-extraction of matrix constituents. An outlier had to be removed from the PAH dataset (1500 psi, Σ15PAH = 3967 µg kg^{-1}dw).

3.2.2 Method validation

3.2.2.1 Limits of quantification and linearity LOQ for individual PAHs were between 0.05 and 0.60 $\mu g\,kg^{-1}$ dw. For all PAHs except ANT, average blank levels were > LOQ (table 1). These compounds exhibited average blank concentrations of 0.11 and 3.72 $\mu g\,kg^{-1}$ dw, respectively, which increases their LOQ to 1.1 and 37.2 $\mu g\,kg^{-1}$ dw (LOQ > 10 times average blank concentrations). These blank levels may seem high and are explained by the limited capacity of a 33 mL ASE cell only accommodating 4–7 g dw of chemically dried compost. Still, these ten fold blank concentrations were, with the exception of NAP, considerably lower than those usually observed in real samples (table 2). The method proved to be linear from LOQ up to 438 $\mu g\,kg^{-1}$ dw for individual PAHs.

3.2.2.2 Precision Precision for individual PAHs was between 12 and 34% ($n = 8$; table 1), which is slightly higher than acceptable (11% at the ppm level, 30% at the ppb level, [51]), and than for analysis for PCBs in compost/digestate. This higher variation is explained by the heterogeneity of the samples (see above).

3.2.2.3 Recoveries Recoveries of isotope-labelled extraction standards (absolute recoveries) increased with increasing molecular weight as found for PCBs (24–68%, table 1). These recoveries are comparable to those found in [32], especially if taking into account that in the optimised method of this study, samples had to be concentrated once more, i.e., after water removal by liquid–liquid extraction. Losses of analytes were compensated by the use of each of their respective deuterated analogues as extraction standards. Consequently relative recoveries of PAHs were good (85–99%, table 1). Quantification of DBA was difficult since absolute recoveries of the extraction standards were low (1–5%). DBA recoveries were also low in method blanks. During routine analysis DBA recoveries increased, which might be explained by shorter silica gel columns used. However, DBA usually accounts for 1–2% of the total sum of the 16 EPA PAHs [7, 32] only, and consequently, the sum of 15 PAHs is reported in this study.

3.2.2.4 Extraction completeness PAH re-extracts were 1% or 2% (for all PAHs heavier than FLT) to 25% for NAP of the first extract, whereas method blanks accounted for 0% (for all PAHs heavier than PHE) to 22% (NAP) of the first extraction. These findings indicate that the extraction is complete under the parameters applied. However, as explained above for PCBs, a non-extractable fraction of PAHs in compost cannot be excluded.

3.2.2.5 Sample stability PAH contents were analysed in compost and digestate dried with sodium sulphate at the beginning of the experiment ($n = 3$), after three ($n = 1$–2), eight ($n = 1$–3) and 17 months ($n = 2$). Extraction was performed according to the EPA Method 3545a. PAH concentration in all samples remained apparently constant up to eight months, but decreased by 26–51% (Σ15PAHs) over a period of 17 months. In this study, all samples were analysed within five months.

3.2.2.6 Robustness Due to the lack of certified reference material for compost, robustness was tested by triplicate analysis of five compost/digestate samples with varying PAH and OM contents (sample C, F–I, table 2). Relative standard deviations were higher than method precision for some single compounds (table 2) and an outlier

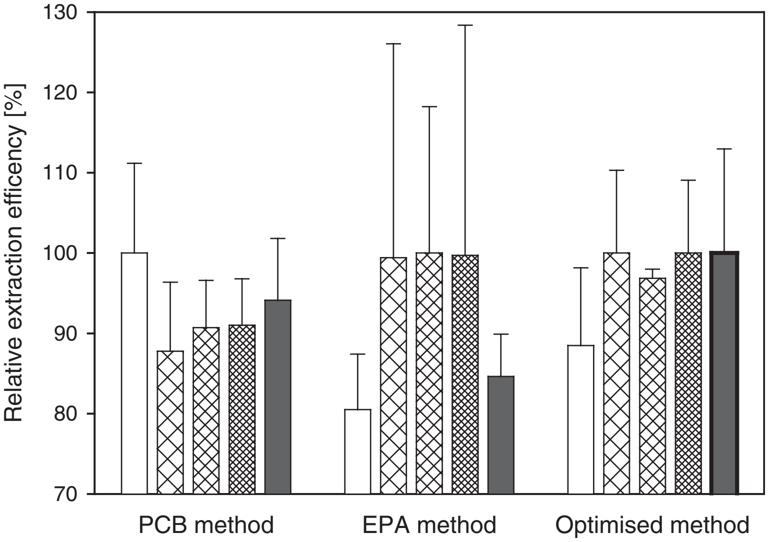

Figure 6. Relative extraction efficiencies and standard deviations of PAHs in different compost samples (□ low PAH concentration, low OM content; ▨ low PAH concentration, medium OM content; ▨ low PAH concentration, high OM content; ▩ medium PAH concentration, medium OM content; ■ high PAH concentration, medium OM content) determined with the optimised PCB ($n=3$; $n=3$; $n=5$; $n=3$; $n=3$), the EPA ($n=5$; $n=6$; $n=6$; $n=6$; $n=3$) and the optimised PAH method of this study ($n=3$; $n=5$; $n=3$; $n=3$; $n=3$).

had to be removed from the dataset (sample G: Σ 15PAH = 1779.1 μg kg^{-1} dw). Based on this observation, along with varying PAH results in repeated analysis as observed above (optimisation of ASE parameters, samples stability), PAH measurements were always confirmed by a second analysis. If results varied more than method precision for five or more individual PAHs, two additional analyses were carried out and outliers removed by the Grubbs outlier test.

The optimised PAH extraction method was tested against the EPA Method 3545a as well as compared with the optimised PCB method for the five samples used in the robustness test (see above). None of these extraction methods appeared to be consistently most efficient for all five compost samples (figure 6), which is in contrast to the results for PCBs (see above and figure 3). However, for three out of five samples, the method optimised in this study was found to extract most PAHs. The average relative extraction efficiency for the optimised method presented here ($n=5$) was at 97%, for the other two methods it was at 93%. However, the differences between the extraction methods were not significant except for sample F. In general standard variations remained high even though outliers (EPA: sample F: Σ15PAH = 1570.7 μg kg^{-1} dw, optimised PAH method: sample G: see above) were removed by the Grubbs outlier's test. Due to the slightly higher relative extraction efficiencies and the lower relative standard variations, it is suggested to prioritize the method optimised in this study over the EPA method and the method optimised for PCB extraction (see above). Even though the latter would allow for co-extraction of PCBs and PAHs, the overall time reduction would be minimal, since no joint clean-up could be found with acceptable recovery rates.

Besides inhomogeneity, differences in speciation of PAHs in various composts could be a reason of varying extraction efficiencies of the tested methods. PAHs originating from aerial deposition (both from particle bound aerosols or condensation from gas phase) probably ask for other extraction conditions than PAHs associated or incorporated into, e.g., charcoals, or ashes, which are occasional input materials of compost. However, molecular marker analysis [32] of the composts in question gave no indication of different PAH sources. Furthermore, PAHs might be differently sequestered during composting and/or digestion depending on the management of the process.

3.3 *Initial results from a nation wide compost screening study*

Sample selected specifically for the robustness test were also analysed for the other group of organic pollutants resulting in a comprehensive dataset covering a wide range of compost regarding input material, degradation process and catchment area (table 2). Almost all single PCB values (sample F–I) were slightly below the literature values [7] which may be explained by generally decreasing amounts of PCBs in the environment [53, 54]. PAH concentrations (sample A, B, D, F) were well within the literature values [7]. Different feedstocks (with or without kitchen waste), degradation processes (digestion versus composting), and catchment areas (rural vs urban) did not seem to have a systematic influence on PCB and PAH concentrations. However, further measurements are required and currently carried out in our laboratory in order to assess possible influences of these parameters more systematically.

4. Conclusions

This work illustrates that different types of solid samples need to be considered individually when establishing methods for the quantification of organic pollutants in such matrices. Although international harmonisation efforts for the establishment of standardised methods are needed (e.g., for sample preparation and storage, method reporting, etc.), uniform treatment of different types of solid samples is not adequate. Furthermore, sampling and drying have to be carried out very carefully if ubiquitous and semivolatile compounds such as PCBs and PAHs are to be analysed. Chemical drying is an alternative technique which does not expose the sample to high temperature nor to ambient air. ASE is an efficient, low solvent consuming and fast extraction technique well suited for the extraction of PCBs and PAHs from chemically dried compost/digestate. The method presented here proved to be a rugged and reliable routine screening tool for the analysis of PCBs. Method optimisation for the extraction of PAHs from compost was more difficult due to sample inhomogeneity and further larger efforts in sample preparation and extraction would be needed to reduce this problem. However, the performance of the method presented is still suitable to assess the sources and fate of PAHs in compost.

Acknowledgements

We would like to acknowledge Hans Jörg Bachmann, Franziska Blum, Marianne Erbs and Niccolo Hartmann for helpful comments on the manuscript and analytical support, Markus Zennegg, Erika Gujer and Peter Schmid (Laboratory of Organic Chemistry at the Swiss Federal Laboratories for Material Testing and Research, EMPA) for the inter-laboratory comparison, and the Swiss Agency for the Environment, Forest and Landscape (SAEFL) and the Swiss Federal Office of Energy (SFOE) for their financial support.

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4 Paper 3

Two-dimensional gas chromatography coupled to triple quadrupole mass spectrometry for the unambiguous determination of atropisomeric polychlorinated biphenyls in environmental samples

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Journal of Chromatography A, 2006, 156-164.

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Journal of Chromatography A, 1110 (2006) 156–164

JOURNAL OF CHROMATOGRAPHY A

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Two-dimensional gas chromatography coupled to triple quadrupole mass spectrometry for the unambiguous determination of atropisomeric polychlorinated biphenyls in environmental samples

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Received 14 November 2005; received in revised form 12 January 2006; accepted 13 January 2006
Available online 10 February 2006

Abstract

Two-dimensional gas chromatography coupled to triple quadrupole mass spectrometry (GC–GC–MS–MS) is presented as a robust, selective and sensitive method for the accurate quantification of enantiomeric fractions (EFs) of atropisomeric polychlorinated biphenyls (PCBs) in a range of environmental matrices. The method was subjected to a set of quality control and validation experiments. EF precision of the atropisomers 95, 149, 132, and 174 ranged from 0.7 to 1.4% in soil samples. Quantified amounts of these congeners in soil and compost samples ($59 < n < 100$) were on average within 3–26% of the numbers gathered with conventional (achiral) bench top GC–MS. However, significant deviations were observed between EFs obtained by GC–GC–MS–MS and those by GC–GC–MS, GC–MS–MS, and GC–MS. The method was successfully applied to a variety of sample types, such as soil, air, herring, human milk, and, for the first time, compost. EFs in soils are shown to vary with land use and correlations with soil pH were observed. EFs in compost samples were mostly close to, or racemic.

Keywords: Heart-cut gas chromatography; Deans switching; Chiral PCBs; Enantiomeric ratio; Enantioselective biodegradation

1. Introduction

Polychlorinated biphenyls (PCBs) belong to the 12 most harmful persistent organic pollutants as specified in the Stockholm convention [1]. They have been widely used in quantities of around 1.3 million tonnes [2] since the 1930s mainly as insulators in transformers and capacitors, as heat exchange fluids, as paint additives, and in plastics. PCBs are nowadays ubiquitously present in the environment and accumulate throughout the food chain. Animal and human health is impaired through adverse effects of PCBs on the endocrine, immune, nervous, and reproductive systems, and their ability to cause cancer [3,4].

Nineteen tri- and tetra-*ortho*-chlorine substituted PCBs exhibit rotational energy barriers of the central C–C-bond high enough to distinguish two stable conformational isomers under environmentally prevalent temperatures [5,6]. Such atropisomeric PCBs were determined in a wide range of environmental samples, such as sediments [7–9], organisms at various trophic levels [10–12], and several top predators [13–19]. Further matrices investigated include dairy food products [20], and human milk [21,22]. Relatively little work has been done in air and soil [23,24], and no data is available for compost, where it is still controversial whether degradation of PCBs takes place [25]. The fact that the individual enantiomers of atropisomeric PCBs were originally released as racemates into the environment, but are often detected in non-racemic proportions in such matrices is generally regarded as evidence for enantioselective biodegradation or metabolism [26,27].

Two-dimensional gas chromatography (GC–GC), also known as “heart-cutting” or “multidimensional” GC, is a relatively old coupling technique and has been reviewed extensively throughout its history [28–31]. GC–GC has been widely applied for separation of chiral PCBs, usually with electron capture detection (ECD) [7,8,20,32] or single quadrupole mass spectrometers (MS) [9,11,21,22,24]. Although ion trap mass spectrometry has been used in recent years in combination with one-dimensional GC for the analysis of achiral PCBs (e.g., [33–35]), two-dimensional, and specifically triple quadrupole mass spectrometers (MS–MS) have not yet been combined with GC–GC to quantify atropisomeric PCBs. Here, we provide a

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doi:10.1016/j.chroma.2006.01.069

combination of both two-dimensional separation and detection and illustrate the advantage of this technique over other coupling combinations for the analysis of such compounds. This GC–GC–MS–MS method is quality controlled and applied to a wide range of environmental matrices, including an extensive set of soil and compost samples.

2. Experimental

2.1. Chemicals and materials

Mixtures containing each of the seven Institute of Reference Materials and Measurements (IRMM) PCBs (i.e., PCB 28, 52, 101, 118, 138, 153, 180) at 10 μg/mL in isooctane and each of the respective individual $^{13}C_{12}$-labeled IRMM PCBs at 40 ± 2 μg/mL in nonane were obtained from LGC Promochem (Wesel, Germany). The chiral PCBs 95, 149, 132, and 174, as well as the recovery standard 1,2,3,4-tetrachloronaphthalene (TCN) were purchased from the same supplier as individual solutions at 100 μg/mL in 1.2 mL hexane, and 1.5 mL isooctane, respectively. Hexane (96%, for pesticide residue analysis) was obtained from Scharlau (Barcelona, Spain). Acetone, toluene (both suprasolv, for gas chromatography), sodium sulphate, potassium hydroxide pellets, sulphuric acid (all for analysis), and silica gel 60 (0.063–0.200 mm) for column chromatography were purchased from Merck (Darmstadt, Germany). Deionised water was further treated with a Milli-Q Gradient A10 water purification system (Millipore, Billerica, MS, USA). Helium (4.6) and nitrogen (6.0) were from Pangas (Dagmarsellen, Switzerland).

2.2. Samples and sample preparation

Swiss soil samples were taken and stored as described in [36]. PCBs were Soxhlet extracted for 32 h with hexane. The concentrated extracts were cleaned over sodium sulphate, and deactivated (10% Milli-Q water), potassium hydroxide-, and sulphuric acid-impregnated silica gel [37]. Czech soil samples were collected in spring 2005 close to Brno. The samples were Soxtec extracted with dichloromethane/hexane 1:1 (v/v) and the extracts cleaned over sulfuric acid-impregnated silica gel.

Compost ($n = 65$) and digestate ($n = 14$) samples were taken from about 40 commercial plants in Switzerland. The samples were prepared and extracted as described in [37]. Briefly, accelerated solvent extraction of PCBs was performed from 4–7 g of chemically dried compost using the following conditions: toluene/acetone 1:3 (v/v), 120 °C, 2000 psi, 3 × 5 min static cycles, and 50% flush volume. Extract cleanup was performed as described in [37].

Air samples were obtained from the eastern Mediterranean Sea region and PCBs extracted as described in [38]. Baltic herring, guillemot eggs (*Uria aalge*), and sediment samples were collected from the Baltic Sea area and PCBs extracted and cleaned as described in [39].

Human milk samples were collected from four Swiss women aged 25–36 in August 2002. Milk fat was extracted using the method of [40] and further cleaned with gel permeation chromatography.

2.3. GC–GC–MS–MS

The GC–GC system consisted of two Varian CP3800 gas chromatographs (Varian, Walnut Creek, CA, USA). In the first GC, a Deans switching systems was mounted to divert selected chromatographic fractions over a heated transfer capillary into the second GC. Two electric pressure control (EPC) units regulated the pressure at the column inlet and at the Deans switching system, respectively. The Deans switching EPC was set at 25 psi at all times to allow the complete transfer of analytes to either of the detectors. A programmable temperature vaporization injector was used in the on-column injection mode (temperature program: 0.1 min at 80 °C, to 300 °C at 200 °C/min, 10 min at 300 °C). The split valve was closed upon injection of 1 μL of sample, opened with a ratio of 50 after 2.5 min, and kept at 20 after 2.5 more min. The achiral separation of PCBs was carried out in the first GC on a HT-8 capillary column (50 m, 0.22 mm I.D., 0.25 μm film thickness, SGE International, Ringwood, Australia). As a retention gap, a 2 m fused silica capillary column (Agilent, 0.53 mm I.D.) was mounted prior to the separation column. Helium was used as a carrier gas at a constant flow of 1 mL/min. The oven temperature of the first GC was programmed as follows: 1 min at 90 °C, to 200 °C at 20 °C/min, 10 min at 200 °C, to 285 °C at 3 °C/min, to 310 °C at 10 °C/min and 20 min at 310 °C. During the time of achiral separation, the temperatures at the transfer capillary and in the second GC were held constant at 300 and 40 °C, respectively. The atropisomeric PCBs as well as their respective internal standards were heart-cut by Deans switching at their respective retention times (time windows of 0.75–1.00 min), transferred via a 1 m fused silica capillary column (Agilent, 0.25 mm I.D.) and condensed at the begin of the chiral column (Chirasil Dex, 25 m, 0.25 mm I.D., 0.25 μm film thickness, Varian) mounted in the second GC. Once the transfer of all atropisomeric PCBs and their respective internal standards (see below) was completed, the oven program of the second GC was run as follows: from 40 to 160 °C at 30 °C/min, 5 min at 160 °C, to 180 °C at 0.5 °C/min, and 40 min at 180 °C.

The achiral PCBs were detected with ECD mounted on the first GC. The ECD was kept at 320 °C and nitrogen was used as make-up gas. The chiral PCBs, together with their internal standards (see below), were detected with a triple quadrupole mass spectrometer (Varian 1200, Varian) in the electron impact mode with 70 eV ionization energy. Multiple reaction monitoring was performed with $[M]^+$ as precursor ion and $[M\text{–}2Cl]^+$ as product ion for all PCBs. Collision energy was set to −30 V using argon as collision gas. For single ion monitoring, the quantifier ion was $[M]^+$ and the qualifier ion was $[M + 2]^+$.

2.4. Quantification, analytical quality control, and data presentation

In Swiss soil and compost samples, the seven IRMM PCBs were quantified by the internal standard method, using the seven respective $^{13}C_{12}$-labeled congeners as internal standards [37]. The atropisomeric PCBs 95, 149, 132, and 174 were quantified in the same way, using $^{13}C_{12}$-labeled PCBs 101 (for PCB 95), 153 (for PCB 149 and 132), and 180 (for PCB 174) as internal standards. For each sample, the sum of both enantiomers was compared with the amount quantified by conventional GC–MS [37]. The validation parameters (e.g., recoveries and extraction completeness) obtained for the analysis of seven IRMM PCBs in the very same compost samples [37] are regarded as indicative for the performance of the here presented method for atropisomeric PCBs. In all other sample types (extracts used as received by donors listed in the acknowledgment), concentrations of (atropisomeric) PCBs were not quantified due to the lack of appropriate internal standards.

The enantiomeric fraction (EF; [26]) is used as descriptor of enantiomeric PCB signatures where:

$$\mathrm{EF} = \frac{E_1}{(E_1 + E_2)} \quad \text{or} \quad \mathrm{EF} = \frac{E_+}{(E_+ + E_-)}$$

with E_1 and E_2 being the first and the last eluting enantiomer if the identity of the (+) and (−) forms are unknown. The EF ranges from 0 to 1.0 with EF = 0.5 representing a racemic mixture. All EFs were determined using the peak areas of the respective enantiomers (E_1, E_2, and E_+, E_-, respectively). For data comparison, enantiomeric ratios (ER) reported in the literature were transferred to EFs as follows:

$$\mathrm{EF} = \frac{\mathrm{ER}}{(1 + \mathrm{ER})}$$

Precision of EF quantification was determined as the relative standard deviation of (1) multiple analyses of PCB standard solutions at concentrations from 10 to 250 pg/μL (apparative precision), (2) analyses of multiple extracts from individual soil samples (extraction and cleanup precision), and (3) analyses of individual extracts from four soil samples collected at the same sampling site (sampling precision).

3. Results and discussion

3.1. GC–GC–MS–MS

Fig. 1 illustrates the first (a–c), and second column separation (d–f) of the seven IRMM and the four atropisomeric PCBs investigated, and Table 1 compiles the respective peak assignments, retention times, heart-cutting windows, and ions monitored. The four atropisomeric PCBs 95, 149, 132, and 174, together with their internal standards $^{13}C_{12}$-PCB 101, 153, and 180 were heart-cut from the HT-8 column (first column; Fig. 1a–c) in six portions (Fig. 1a–c, A–F) and transferred to the Chirasil Dex column (second column; Fig. 1d–f), on which the two enantiomers of the PCBs 95 (Peaks no 4 and 5), 149 (no 7 and 8), and 132 (no 11 and 12) were baseline-separated. Only a partial separation of the PCB 174 enantiomers (no 14 and 15) could be achieved (Fig. 1d–f). This is in accordance with the earlier reported capability of Chirasil Dex for separation of atropisomeric PCBs [41,42]. The elution order of the (+/−)-enantiomers of the PCBs 149, 132, and 174 on Chirasil Dex [9,41] is specified in Table 1.

Several advantages of the heart-cutting technique in combination with triple quadrupole detection are apparent and visualized in Fig. 1:

(1) The second column chromatograms are hardly affected by even heavily loaded matrices, such as compost samples (Fig. 1c).
(2) No interference by co-eluting PCBs on Chirasil Dex (171 and 197 with PCB 174; 176 with PCB 132; [42]) is discernable (Fig. 1d–f). These congeners are effectively separated

Table 1
Peak assignments, retention times, heart-cut windows, and ions monitored with GC–GC–MS–MS

Peak assignment	Analyte	PCB retention time on first column (min)	Heart-cut window on first column (min)	PCB retention time on second column (min)	Ions monitored
1	PCB 28	29.1	–	–	ECD
2	PCB 52	31.0	–	–	ECD
3	TCN	33.6	–	–	ECD
4	PCB 95 (E_1)	35.3	35–36 (A)	83.2	326 → 256
5	PCB 95 (E_2)	35.3	35–36 (A)	83.7	326 → 256
–	$^{13}C_{12}$-PCB 101	37.2	37–38 (B)	86.5	338 → 268
6	PCB 101	37.3	37–38 (B)	86.6	326 → 256
7	PCB 149 (−)	41.0	40.75–41.75 (C)	97.6	360 → 290
8	PCB 149 (+)	41.0	40.75–41.75 (C)	98.2	360 → 290
9	PCB 118	42.2	–	–	ECD
–	$^{13}C_{12}$-PCB 153	43.2	42.7–43.7 (D)	102.1	372 → 302
10	PCB 153	43.3	42.7–43.7 (D)	102.2	360 → 290
11	PCB 132 (−)	42.9	42.7–43.7 (D)	106.9	360 → 290
12	PCB 132 (+)	42.9	42.7–43.7 (D)	107.9	360 → 290
13	PCB 138	45.1	–	–	ECD
14	PCB 174 (+)	47.0	46.75–47.5 (E)	123.3	394 → 324
15	PCB 174 (−)	47.0	46.75–47.5 (E)	124.0	394 → 324
–	$^{13}C_{12}$-PCB 180	49.2	49–49.75 (F)	132.3	406 → 336
16	PCB 180	49.3	49–49.75 (F)	132.4	394 → 324

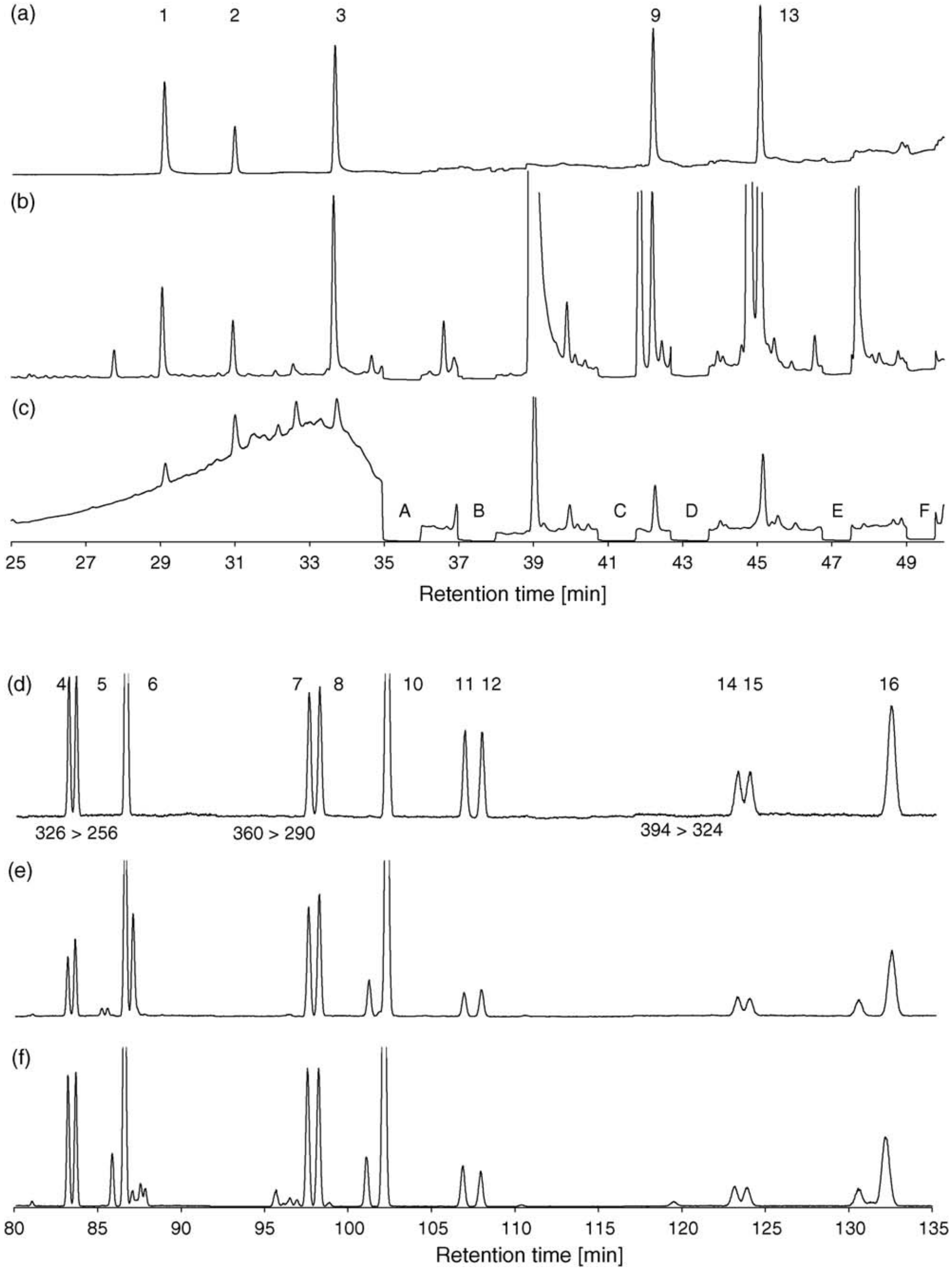

Fig. 1. First column GC-ECD chromatograms (a–c) and second column GC–MS–MS chromatograms (d–f) of heart-cut fractions diverted from the first column. Chromatograms were obtained from injection of a 10 pg/uL standard solution (a and d), a Swiss soil (b and e), and a Swiss compost extract (c and f). Peak and heart-cut assignments are specified in Table 1.

on HT-8 [43] and, thus, not transferred to the second column. Moreover, the congeners 197 and 176 hold one more chlorine atom than the congeners of interest and, hence, do not appear in the (tandem) mass traces.

(3) With 145 min, the total run time remains relatively short, compared to one-dimensional GC runs of 100–135 min (e.g., [14,24,41]).

Moreover, a high reproducibility and robustness was achieved, as little matrix and no high boiling-point analytes were loaded onto the temperature-sensitive chiral column. Several hundred injections were made without any discernable effect on the separation power of the chiral column, although the first column usually exhibited increased tailing after a couple of dozen on-column injections due to activation of the precolumn. This was accounted for by its regular replacement.

3.2. Analytical quality control

Detection limits as determined by the signal to noise ratio (S/N) of 3 averaged from 22 individual chromatograms of a low calibration standard (10 pg/μL) were 0.18, 0.16, 0.28, and 0.69 pg for each of the enantiomers of the four atropisomeric PCBs 95, 149, 132, and 174, respectively. These detection limits obtained with separation on Chirasil Dex are at the higher end of what can be achieved when installing a HT-8 column on the same instrument (0.06–0.15 pg; S/N = 3). The reason for this are the much broader peaks obtained when performing chiral separation (0.5 min < peak width < 1.5 min). The MS–MS detection limits obtained with the given application (on-column injection, EI^+ ionization mode) compare favorably with those of conventional single quadrupole instruments (roughly 0.3–3 pg, data obtained with various instruments either in our lab or during evaluations with different companies) due to the drastic reduction of the noise level. Linearity of quantification for individual enantiomers was confirmed from their detection limits up to 112.1 (PCB 95), 114.2 (PCB 149), and 124.5 pg/μL (PCB 132 and 174).

Blank samples that were analyzed in parallel to the Swiss soil samples exhibited minimum, median, and maximum concentrations of 0.2, 0.3, and 0.4 pg/μL (PCB 95), and 0.4, 0.8, and 1.3 pg/μL (PCB 149) for individual PCB atropisomers ($n = 11$). PCB 132 and 174 were present at levels below detection limits. Respective numbers in soil extracts were 0.2, 2.1, and 10.7 pg/μL (PCB 95; $n = 181$), and 0.7, 2.6, and 18.5 pg/μL (PCB 149; $n = 181$). Hence, in certain cases, blank levels were higher than one-tenth of soil extract concentrations, which is a common analytical quality control requirement. However, blank PCBs were always racemic (EFs = 0.50 ± 0.01 for all four atropisomeric PCBs, $n = 11$). The risk for alteration in EFs quantified in soils due to contamination with racemic PCBs can thus be considered minor. For compost samples, the PCB blank concentration level was essentially equal to the one observed in soils. However, compost extracts were much more concentrated (minimum concentrations 1.5 and 2.6 pg/μL for PCB 95 and PCB 149, respectively). If anything, the more concentrated extracts might have been prone to cross contamination within the GC–GC–MS–MS. This was repeatedly tested by injecting solvent or low PCB standards right after analysis of concentrated extracts. Peak areas of atropisomeric PCBs in the resulting chromatograms were always $\ll$10% of those of the preceding runs. Nevertheless, special care was taken not to mix low and high concentrated samples during analysis.

Quantification of atropisomeric PCBs in Swiss soil and compost extracts by GC–GC–MS–MS was compared with results obtained with bench top (achiral) GC–MS. Ratios of the quantified amounts in soil extracts were 116 ± 17% ($n = 98$), 112 ± 13% ($n = 100$), 103 ± 30% ($n = 59$), and 120 ± 27% ($n = 98$) for the PCBs 95, 149, 132, and 174, respectively. Respective numbers in compost extracts were 123 ± 7% ($n = 87$), 126 ± 8% ($n = 84$), 95 ± 21% ($n = 86$), and 119 ± 23% ($n = 86$). Hence, the data obtained by the two quantification methods corresponded very well.

Apparative precision of EF quantification was found to be concentration dependent and ranged from 0.8% (PCB 95) to 2.2% (PCB 174) at 10 pg/μL ($n = 21$) and 0.2% (PCB 149) to 0.7% (PCB 174) at 250 pg/μL ($n = 3$) for standard solutions. Triplicate extracts from individual soils ($n = 8$) resulted in mean (extraction and cleanup) precisions of 0.7% (PCB 149) to 1.1% (PCBs 95 and 132). Mean (sampling) precisions ($n = 19$) obtained from averaged numbers of individual extracts from four different soil samples collected concomitantly at the same respective location were between 0.8% (PCB 95) and 1.4% (PCB 149). Given that most of the soils investigated exhibited chiral PCB concentrations between <10 and 25 pg/μL, the precisions of EF quantification in these real samples are very much comparable to those obtained with pure PCB standards. This illustrates the robustness of the method against matrix effects. Furthermore, these values are of importance when comparing EFs obtained with different coupling techniques (see below).

The influence of varying PCB concentrations on EF quantification was further evaluated by the analysis of identical soil extracts at different end volumes. Numbers quantified in extract volumes between 100 and 200 μL differed on average ($n = 60$) between 0.6% (PCBs 95 and 174) and 1.3% (PCB 132) from those at 20 μL and hence are in the range described above.

Standard addition of increasing amounts of racemic PCB 95, 149, 132, and 174 to soil and compost extracts caused the expected shift in EFs towards 0.5. Resulting EFs were within 0.3–3.2% of the predicted numbers.

Although many reports on EFs of atropisomeric PCBs are based on extraction techniques that make use of elevated temperatures, such as Soxhlet extraction (e.g., [10,19,24]), only little information is available on whether such harsh extraction conditions might lead to artifact changes in EFs. Glausch et al. [8] tested and excluded racemization of PCB 132 (−) during the extraction of sediment samples using steam distillation-solvent extraction. Indeed, such experiments may seem somewhat unnecessary given the considerable rotational energy barriers resulting in half lives in the order of about 20–120 min at 280 °C [5], i.e., at a temperature substantially higher than those applied during, e.g., Soxhlet extraction. However, since part of our samples were extracted with ASE at both elevated temperature and pressure (120 °C and 2000 psi), we carried out racemization experiments by spiking and extracting enantiopure PCB 132 (−) (EF = 0.018) and 174 (−) (EF = 0.024) from sodium sulphate (blank), and PCB 174 (−) (EF = 0.024) from a soil and a compost sample at a concentration well above those of native compounds. The resulting EFs in the Soxhlet and ASE extracted blanks were 0.025 and 0.023, respectively, for PCB 132 (−), and twice 0.025 for PCB 174 (−). EFs obtained for PCB 174 in the spiked soil were 0.031 for Soxhlet and 0.029 for ASE extraction. Respective numbers obtained with the compost sample were 0.041 and 0.036. Overall, the slight increase of EFs in soil and compost as compared to the blank can be attributed to the presence of native (+) enantiomers of the investigated PCBs in these samples. It can thus be concluded that there was no risk of racemization under the extraction conditions applied here.

3.3. Comparison of GC–GC–MS–MS with other GC and MS coupling configurations

The separation and detection power of GC–GC–MS–MS was compared with that of other possible coupling configurations, i.e., GC–GC–MS, GC–MS–MS, and GC–MS. For this purpose, a selection of samples from different environmental compartments that underwent different extraction and cleanups steps

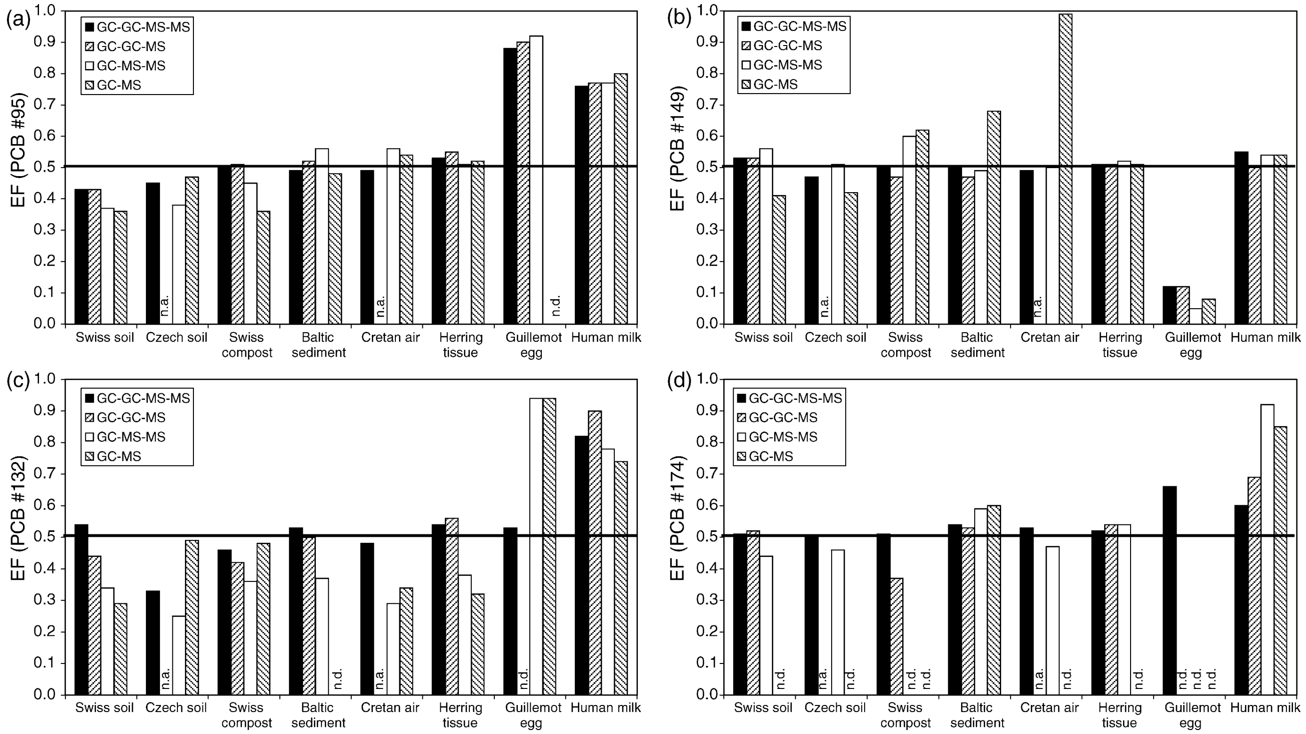

Fig. 2. Enantiomeric fractions (EFs) of PCB (a) 95, (b) 149, (c) 132, and (d) 174 determined with GC–GC–MS–MS (■), GC–GC-MS (▨), GC–MS–MS (□), and GC–MS (▧). The black line indicates a racemic distribution of PCB enantiomers. n.a.: not analyzed; n.d.: not detected.

was analyzed with these four techniques. Fig. 2 compiles the EFs that were quantified from the chromatograms obtained, and Fig. 3 illustrates the chromatographic differences for a Swiss soil sample. Note that we do not claim the EFs obtained with GC–GC–MS–MS to be free of artifacts and thus correct. As a matter of fact, the true EFs in these samples are unknown. However, we are convinced that GC–GC–MS–MS, being the most selective of the four techniques, has the best chances of getting close to these true EFs. Significant (i.e., larger than EF quantification precision achieved with GC–GC–MS–MS; see above) differences in EFs between the various coupling techniques were observed for all four atropisomeric PCBs investigated. For most samples and analytes, the deviations from the original GC–GC–MS–MS data were smallest when using GC–GC–MS. This latter coupling technique provided EFs that were within 5% (PCB 95), 10% (PCB 149), 20% (PCB 132), and 25% (PCB 174) of the data obtained with GC–GC–MS–MS (Fig. 2). However, even errors in the order of 5–25% may be intolerable when enantioselective degradation processes in the environment are to be studied. EFs determined with GC–MS–MS differed even more from the data generated with GC–GC–MS–MS, i.e., up to 15% for PCB 95, and up to 50–70% for the other congeners (Fig. 2). This might indicate that the second chromatographic dimension contributes more to the overall method selectivity than the triple quadrupole detection. However, MS–MS added to the sensitivity of the method, and single quadrupole MS was often unable to detect the analytes of interest (Fig. 2d, PCB 174, and Fig. 3d). Finally, analysis by GC–MS produced EFs that deviated up to 100% (Fig. 2b, PCB 149 in Cretan air sample) from the data obtained with GC–GC–MS–MS.

A rigorous extract cleanup might be a valuable alternative to sophisticated multidimensional separation and detection. Indeed, Fig. 2 presents some examples where presumably clean extracts yielded EFs of high consistency irrespective of the analytical techniques applied. For instance, the herring and human milk extract exhibited pretty much constant EFs for the PCBs 95 and 149. However, results obtained for the two other atropisomeric PCBs were not satisfactory (PCB 132: up to 40% deviation in herring (Fig. 2c); PCB 174: up to 50% deviation in human milk (Fig. 2d)).

The limits of one-dimensional separation and/or detection of atropisomeric PCBs in real samples are further illustrated in Fig. 3, showing soil sample chromatograms obtained with the four coupling techniques investigated. Three main features are worthwhile to point out: (1) The increase in selectivity and sensitivity due to MS–MS. For instance, co-eluting compounds of PCB 132 (+) (Fig. 3a and b) and PCB 149 (−) (Fig. 3c and d) are efficiently eliminated when using MS–MS. Moreover, although the peak shape and intensity of the individual atropisomers of the PCBs 132 and 174 appear to be free of any disturbances in Fig. 3b (GC–GC–MS), the relative abundance of the respective enantiomers changes when using tandem MS (Fig. 3a). Hence, apparently "clean" single quadrupole mass traces do not guarantee an artifact-free quantification of EFs. (2) The improved and lasting separation power for atropisomeric PCBs when using heart-cut two-dimensional chromatography (Fig. 3a and b). In comparison, the peak width and tailing of individual PCB atropisomers obtained with one-dimensional chiral chromatography were not satisfactory (Fig. 3d), even in tandem MS mode (Fig. 3c). In general, the Chirasil Dex column exhibited a

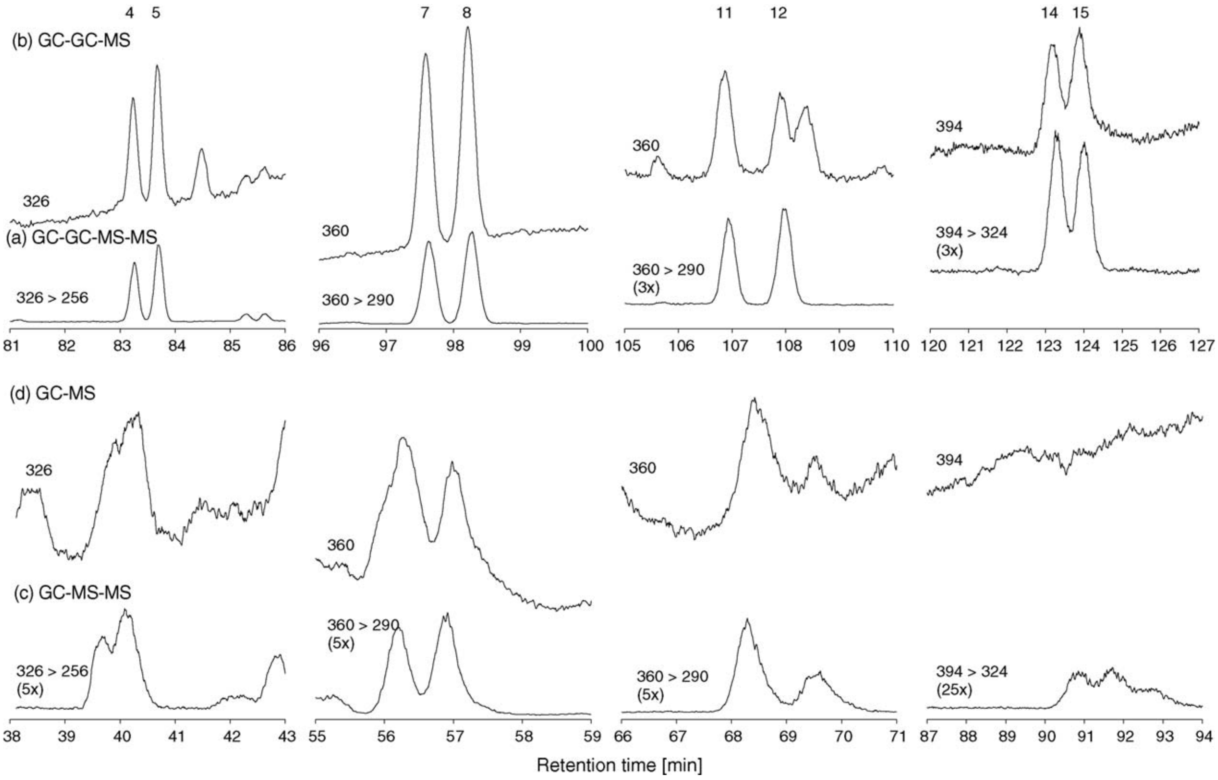

Fig. 3. Chromatograms of a Swiss soil extract analyzed with (a) GC–GC–MS–MS, (b) GC–GC–MS, (c) GC–MS–MS, and (d) GC–MS. Monitored ions are indicated and magnification factors of MS–MS mass traces (a and c) are given in brackets. For peak assignments, see Table 1. The difference in chromatographic quality is apparent and further discussed in the text.

considerable susceptibility to damage by on-column injection of real sample extracts, especially if these were not subjected to a rigorous cleanup. No such problems were observed for any of the sample extracts when only heart-cut fractions were applied. (3) Apart from the higher vulnerability of the Chirasil Dex towards dirty extracts, its reduced separation power of approximately a factor of four (based on theoretical plate numbers calculated from PCB standard injection) as compared to, e.g., a conventional HT-8, makes it a priori a worse choice for separation of complex mixtures.

3.4. Application of GC–GC–MS–MS to environmental samples

The presented GC–GC–MS–MS coupling technique was applied to extracts from a large variety of environmental samples, including soil, compost, sediment, air, herring, guillemot egg, and human milk. The EFs obtained for the different sample types are compiled in Table 2.

The EFs different from 0.5 indicate that enantioselective degradation of PCBs takes place in Swiss soils. A closer inspection of the data suggests that the degree and enantiomer prevalence of the observed enantiomeric shifts differ between different types of land use (Fig. 4). For instance, 50% of the EFs of PCB 95 in deciduous forests were >0.5. In contrast, most other soil types exhibited EFs < 0.5 (Fig. 4a). For PCB 149, EFs < 0.5 were almost exclusively observed in forest soils (Fig. 4b). Most other soils showed EFs > 0.5. Enantiomeric shifts of PCB 132 were most pronounced in forest soils (Fig. 4c). The soil pH appeared to have some influence on the EFs of PCB 95, 149, and 132. However, linear correlations were very weak, although p-values indicated significance (PCB 95: $\mathrm{EF} = -0.0078\ \mathrm{pH} + 0.5349$; $R^2 = 0.2234$, p-value = 0.0000006, $n = 101$; PCB 149: $\mathrm{EF} = 0.0067\ \mathrm{pH} + 0.4653$; $R^2 = 0.0931$, p-value = 0.00192, $n = 101$, and PCB 132: $\mathrm{EF} = -0.0044\ \mathrm{pH} + 0.541$; $R^2 = 0.0831$, p-value = 0.00347, $n = 101$). Such a pH-dependence of enantioselective degradation was earlier reported for chiral pesticides [44].

Results for Swiss soil samples can be compared with those obtained for Czech soils (this work; Table 2) and data from Robson and Harrad [24] for U.K. soils. Interestingly, differences in the prevalent enantiomers and the extent of enantiomeric shift could be observed for each of the three comparable atropisomeric PCBs 95, 149, and 132. In Swiss soils, roughly 10% of all samples exhibited an EF > 0.5 for PCB 95. This occasional prevalence of the E_1 was not observed in either of the Czech or the U.K. soils. However, at these locations, EFs for PCB 95 as low as 0.36 (Table 2) and 0.39 [24], respectively, were measured. These enantiomeric shifts were more pronounced than those detected in Swiss soils (minimum EF = 0.45). Similar differences between Swiss and Czech soils were observed for PCB 149 and PCB 132 (Table 2). A significant correlation between soil pH and EF of PCB 149 was observed in the Czech soils ($\mathrm{EF} = 0.0264\ \mathrm{pH} + 0.3058$; $R^2 = 0.6702$, p-value = 0.00113, $n = 12$). The EFs of PCB 149 were roughly in the same range in Swiss (Table 2) and U.K. soils ($0.47 < \mathrm{EF} < 0.57$; [24]). The

Table 2
Range of enantiomeric fractions observed in various matrices

Sample type	Number of samples	PCB 95	PCB 149	PCB 132	PCB 174	Sample donors
PCB standards	28	0.50–0.51	0.49–0.51	0.49–0.51	0.49–0.53	Own solutions
Swiss NABO soils	105	0.45–0.55	0.44–0.56	0.49–0.57	0.48–0.53	Stefan Ammann
Czech soils	12	0.36–0.51	0.42–0.51	0.22–0.49	n.d.	Jana Klanova
Swiss compost and digestate	79	0.48–0.51	0.46–0.51	0.46–0.52	0.47–0.53	Own samples
Baltic sediment (Saxarfjärden, Stockholm)	1	0.49	0.50	0.52	0.54	Lillemor Asplund
Crete air samples	13	0.49–0.51	0.48–0.50	0.46–0.50	0.47–0.53	Manolis Mandalakis
Baltic herring	2	0.50, 0.53	0.51	0.54	0.50, 0.52	Lillemor Asplund
Baltic guillemot egg	1	0.88	0.12	0.53	0.64	Lillemor Asplund
Swiss human milk	4	0.64–0.76	0.52–0.55	0.67–0.82	0.59, 0.62 ($n = 2$)	Peter Schmid

n.d.: not detected.

observation of an inverse relationship between the degree of urbanization and extent of enantioselective degradation [23] was not reflected in our data.

To the best of our knowledge, this is the first time that atropisomeric PCBs were determined in compost samples. In general, enantiomeric shifts (Table 2) were weak and occurred in only about 20% of all samples investigated. This is somewhat surprising, as the compost process takes place in a highly active microbial environment. However, the enantioselective microbial degradation rates might be too low to cause more pronounced EFs under the usual compost processing time (roughly 4 months in a commercial compost plant).

Although the sediment EFs were well within the range reported in the literature (e.g., [9]), the EFs observed in two Baltic herring samples (Table 2) differed from similar data reported for lake herring (*Coregonus artedii* from Lake Superior; [12]). Specifically, EFs ≥ 0.5 were measured in the Baltic samples for both PCBs 95 and 149, whereas EFs < 0.5 were quantified in the Lake Superior samples.

With EFs of 0.88 for PCB 95 and of 0.12 for PCB 149 (Table 2), the Guillemot egg exhibited the most extreme enantiomeric shifts of all samples investigated. Unfortunately, we were unable to find any further data on atropisomeric PCBs in bird eggs to compare our data with, although the presence of PCB 149 was earlier reported in Norwegian birds of prey [45]. Recently, an enantioselective enrichment of the polybrominated biphenyl 149 (EF of the first eluting enantiomer of 0.42–0.43) was observed in the extract of a white-tailed sea eagle egg [46].

The human milk samples exhibited enantioselective shifts (Table 2) that were more pronounced than observed previously

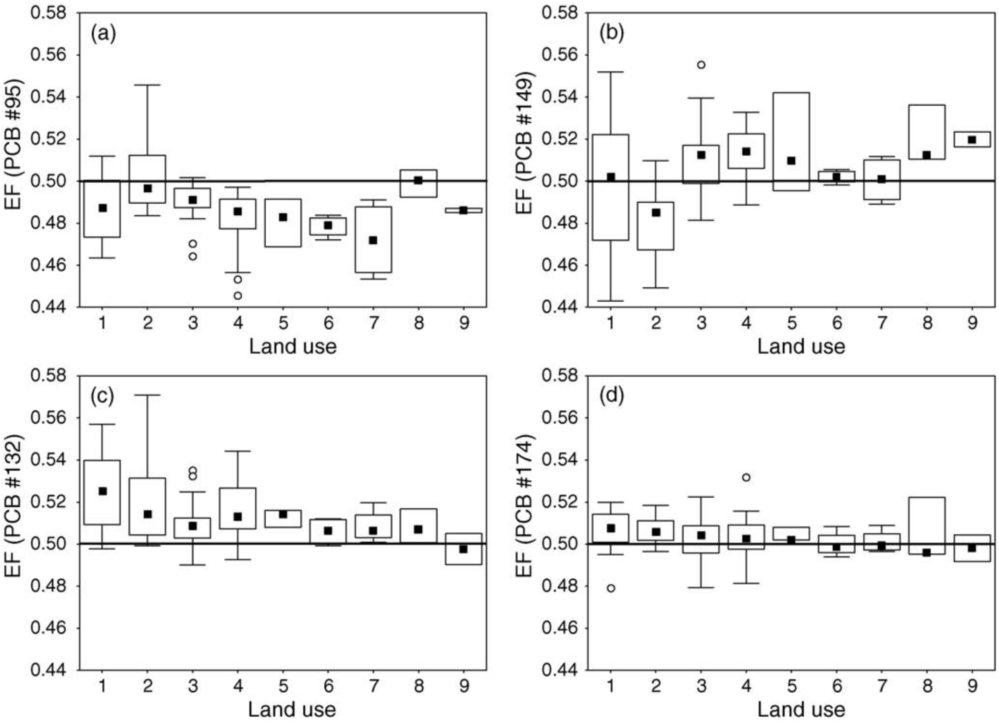

Fig. 4. Enantiomeric fractions (EFs) of (a) PCB 95, (b) PCB 149, (c) PCB 132, and (d) PCB 174 in Swiss soils. Land use numbers represent: deciduous forests (1; $n = 12$), coniferous forests (2; $n = 16$), permanent and pasture grassland (3; $n = 28$), agriculture (4; $n = 29$), fruit-growing (5; $n = 3$), viticulture (6; $n = 4$), horticulture (7; $n = 4$), marsh (8; $n = 3$), and city park (9, $n = 2$). Black square: median; box: 25th and 75th percentile; lines and whiskers: non-outlier range; empty dots: outliers. The black line indicates a racemic distribution of PCB enantiomers.

with heart-cut two-dimensional gas chromatography and MS in the SIM mode: $0.51 < \text{EF (PCB 95)} < 0.58$; $0.49 < \text{EF (PCB 149)} < 0.53$ (calculated from [21]); $0.53 < \text{EF (PCB 132)} < 0.71$ (calculated from [22]).

4. Conclusions

The coupling of two-dimensional GC with triple quadrupole MS presented here proved to be superior to coupling techniques with less dimensions. Extracts from a range of environments could unequivocally be quantified for atropisomeric PCBs almost irrespective of their origin and cleanup quality. The extensive quality control measures put the presented method on solid ground and render the quantified EF data highly reliable. This work refutes the common perception of heart-cut two-dimensional GC being too sophisticated, demanding and awkward in maintenance, and therefore unsuitable for routine application. Hundreds of extracts from soil and compost samples were successfully analyzed with the same ease as when using bench top GC–MS.

Acknowledgments

We are thankful to Hans Jörg Bachmann (FAL), Luiz Felipe De Alencastro (Ecole Polytechnique Fédérale de Lausanne), Marianne Erbs (FAL), Wayne Garrison (National Exposure Research Laboratory, US EPA), Peter Haglund (Department of Chemistry, Umeå University), Peter Schmid (Swiss Federal Institute of Materials Science and Technology, Dübendorf), Franz X. Stadelmann (FAL), and Felix Wettstein (FAL) for their feedback on this manuscript. We gratefully acknowledge the various sample donors: Stefan Ammann and André Desaules (Swiss Soil Monitoring Network, FAL), Lillemor Asplund (Department of Applied Environmental Sciences, Stockholm University), Jana Klanova (Research Centre for Environmental Chemistry and Ecotoxicology, Brno), Manolis Mandalakis (Department of Chemistry, University of Crete), and Peter Schmid. Peter Haglund and Wayne Garrison are thanked for their donation of enantiopure PCB atropisomers. Franziska Blum is thanked for her help with the analysis of soil and compost samples. Thanks due to G. Karlaganis, J. Zihler, and J. Dettwiler (Federal Office for the Environment, FOEN) for their financial support and interest in our work.

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5 Manuscript 1

Organic pollutants in Swiss compost and digestate;
1. Polychlorinated biphenyls, polycyclic aromatic hydrocarbons and molecular markers, determinant processes, and source apportionment

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5.1 Manuscript 1: Text

Abstract

In Europe 9.3×10^6 $t_{\text{dry weight (dw)}}$ of compost and digestate are produced per year. Most of this is applied to agricultural land, which can lead to considerable inputs of organic pollutants, such as polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) to soil. This paper presents an inventory of the pollutant situation in source-separated composts and digestates in Switzerland by a detailed analysis of over 80 samples. PCB concentrations (ΣPCB 28, 52, 101, 118, 138, 153, 180) were significantly higher in urban (median: 30 $\mu g/kg_{dw}$, n=52) than in rural samples (median: 14 $\mu g/kg_{dw}$, n=16). Together with low concentrations in general this points to aerial deposition on compost input material as the major contamination pathway. Enantiomeric fractions of atropisometric PCB were close to racemic. Median PAH concentration was 3010 $\mu g/kg_{dw}$ (Σ15PAH, n=69) and one fourth of the samples exhibited concentrations above the relevant guide value (4000 $\mu g/kg_{dw}$). The levels were influenced by the treatment process (digestate>compost), the season of input material collection (spring/summer>winter>autumn), the particle size (coarse-grained>fine-grained), and maturity (mature>less mature). The main source of PAH in compost was pyrogenic, probably influenced mainly by liquid fossil fuel combustion and some asphalt abrasion as suggested by multiple linear regression. This study provides, together with a companion paper, a starting point for a better risk-benefit estimation of the application of compost and digestate to soil in Switzerland.

Introduction

Composting (aerobic treatment) of crude organic kitchen waste and green waste represents an important and well-established part of waste management in Europe. Digestion (anaerobic treatment with or without subsequent aerobic treatment) has been promoted in recent years due to increasing efforts to combine recycling of organic materials with production of renewable energy. Some $31.5*10^6$ t/y of municipal were composted in the 25 European Union member states (EU25, (*1*)), which .results in some $9.3*10^6$ tonnes dry weight (t_{dw}) of compost, considering a mass loss during decomposition of 40% (*2*) and a dry matter content of 50%. This amount is expected to increase, due the EC Council Directive on the Landfill of Waste (*3*), which has implemented strict limits on the amount of biodegradable municipal waste that can be disposed of via landfill. Most compost and digestate, including the liquid fraction of the digestion process (presswater), is applied to agricultural land or is used in horticulture and landscaping. Utilization of these products follows the recycling principle and can have positive effects on physical, chemical and biological soil parameters. However, compost can contain significant amounts of pollutants (*4,5*) that are introduced to the soil ecosystem by its application. The problem related to heavy metals has been recognized and statutory as well as voluntary quality standards have been put in place. It was shown that reduction of the heavy metal contents can only be achieved by thorough separation of the input materials at the source (*6*), i.e., by excluding municipal solid waste, sewage sludge etc. A recent literature review has shown that knowledge on organic pollutants in this so-called ‘source-separated compost’ is limited (*5*). Information on digestate is completely lacking. From a (soil) risk assessment point of view, this gap of knowledge is problematic.

Plausible input pathways of organic pollutants to compost and digestate are aerial deposition on green waste, accidental (i.e., improper separation of input materials, e.g., plastic debris) and/or deliberate input (e.g., pesticide application to fruits and vegetables). The situation is further aggravated by, at least for persistent organic pollutants, the expected increases of concentrations during aerobic and anaerobic treatment as a consequence of organic mass degradation (see above).

We made an inventory of the content of a wide range of the organic pollutants of most concern today in compost and digestate in Switzerland. This paper presents results for polychlorinated biphenyls (PCB) including four atropisometric congeners, and polycyclic aromatic hydrocarbons (PAH). Molecular markers and characteristic ratios were added as an attempt to identify sources of PAH in compost. This concept was originally based on emission data (for review see, e.g., (*7*)). Here, we investigate to what extent these ratios preserve their diagnostic potential in environmental recipient matrices such as compost and digestate and whether the application of correction factors as suggested by Zhang et al. (*8*) could be helpful. A companion paper (*9*) reports on data for polychlorinated dibenzo-*p*-dioxins and -furans, brominated flame retardants, perfluorinated alkyl substances, pesticides and other organic contaminants in a subset of samples. The present study aims at (i) assessing the variables that influence PAH and PCB concentrations in compost and digestate, (ii) apportioning relevant sources of PCB and PAH in these products, (iii) comparing the obtained data to literature and legislative values and (iv) relating organic pollutant input to soil by compost application to other input pathways.

Materials and Methods

Experimental Design

Over 80 samples of compost, digestate and presswater derived from source separated green (organic waste from private gardens and public green areas) and kitchen waste (crude organic waste originating from private kitchens) were collected from 39 commercial composting and digestion plants in Switzerland (for location, number of samples per plant, a thorough description of the samples and of the composting and digestion process see Supporting information, Figure 1, Table 1 and Text 1). Small amounts of other types of organic waste, originating mainly from food processing industry, in the input material were included in the input materials of some plants. Sample selection accounted for variables hypothesized to be key determinants for organic pollutant content in compost and digestate (*5*): treatment process (anaerobic/aerobic), composition of input materials (green waste with/without organic kitchen waste), origin of input material (urban/rural) and season of input material collection (spring/summer -united because of sampling limitations-, autumn, winter).

Sampling and sample preparation

Sampling procedure for windrow composting was described in Brändli et al. (*10*). Where other processes were applied (e.g., box and table windrow composting), multiple subsamples (two to six) were taken and jointed. Presswater, sampled from its storage tank, was dried at 40 ºC for seven days for analysis of heavy metals and nutrients, or mixed with hydromatrix (diatomaceous earth, Varian, Inc. Walnut Creek, CA, USA, 2:1 w/w) for analysis of PCB and PAH. Samples were stored in the dark at 4 ºC until analysis within 1 to 26 weeks.

Analytical procedure

Concentrations, ratios, and enantiomeric fractions (EF) of the following organic pollutants were determined as described earlier (*10*-*12*): (i) PAH (naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IPY), dibenzo[*a,h*]anthracene (DBA), benzo[*ghi*]perylene (BPE), retene (RET), coronene (COR), ratio of methylPHE and –ANT to PHE (MPHE&ANT)/PHE), ratio of methylFLT and -PYR to PYR (MFLT&PYR)/PYR), ratio of 1,7- to 1,7- and 2,6-dimethylPHE (1,7-/(1,7-&2,6-)DmPHE), (ii) PCB (PCB 28, 52, 95, 101, 118, 132, 138, 149, 153, 174, 180), and (iii) EF of PCB 95, 132, 149. 4-H-cyclopenta[*def*]PHE (CPHE), cyclopenta[*cd*]PYR (CPYR), and perylene (PER) were quantified analogously to the previously mentioned PAH, using deuterated ANT, BaA and PYR, respectively as internal standards. Chemically dried presswater was filled in three 33-ml Accelerated Solvent Extraction cells and the internal standard was divided between them. Extraction was performed as described in Brändli et al. (*10*), extracts were pooled and following clean-up steps performed as for compost. To test potential correlations with organic pollutants, to characterize samples and to support source identification, heavy metals (Cd, Co, Cr, Cu, Ni, Pb and Zn), nutrients (N, P, K, Mg, Ca), pH and electrical conductivity were determined. Their analysis was carried out according to the Swiss references methods (*13*). Impurities were determined on a percentage per weight basis and maturity of compost by the ratio of NO_3^-/NH_4^+ (both (*14*)). All values were related to dry weight content, determined directly after sampling by air-drying at 105 ºC.

Mass fluxes of organic pollutants to soil

Annual inputs of organic pollutants to agricultural soil by compost, digestate and presswater application can be related to other input pathways, such as aerial deposition and input via sewage sludge or manure. Mean, minimum and maximum total loads to the Swiss agricultural area (comprising all arable soils, grassland, horticulture, orchards, and vineyards) and loads per hectare (ha, surface specific loads, based on a standard fertilisation) were calculated. Whereas the total loads reflect the contribution for different contamination sources to agricultural soils on a national scale, the surface specific loads are relevant for plots where compost is effectively applied for fertilising. Additionally, time to reach Swiss trigger or guide values for organic pollutants in soil as defined in the Ordinance relating to the Impact on the soil (OIS) (*15*) solely by compost application and aerial deposition was estimated. For calculations and relevant data see Supporting information Text 2 and Table 2and 3.

Uncertainty, data processing and statistics

Uncertainties of the results presented here are associated with sampling, sample preparation and analysis (for a thorough discussion see Brändli et al. (*16*). Such errors were found to be in the order of 30% for PAH and PCB analysis in compost (*17*). Samples that contained manure or green waste collected exclusively from highway areas were eliminated from the dataset because they do not match the definition of 'source-separated compost' and because highway areas are normally more contaminated (*18*). It resulted a dataset of n=69. PCB, PAH, heavy metal and nutrients contents were tested for linear correlation. Samples with different congener/compound pattern were identified by principal component analysis (PCA, Statistica 6.1, StatSoft, Inc, Tulsa, USA). Since PCB 28 was detected only in few samples, contributions of the ten congeners (PCB 52, 95, 101, 118, 132, 138, 149, 153, 174, 180) relative to their sum were taken into account for this evaluation. For PAH, PCA is based on 15 PAH (16 EPA PAH, except DBA see below). The linear models applied to identify relevant variables influencing organic pollutant concentrations in compost are described in the Supporting information Text 3.

Source apportionment for PAH

There are three types of characteristic PAH ratios, which can easily be integrated in conventional PAH analysis and may be used for source apportionment. They distinguish between: i) petrogenic and pyrogenic origin, ii) different fuels such as petroleum, coal and wood and iii) traffic and non-traffic sources of PAH (Supporting information, Table 4). Conversion factors (for air particulate matter) representing environmental processes between sources and the recipient matrix (i.e., input material) where taken from Zhang et al. (*8*) (for conversion see Supporting information Text 4). Processes during digestion and composting were considered as discussed in Brändli et al. (*16*). We also included molecular marker substances that were suggested to be characteristic for specific sources (Supporting information, Table 5). Additionally, a linear mixing model taking into account the whole PAH profile was fitted to the data. This method allows for identifying a few potential sources and their contributions to PAH concentrations from the data. For a further description of this approach, see Supporting information, Text 5.

Results and Discussion

PCB and PAH concentrations in Swiss compost and digestate are first compared to data from the literature and to concentrations in soil, which is the primary recipient of compost. Afterwards, PCB and PAH input via compost application to soil is related to other input pathways. Finally, possible key determinants influencing PCB and PAH concentrations in compost and digestate are discussed. For PAH, a thorough source apportionment is carried out, using characteristic PAH ratios, molecular markers, and a linear unmixing model.

PCB

Median values and input to soil

Median PCB concentration (Sum of PCB 28, 52, 101, 118, 138, 153, 180; Σ7PCB) in Swiss compost and digestate was 26 $\mu g/kg_{dw}$ (n=68, range: 8.1-102 $\mu g/kg_{dw}$, Figure 1, for detailed data see Supporting information, Table 1). Sample no. 56 exhibiting very high and in repetitive analysis varying concentrations was excluded from the dataset. PCB concentrations in presswater were in the same range as for compost (21-36 $\mu g/kg_{dw}$, n=3). There was no correlation of PCB concentrations with heavy metal or nutrient contents. The median PCB value for compost in the literature was slightly higher (38 $\mu g/kg_{dw}$, Sum of PCB 28, 52, 101, 138, 153, 180, Σ6PCB, (*5*)) than in the present study (median: 22 $\mu g/kg_{dw}$, Σ6PCB). This may be a consequence of the generally decreasing PCB levels in the environment (*19*). PCB contents in Swiss soils were roughly ten times lower than concentrations in compost (*20*).

Sample nos 4 and 48 exhibited different congener patterns compared the other samples (identified by PCA, Supporting information, Figure 2), which points to a different mixture of contributing PCB sources to these composts. In sample no. 4, the level of PCB 180 was elevated relative to the other congeners. This sample contained small amounts of residues from the production of potato chips; however, it is unclear whether this altered the congener pattern. Sample no. 48 had higher relative content of PCB 52 and it was one of the few samples, where PCB 28 was detected. This different pattern might be due to small amounts of paper sludge in the input material, which can contain high relative amounts of PCB 52 (own unpublished results).

Total input of PCB to Swiss agricultural soil was dominated by manure application and aerial deposition (Figure 2a). However, if surface specific loads are considered, compost and digestate application were the most important inputs, outweighing aerial deposition by more than a factor of 25. Input by presswater was in the same range as input via sewage sludge. Time to reach the Swiss trigger value for plant production (0.2 mg/kg_{dw}, OIS (*15*)) by compost or digestate application (surface specific load scenario) and aerial deposition, which accounted for 4% of the total surface specific load, was estimated to 1400 years (for starting level in soil and deposition rate see Supporting information Table 1). This period was significantly reduced if dioxin-like PCB were considered (*9*).

Variables influencing PCB concentrations in compost and digestate

Sample no. 30 exhibited a considerably higher PCB content compared to the remaining dataset and was eliminated as an outlier before applying the linear model. The variables 'origin of input material' (urban/rural), 'composition of the input material' (green waste with/without kitchen waste) and 'duration of the treatment process' were identified as explanatory (for *p* values see Table 1, for coefficients, see Supporting information Table 6). For all congeners, concentrations were significantly higher in urban compared to rural samples. This is in line with the literature (*5*) and the generally higher burden of PCB in urban areas (*21*). Green waste composts had slightly higher PCB concentrations than compost with organic kitchen waste in the input material. This could indicate proper separation of organic kitchen waste in Switzerland and contrasts with the literature (*5*). However, the difference was significant for three congeners only (Table 1). The longer the composting process lasted, the lower were the PCB values in general. This can be explained by either increasing losses (degradation/volatilisation) during the process, or by the formation of increasing amounts of non-extractable residues over time as found previously (*22*). Again, the effect was significant for a few congeners only.

The variables that influenced the relative PCB contents (individual PCB/Σ10PCB) were 'particle size', 'organic matter content' and 'maturity' (for *p* values see Table 1, for coefficients Supporting information Table 6). In coarse-grained (unsieved or sieved to > 20 mm) compost and digestate, the less chlorinated PCB (52-118) contributed more, and higher chlorinated ones (132-180) less, to the total sum, compared to fine-grained (0-20mm) compost. This may be explained by heavier PCB being bound more effectively (due to higher K_{oc} values) to small, organic rich (soil) particles than to bigger (wood) parts. However, this was not reflected by the variable ‘organic matter content’, whose coefficients altered between positive and negative for the different congeners (Table 1). Ratios of the less chlorinated PCB (52 to 118) were generally lower and fractions of higher chlorinated PCB (132 to 180) higher in compost and digestate with higher NO_3^-/NH_4^+ ratios, i.e., which were more mature. This might reflect increased losses of the less chlorinated PCB during composting compared to higher chlorinated congeners as indicated above and reported previously (*23*). However, the difference was significant for some congeners only (Table 1) and in a field study, increasing levels of tetra- and pentachlorianted PCB during composting were observed (*16*).

Enantiomeric fractions of atropisometric PCB and influencing variables

EF of PCB 95, 149 and 132 varied little and were close to 0.5 in compost and digestate (Supporting information, Figure 3). This is surprising since composting and digestion are biologically very active processes and microbial transformation of PCB could be expected. However, duration of composting and digestion (four to eight weeks) might be insufficiently short to significantly change EFs. Still, ‘treatment process’ (anaerobic/aerobic) was the most important variable within the linear model (significant for EF 95, 149, Supporting information, Table 7). The EFs of PCB 95 were higher in digestate than in compost, whereas for PCB 149 the opposite was observed (Supporting information, Table 7). This may point to different degradation mechanisms under aerobic and anaerobic conditions. ‘Season of input material collection’ played a minor role and ‘duration of the degradation process’ influenced none of the EFs significantly (Supporting information, Table 7).

PAH

Median values and input to soil

Median PAH concentration in compost and digestate (Σ16EPA PAH except DBA, Σ15PAH) was 3010 $\mu g/kg_{dw}$ (n=69, range: 600 – 12470 $\mu g/kg_{dw}$, Figure 1, for detailed data see Supporting information, Table 1). DBA could not be determined due to low recoveries, however it only contributes 1-2% to the Σ16PAH in compost (*5*). One fourth of the samples exceeded the Swiss guide value for compost (4000 $\mu g/kg_{dw}$ (*24*)). Concentrations in presswater were higher than in compost and digestate (5780-9310 $\mu g/kg_{dw}$, n=3).

PAH levels did not correlate with respective PCB, heavy metal and nutrient contents. The median concentration of PAH in compost in the literature was lower than in this study (1870 $\mu g/kg_{dw}$, Σ16PAH, (*5*)). Different composition of input materials or a more efficient extraction technique (optimized for compost (*10*)) might contribute to these higher levels. Spatial (most literature data originated from Germany and Austria) and temporal differences in PAH emission seemed to be of minor importance (*25,26*). Median values of EPA PAH and molecular markers (RET, COR) were six to 40 times higher in compost and digestate than in Swiss soil (*12*).

Samples no. 5, 11, 49, 80, 84 and 89 had a different relative PAH pattern (Supporting information, Figure 4). Ratios of the lighter PAH to Σ15PAH were higher in samples no. 5, 49, 80, 84, and 89 than in the remaining dataset. All of these samples were digestates, containing no detectable NO_3^-, which points to insufficient aerobic stabilisation after digestion. However, there were also composts with the same characteristics in respect to stabilisation, e.g., sample nos. 1, 6 and 9, which had an inconspicuous PAH pattern. Maybe low molecular weight (LMW) PAH were sequestered, e.g., by organic matter glassy – rubbery transition at elevated temperatures as suggested by Delapp et al. (*27*) during digestion in the closed system, hindering evaporation in the subsequent stabilization, whereas in the open compost system evaporation was possible at all times. Sample no. 11 had high relative NAP concentration, which may be due to low temperature during composting. The other two samples close to sample no. 11 in the PCA (no. 39, 40, Supporting information, Figure 4) were subject to low temperature during composting as well.

Total PAH loads introduced by compost, digestate and presswater application to Swiss agriculture accounted for 33% of the input from aerial deposition and exceeded loads by manure and sewage sludge application (Figure 2b). As for PCB, compost, digestate and presswater application were the most important input pathway if considering surface specific loads. They outweighed aerial deposition by more than a factor of 20 (Figure 2b). If the only inputs of PAH to soil were compost application (96% of the total surface specific load) and aerial deposition (4% of the surface specific load, for deposition rate and starting level in soil see Supporting information, Table 1), it would take less than 50 years to reach the Swiss guide value for soil (1 mg/kg_{dw}, OIS, (*15*)). At this level the law calls for actions to prevent further increase of the PAH.

Variables influencing the PAH concentrations in compost and digestate

The linear model determined other variables as influencing PAH concentrations in compost and digestate than for PCB: ‘treatment process’, ‘season of input material collection’, ‘particle size’ and ‘maturity’ (for *p* values see Table 2, for coefficients Supporting information Table 8). ‘Maturity’ did only correlate weakly but significantly (r^2 = 0.26, $p< 0.001$) with the ‘duration of the degradation process’, which was identified as influencing PCB levels.

Significantly higher concentrations of especially the LMW PAH (NAP-CHR) were detected in digestate compared to compost. A hypothesis for this has been outlined earlier in this paper. However, PAH concentration did not evolve differently in a full-scale composting of primarily digested compared to non-digested organic kitchen and green waste (*16*). However, PAH concentration did not evolve differently in a full-scale composting of primarily digested compared to non-digested organic kitchen and green waste (*16*). PAH concentrations were in general higher in compost and digestate derived from input material collected in spring/summer compared to input material gather during the rest of the year. Lower concentrations than the rest of the year was obtained from autumn input material (Table 2). Considering the prerequisite that coefficients sum to zero (see description of the model, Supporting information, Text 3) this results in the following order of PAH concentrations in compost: input material collected in spring/summer > winter > autumn. This is not in line with emission data, which are higher in winter than in summer (*28*). However, it was found previously that contents in compost input material were highest in seasons with lower releases (*5*). Coefficients of LMW PAH were slightly higher than of high molecular weight (HMW) compounds in all seasons (Supporting information, Table 8), which may reflect higher mobility of the LMW PAH. Coarse-grained compost and digestate had overall higher PAH contents than fine-grained material. This holds particularly true for the HMW compounds (PYR-BPE and RET-COR) and is unexpected considering physical-chemical properties of PAH and small particles exhibiting a relatively high sorption capacity. The higher the NO_3^-/NH_4^+ ratio, i.e., the more mature the compost was, the lower were the PAH concentrations. This effect was more pronounced for the LMW PAH (ACE-PYR and CPHE) than for the HMW compounds (Table 2). In addition to preferential evaporation, LMW PAH were also reported to be more effectively degraded during the maturation stage (*29,30*).

In contrast to the PCB, two variables already explaining total PAH concentrations remained explanatory also for the PAH compound patterns (for *p* values see Table 2, for coefficients see Supporting information Table 8), namely ‘organic matter degradation process’ and ‘maturity’.. Sample no. 5 was eliminated as an outlier due to very different pattern of single compounds (see PCA, Supporting information Figure 4). Findings (and explanations) go in line with the total concentrations (see above).

Characteristic PAH ratios and molecular markers

In general, characteristic PAH ratios and molecular markers in Swiss compost compared well with compost literature data (*5*) and values from Swiss soils (*12*) (Supporting information, Figure 5) even before taking into account possible alteration due to environmental processes and degradation during composting. However, not all ratios proved to be stable and they did not change consistently during composting and digestion (*16*). Among the constant ones, and hence possibly suitable for source apportionment in finished compost, were BaA/(BaA&BPE), FLT/(FLT&PYR), IPY/(IPY&BPE), 1,7-/(1,7-&2,6-)DmPHE and BaP/BPE. The remaining characteristic PAH ratios (ANT/(ANT&PHE), RET/(RET&CHR), (MFLT&PYR)/PYR, (MPHE&ANT)/PHE, ComPAH/Σ15PAH) changed inconsistently in three different composting studies (*16*) and are therefore not discussed here, but they are listed in the Supporting information Table 5 and 9.

PAH ratios differentiating between petrogenic and pyrogenic sources (FLT/(FLT&PYR), BaA/(BaA&CHR), IPY/(IPY&BPE), 1,7-/(1,7-&2,6-)DmPHE pointed, before and after conversion (where possible), towards a pyrogenic origin of PAH in compost (Supporting information, Table 5, for conversion see Supporting information, Text 4). There was no correlation between any of these ratios, before and after conversion, which could have been expected since they should all differentiate between the same sources.

It was not straightforward to distinguish between varying fuels as sources of PAH in compost. FLT/(FLT&PYR) ratios (median 0.6) were mostly in the grass/wood/coal combustion range, whereas for IPY/(IPY&BPE) about 46% of the samples had values below 0.5, indicating liquid fossil fuel combustion (Supporting information, Table 5). Conversion as suggested by Zhang (*8*), shifted FLT/(FLT&PYR) ratios more towards liquid fossil fuel combustion (about 0.13 units), which is reasonable for the PAH emission situation in Switzerland. However, IPY/(IPY&BPE) ratios were all above 0.5 after conversion, identifying grass/coal/wood combustion as the major PAH source.

None of the 1,7-/(1,7-&2,6-)DmPHE ratios in compost and digestate was <0.45, which would identify vehicle emission but most, and after conversion, all BaP/BPE ratios indicated traffic sources of PAH . Values below 0.45 for 1,7-/(1,7-&2,6-)DmPHE ratios were expected at least for composts containing material from highways in the input material (special case: sample no. 31 and no. 47). High COR concentrations did not correspond with low 1,7-/(1,7-&2,6-)DmPHE ratios. Furthermore, the value of COR as a marker for vehicle exhaust debated (*31*). In general normalisation of molecular markers might be more informative than comparison of absolute values. However ratios obtained by normalisation to the total sum (since no other parameters have been suggested, CPHE/Σ15PAH, CPYR/ Σ15PAH, PER/ Σ15PAH, COR/ Σ15PAH) were not stable and they did not change consistently during composting (*16*), hampering source apportionment.

Difficulties were also encountered if variables influencing characteristic PAH ratios were determined by the linear model. Results were contradictory and ratios identifying the same sources were influenced in opposite directions by the same variable (see Supporting information Table 9). Overall, the application of PAH ratios and related molecular markers, originally derived from, and determined for characterization of specific emission sources, to recipient matrices such as compost or soils for the purpose of source diagnosis of PAH seems to be of limited use. Correction factors such as those introduced recently by Zhang et al. (*8*) as well as factors accounting for processes during composting (*16*) may be conceptually correct, but appear too simplistic for successful application to our compost data.

Source apportionment by linear unmixing analysis

Since differences in compound patterns were observed between digestate and compost, only compost data were used for the following linear unmixing model (n=55, sample no. 56 excluded). Four characteristic PAH source profiles were identified in compost (Supporting information, Figure 6). Source A corresponded well with a profile from asphalt (*32*), before applying any conversion factors. This might be due to abrasion of roads surfaces induced by traffic that end up on plant material subsequently composted or of the composting plants pavement. However, asphalt is only one fraction of all particles/aerosols produced by traffic, such as tire rubbers, brakes, soot, etc., many of which also contain considerable amounts of PAH. Source B and D were similar to PAH profiles originating from green waste combustion (*33*) and traffic emission (*34*) after accounting for processes during composting (*16*). Traffic emission indeed seems to be a plausible source, whereas green waste combustion might be of minor importance. Source C did not match any of the emission profiles from the literature (Supporting Information, Table 4) even if processes during composting (*16*) and between emission and deposition on input material (*8*) were taken into account.

Synopsis and Recommendation

Overall, the data presented here provide a basis that allows for better balancing beneficial effects of compost application (e.g., soil improving and fertilizing effects, recycling of nutrients) against hazardous impacts. Even though PCB inputs to agricultural soils by compost application may outweigh inputs via aerial deposition and other recycling fertilizer application, loads were low and are even expected to decrease over the next decades due to the banning of PCB. Sources of PCB in compost and digestate are diffuse and aerial deposition is suggested to be the main input pathway. In contrast, PAH inputs to agricultural land by compost application can be considerable. Important sources may be emissions from traffic (asphalt and emissions from vehicles) as well as diffuse sources. Therefore, thorough studies to identify sources of PAH in compost are needed to lower PAH concentrations therein. The most realistic way of doing this seems to be a detailed investigation of input material at composting sites where PAH concentrations were high in repeated analyses, since indirect methods (characteristic PAH ratios, molecular markers, linear (unmixing) model) did not reveal clear results. Digestion and presswater need to be included in these evaluations since they were prone to even higher PAH concentrations.

Acknowledgements:

The Federal Office for the Environment and the Swiss Federal Office of Energy are acknowledged for financial support and Franziska Blum for the help with analyses. Thanks due to Henrik Kylin for reviewing this manuscript.

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5.2 Manuscript 1: Figures and Tables

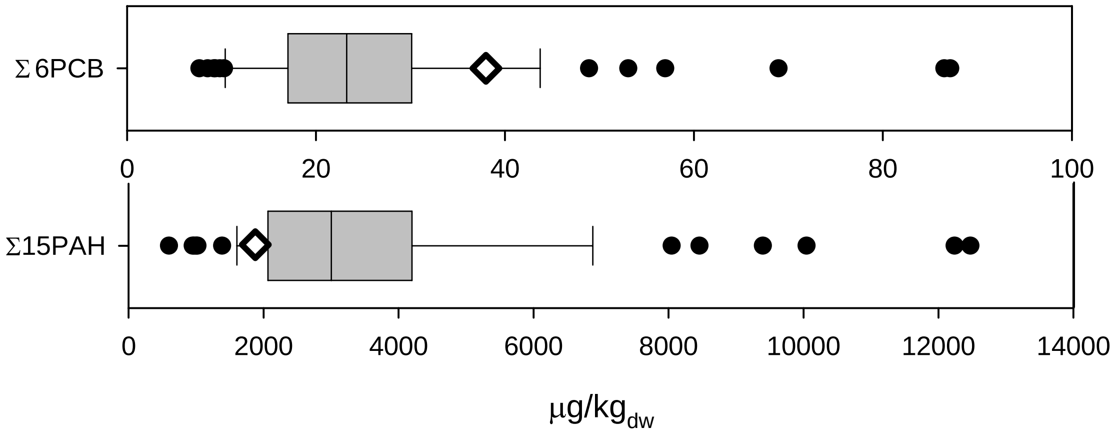

Figure 1: Concentrations of PCB (Sum of PCB 28, 52, 101, 138, 153, 180, Σ6PCB, n=68) and PAH (Sum of 16 PAH defined by US EPA except DBA, Σ15PAH, n=69) in compost and digestate (median; box: 25th and 75th percentile; lines with whiskers 10th and 90th percentile, dots: outliers, diamond: median literature value (*5*)).

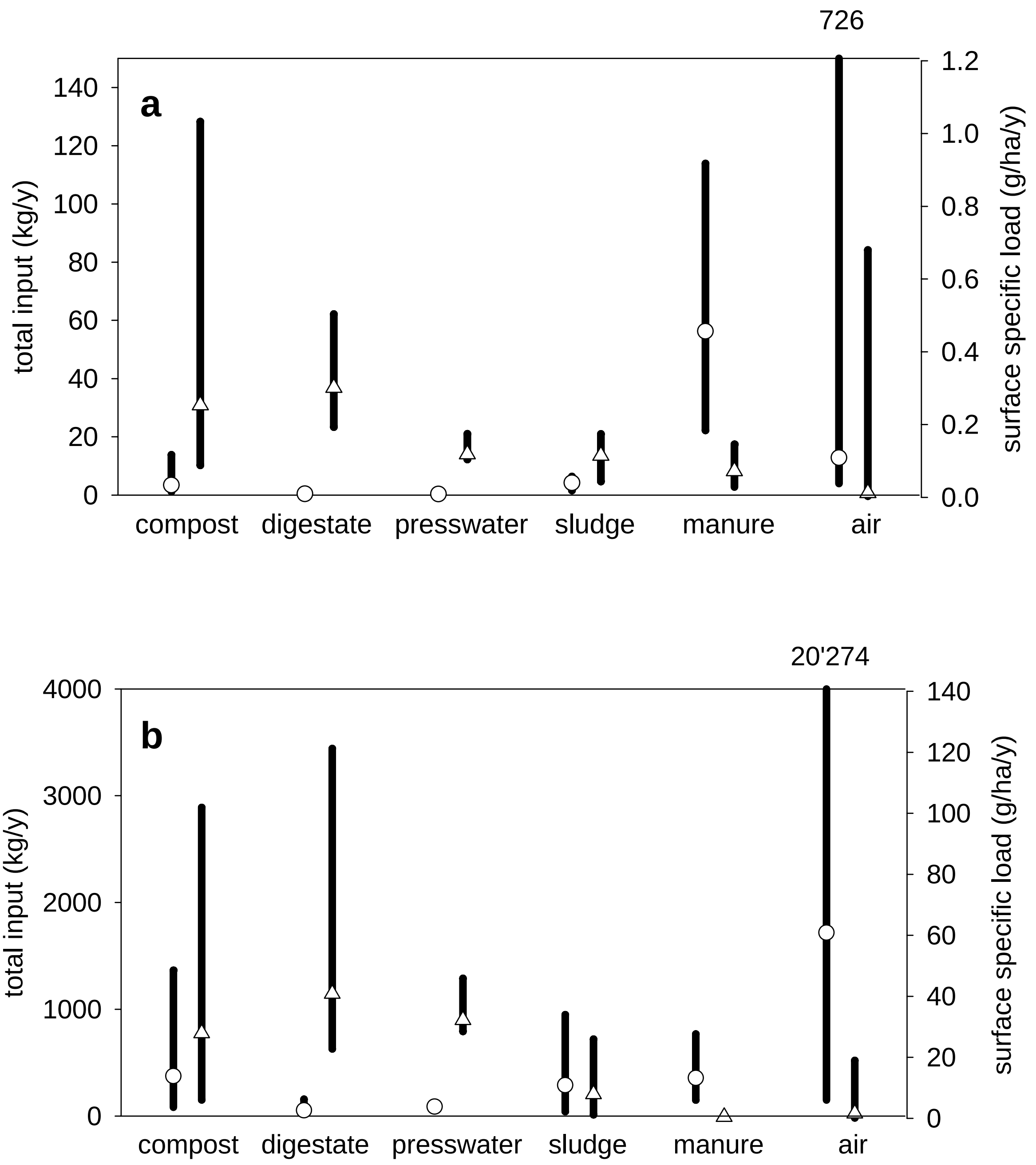

Figure 2: Mean annual loads of a) PCB (Sum of PCB 28, 52, 101, 118, 138, 153, 180, Σ7PCB) and b) PAH (Sum of 16 PAH defined by US EPA except DBA, Σ15PAH) from different sources: application of compost, digestate, presswater, sewage sludge (sludge), farmyard manure (manure) and atmospheric deposition (air) into agricultural soil. ○ average total loads to the Swiss agricultural area; △ average surface specific loads (input per hectare based on a standard fertilization). The bars represent minimum and maximum values. For assumptions/calculations see text.

Table 1: Significant factors influencing PCB and relative PCB concentrations in compost and digestate.

PCB concentrations	PCB 52	PCB 95	PCB 101	PCB 118	PCB 132	PCB 138	PCB 149	PCB 153	PCB 174	PCB 180	Σ11PCB
Origin of input materials (urban/rural)	++	++	++	++	++	++	++	++	++	++	++
Composition of input materials (green waste with/without org. kitchen waste)	++	+							+		
Duration of the treatment process	-	-							--		
r^2 of the model[a]	0.25	0.34	0.32	0.31	0.30	0.30	0.25	0.20	0.23	0.12	0.30
Individual PCB/Σ10PCB											
Particle size (>20 mm/≤20mm)	++	++			--			--		--	na
Organic matter content			++		--		+	--		--	na
Maturity (NO_3^-/NH_4^+)				--	++		++			++	na
r^2 of the model[a]	0.16	0.15	0.31	0.14	0.08	0.02	0.31	0.24	0.11	0.35	na

++ first term named/with increasing continuous coefficient: significantly higher concentration on 95% level, + first term named/with increasing continuous coefficient: significantly higher concentration on 90% level

-- first term named/with increasing continuous coefficient: significantly lower concentration on 95% level, - first term named/with increasing continuous coefficient: significantly lower concentration on 90% level

a) r^2 is the fraction of explained variation by the model. It varies between 0 and 1 with the higher the value the more successful is the linear model in explaining the variation in the responses

Table 2: Significant factors influencing PAH and relative PAH concentration in compost and digestate.

PAH concentration	NAP	ACY	ACE	FLU	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IPY	BPE	Σ15PAH	CPHE	RET	PER	CPYR	COR
Treatment process (anaerobic/aerobic)	++	++	++	++	+	++	++	++	++	++						++	++				
Season of input material collection (autumn/ remaining year)	--	--	-	-		--	-	--	--	--	--	--	--	--	-	--	--		--		
Season of input material collection ((summer/ spring)/remaining year)			-					++	++	++	++	++	++	++		++					
Particle size (>20 mm/≤20mm)		++				+		++	++	++	++	++	++	++	++	++		++	++	++	++
Maturity (NO_3^-/NH_4^+)			--	--	--	--	--	--	-				--			--	--		-		
r^2 of the model[a]	0.34	0.33	0.44	0.40	0.53	0.43	0.45	0.50	0.23	0.19	0.15	0.16	0.21	0.18	0.13	0.40	0.42	0.17	0.25	0.19	0.16
Individual PAH/Σ20PAH																					
Treatment process (anaerobic/aerobic)			++	++	++	++		++	--	--	--	--	--	--	--	na		--		--	--
Maturity (NO_3^-/NH_4^+)	++	++	--	--	--	--	--	--	++	++	++	++	++	++	++	na	--		++	++	++
r^2 of the model[a]	0.17	0.19	0.38	0.38	0.56	0.45	0.36	0.43	0.23	0.53	0.45	0.34	0.31	0.30	0.56	na	0.27	0.08	0.21	0.40	0.55

++ first term named/with increasing continuous coefficient: significantly higher concentration on 95% level, + first term named/with increasing continuous coefficient: significantly higher concentration on 90% level

-- first term named/with increasing continuous coefficient: significantly lower concentration on 95% level, - first term named/with increasing continuous coefficient: significantly lower concentration on 90% level

a) r^2 is the fraction of explained variation by the model. It varies between 0 and 1 with the higher the value the more successful is the linear model in explaining the variation in the responses

5.3 Manuscript 1: Supporting Information

Text 1

The composting and digestion process

On composting plants, delivered green and kitchen waste is chopped and mixed with wooden material to achieve an adequate porosity of the substrate for an aerobic degradation process. Different systems for composting are employed: open triangle and table windrows, aerated boxes and trenches etc. Independently of the system, the substrate is regularly turned or aerated during the process to guarantee sufficient oxygen supply and consequently an aerobic decomposition. If necessary, water is added to achieve efficient degradation. The composting process can be divided in four stages according to the temperature evolution: mesophilic, thermophilic, cooling down and maturation (*1*). It usually lasts between five and eight weeks. Finished compost is screened according to requirements of the application (*2*).

Different systems are employed for digestion (i.e., anaerobic treatment coupled with biogas production): thermophilic, mesophilic, solid and liquid digestion. The most common system for the treatment of organic kitchen and green waste is thermophilic solid digestion (*3*). In this process, input materials are chopped and ferrous impurities removed. They are mixed with recycled presswater and fresh water to achieve a pumpable mixture, which is then inoculated with digestate. This substrate is pumped to a fermenter, where it is continuously forwarded by an archimedic spiral. Thermophilic digestion lasts about two weeks at a temperature of approximately 55 °C. The output material undergoes solid-liquid separation. The solid fraction is often submitted to aerobic treatment similar techniques as for composting, whereas presswater is stored in a tank until application to agricultural fields.

Text 2

Relevant data for calculation of input loads of organic pollutants to agricultural soil in Switzerland

The relevant data for determination of the total annual loads in Switzerland was: (i) for aerial deposition: the total agricultural surface of 2003 (1'067'055 ha; (*4*)) and organic pollutant deposition rates obtained from the literature (Supporting information, Table 1), (ii) for farmyard manure: the total amount of cattle and swine manure produced in 2000 (2'264'776 t_{dw}, determined on the basis of (*5*)) and organic pollutant concentrations therein (Supporting information, Table 1, where available Swiss data was used), (iii) for sewage sludge: 21% of the total production of stabilized sewage sludge applied to agricultural soils in 2002 (199'500 t_{dw}; (*6*)) and organic pollutant concentrations in sewage sludge (Supporting information, Table 1 where available Swiss data was used), and (iv) for compost: 88% (portion treated aerobically (*3*)) of the total amount of organic waste processed in 2004 (770'000 t wet weight (ww) (*7*)), taking into account a mass loss of 40% during treatment (*3*), a dry matter content of compost of 50%, percentage of compost applied to agricultural soil of 65% (*3*) and organic pollutant concentrations as in this study, (v) for digestate and presswater: the total amount of aerobically treated organic waste in 2004 (12% (*3*) of 770'000 t ww (*7*)) assuming a mass loss during digestion based on dw of 10% (*8*) and during subsequent aerobic stabilisation of 30%, an output ratio of digestate to presswater of 57% to 43%1.326 (ww) (*8*), percentage of digestate and presswater applied to agricultural soil of 100% and mean organic pollutant concentrations as presented in this study.

Comparison of surface specific load per year was based on a standard fertilization of 70 kg P_2O_5. This corresponded to an application rate for farmyard manure of 2.9 t_{dw} (based on (*5*) and (*9*)), for sewage sludge of 1.1 t_{dw}/ha (P_2O_5 content of sewage sludge: 61 g/kg_{dw} (*10*)) for a compost of 10.1 t_{dw}/ha (median P_2O_5 content in this study 6.9 g/kg_{dw}, Supporting information, Table 2), for digestate of 9.7 t_{dw}/ha (median P_2O_5 content in this study 7.2 g/kg_{dw}, Supporting information, Table 2), and for presswater of 4.9 t_{dw}/ha (median P_2O_5 content in this study 14.2 g/kg_{dw}, Supporting information, Table 2, which is about 40m^3, if assuming dry weight content of presswater of 13% and density of 1.05) . For PCB and PAH deposition rates, and concentrations in sludge, manure, and compost, see above.

The time period needed to reach Swiss guide or trigger values for PCB and PAH in soils was calculated assuming aerial deposition and compost applications as their sole input sources. PCB and PAH were considered non-degradable and non-mobile. Initial concentrations in background soils were taken from the literature (Supporting information, Table 1). Soil depth considered was 20 cm, with a density of 1.5 g/cm^3 and dry matter content of 75%.

Text 3

Linear model to determine relevant variables influencing organic pollutant concentrations in compost and digestate

The variables hypothesized to influence organic pollutant concentrations in compost and digestate were assessed with a linear model (*11,12*). These were: treatment process (anaerobic/aerobic), composition of input materials (green waste with/without org. kitchen waste), origin of input material (urban/rural), season of input material collection (spring&summer/autumn/winter), particle size of the samples (two classes: (i) coarse-grained: final product sieved to >20mm or unsieved and (ii) fine-grained: final product sieved to ≤20mm), organic matter and impurity content, maturity (expressed as $NO_3^-/(NO_3^- + NH_4^+)$) and duration of the treatment process (in days). Due to weak correlation of 'maturity' and 'duration of the treatment process' ($r^2 = 0.26$, $p < 0.001$), both variables were considered in the initial model. To stabilize variances, data were log-transformed (except for fractions and ratios). The log-transformed specific loads, denoted as $\log(Y_i^{(j)})$ (*j*th organic pollutant's log-concentration in the *i*th compost sample) were modelled as follows:

$$\log(Y_i^{(j)}) = \mu + \alpha_k^{(j)} + \beta_l^{(j)} + \ldots + \gamma^{(j)}x_{1i} + \delta^{(j)}x_{2i} + \ldots + E_i^{(j)}$$

where μ was the global mean, $\alpha_k^{(j)}$; $\beta_l^{(j)}$,… were effects associated to the *k*th, *l*th,… variable (i.e. treatment process, region of input material collection, input material composition, season of input material collection, particle size), $\gamma^{(j)}$, $\delta^{(j)}$, ..., were coefficients related to continuous factors (i.e. duration of the process, maturity, organic matter and impurity content, with x_{1i} , x_{2i} etc.). $E_i^{(j)}$ was a normal random error with mean zero associated to all coefficients, accounting for measurement error and not modelled variability (for discussion about normality see Kupper et al. 2004 (*13*)). As the model is not uniquely defined, we impose that the effects of each variable sum to zero. For all response variables assessed (total concentrations, relative contributions of the compounds/congeners to the total sum, enantiomeric fractions, characteristic ratios), we estimated the coefficients ($\alpha^{(j)}$ to $\gamma^{(j)}$) with ordinary least squares. After initial determination of all coefficients, variables explaining most of the variations were kept in a final model and tested for significance (level of significance 0.05). R^2 represents the fraction of variation explained by the model and is defined by one minus the sum of squared deviations about the fitted model divided by the sum of squared deviations about the mean. Note that the design in our study is not balanced, i.e. we do not have the same number of observations for all variables. For consequences see (*13*).

Text 4

Conversion of characteristic PAH to ratios in input material

Since some ratios changed inconsistently during composting in the field (*8*), only stable PAH ratios were selected. To account for altered characteristic PAH ratios between emission and input material of compost, rectification factor as defined by Zhang et al. (*14*) for air particles were applied. Ratios determined in compost of the form x/(x+y) (i.e. FLT/(FLT&PYR), BaA(BaA&CHR), (IPY/(IYP&BPE)) were converted to sources ratios as follows:

$$r_{source=}\ r_{input\ material}/(RF_{Zhang}+r_{input\ material}-RF_{Zhang}*r_{input\ material})$$

where r_{source} is the characteristic PAH ratio at the emission source, $r_{input\ material}$ is the PAH ratio in compost input material and RF_{Zhang} is the rectification factor (for ANT/PHE 2.16, for FLT/PYR 1.68, for BaA/CHR 0.59, for IPY/BPE 0.92). BaP/BPE ratios were converted by deviding the $BaP/BPE_{input\ material}$ by $RF_{ZhangBaP/BPE}$ (0.60).

Text 5

Linear unmixing analysis for source apportionment

A linear mixing model was fitted to PAH concentrations as an attempt to identify emission sources. This model is based on the idea that there are a few *(p)* sources, each of which releases PAH in constant proportions ($C_k^{(j)}$) giving rise to the source's 'profile'. If not altered during transport to compost input material and during composting, the measurements $Y_i^{(j)}$ will consist, up to random errors $E_i^{(j)}$, of a linear mixture of these profiles:

$$Y_i^{(j)} = \Sigma_{k=1}^{p}\ S_i^{(k)}\,C_k^{(j)} + E_i^{(j)}$$

If available, source profiles obtained from the literature can be used, and the model may be fitted by adjusting the 'scores' $S_i^{(k)}$ to the data. Such methods were described under the keyword of a 'chemical mass balance model' in chemometrics. In our case, we preferred to estimate the profiles of sources that contributed to our compost samples from the data, (i) since the main sources were not clear beforehand, (ii) there were many candidates in the literature (Supporting information, Table 4), and (iii) the proportions may change between emissions and measurement, see below. Suitable procedures to identify source profiles and scores at the same time can be called 'linear unmixing' methods.

We applied two approaches here to match the compost source profiles with emission profiles: First, we fitted a model based on a multivariate lognormal distribution for the scores, introduced by Wolbers and Stahel (*15*). Second, we used some ad-hoc methods based on the fact that all quantities in the foregoing equation, except for the error term, must be non-negative, and on graphical aids. The results of the second approach turned out to be more easily interpretable and are therefore reported here.

The resulting source profiles were then compared to values reported in the literature for emissions of various potential sources. Note that the proportions may change from emissions to deposition on input material for compost (*14*), and again during the composting process (*8*). Adjusting factors derived from the two papers can be applied to obtain the expected PAH source profile in mature compost if some of these sources of pollution were among the main contributors to the contamination of our compost samples. The literature profiles were each used (i) uncorrected, (ii) corrected for the composting process using the factors derived from Brändli et al. (*8*), and (iii) corrected by the product of Brändli's and Zhang's (*14*) factors to adjust for both effects. Note, however, that these factors give rough figures for a general picture and should not be expected to hold for a particular situation.

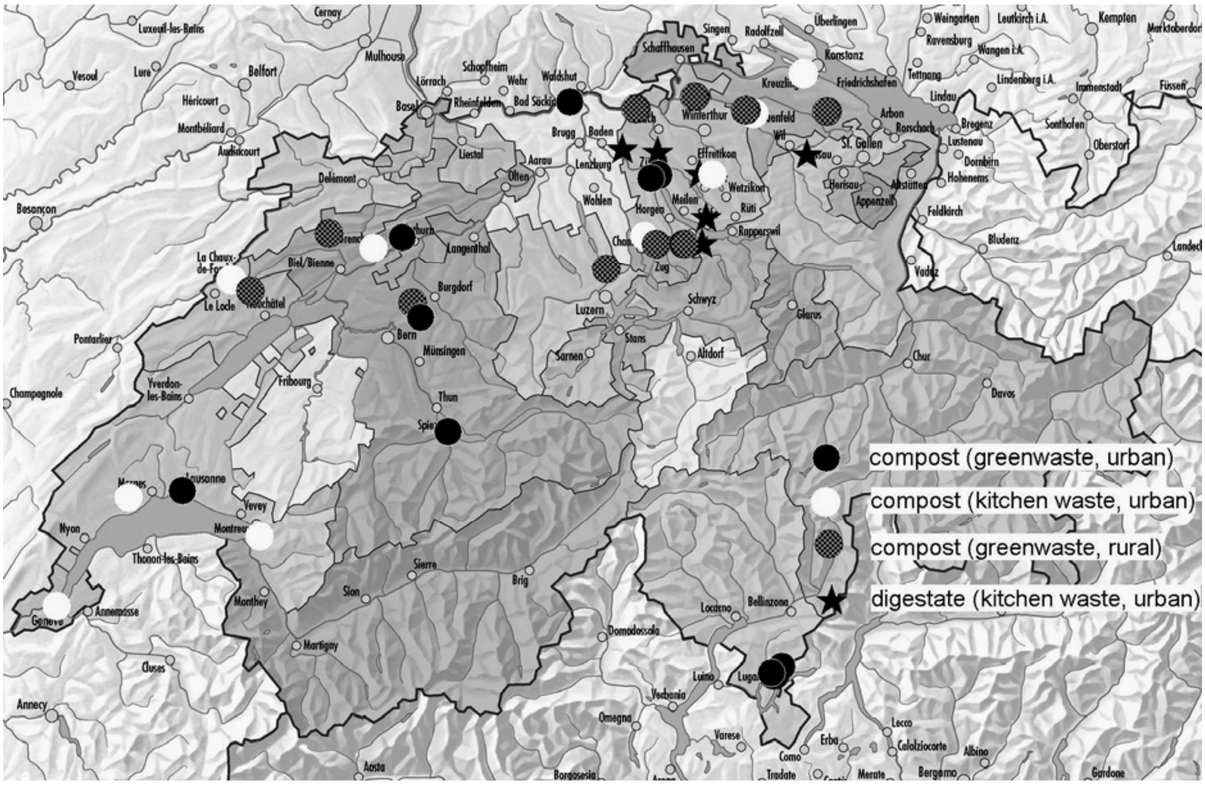

Figure 1: Sampling locations (n=39) of compost and digestate in Switzerland, some plants were sampled once, others three times to account for different seasons. For further information on individual plants, see Table 1, status May 2006

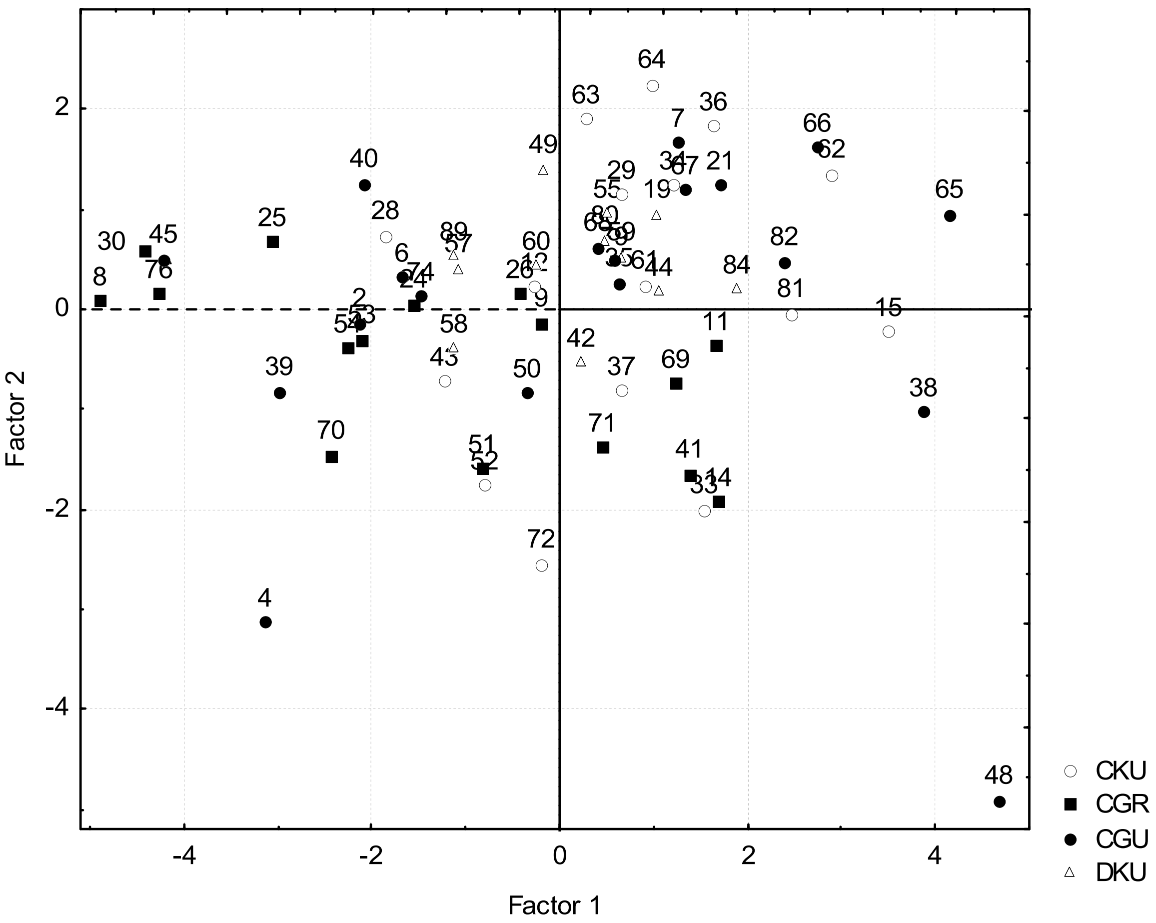

Figure 2: Factor 1 and 2 of the principal component analysis of the ratios of individual PCB (PCB 52, 95, 101, 118, 132, 138, 149, 153, 174, 180) to the total sum of 10PCB in Swiss compost and digestate (n=63). Number = sample number specified in Table 1, CKU: compost containing organic kitchen and green waste in the input material originating from urban areas, CGR: green waste compost originating from rural areas, CGU: green waste compost originating from urban areas, DKU: digestate derived from urban green and organic kitchen waste.

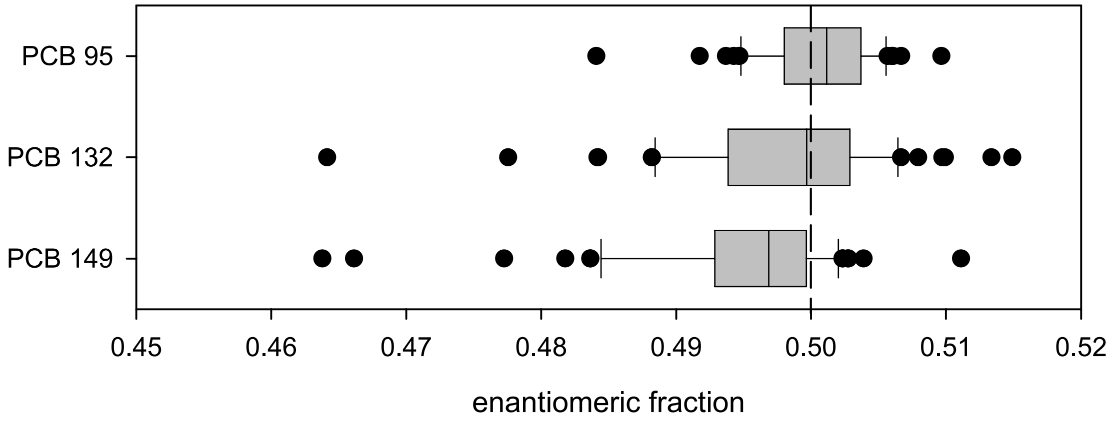

Figure 3: Enantiomeric fractions (EFs) of three antropisomeric PCB in Swiss compost and digestate (n=68).

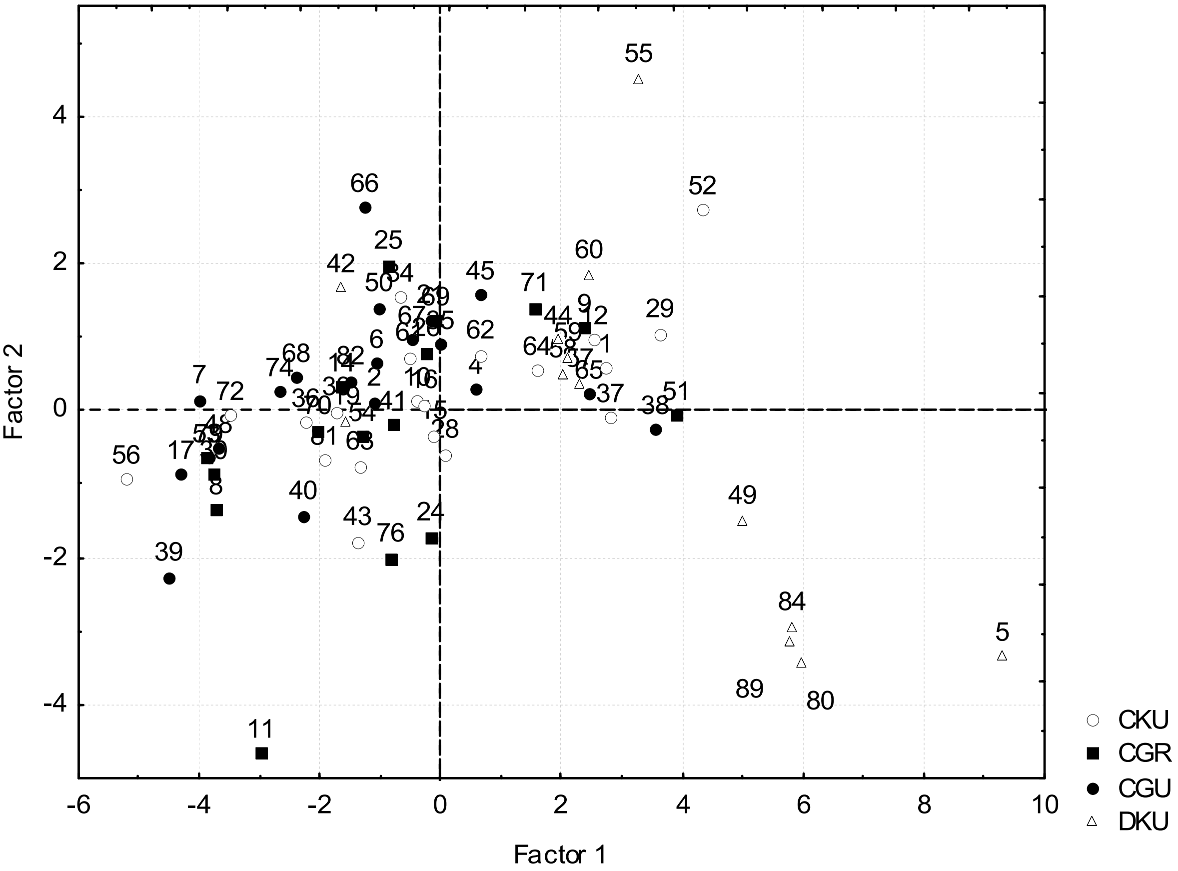

Figure 4: Factor 1 and 2 of the principal component analysis of the ratios of single PAH compounds to the total sum (Sum of 16 EPA PAH except dibenz[*a,h*]anthracene) in Swiss compost and digestate (n=69). Number = sample number specified in Table 1, CKU: compost containing organic kitchen and green waste in the input material originating from urban areas, CGR: green waste compost originating from rural areas, CGU: green waste compost originating from urban areas, DKU: digestate derived from urban green and organic kitchen waste.

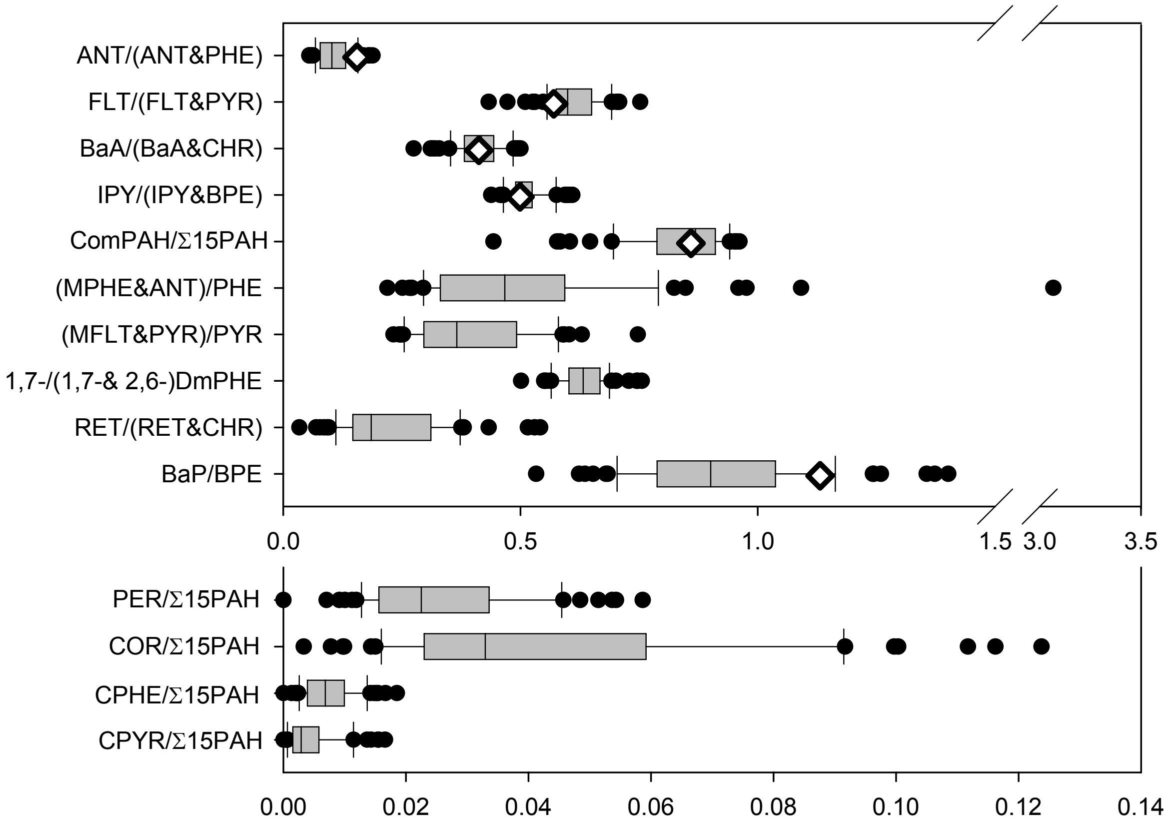

Figure 5: Characteristic PAH ratios in Swiss compost and digestate (n=69, line: median; box: 25th and 75th percentile; lines with whiskers 10th and 90th percentile, dots: outliers, diamond: median literature value, ANT: anthracene, PHE: phenanthrene, fluoranthene (FLT), pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), indeno[*1,2,3-cd*]pyrene (IPY), benzo[*ghi*]perylene (BPE), ComPAH: sum of FLT, PYR, BaA, CHR, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene (not included here), Σ15PAH: sum of 16 EPA PAH except dibenzo[*a,h*]anthracene, MPHE&ANT: methylated phenanthrene and anthracene, MFLT&PYR: methylated fluoranthene and pyrene, 1,7-/(1,7-&2,6-DmPHE): 1,7-/(1,7-& 2,6-dimethylphenanthrene), RET: retene, benzo[*a*]pyrene (BaP), benzo[*ghi*]perylene (BPE), PER: perylene, COR: coronene COR, CPHE: 4-H cyclopenta[*def*]PHE, CPYR: cyclopenta[*cd*]PYR.

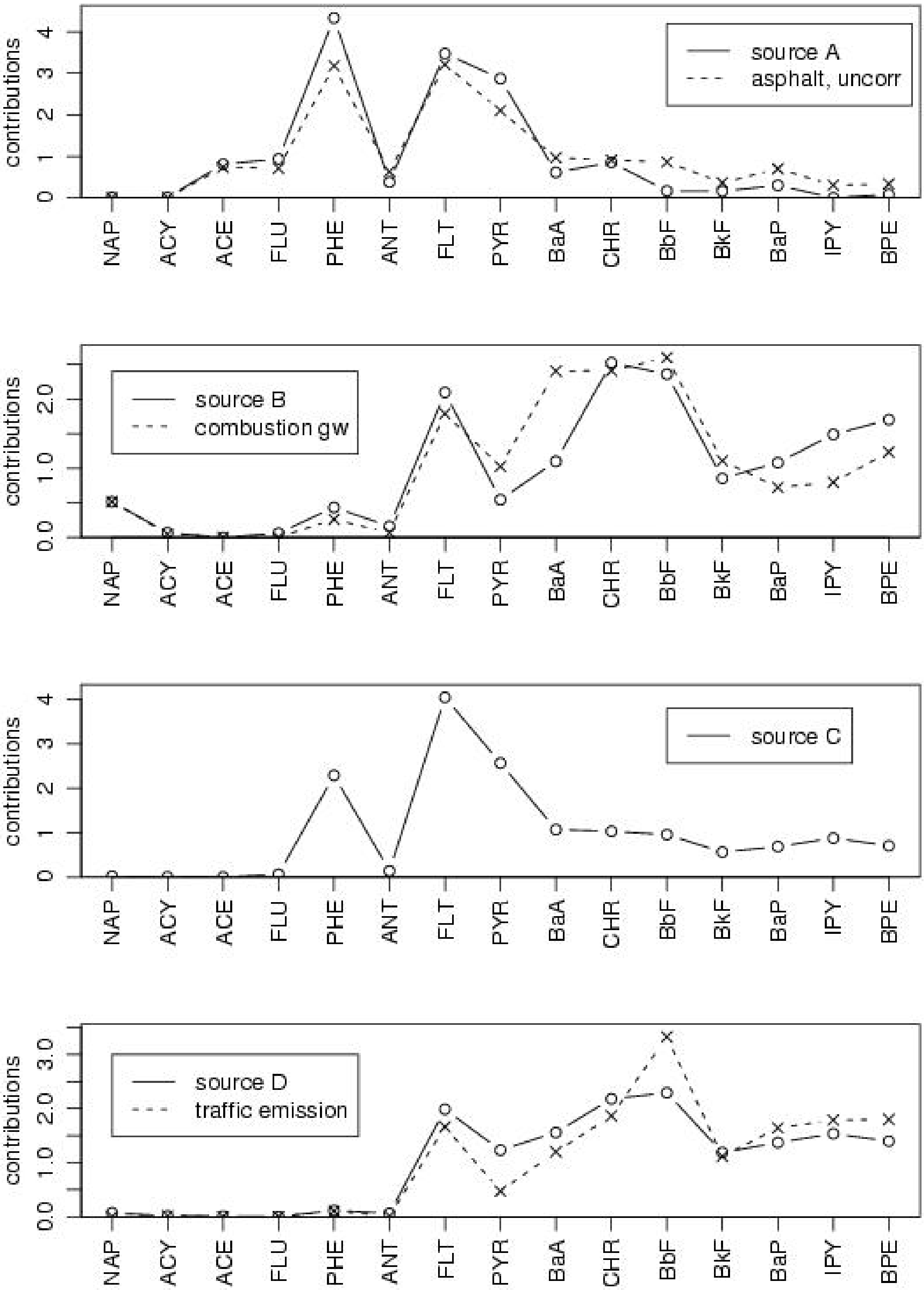

Figure 6: characteristic PAH source profiles in compost (n=55), including matching source's profiles. Combustion gw and traffic emissions are corrected for processes during composting (uncorr: uncorrected for environmental processes and alteration during composting, gw: green waste).

Table 1: Sample description, PCB, PAH, heavy metal and nutrient contents of compost, digestate and presswater samples in Switzerland

Sample No.	1	2	3[k]	4	5	6	7	8	9	10
Product[a]	Com	Com	Dig	Com	Dig	Com	Com	Com	Com	Com
Plant code and number[b]	CKU01	CGU01	DGR01	CGU10	DKU01	CGU03	CGU03	CGR01	CGR12	CKU02
Input material[c]	kw, gw, iw	gw, iw	gw	gw, iw	kw, gw, iw	gw	gw	gw	gw	kw, gw
Origin of input material[d]	urban	urban	rural	urban	urban	urban	urban	rural	rural	urban
Season[e]	winter	winter	winter	winter	winter	winter	summer	winter	summer	winter
Plant type[f]	twl	twl	mcd	tbw	tad	twh	twh	twl	ab	ab
Process duration (days)[h]	53	53	na	118	42	35	231	56	28	77
Water content [% ww]	50	46	37	46	49	54	42	48	45	45
Org matter content [% dw]	62	36	58	30	46	55	37	36	47	57
Impurity content [% dw]	0.15	0.076	0.047	0.065	0.32	0.25	0.41	0.30	0.18	0.062
Maturity (NO_3^-/NH_4^+)	nd[i]	15	0.43	10	nd[i]	nd[i]	2.2	5.9	nd[i]	nd[i]
Particle size [mm][j]	<40	<10	not	<20	<40	<40	<20	<25	not	<20
PCB (µg/kg$_{dw}$)										
PCB 28	nd	nd	nd	7.9	nd	nd	nd	nd	nd	nd
PCB 52	0.97	2.0	0.66	8.8	1.9	3.4	6.2	2.2	3.1	2.4
PCB 95	na	2.2	0.96	7.7	na	4.5	9.9	6.1	4.2	na
PCB 101	2.8	3.1	1.2	8.5	4.4	6.0	13	7.7	5.5	6.1
PCB 118	1.6	2.3	1.0	4.8	3.6	4.9	9.2	3.6	3.8	5.9
PCB 132	na	2.2	1.3	5.4	na	4.9	8.0	7.0	3.7	na
PCB 138	4.5	4.7	2.5	11	7.8	8.6	13	12	4.7	7.8
PCB 149	na	3.8	2.1	12	na	6.3	11	11	4.8	na
PCB 153	3.3	5.4	2.9	19	5.2	10	17	16	7.6	6.7
PCB 174	na	1.3	0.85	4.0	na	2.4	3.1	3.9	2.1	na
PCB 180	1.5	2.8	1.6	14	2.5	6.2	7.5	12	4.4	3.7
EF PCB 95	0.50	0.50	0.50	0.50	0.51	0.50	0.50	0.51	0.50	0.49
EF PCB 132	0.50	0.50	0.50	0.50	0.50	0.51	0.50	0.50	0.50	0.50
EF PCB 149	0.49	0.50	0.50	0.49	0.49	0.50	0.50	0.50	0.49	0.48
PAH (µg/kg$_{dw}$)										
NAP	19	16	27	32	120	27	12	42	25	48
ACY	3.0	2.3	3.3	5.7	11	3.8	2.7	4.9	2.3	14
ACE	17	6.8	36	50	740	36	4.5	7.9	38	17
FLU	43	13	33	61	1000	18	4.8	12	80	46
PHE	350	160	210	340	4200	150	62	150	770	910
ANT	45	18	31	64	700	29	10	21	45	140
FLT	620	410	410	760	2400	710	360	430	900	1700
PYR	260	170	300	600	1400	380	230	220	600	1200
BaA	130	130	120	270	350	240	250	240	240	650
CHR	180	220	170	360	360	340	460	380	330	680
BbF	130	210	230	370	240	340	320	440	240	760
BkF	69	93	160	210	130	190	150	230	130	530
BaP	83	100	200	190	200	190	160	220	170	590
IPY	96	130	190	190	140	190	260	230	200	600
BPE	110	140	200	220	170	200	230	240	190	530
CPHE	29	13	22	45	na	30	6.0	9.7	54	64
RET	89	170	26	210	56	93	71	65	190	150
CPYR	6.7	5.0	5.1	6.3	na	6.6	8.6	5.3	9.6	33
PER	32	33	68	63	na	64	54	70	55	200
COR	62	67	89	110	41	90	99	110	76	210
(MPHE/ANT)/PHE [-]	0.37	0.56	0.55	0.96	0.25	0.98	0.82	0.54	0.33	0.36
(MFLT/PYR)/PYR [-]	0.35	0.50	0.37	0.39	0.31	0.42	0.58	0.63	0.30	0.25
1,7-/(1,7-&2,6-DmPHE) [-]	0.66	0.68	0.62	0.60	0.50	0.65	0.65	0.68	0.64	0.64

Heavy metals (mg/kg$_{dw}$)										
Cd	0.13	0.13	0.34	0.025	nd	0.081	0.1	0.021	0.34	0.53
Co	2.2	3.9	3.2	3.6	3.2	3.2	4.4	3.8	5.1	3.6
Cr	11	16	22	23	14	13	21	17	25	15
Cu	31	47	64	86	35	43	60	37	71	55
Ni	9.5	14	16	12	11	12	17	14	21	11
Pb	19	33	280	30	22	59	66	26	54	100
Zn	76	110	160	150	89	130	190	120	190	250
nutrients (g/kg$_{dw}$)										
N	15	14	14	9.2	11	12	19	15	14	19
P	1.8	2.3	6.7	3.9	2.6	1.7	3.3	2.3	2.5	2.8
K	6.9	8.7	16	6.4	7.7	5.7	14	9.9	9.1	14
Mg	4.1	4.9	7.0	5.0	6.5	5.8	8.8	6.9	4.0	4.1
Ca	68	82	47	92	65	50	64	64	68	41
Further elements (g/kg$_{dw}$)										
Fe	4.5	8.9	7.0	11.0	7.6	7.1	10	9.2	11	8.2
Mn	0.31	0.44	0.47	0.34	0.40	0.34	0.44	0.69	0.43	0.37
Na	0.64	0.55	1.1	0.47	1.60	0.34	0.58	0.61	0.59	0.71
Ancillary data										
pH	8.3	8.4	8.5	8.2	8.3	8.3	8.1	8.2	7.8	8.2
Conductivity (μS/cm)	1400	1800	2000	1800	3000	920	3600	2600	1800	2100

a) Com: compost, Dig: digestate, all digestate samples were submitted to subsequent aerobic treatment except for samples 80 and 89, PW: presswater
b) plant code: C: compost, K: organic kitchen waste and green waste as input materials, G: pure green waste compost, U: urban area of input material collection, R: rural area of input material collection, SP: special compost if not compatible with factors described in the section 'experimental design'
c) kw: kitchen waste, gw: green waste, iw: industrial waste including paper sludge, coffee ground, tea leaves, residues from potato chips production, biodegradable plastics, edible oil, cacao
d) characterisation of the area where the input material was collected
e) season of input material collection
f) plant type: ab: aerated boxes, atc: aerated trench composting in sheds, bwc: combined box and windrow composting, fec: field-edge composting, mcd: mesophilic aerobic co-digestion, tad: thermophilic aerobic digestion, tbw: table windrows, twh: triangle windrows higher than 2 meters, twl: triangle windrows lower than 2 meters, vc: vermicomposting
g) contains small amounts of digested material in the compost input material
h) duration of the treatment process in days
i) NO_3^- nd
j) sieve-width in mm, not: unsieved
k) this product contains important amounts of feedstock materials other than organic kitchen waste or green waste (e.g. farmyard manure)
l) NH_4^+ nd
m) input material from highway areas
n) only compost derived from green and kitchen waste collected in rural areas

NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[1,2,3-*cd*]pyrene, BPE: benzo[*ghi*]perylene, CPHE: 4-H-cyclopenta[*def*]PHE, RET: retene, CPYR: cylopenta[*cd*]PYR, COR: coronene, (MPHE&ANT)/PHE: ratio of methylPHE and –ANT to PHE, (MFLT&PYR)/PYR: ratio of methylFLT and -PYR to PYR, 1,7-/(1,7-&2,6-)DmPHE: the ratio of 1,7- to 1,7- and 2,6-dimethylPHE, nd: not detected, na: not available, EF enantiomeric fraction, ww: wet weight, dw: dry weight

Table 1 (cont.): Sample description, PCB, PAH, heavy metal and nutrient contents of compost, digestate and presswater samples in Switzerland

Sample No.	11	12	13[k]	14	15	16	17	18[k]	19	21
Product[a]	Com	Com	Com	Com	Com	Com	Com	Com	Dig	Com
Plant code and number[b]	CGR06	CKU05	CGR05	CGR02	CKU03	CKU04	CGU04	CKU05	DKU02	CGU6
Input material[c]	gw	kw, gw, iw	gw, iw	gw	kw, gw	kw, gw	gw	kw, gw, iw	kw, gw	gw
Origin of input material[d]	rural	urban	rural	rural	urban	urban	urban	urban	urban	rural
Season[e]	winter	autumn	winter	winter	summer	autumn	autumn	winter	winter	winter
Plant type[f]	fec	bwc	fec	twh	atc[g]	twh	tbw	bwc	tad	twh
Process duration (days)[h]	98	136	231	83	63	210	127	112	105	87
Water content [% ww]	58	59	42	49	27	47	53	43	45	36
Org matter content [% dw]	53	45	22	40	32	41	40	53	42	37
Impurity content [% dw]	0.43	0.19	0.071	0.18	0.14	0.39	0.19	0.35	na	0.27
Maturity (NO_3^-/NH_4^+)	15	0.31	67	nd[i]	0.0079	2.5	1.1	0.097	35	0.16
Particle size [mm][j]	not	<20	not	<20	<10	<10	<20	<40	<10	<12
PCB (μg/kg$_{dw}$)										
PCB 28	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB 52	2.1	2.0	1.6	5.1	2.8	2.4	1.8	1.1	4.6	3.7
PCB 95	1.9	2.8	2.1	3.1	4.3	na	na	1.7	7.3	4.7
PCB 101	2.7	3.8	3.7	3.9	6.2	6.3	5.2	2.2	9.9	6.0
PCB 118	3.6	3.1	3.7	3.1	13	6.0	4.6	1.8	8.7	5.0
PCB 132	1.9	2.7	2.9	2.1	3.1	na	na	1.6	6.3	3.9
PCB 138	3.2	3.5	4.8	4.4	8.0	8.3	6.1	3.1	8.6	6.6
PCB 149	2.2	3.5	3.2	3.5	4.8	na	na	2.2	8.6	5.2
PCB 153	3.9	5.3	5.1	5.4	7.7	6.3	5.1	3.2	13	7.6
PCB 174	0.80	1.3	1.2	1.2	1.3	na	na	0.81	2.1	1.3
PCB 180	1.7	3.0	3.2	2.8	3.6	2.7	2.1	2.1	6.9	3.8
EF PCB 95	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.51
EF PCB 132	0.51	0.49	0.5	0.5	0.49	0.50	0.50	0.50	0.49	0.49
EF PCB 149	0.48	0.50	0.5	0.50	0.50	0.48	0.49	0.50	0.50	0.50
PAH (μg/kg$_{dw}$)										
NAP	91	21	16	22	27	19	15	14	49	14
ACY	2.1	3.2	2.3	3.9	5.1	3.0	2.4	2.5	6.0	2.5
ACE	1.1	33	1.7	9.0	86	9.7	4.4	28	20	15
FLU	4.2	50	4.1	11	78	22	9.3	21	28	32
PHE	69	390	62	160	650	140	130	290	340	300
ANT	5.9	29	10	28	110	21	16	27	44	25
FLT	170	600	170	510	990	420	380	670	760	610
PYR	54	380	96	420	660	190	190	530	480	410
BaA	54	150	85	230	470	130	190	180	350	230
CHR	120	240	120	270	470	220	390	250	540	360
BbF	120	150	110	270	530	180	410	160	480	250
BkF	64	74	67	170	320	52	220	81	240	160
BaP	70	77	84	220	420	110	190	91	250	130
IPY	110	120	99	220	330	110	310	120	320	190
BPE	100	120	92	210	300	130	270	120	290	170
CPHE	7.0	23	6.7	18	54	18	11	20	16	17
RET	28	130	13	67	76	81	150	270	100	200
CPYR	9.3	14	8.9	9.0	4.1	5.4	7.6	11	6.4	7.3
PER	28	32	30	69	120	44	60	34	92	45
COR	45	77	51	90	110	40	110	84	130	76
(MPHE/ANT)/PHE [-]	0.35	0.38	0.42	0.66	0.59	0.79	0.48	0.50	0.39	0.58
(MFLT/PYR)/PYR [-]	0.57	0.30	0.49	0.32	0.49	0.57	0.48	0.24	0.39	0.38
1,7-/(1,7-&2,6-DmPHE) [-]	0.70	0.61	0.65	0.69	0.6	0.68	0.75	0.63	0.65	0.68

Heavy metals (mg/kg$_{dw}$)										
Cd	0.12	0.032	0.094	0.20	0.21	0.22	0.16	nd	0.18	0.064
Co	3.6	3.5	5.5	4.6	5.5	4.9	4.3	2.2	3.6	4.6
Cr	16	21	17	16	29	25	18	12	25	18
Cu	40	49	27	34	72	91	58	72	160	53
Ni	13	15	21	17	27	22	16	7.8	17	15
Pb	30	27	30	71	70	49	36	19	48	37
Zn	140	140	100	170	180	170	150	120	210	210
nutrients (g/kg$_{dw}$)										
N	22	18	9.4	9.5	16	17	16	16	19	16
P	3.3	3.5	3.0	1.7	3.4	2.9	2.7	2.5	3.6	3.2
K	13	12	7.1	5.1	9.9	11	11	7.3	13	13
Mg	6.9	6.6	6.6	6.4	4.7	5.6	6.2	4.8	9.4	5.8
Ca	64	59	51	60	51	65	66	43	59	69
Further elements (g/kg$_{dw}$)										
Fe	9.9	9.2	13	11	16	11	9.1	5.8	10	12
Mn	0.46	0.41	0.65	0.48	0.43	0.40	0.46	0.32	0.50	0.45
Na	0.74	1.6	0.73	0.31	0.61	1.0	0.62	1.6	1.40	0.70
Ancillary data										
pH	8.2	8.1	8.2	8.5	8.3	8.3	8.4	8.4	8.4	8.4
Conductivity (µS/cm)	2500	2900	3400	1300	2800	2900	2700	4300	3700	3600

a) Com: compost, Dig: digestate, all digestate samples were submitted to subsequent aerobic treatment except for samples 80 and 89, PW: presswater
b) plant code: C: compost, K: organic kitchen waste and green waste as input materials, G: pure green waste compost, U: urban area of input material collection, R: rural area of input material collection, SP: special compost if not compatible with factors described in the section ‘experimental design’
c) kw: kitchen waste, gw: green waste, iw: industrial waste including paper sludge, coffee ground, tea leaves, residues from potato chips production, biodegradable plastics, edible oil, cacao
d) characterisation of the area where the input material was collected
e) season of input material collection
f) plant type: ab: aerated boxes, atc: aerated trench composting in sheds, bwc: combined box and windrow composting, fec: field-edge composting, mcd: mesophilic aerobic co-digestion, tad: thermophilic aerobic digestion, tbw: table windrows, twh: triangle windrows higher than 2 meters, twl: triangle windrows lower than 2 meters, vc: vermicomposting
g) contains small amounts of digested material in the compost input material
h) duration of the treatment process in days
i) NO_3^- nd
j) sieve-width in mm, not: unsieved
k) this product contains important amounts of feedstock materials other than organic kitchen waste or green waste (e.g. farmyard manure)
l) NH_4^+ nd
m) input material from highway areas
n) only compost derived from green and kitchen waste collected in rural areas

NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[1,2,3-*cd*]pyrene, BPE: benzo[*ghi*]perylene, CPHE: 4-H-cyclopenta[*def*]PHE, RET: retene, CPYR: cylopenta[*cd*]PYR, COR: coronene, (MPHE&ANT)/PHE: ratio of methylPHE and –ANT to PHE, (MFLT&PYR)/PYR: ratio of methylFLT and -PYR to PYR, 1,7-/(1,7-&2,6-)DmPHE: the ratio of 1,7- to 1,7- and 2,6-dimethylPHE, nd: not detected, na: not available, EF enantiomeric fraction, ww: wet weight, dw: dry weight

Table 1 (cont.): Sample description, PCB, PAH, heavy metal and nutrient contents of compost, digestate and presswater samples in Switzerland

Sample No.	22[k]	23[n]	24	25	26	27[k]	28	29	30	31[m]
Product[a]	Com	Com	Com	Com	Com	Com	Com	Com	Com	Com
Plant code and number[b]	CGR09	CSP01	CGR03	CGR08	CGR04	CGR10	CKU02	CKU01	CGR01	CSP02
Input material[c]	gw	kw, gw	gw	gw	gw	gw	kw, gw	kw, gw, iw	gw	gw
Origin of input material[d]	rural	rural	rural	rural	rural	rural	urban	urban	rural	rural
Season[e]	autumn	autumn	winter	winter	autumn	autumn	summer	summer	summer	autumn
Plant type[f]	fec	fec	twh	twl	twh	vc	ab	twl	twl	atc
Process duration (days)[h]	244	164	87	74	203	192	55	50	70	254
Water content [% ww]	43	50	52	38	40	68	45	49	35	42
Org matter content [% dw]	25	37	37	31	27	53	51	51	27	52
Impurity content [% dw]	0.29	0.41	0.2	0.15	0.074	0.48	0.078	0.017	0.15	0.062
Maturity (NO_3^-/NH_4^+)	41	20	1.1	4.9	0.59	67	0.38	nd[i]	2.0	0.33
Particle size [mm][j]	<10	<30	<20	<20	<20	not	<20	<40	<25	<20
PCB (μg/kg$_{dw}$)										
PCB 28	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB 52	0.38	0.59	0.86	0.56	0.88	1.6	1.5	2.0	5.1	1.0
PCB 95	0.62	1.6	1.3	1.0	1.3	2.8	2.6	3.1	13	3.0
PCB 101	0.84	2.2	1.8	1.4	1.9	3.4	3.4	3.8	15	4.2
PCB 118	0.59	2.6	1.4	0.98	1.5	2.6	2.4	2.9	6.0	6.4
PCB 132	0.58	1.9	1.2	1.2	1.0	2.3	2.4	2.4	15	2.3
PCB 138	1.3	3.6	2.1	2.3	2.0	3.5	5.2	4.6	17	6.9
PCB 149	1.0	2.7	1.9	1.7	1.8	3.3	3.8	3.5	22	4.8
PCB 153	1.7	4.1	2.9	2.6	2.9	4.6	5.8	4.9	31	9.3
PCB 174	0.36	0.84	0.62	0.56	0.48	0.71	1.0	1.1	6.0	1.4
PCB 180	0.98	2.5	1.7	1.7	1.5	2.1	3.8	2.8	20	5.3
EF PCB 95	0.49	0.50	0.50	0.50	0.49	0.50	0.50	0.50	0.50	0.50
EF PCB 132	0.52	0.52	0.50	0.51	0.50	0.49	0.46	0.48	0.50	0.50
EF PCB 149	0.50	0.49	0.50	0.49	0.50	0.49	0.50	0.50	0.50	0.50
PAH (μg/kg$_{dw}$)										
NAP	14	18	55	24	19	9.8	36	17	28	12
ACY	1.3	2.0	6.3	14	2.4	1.8	28	3.2	3.6	2.6
ACE	2.2	2.2	24	34	8.3	3.6	23	120	8.6	1.3
FLU	2.7	3.9	60	33	13	4.5	73	35	15	2.8
PHE	38	43	430	200	190	58	1100	350	160	63
ANT	5.3	5.2	33	45	22	11	210	26	24	16
FLT	90	100	470	1000	470	190	2000	600	500	370
PYR	53	58	300	1100	240	140	1500	460	250	260
BaA	52	46	180	810	130	130	770	130	270	260
CHR	88	110	330	1100	290	150	810	190	430	450
BbF	75	100	300	540	220	140	890	150	500	430
BkF	31	41	120	280	83	92	480	71	230	200
BaP	51	54	150	260	88	120	620	84	260	230
IPY	59	82	220	230	120	150	960	99	320	330
BPE	62	88	190	180	120	110	540	93	290	320
CPHE	5.8	7.7	23	18	5.5	11	88	37	6.6	7.5
RET	15	21	51	37	41	11	68	94	85	23
CPYR	6.7	12	6.4	11	1.8	7.4	31	1.5	2.6	9.2
PER	22	27	42	75	28	39	180	27	87	65
COR	37	54	120	57	58	43	190	39	120	180
(MPHE/ANT)/PHE [-]	0.42	0.37	0.32	0.76	0.37	0.50	0.36	0.44	0.44	0.72
(MFLT/PYR)/PYR [-]	0.59	0.49	0.39	0.42	0.34	0.48	0.30	0.25	0.51	0.48
1,7-/(1,7-&2,6-DmPHE) [-]	0.70	0.68	0.62	0.61	0.67	0.69	0.58	0.63	0.66	0.62

Heavy metals (mg/kg$_{dw}$)										
Cd	0.051	0.24	0.18	0.29	0.15	0.09	0.25	nd	0.099	0.16
Co	5.2	3.9	4.2	4.4	5.0	2.3	4.4	3.4	4.3	2.7
Cr	17	25	18	23	22	10	16	15	20	11
Cu	34	300	57	50	58	51	58	44	59	51
Ni	17	18	14	16	17	8.8	14	13	17	10
Pb	29	37	51	35	32	17	61	29	59	40
Zn	120	260	170	120	130	170	190	110	140	180
nutrients (g/kg$_{dw}$)										
N	12	16	14	12	12	25	26	19	11	28
P	3.2	3.4	2.8	2.2	3.0	8.8	4.3	2.9	2.2	4.0
K	7.3	12	11	6.7	12	28	25	16	7.6	21
Mg	5.2	6.9	10	6.3	11	6.3	5.1	4.1	7.1	8.4
Ca	35	56	70	46	76	38	70	53	58	60
Further elements (g/kg$_{dw}$)										
Fe	13	11	9.1	11.0	11	6.1	9.7	7.2	10	7.0
Mn	0.56	0.47	0.45	0.55	0.93	0.47	0.42	0.34	0.67	0.42
Na	0.53	1.1	0.63	0.48	0.46	1.2	0.81	0.71	0.49	0.64
Ancillary data										
pH	8.0	8.1	8.5	8.4	8.4	8.4	8.5	8.5	8.3	8.1
Conductivity (µS/cm)	3100	3900	2200	1900	3700	3700	4500	3200	1800	5300

a) Com: compost, Dig: digestate, all digestate samples were submitted to subsequent aerobic treatment except for samples 80 and 89, PW: presswater
b) plant code: C: compost, K: organic kitchen waste and green waste as input materials, G: pure green waste compost, U: urban area of input material collection, R: rural area of input material collection, SP: special compost if not compatible with factors described in the section ‘experimental design’
c) kw: kitchen waste, gw: green waste, iw: industrial waste including paper sludge, coffee ground, tea leaves, residues from potato chips production, biodegradable plastics, edible oil, cacao
d) characterisation of the area where the input material was collected
e) season of input material collection
f) plant type: ab: aerated boxes, atc: aerated trench composting in sheds, bwc: combined box and windrow composting, fec: field-edge composting, mcd: mesophilic aerobic co-digestion, tad: thermophilic aerobic digestion, tbw: table windrows, twh: triangle windrows higher than 2 meters, twl: triangle windrows lower than 2 meters, vc: vermicomposting
g) contains small amounts of digested material in the compost input material
h) duration of the treatment process in days
i) NO_3^- nd
j) sieve-width in mm, not: unsieved
k) this product contains important amounts of feedstock materials other than organic kitchen waste or green waste (e.g. farmyard manure)
l) NH_4^+ nd
m) input material from highway areas
n) only compost derived from green and kitchen waste collected in rural areas

NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[1,2,3-*cd*]pyrene, BPE: benzo[*ghi*]perylene, CPHE: 4-H-cyclopenta[*def*]PHE, RET: retene, CPYR: cylopenta[*cd*]PYR, COR: coronene, (MPHE&ANT)/PHE: ratio of methylPHE and –ANT to PHE, (MFLT&PYR)/PYR: ratio of methylFLT and -PYR to PYR, 1,7-/(1,7-&2,6-)DmPHE: the ratio of 1,7- to 1,7- and 2,6-dimethylPHE, nd: not detected, na: not available, EF enantiomeric fraction, ww: wet weight, dw: dry weight

Table 1 (cont.): Sample description, PCB, PAH, heavy metal and nutrient contents of compost, digestate and presswater samples in Switzerland

Sample No.	32[k]	33	34	35	36	37	38	39	40	41
Product[a]	Com	Com	Com	Com	Com	Com	Com	Com	Com	Com
Plant code and number[b]	CGU09	CKU03	CKU04	CGU04	CKU07	CKU07	CGU05	CGU08	CGU07	CGR02
Input material[c]	gw	kw, gw	kw, gw	gw	kw, gw	kw, gw	gw	gw	gw	gw
Origin of input material[d]	urban	urban	urban	urban	urban	urban	urban	urban	urban	rural
Season[e]	autumn	summer	summer	summer	summer	summer	summer	autumn	autumn	summer
Plant type[f]	fec	atc[g]	tbw	twh	twl[g]	twl[g]	atc	twh	twh	twh
Process duration (days)[h]	70	35	91	96	87	107	33	298	168	70
Water content [% ww]	38	39	37	43	43	50	43	45	59	51
Org matter content [% dw]	17	34	36	45	41	53	44	24	42	33
Impurity content [% dw]	0.078	0.13	2.5	0.26	0.22	0.047	0.21	0.17	0.12	0.064
Maturity (NO_3^-/NH_4^+)	5.4	0.032	0.48	nd[i]	46	nd[i]	nd[i]	25	33	0.4
Particle size [mm][j]	not	<10	not	<40	<10	<40	<20	<20	<20	<20
PCB (μg/kg$_{dw}$)										
PCB 28	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB 52	0.49	3.0	1.8	2.0	2.9	2.7	4.7	0.73	1.9	3.5
PCB 95	0.85	3.9	2.3	2.9	4.4	3.4	4.7	2.1	3.7	2.6
PCB 101	1.3	5.3	3.2	4.0	5.9	4.6	6.0	2.3	4.8	3.4
PCB 118	0.91	9.5	2.8	4.0	5.2	3.9	8.3	1.8	3.7	2.4
PCB 132	0.75	3.4	2.0	2.6	3.8	2.3	2.4	1.8	3.1	1.6
PCB 138	1.8	3.8	4.2	3.7	7.2	3.3	6.4	3.9	5.2	3.4
PCB 149	1.3	4.8	2.6	3.4	4.8	4.1	4.5	2.9	4.8	2.9
PCB 153	2.3	7.4	4.2	5.8	7.2	6.6	6.6	4.3	7.2	4.5
PCB 174	0.63	1.7	0.76	1.2	1.2	1.5	1.6	0.86	1.5	0.96
PCB 180	1.4	4.9	2.2	2.9	3.8	2.9	3.2	2.3	5.0	2.7
EF PCB 95	0.50	0.48	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.49
EF PCB 132	0.51	0.51	0.50	0.48	0.49	0.50	0.50	0.49	0.51	0.50
EF PCB 149	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.49	0.50
PAH (μg/kg$_{dw}$)										
NAP	7.5	23	9.1	15	20	38	16	27	14	22
ACY	0.80	2.5	1.7	2.2	4.3	2.9	3.7	4.5	1.2	4.3
ACE	0.94	9.0	4.6	32	8.5	120	120	2.1	1.8	14
FLU	1.8	21	4.5	40	17	210	140	4.6	3.1	26
PHE	48	300	220	420	170	870	810	59	38	220
ANT	4.0	28	13	25	35	51	77	11	2.5	23
FLT	96	550	400	650	520	910	760	210	120	520
PYR	67	300	280	490	310	660	560	180	52	260
BaA	42	260	180	250	240	290	240	170	30	170
CHR	68	300	250	340	440	370	310	200	80	280
BbF	76	320	220	320	390	310	220	230	73	260
BkF	42	170	100	160	170	160	110	110	27	110
BaP	48	210	98	200	170	220	160	200	36	150
IPY	71	320	110	230	250	210	150	190	57	180
BPE	70	200	110	200	220	200	170	240	67	170
CPHE	4.9	20	2.7	27	8.9	66	46	12	7.3	11
RET	12	66	93	200	210	170	58	18	43	66
CPYR	6.5	4.7	1.3	2.2	1.9	3.0	8.1	12	9.3	3.7
PER	21	60	34	63	56	68	51	64	23	58
COR	35	78	40	77	87	70	71	140	43	79
(MPHE/ANT)/PHE [-]	0.46	0.52	0.48	0.38	0.73	0.31	0.27	0.62	0.33	0.42
(MFLT/PYR)/PYR [-]	0.37	0.47	0.33	0.33	0.49	0.37	0.30	0.50	0.32	0.41
1,7-/(1,7-&2,6-DmPHE) [-]	0.66	0.62	0.65	0.68	0.69	0.63	0.59	0.57	0.76	0.64

Heavy metals (mg/kg$_{dw}$)										
Cd	nd	0.13	nd	nd	nd	nd	nd	0.032	0.45	0.17
Co	2.9	5.3	4.9	3.9	3.9	3.6	3.4	5.4	6.2	5.4
Cr	10	28	25	15	20	14	19	13	41	21
Cu	21	110	64	48	59	47	36	47	68	48
Ni	10	27	24	15	18	15	14	16	22	18
Pb	15	65	38	39	32	45	32	46	58	53
Zn	72	190	140	130	150	110	140	160	210	120
nutrients (g/kg$_{dw}$)										
N	8.7	16	17	17	19	18	20	9.6	21	13
P	2.4	3.9	3.0	3.0	3.0	2.7	3.6	1.3	3.3	2.5
K	7.5	7.4	14	15	13	14	15	2.2	7.1	8.1
Mg	4.6	4.7	5.0	5.0	7.7	5.9	4.5	9.5	7.0	6.4
Ca	35	53	53	46	75	58	31	41	30	53
Further elements (g/kg$_{dw}$)										
Fe	7.6	15	10	8.9	9.7	8.3	8.9	14	16	12
Mn	0.28	0.43	0.40	0.38	0.38	0.31	0.41	0.32	0.49	0.56
Na	0.44	0.54	0.75	0.65	0.66	0.61	0.75	0.18	0.29	0.43
Ancillary data										
pH	8.0	8.3	8.1	8.2	7.8	8.2	8.3	8.0	8.2	8.4
Conductivity (µS/cm)	3500	2200	4400	5300	4100	4400	4300	680	1400	2100

a) Com: compost, Dig: digestate, all digestate samples were submitted to subsequent aerobic treatment except for samples 80 and 89, PW: presswater
b) plant code: C: compost, K: organic kitchen waste and green waste as input materials, G: pure green waste compost, U: urban area of input material collection, R: rural area of input material collection, SP: special compost if not compatible with factors described in the section 'experimental design'
c) kw: kitchen waste, gw: green waste, iw: industrial waste including paper sludge, coffee ground, tea leaves, residues from potato chips production, biodegradable plastics, edible oil, cacao
d) characterisation of the area where the input material was collected
e) season of input material collection
f) plant type: ab: aerated boxes, atc: aerated trench composting in sheds, bwc: combined box and windrow composting, fec: field-edge composting, mcd: mesophilic aerobic co-digestion, tad: thermophilic aerobic digestion, tbw: table windrows, twh: triangle windrows higher than 2 meters, twl: triangle windrows lower than 2 meters, vc: vermicomposting
g) contains small amounts of digested material in the compost input material
h) duration of the treatment process in days
i) NO_3^- nd
j) sieve-width in mm, not: unsieved
k) this product contains important amounts of feedstock materials other than organic kitchen waste or green waste (e.g. farmyard manure)
l) NH_4^+ nd
m) input material from highway areas
n) only compost derived from green and kitchen waste collected in rural areas

NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[1,2,3-*cd*]pyrene, BPE: benzo[*ghi*]perylene, CPHE: 4-H-cyclopenta[*def*]PHE, RET: retene, CPYR: cylopenta[*cd*]PYR, COR: coronene, (MPHE&ANT)/PHE: ratio of methylPHE and –ANT to PHE, (MFLT&PYR)/PYR: ratio of methylFLT and -PYR to PYR, 1,7-/(1,7-&2,6-)DmPHE: the ratio of 1,7- to 1,7- and 2,6-dimethylPHE, nd: not detected, na: not available, EF enantiomeric fraction, ww: wet weight, dw: dry weight

Table 1 (cont.): Sample description, PCB, PAH, heavy metal and nutrient contents of compost, digestate and presswater samples in Switzerland

Sample No.	42	43	44	45	46[k]	47[m]	48	49	50	51
Product[a]	Dig	Com	Dig	Com	Dig	Com	Com	Dig	Com	Com
Plant code and number[b]	DKU05	CKU08	DKU06	CGU01	DGR01	CSP03	CGU02	DKU01	CGU03	CGR04
Input material[c]	kw, gw, iw	kw, gw	kw, gw, iw	gw, iw	gw	gw	gw, iw	kw, gw, iw	gw	gw
Origin of input material[d]	urban	urban	urban	urban	rural	rural	rural	urban	urban	rural
Season[e]	summer	summer	summer	summer	summer	autumn	summer	summer	summer	summer
Plant type[f]	tad	twl	twl[g]	twl	mcd	twl	twh	tad	twh	twh
Process duration (days)[h]	91	70	28	70	28	28	105	20	49	105
Water content [% ww]	43	43	52	39	25	66	34	44	52	32
Org matter content [% dw]	34	23	43	31	61	79	44	51	51	39
Impurity content [% dw]	1.4	0.10	0.33	0.081	0.036	0.36	0.044	0.40	0.28	0.11
Maturity (NO_3^-/NH_4^+)	0.41	30	0.083	0.28	0.19	nd[i]	0.14	nd[i]	nd[i]	nd[i]
Particle size [mm][j]	<40	<15	<40	not	not	not	<10	<40	<40	not
PCB (μg/kg$_{dw}$)										
PCB 28	nd	nd	nd	nd	nd	nd	21	nd	nd	nd
PCB 52	4.0	1.3	2.1	1.5	0.58	1.2	25	1.5	3.8	0.88
PCB 95	4.4	2.3	2.8	4.1	4.7	1.3	9.4	2.9	4.8	1.4
PCB 101	5.8	2.9	3.7	5.3	6.0	2.1	10	4.4	6.6	1.8
PCB 118	4.1	3.5	2.8	2.4	2.6	3.6	15	4.1	5.3	1.6
PCB 132	2.9	1.9	1.8	4.1	8.2	1.3	5.4	2.7	3.2	0.60
PCB 138	6.1	3.5	4.0	8.3	21	2.1	9.4	6.1	7.2	1.8
PCB 149	5.5	3.4	3.2	7.4	13	1.7	9.4	3.9	6.5	1.8
PCB 153	8.4	5.2	4.6	10	22	3.0	13	6.7	9.5	3.9
PCB 174	1.6	1.0	0.99	2.3	6.2	1.1	2.5	1.3	2.2	0.50
PCB 180	4.8	2.9	2.7	6.7	22	1.4	8.0	2.7	5.8	1.5
EF PCB 95	0.50	0.50	0.50	0.50	0.50	0.51	0.50	0.50	0.50	0.50
EF PCB 132	0.50	0.50	0.51	0.50	0.49	0.50	0.50	0.50	0.49	0.50
EF PCB 149	0.50	0.50	0.49	0.50	0.50	0.50	0.51	0.49	0.50	0.49
PAH (μg/kg$_{dw}$)										
NAP	11	25	22	18	32	14	22	65	13	13
ACY	1.8	3.0	3.1	2.8	3.1	2.2	3.5	8.9	1.8	4.1
ACE	4.1	8.8	56	11	35	0.96	5.5	220	18	110
FLU	4.2	25	64	15	52	1.8	9.0	210	15	110
PHE	73	140	410	240	360	96	77	1300	230	800
ANT	14	17	41	22	53	3.7	11	180	24	66
FLT	450	240	760	650	580	160	310	1100	660	770
PYR	410	110	490	420	420	110	410	800	500	540
BaA	170	110	200	150	170	52	190	240	250	160
CHR	290	170	300	240	270	110	300	340	340	270
BbF	290	160	240	220	470	94	380	290	330	230
BkF	140	61	120	110	210	49	190	150	190	120
BaP	110	93	130	120	370	53	190	200	200	120
IPY	220	110	200	200	450	84	400	210	270	160
BPE	140	110	130	130	310	110	250	160	200	120
CPHE	5.0	8.3	38	11	27	8.7	7.4	68	19	46
RET	110	18	56	54	30	14	320	68	67	120
CPYR	1.7	8.6	5.0	2.6	3.0	15	4.2	6.3	8.6	2.7
PER	37	34	37	30	110	32	51	55	59	33
COR	54	63	52	65	100	83	130	54	81	51
(MPHE/ANT)/PHE [-]	1.1	0.22	0.36	0.57	0.46	0.25	3.1	0.30	0.53	0.33
(MFLT/PYR)/PYR [-]	0.28	0.51	0.29	0.25	0.43	0.23	0.36	0.29	0.28	0.28
1,7-/(1,7-&2,6-DmPHE) [-]	0.65	0.68	0.62	0.62	0.58	0.57	0.67	0.57	0.64	0.61

Heavy metals (mg/kg$_{dw}$)										
Cd	0.022	0.11	0.013	0.21	0.01	0.01	0.16	0.01	0.025	0.015
Co	5.1	5.9	2.9	5.4	2.3	1.0	3.2	5.3	3.8	4.1
Cr	24	24	13	20	11	2.3	17	31	16	18
Cu	69	36	35	55	29	28	110	31	49	55
Ni	20	22	9.7	18	9.1	2.9	10	9.2	14	14
Pb	40	38	25	34	8.1	11	45	17	53	27
Zn	120	110	90	140	91	110	120	79	160	140
nutrients (g/kg$_{dw}$)										
N	13	10	14	15	15	26	12	15	19	15
P	3.6	2.1	2.8	3.9	3.6	3.7	1.7	3.3	3.1	3.1
K	11	6.6	12	11	9.4	23	6.9	12	16	16
Mg	9.5	13	8.9	4.4	3.7	3.6	4.4	7.3	7.3	9.0
Ca	66	62	84	39	23	24	44	58	52	63
Further elements (g/kg$_{dw}$)										
Fe	11	13	6.9	13.0	5.7	2.9	5.4	7.2	8.8	9.2
Mn	0.58	0.71	0.38	0.61	0.41	0.21	0.24	0.35	0.37	0.57
Na	1.0	0.44	0.95	0.55	0.54	0.65	0.65	1.4	0.50	0.47
Ancillary data										
pH	8.0	8.4	8.5	8.3	8.4	8.4	8.2	8.6	8.5	8.5
Conductivity (µS/cm)	4000	2000	3700	3900	1200	4300	1800	3000	3400	4200

a) Com: compost, Dig: digestate, all digestate samples were submitted to subsequent aerobic treatment except for samples 80 and 89, PW: presswater
b) plant code: C: compost, K: organic kitchen waste and green waste as input materials, G: pure green waste compost, U: urban area of input material collection, R: rural area of input material collection, SP: special compost if not compatible with factors described in the section ‘experimental design’
c) kw: kitchen waste, gw: green waste, iw: industrial waste including paper sludge, coffee ground, tea leaves, residues from potato chips production, biodegradable plastics, edible oil, cacao
d) characterisation of the area where the input material was collected
e) season of input material collection
f) plant type: ab: aerated boxes, atc: aerated trench composting in sheds, bwc: combined box and windrow composting, fec: field-edge composting, mcd: mesophilic aerobic co-digestion, tad: thermophilic aerobic digestion, tbw: table windrows, twh: triangle windrows higher than 2 meters, twl: triangle windrows lower than 2 meters, vc: vermicomposting
g) contains small amounts of digested material in the compost input material
h) duration of the treatment process in days
i) NO_3^- nd
j) sieve-width in mm, not: unsieved
k) this product contains important amounts of feedstock materials other than organic kitchen waste or green waste (e.g. farmyard manure)
l) NH_4^+ nd
m) input material from highway areas
n) only compost derived from green and kitchen waste collected in rural areas

NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[1,2,3-*cd*]pyrene, BPE: benzo[*ghi*]perylene, CPHE: 4-H-cyclopenta[*def*]PHE, RET: retene, CPYR: cylopenta[*cd*]PYR, COR: coronene, (MPHE&ANT)/PHE: ratio of methylPHE and –ANT to PHE, (MFLT&PYR)/PYR: ratio of methylFLT and -PYR to PYR, 1,7-/(1,7-&2,6-)DmPHE: the ratio of 1,7- to 1,7- and 2,6-dimethylPHE, nd: not detected, na: not available, EF enantiomeric fraction, ww: wet weight, dw: dry weight

Table 1 (cont.): Sample description, PCB, PAH, heavy metal and nutrient contents of compost, digestate and presswater samples in Switzerland

Sample No.	52	53	54	55	56[k]	57	58	59	60	61
Product[a]	Com	Com	Com	Dig	Com	Dig	Dig	Dig	Dig	Com
Plant code and number[b]	CKU09	CGR08	CGR03	DKU02	CKU06	DKU01	DKU03	DKU04	DKU02	CKU03
Input material[c]	kw, gw	gw	kw, gw	kw, gw	kw, gw	kw, gw, iw	kw, gw, iw	kw, gw, iw	kw, gw	kw, gw
Origin of input material[d]	urban	rural	rural	urban	urban	urban	urban	urban	urban	urban
Season[e]	summer	summer	summer	summer	summer	autumn	autumn	autumn	autumn	autumn
Plant type[f]	ab	twl	twg	tab	tbw[g]	tad	tad	tad	tad	atc
Process duration (days)[h]	43	113	134	126	174	19	29	7	49	43
Water content [% ww]	45	47	49	34	37	47	31	55	41	52
Org matter content [% dw]	43	30	35	47	26	50	34	51	49	46
Impurity content [% dw]	0.082	0.061	0.13	2.3	0.086	0.35	0.062	0.32	0.038	0.29
Maturity (NO_3^-/NH_4^+)	nd[i]	68	0.43	0.22	11	nd[i]	0.72	0.016	0.22	0.076
Particle size [mm][j]	<10	<10	<20	not	<10	<20	<10	<20	not	<10
PCB (µg/kg$_{dw}$)										
PCB 28	1.8	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB 52	4.9	0.58	0.78	3.3	6.2	3.5	3.6	3.1	2.9	2.8
PCB 95	3.7	1.1	1.4	5	31	5.1	4.8	3.6	4.8	4.1
PCB 101	4.9	1.3	2.0	6.8	73	6.6	6.1	4.9	6.3	5.5
PCB 118	3.2	1.1	1.7	5.9	130	5.0	4.9	3.4	5.1	4.8
PCB 132	2.8	0.78	1.2	4.0	69	4.9	4.2	2.9	3.9	3.1
PCB 138	5.6	1.9	2.9	8.6	130	7.9	6.9	5.2	7.1	5.6
PCB 149	5.5	1.6	2.2	6.2	78	7.0	6.5	4.3	6.1	4.7
PCB 153	8.0	2.5	3.6	9.5	140	9.8	9.4	6.3	8.9	6.9
PCB 174	1.5	0.5	0.74	1.6	17	2.4	2.3	1.5	2.1	1.6
PCB 180	5.0	1.4	2.2	5.1	57	6.0	6.1	2.9	5.0	4.2
EF PCB 95	0.50	0.49	0.50	0.50	0.50	0.51	0.50	0.51	0.50	0.50
EF PCB 132	0.49	0.49	0.50	0.50	0.50	0.49	0.50	0.50	0.48	0.50
EF PCB 149	0.50	0.49	0.50	0.50	0.50	0.49	0.50	0.49	0.50	0.50
PAH (µg/kg$_{dw}$)										
NAP	26	17	46	31	20	31	56	40	25	14
ACY	5.1	4.1	6.7	6.1	3.0	4.9	4.3	3.7	3.8	1.6
ACE	140	8.7	42	69	5.9	33	21	75	41	4.3
FLU	200	9.2	71	55	9.7	53	34	98	33	8.0
PHE	870	56	450	1200	91	710	550	980	550	180
ANT	94	13	53	100	15	72	46	72	42	13
FLT	2200	200	830	3900	350	840	730	1100	920	370
PYR	1300	190	660	3000	220	580	470	830	680	180
BaA	500	220	410	930	360	220	190	340	230	120
CHR	510	380	580	1100	440	310	310	450	310	180
BbF	270	220	570	660	470	280	240	370	250	150
BkF	160	120	270	360	250	130	110	190	120	69
BaP	210	120	370	330	320	170	110	270	130	94
IPY	180	140	420	360	300	180	140	270	170	110
BPE	190	130	320	260	310	180	140	260	160	120
CPHE	100	8.3	29	100	7.5	25	8.2	45	18	6.8
RET	110	29	73	110	65	110	68	89	140	98
CPYR	18	11	7.9	6	9.6	8.8	5.3	8.3	5.8	6.2
PER	69	41	87	88	88	58	37	84	48	35
COR	93	58	150	97	160	84	69	120	83	61
(MPHE/ANT)/PHE [-]	0.51	0.75	0.43	0.52	0.58	0.32	0.32	0.29	0.37	0.51
(MFLT/PYR)/PYR [-]	0.31	0.6	0.37	0.25	0.75	0.28	0.25	0.28	0.23	0.38
1,7-/(1,7-&2,6-DmPHE) [-]	0.56	0.61	0.64	0.58	0.63	0.6	0.57	0.60	0.62	0.67

Heavy metals (mg/kg$_{dw}$)										
Cd	0.092	0.088	0.17	0.01	0.13	0.010	0.010	0.12	0.065	0.12
Co	4.2	4.6	4.5	3.4	5.3	2.7	2.6	3.1	3.2	4.2
Cr	19	24	40	21	22	21	21	21	24	24
Cu	57	46	59	56	59	50	44	59	50	86
Ni	13	17	25	15	18	13	14	15	15	22
Pb	54	45	62	36	70	19	22	32	42	48
Zn	150	140	170	130	160	110	120	130	130	170
nutrients (g/kg$_{dw}$)										
N	17	16	14	18	13	18	16	16	17	18
P	2.9	3.1	3.1	3.9	2.9	3.6	3.7	2.9	3.6	3.4
K	15	14	14	16	9.7	13	14	12	15	12
Mg	8.1	7.1	11	10	9.3	8.0	7.6	6.8	9.7	5.1
Ca	69	45	69	56	61	67	150	68	60	61
Further elements (g/kg$_{dw}$)										
Fe	8.4	12	10	9.0	12	8.9	9.2	9.5	9.7	10
Mn	0.36	0.59	0.49	0.45	0.59	0.42	0.40	0.41	0.44	0.37
Na	0.86	1.0	0.59	1.2	0.50	2.0	1.5	1.5	1.3	0.90
Ancillary data										
pH	8.5	8.2	8.5	8.3	8.2	8.4	8.1	8.5	8.2	8.6
Conductivity (μS/cm)	4200	4900	3500	4300	2800	3200	3900	2900	3400	2400

a) Com: compost, Dig: digestate, all digestate samples were submitted to subsequent aerobic treatment except for samples 80 and 89, PW: presswater
b) plant code: C: compost, K: organic kitchen waste and green waste as input materials, G: pure green waste compost, U: urban area of input material collection, R: rural area of input material collection, SP: special compost if not compatible with factors described in the section ‘experimental design’
c) kw: kitchen waste, gw: green waste, iw: industrial waste including paper sludge, coffee ground, tea leaves, residues from potato chips production, biodegradable plastics, edible oil, cacao
d) characterisation of the area where the input material was collected
e) season of input material collection
f) plant type: ab: aerated boxes, atc: aerated trench composting in sheds, bwc: combined box and windrow composting, fec: field-edge composting, mcd: mesophilic aerobic co-digestion, tad: thermophilic aerobic digestion, tbw: table windrows, twh: triangle windrows higher than 2 meters, twl: triangle windrows lower than 2 meters, vc: vermicomposting
g) contains small amounts of digested material in the compost input material
h) duration of the treatment process in days
i) NO_3^- nd
j) sieve-width in mm, not: unsieved
k) this product contains important amounts of feedstock materials other than organic kitchen waste or green waste (e.g. farmyard manure)
l) NH_4^+ nd
m) input material from highway areas
n) only compost derived from green and kitchen waste collected in rural areas

NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[1,2,3-*cd*]pyrene, BPE: benzo[*ghi*]perylene, CPHE: 4-H-cyclopenta[*def*]PHE, RET: retene, CPYR: cylopenta[*cd*]PYR, COR: coronene, (MPHE&ANT)/PHE: ratio of methylPHE and –ANT to PHE, (MFLT&PYR)/PYR: ratio of methylFLT and -PYR to PYR, 1,7-/(1,7-&2,6-)DmPHE: the ratio of 1,7- to 1,7- and 2,6-dimethylPHE, nd: not detected, na: not available, EF enantiomeric fraction, ww: wet weight, dw: dry weight

Table 1 (cont.): Sample description, PCB, PAH, heavy metal and nutrient contents of compost, digestate and presswater samples in Switzerland

Sample No.	62	63	64	65	66	67	68	69	70	71
Product[a]	Com	Com	Com	Com	Com	Com	Com	Com	Com	Com
Plant code and number[b]	CKU03	CKU02	CKU01	CGU05	CGU05	CGU02	CGU02	CGR02	CGR03	CGR04
Input material[c]	kw, gw	kw, gw	kw, gw, iw	gw	gw	gw, iw	gw, iw	gw	gw	gw
Origin of input material[d]	urban	urban	urban	rural	rural	rural	rural	rural	rural	rural
Season[e]	winter	autumn	autumn	autumn	winter	autumn	winter	autumn	autumn	winter
Plant type[f]	atc	ab	twl	atc	atc	tbw	tbw	twh	twh	twh
Process duration (days)[h]	56	73	73	12	18	94	63	103	72	84
Water content [% ww]	42	57	59	44	50	57	58	51	53	41
Org matter content [% dw]	53	52	46	43	48	52	40	35	29	38
Impurity content [% dw]	0.17	0.0089	0.021	0.082	0.4	0.036	nd	0.034	0.21	0.017
Maturity (NO_3^-/NH_4^+)	nd[i]	nd[i]	nd[i]	nd[i]	nd[i]	nd[i]	0.47	13	1.2	nd[i]
Particle size [mm][j]	<10	<20	<40	<20	<20	<20	<20	<20	<20	not
PCB (µg/kg$_{dw}$)										
PCB 28	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB 52	2.9	2.2	2.5	5.9	3.6	2.6	2.6	1.8	0.92	1.4
PCB 95	4.5	3.9	4.4	5.9	4.7	3.5	3.2	2.0	1.4	1.6
PCB 101	6.6	5.6	6.5	7.4	6.0	4.3	4.0	2.7	1.9	2.2
PCB 118	6.5	3.9	7.6	5.1	3.9	3.1	2.8	2.4	1.4	2.1
PCB 132	3.4	3.8	4.4	3.3	3.2	2.7	2.6	1.3	1.1	1.1
PCB 138	6.3	5.1	11	7.1	5.9	4.7	4.4	2.5	2.1	2.1
PCB 149	4.8	4.6	5.3	5.1	4.5	3.7	3.7	2.2	2.2	1.9
PCB 153	6.9	9.0	10	7.2	6.5	5.5	5.5	3.5	3.2	2.9
PCB 174	1.4	1.1	1.3	1.8	1.2	1.2	1.2	0.96	0.85	0.87
PCB 180	3.2	3.3	3.8	2.5	3.0	2.4	2.8	1.7	2.1	1.7
EF PCB 95	0.51	0.49	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
EF PCB 132	0.50	0.51	0.50	0.49	0.50	0.50	0.50	0.50	0.50	0.50
EF PCB 149	0.49	0.50	0.50	0.49	0.49	0.50	0.49	0.50	0.50	0.49
PAH (µg/kg$_{dw}$)										
NAP	17	54	15	19	18	24	10	5.5	16	11
ACY	2.1	14	2.4	3.0	2.8	3.8	3.0	0.81	2.1	1.4
ACE	13	6.8	29	84	4.0	39	5.4	5.5	7.7	7.0
FLU	20	21	59	120	8.1	48	11	7.6	16	7.6
PHE	270	540	430	860	160	300	190	93	120	120
ANT	23	89	31	82	18	44	22	10	14	11
FLT	420	1200	580	910	1100	880	630	200	280	240
PYR	290	630	370	620	630	610	340	140	170	190
BaA	150	540	170	310	570	360	280	80	150	66
CHR	190	590	230	360	650	480	410	110	210	97
BbF	150	600	200	300	430	380	380	73	150	62
BkF	80	310	94	160	230	200	170	44	89	37
BaP	110	420	130	230	230	280	260	48	110	39
IPY	110	470	150	200	250	280	280	59	130	54
BPE	110	460	150	200	250	270	260	68	150	62
CPHE	16	21	34	44	18	50	18	7.9	10	7.8
RET	100	78	81	81	100	120	99	34	35	60
CPYR	6.0	20	6.1	4.5	12	6.1	5.7	7.0	12	6.1
PER	38	140	49	70	60	81	81	20	31	14
COR	61	210	76	87	110	120	120	41	98	38
(MPHE/ANT)/PHE [-]	0.50	0.30	0.33	0.30	0.74	0.60	0.6	0.47	0.48	0.47
(MFLT/PYR)/PYR [-]	0.36	0.29	0.35	0.39	0.51	0.46	0.55	0.33	0.44	0.24
1,7-/(1,7-&2,6-DmPHE) [-]	0.65	0.66	0.62	0.59	0.61	0.63	0.63	0.62	0.65	0.69

Heavy metals (mg/kg_{dw})										
Cd	0.058	0.49	0.10	0.11	0.076	0.053	0.52	0.11	0.28	0.28
Co	3.6	4.2	3.5	3.6	2.9	2.9	3.8	4.3	4.2	4.2
Cr	22	21	21	26	21	17	20	23	25	25
Cu	110	64	45	48	51	44	51	47	53	87
Ni	20	15	15	17	15	12	14	16	15	20
Pb	150	98	29	41	38	38	42	31	42	42
Zn	160	230	120	170	170	130	150	140	140	140
nutrients (g/kg_{dw})										
N	16	20	16	17	18	14	15	15	9.8	13
P	2.9	3.5	2.5	3.7	3.2	2.6	2.9	2.8	2.5	3.1
K	7.9	17	10	16	13	10	12	12	12	15
Mg	4.6	4.9	4.4	4.7	4.6	5.3	6.0	6.2	10	9.2
Ca	56	77	71	40	53	75	82	64	38	70
Further elements (g/kg_{dw})										
Fe	9.3	11	8.9	11	9.1	7.6	10	12	10	9.7
Mn	0.36	0.45	0.37	0.46	0.48	0.32	0.39	0.52	0.45	1.0
Na	0.88	0.61	0.49	0.59	0.71	0.49	0.50	0.34	0.52	0.34
Ancillary data										
pH	8.5	8.5	8.6	8.7	8.6	8.5	8.4	8.6	8.5	8.7
Conductivity (μS/cm)	1800	3400	2100	3300	2400	1800	1900	2400	3100	2600

a) Com: compost, Dig: digestate, all digestate samples were submitted to subsequent aerobic treatment except for samples 80 and 89, PW: presswater
b) plant code: C: compost, K: organic kitchen waste and green waste as input materials, G: pure green waste compost, U: urban area of input material collection, R: rural area of input material collection, SP: special compost if not compatible with factors described in the section ‘experimental design’
c) kw: kitchen waste, gw: green waste, iw: industrial waste including paper sludge, coffee ground, tea leaves, residues from potato chips production, biodegradable plastics, edible oil, cacao
d) characterisation of the area where the input material was collected
e) season of input material collection
f) plant type: ab: aerated boxes, atc: aerated trench composting in sheds, bwc: combined box and windrow composting, fec: field-edge composting, mcd: mesophilic aerobic co-digestion, tad: thermophilic aerobic digestion, tbw: table windrows, twh: triangle windrows higher than 2 meters, twl: triangle windrows lower than 2 meters, vc: vermicomposting
g) contains small amounts of digested material in the compost input material
h) duration of the treatment process in days
i) NO_3^- nd
j) sieve-width in mm, not: unsieved
k) this product contains important amounts of feedstock materials other than organic kitchen waste or green waste (e.g. farmyard manure)
l) NH_4^+ nd
m) input material from highway areas
n) only compost derived from green and kitchen waste collected in rural areas

NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[1,2,3-*cd*]pyrene, BPE: benzo[*ghi*]perylene, CPHE: 4-H-cyclopenta[*def*]PHE, RET: retene, CPYR: cylopenta[*cd*]PYR, COR: coronene, (MPHE&ANT)/PHE: ratio of methylPHE and –ANT to PHE, (MFLT&PYR)/PYR: ratio of methylFLT and -PYR to PYR, 1,7-/(1,7-&2,6-)DmPHE: the ratio of 1,7- to 1,7- and 2,6-dimethylPHE, nd: not detected, na: not available, EF enantiomeric fraction, ww: wet weight, dw: dry weight

Table 1 (cont.): Sample description, PCB, PAH, heavy metal and nutrient contents of compost, digestate and presswater samples in Switzerland

Sample No.	72	74	75[j]	76	79	80	81	82	84	85
Product[a]	Com	Com	Dig	Com	Com	Dig	Com	Com	Dig	PW
Plant code and number[b]	CKU06	CGU01	DGR01	CGR01	CGU03	DKU03	CKU04	CGU04	DKU04	DKU04
Input material[c]	kw, gw, iw	gw, iw	kw, gw	gw	gw	kw, gw	kw, gw	gw	kw, gw, iw	kw, gw, iw
Origin of input material[d]	urban	rural	rural	rural	urban	urban	urban	urban	urban	urban
Season[e]	autumn	autumn	winter	winter	autumn	summer	winter	winter	winter	summer
Plant type[f]	tbw[g]	twl	mcd	twl	twh	tad	tbw	twh	tad	tad
Process duration (days)[h]	142	173	na	na	179	16	84	121	49	35
Water content [% ww]	41	44	52	39	47	52	51	54	51	93
Org matter content [% dw]	32	28	73	24	40	29	56	45	48	47
Impurity content [% dw]	0.012	0.0069	0.0094	0.012	0.015	0.078	0.05	0.014	0.2	na
Maturity (NO_3^-/NH_4^+)	14	nd[l]	1.2	38	33	nd[i]	nd[i]	nd[i]	nd[i]	na
Particle size [mm][j]	<10	<10	<20	<10	<20	<20	<40	<20	<10	not
PCB (μg/kg$_{dw}$)										
PCB 28	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB 52	5.2	1.5	0.62	2.2	4.2	2.3	1.5	2.1	3.3	3.2
PCB 95	4.4	2.6	0.6	8.2	6.5	3.9	1.9	2.6	3.6	4.1
PCB 101	5.5	3.2	0.88	9.3	8.2	4.1	2.6	3.6	4.6	6.0
PCB 118	4.1	2.2	0.76	3.8	6.0	3.7	2.5	3.4	4.3	5.1
PCB 132	2.9	2.1	0.44	6.9	4.6	2.9	1.3	1.9	2.5	3.3
PCB 138	5.0	4.0	0.99	11	8.5	4.8	2.3	3.4	5.5	6.8
PCB 149	5.4	3.5	1.0	14	7.4	3.8	2.0	2.7	3.7	6.0
PCB 153	7.8	5.2	1.5	18	11	6.9	2.9	4.0	6.0	9.3
PCB 174	2.1	1.2	0.56	3.9	2.2	1.3	0.66	0.99	1.3	1.7
PCB 180	6.1	3.1	1.2	12	6.2	3.1	1.6	2.0	3.0	5.1
EF PCB 95	0.49	0.50	0.50	0.50	0.50	0.50	0.50	0.51	0.51	0.51
EF PCB 132	0.49	0.50	0.48	0.49	0.50	0.50	0.49	0.50	0.50	0.50
EF PCB 149	0.50	0.50	0.50	0.49	0.49	0.46	0.48	0.47	0.48	0.49
PAH (μg/kg$_{dw}$)										
NAP	8.0	11	11	140	16	88	15	12	150	390
ACY	1.8	2.0	1.2	3.0	2.4	14	2.1	2.1	21	18
ACE	7.3	2.0	8.6	50	2.4	160	9.2	9.9	540	750
FLU	7.4	3.3	14	46	4.9	200	13	23	490	750
PHE	73	42	150	330	80	1000	170	200	1800	2000
ANT	13	5.6	14	72	10	110	14	14	210	210
FLT	230	170	190	510	350	720	290	410	1600	1500
PYR	160	100	150	340	150	530	150	300	1100	1200
BaA	190	120	62	320	160	170	140	190	430	480
CHR	230	180	84	380	320	220	180	270	450	560
BbF	170	92	59	320	300	140	160	230	360	340
BkF	110	53	33	170	120	70	85	120	190	220
BaP	120	51	49	240	160	110	130	160	280	300
IPY	130	66	54	220	220	89	140	180	230	310
BPE	150	77	57	230	220	96	140	190	220	330
CPHE	5.1	4	130	25	6.7	69	13	19	120	130
RET	46	35	94	74	59	50	200	320	110	94
CPYR	6.4	7.3	33	9.6	8.6	20	13	13	13	33
PER	38	18	100	69	50	40	43	52	93	100
COR	84	56	210	110	130	42	68	100	120	210
(MPHE/ANT)/PHE [-]	0.85	0.6	0.23	0.43	0.66	0.3	0.45	0.47	0.27	0.23
(MFLT/PYR)/PYR [-]	0.59	0.59	0.36	0.53	0.59	0.38	0.56	0.39	0.31	0.36
1,7-/(1,7-&2,6-DmPHE) [-]	0.56	0.56	0.56	0.62	0.66	0.55	0.73	0.74	0.56	0.56

Heavy metals (mg/kg$_{dw}$)										
Cd	0.14	0.13	0.17	0.26	0.15	0.13	0.01	0.022	0.0090	0.46
Co	5.4	5.0	1.4	4.4	3.8	2.0	2.9	3.3	2.8	8.0
Cr	24	23	8.0	19	20	12	19	18	20	50
Cu	64	51	53	38	63	21	54	52	69	100
Ni	18	19	10	16	16	8.2	15	15	14	39
Pb	48	37	6.6	25	47	19	26	30	25	73
Zn	160	150	130	120	190	60	110	140	120	340
nutrients (g/kg$_{dw}$)										
N	21	15	20	12	18	9.4	13	16	13	25
P	4.0	3.4	8.0	2.6	2.9	2.0	1.9	2.6	2.8	6.5
K	15	10	21	9.7	12	6.4	8.8	11	8.5	33
Mg	11	4.7	6.8	6.7	8	6.2	3.7	5.3	5.7	9.1
Ca	71	66	38	61	66	150	47	61	59	31
Further elements (g/kg$_{dw}$)										
Fe	14	12	3.7	11	10	5.4	7.7	8.8	9.7	19
Mn	0.53	0.58	1.3	0.55	0.45	0.27	0.32	0.38	0.40	0.80
Na	0.65	0.44	1.1	0.41	0.30	1.2	0.55	0.54	1.7	4.2
Ancillary data										
pH	7.9	8.3	8.3	8.4	8.5	8.5	8.6	8.6	8.5	na
Conductivity (µS/cm)	6200	2900	2900	3300	2500	3000	1600	2300	2900	na

a) Com: compost, Dig: digestate, all digestate samples were submitted to subsequent aerobic treatment except for samples 80 and 89, PW: presswater
b) plant code: C: compost, K: organic kitchen waste and green waste as input materials, G: pure green waste compost, U: urban area of input material collection, R: rural area of input material collection, SP: special compost if not compatible with factors described in the section ‘experimental design’
c) kw: kitchen waste, gw: green waste, iw: industrial waste including paper sludge, coffee ground, tea leaves, residues from potato chips production, biodegradable plastics, edible oil, cacao
d) characterisation of the area where the input material was collected
e) season of input material collection
f) plant type: ab: aerated boxes, atc: aerated trench composting in sheds, bwc: combined box and windrow composting, fec: field-edge composting, mcd: mesophilic aerobic co-digestion, tad: thermophilic aerobic digestion, tbw: table windrows, twh: triangle windrows higher than 2 meters, twl: triangle windrows lower than 2 meters, vc: vermicomposting
g) contains small amounts of digested material in the compost input material
h) duration of the treatment process in days
i) NO_3^- nd
j) sieve-width in mm, not: unsieved
k) this product contains important amounts of feedstock materials other than organic kitchen waste or green waste (e.g. farmyard manure)
l) NH_4^+ nd
m) input material from highway areas
n) only compost derived from green and kitchen waste collected in rural areas

NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[1,2,3-*cd*]pyrene, BPE: benzo[*ghi*]perylene, CPHE: 4-H-cyclopenta[*def*]PHE, RET: retene, CPYR: cylopenta[*cd*]PYR, COR: coronene, (MPHE&ANT)/PHE: ratio of methylPHE and –ANT to PHE, (MFLT&PYR)/PYR: ratio of methylFLT and -PYR to PYR, 1,7-/(1,7-&2,6-)DmPHE: the ratio of 1,7- to 1,7- and 2,6-dimethylPHE, nd: not detected, na: not available, EF enantiomeric fraction, ww: wet weight, dw: dry weight

Table 1 (cont.): Sample description, PCB, PAH, heavy metal and nutrient contents of compost, digestate and presswater samples in Switzerland

Sample No.	89	90	91
Product[a]	Dig	PW	PW
Plant code and number[b]	DKU04	DKU04	DKU02
Input material[c]	kw, gw, iw	kw, gw, iw	kw, gw
Origin of input material[d]	urban	urban	urban
Season[e]	summer	summer	summer
Plant type[f]	tad	tad	tad
Process duration (days)[h]	na	7	7
Water content [% ww]	51	85	85
Org matter content [% dw]	44	39	42
Impurity content [% dw]	0.15	na	na
Maturity (NO_3^-/NH_4^+)	nd[i]	na	na
Particle size [mm][j]	<40	not	not
PCB ($\mu g/kg_{dw}$)			
PCB 28	nd	nd	nd
PCB 52	2.4	2.0	2.0
PCB 95	4.0	2.6	2.9
PCB 101	5.4	3.5	3.9
PCB 118	3.3	3.0	3.6
PCB 132	3.0	2.2	2.4
PCB 138	6.6	3.9	4.5
PCB 149	5.5	3.7	4.1
PCB 153	8.7	5.6	6.4
PCB 174	1.5	1.1	1.3
PCB 180	4.6	3.1	3.7
EF PCB 95	0.51	0.49	0.50
EF PCB 132	0.50	0.50	0.49
EF PCB 149	0.50	0.49	0.49
PAH ($\mu g/kg_{dw}$)			
NAP	200	240	280
ACY	14	11	11
ACE	610	390	260
FLU	660	500	290
PHE	2100	1400	1200
ANT	300	220	140
FLT	1600	1100	1000
PYR	1200	810	770
BaA	520	320	290
CHR	540	370	350
BbF	440	310	290
BkF	240	160	150
BaP	370	250	250
IPY	280	210	220
BPE	270	210	220
CPHE	160	110	86
RET	72	50	45
CPYR	9.3	10	13
PER	120	80	81
COR	120	140	130
(MPHE/ANT)/PHE [-]	0.27	0.27	0.26
(MFLT/PYR)/PYR [-]	0.35	0.39	0.37
1,7-/(1,7-&2,6-DmPHE) [-]	0.55	0.55	0.58

Heavy metals (mg/kg_{dw})			
Cd	0.0059	0.23	0.16
Co	3.6	6.1	5.6
Cr	24	40	37
Cu	50	77	72
Ni	17	31	27
Pb	32	57	60
Zn	110	250	260
nutrients (g/kg_{dw})			
N	12	21	23
P	3.1	5.2	6.2
K	11	26	31
Mg	6.4	8.5	11
Ca	64	32	37
Further elements (g/kg_{dw})			
Fe	12	16	13
Mn	0.52	0.63	0.62
Na	1.3	2.8	2.7
Ancillary data			
pH	8.6	na	na
Conductivity (μS/cm)	2600	na	na

a) Com: compost, Dig: digestate, all digestate samples were submitted to subsequent aerobic treatment except for samples 80 and 89, PW: presswater
b) plant code: C: compost, K: organic kitchen waste and green waste as input materials, G: pure green waste compost, U: urban area of input material collection, R: rural area of input material collection, SP: special compost if not compatible with factors described in the section ‘experimental design’
c) kw: kitchen waste, gw: green waste, iw: industrial waste including paper sludge, coffee ground, tea leaves, residues from potato chips production, biodegradable plastics, edible oil, cacao
d) characterisation of the area where the input material was collected
e) season of input material collection
f) plant type: ab: aerated boxes, atc: aerated trench composting in sheds, bwc: combined box and windrow composting, fec: field-edge composting, mcd: mesophilic aerobic co-digestion, tad: thermophilic aerobic digestion, tbw: table windrows, twh: triangle windrows higher than 2 meters, twl: triangle windrows lower than 2 meters, vc: vermicomposting
g) contains small amounts of digested material in the compost input material
h) duration of the treatment process in days
i) NO_3^- nd
j) sieve-width in mm, not: unsieved
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Table 2: Aerial deposition rates of PCB and PAH and their content in manure, sewage sludge and background soils.

	deposition rate, mean (min, max)	Ref	manure, mean (min, max)	Ref	sewage sludge, mean (min, max)	Ref	soil (mean)	Ref
Σ7PCB[a]	12 mg/ha/y (3.72-68)	(*16,17*)	20 μg/kg$_{dw}$ (8-42)	(*18*)	100 μg/kg$_{dw}$ (38-152)	(*19*)	2.5 μg/kg$_{dw}$	(*20*)
Σ16PAH[b]	1.61 g/ha/y (0.14[c]-19[d])	(*21-23*)	150 μg/kg$_{dw}$ (66-339)	(*18*)	6.9 μg/kg$_{dw}$ (1.01-22.64)	(*19*)	225 μg/kg$_{dw}$	(*24*)

a) Sum of PCB 28, 52, 101, 118, 138, 153, 180
b) Sum of 16 PAH defined by the US EPA
c) Σ16PAH except naphthalene, but with acefenantrilene, benzo[*a*]fluorene, benzo[*ghi*]fluoranthene, cyclopenta[*cd*]pyrene, triphenylene, benzo[*b*]fluoranthene, benzo[*e*]pyrene, perylene, indeno[*7,1,2,3-cd*]chrysene, coronene
d) Σ16PAH without naphthalene and indeno[*1,2,3-cd*]pyrene

Table 3: Phosphate content of manure, sewage sludge, compost, digestate and presswater and resulting application rates per hectare (ha).

	phosphate content (P_2O_5) (g/kg$_{dw}$)	Reference	Application rate (t$_{dw}$/ha) for a fertilizing effect of 70kg/ha P_2O_5
manure	dairy cow manure: 20 dairy followers manure: 20 suckler cow manure: 19 beef cattle manure: 19 gestating sow manure: 64 nursing sow manure: 64 boar manure: 64 piglets manure (till 25kg): 88 fattening pig manure: 88	(*9*)	2.9
sewage sludge	61	(*10*)	1.1
compost	6.9	median this study	10.1
digestate	7.2	median this study	9.7
presswater	14.2	median this study	4.9

Table 4: References of emission profiles used to compare PAH source profiles from compost with

asphalt	(*25*)
break particles	(*26*)
coal	(*27*)
coal combustion	(*27-33*)
coal tar	(*34*)
Diesel	(*35-40*),
Diesel soot	(*28,35,36,38,40-45*)
dust	(*34*)
gasoline	(*37,46*)
gasoline soot	(*28,41,43,44,46-51*)
green waste combustion	(*33,52,53*)
kerosene	(*39*)
kerosene combustion	(*54*)
lawn mower	(*55*)
oil	(*35,39,56*)
oil burning soot	(*41,48*)
orimulsion®*	(*39*)
residue of Diesel burning	(*40*)
road dust	(*26*)
tar	(*35*)
tire wear	(*26*)
traffic emission	(*28,57*)
waste combustion	(*33,57,58*)
weathered oil	(*39*)
wood ash	(*59*)
wood combustion	(*28-31,41,54,58,60-67*)

*bitumen-based fuel

Table 5: Characteristic PAH ratios, molecular markers, and respective values in compost and digestate

	petrogenic[a]	**pyrogenic**[a]	**Swiss compost**[b]	**compost con**[c]
ANT/(ANT&PHE)	<0.1 [d]	>0.1 [d]	0.10 (0.05;0.19)	<; 0.05 (0.03;0.10)
BaA/(BaA&CHR)	<0.2 [d]	>0.35 [d]	0.42 (0.27;0.50)	=; 0.55 (0.39;0.63)
FLT/(FLT&PYR)	<0.4 [d]	>0.4 [d]	0.60 (0.45;0.75)	=; 0.47 (0.31;0.64)
IPY/(IPY&BPE)	<0.2 [d]	>0.2 [d]	0.50 (0.44;0.61)	=; 0.58 (0.46;0.63)
ComPAH/Σ16PAH	0.3 [d]	0.7 [d]	0.87 (0.43;0.96) [e]	<; na [f]
(MPHE&ANT)/PHE	5 [d]	0.5 [d]	0.47 (0.22;3.07)	>/<; na [f]
(MFLT&PYR)/PYR	4 [d]	0.3 [d]	0.37 (0.23;0.75)	=/>; na [f]
1,7-/(1,7-&2,6-)DmPHE	0.45-0.7 [d,g]	<0.45 or 0.7-0.9 [d]	0.63 (0.50;0.76)	=; na [f]

	fuel combustion	**grass/wood/coal combustion**		
FLT/(FLT&PYR)	0.4-0.5 [d]	>0.5 [d]	0.6 (0.43;0.75)	=; 0.47 (0.31;0.64)
IPY/(IPY&BPE)	0.2-0.5 [d]	>0.5 [d]	0.5 (0.44;0.61)	=; 0.58 (0.46;0.63)
RET/(RET&CHR)	0.15-0.5 [h]	0.83 [i]/0.96 [h, i]	0.19 (0.03;0.54)	>/=; na [f]
1,7-/(1,7-&2,6-)DmPHE	<0.45 [d, j]	0.7-0.9 [d, i]		=; na [f]

	diagenetic	**pyrogenic**		
PER/Σ16PAH	>0.05 [k]	<0.05 [k]	0.02 (0, 0.06)	>/<; na [f]

	non-traffic	**traffic**		
BaP/BPE	<0.6 [d,]	>0.6 [d,]	0.90 (0.53;1.4)	=; 1.50 (0.89;2.34)
1,7-/(1,7-&2,6-)DmPHE	>0.45 [d,]	<0.45 [d,]		=; na [f]

Markers			
COR/Σ15PAH	COR: vehicle exhaust [e]	0.03 (0.003;0.12) [e]	</=; na [e]
CPHE/Σ15PAH	CPHE: pyrogenic marker[l]	0.01 (0;0.02) [e]	>; na [e]
CPYR/Σ15PAH	CPYR: wood or traffic marker [m]	0.003 (0;0.017) [e]	>; na [e]

a) prevalent discrimination levels, b) median (min, max) n=69 c) quantitative alteration during composting (*8*) and ratios after applying conversion factor for air particles suggested by (*14*), d) characteristic ratio according to Ref (*24*) and references therein, e) dibenzo(*a,h*)anthracene was not determined, instead of Σ16PAH it is referred to Σ15PAH, f) conversion factor not available, g) also mixed combustion sources, h) (*68*), i) softwood combustion, j) vehicle emission, k) (*69*), l) (*70*), m) (*63,71*)

ANT: anthracene, PHE: phenanthrene, BaA: benzo[*a*]anthracene; CHR: chrysene; FLU: fluoranthene, PYR: pyrene, IPY: indeno[*1,2,3-cd*]pyrene, BPE: benzo[*ghi*]perylene (BPE), ComPAH (Sum of FLT, PYR, BaA, CHR, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene (BaP), IPY, BPE), M: methylated, Dm: dimethylated, RET: retene, PER: perylene, COR: coronene COR, CPHE: 4-H cyclopenta[*def*]PHE, CPYR: cyclopenta[*cd*]PYR

Table 6: Coefficients of variables kept in the final linear model influencing PCB and relative PCB concentrations in compost and digestate[a].

PCB concentrations	PCB 52	PCB 95	PCB 101	PCB 118	PCB 132	PCB 138	PCB 149	PCB 153	PCB 174	PCB 180	Σ11PCB
Origin of input materials (urban/rural)	0.41	0.37	0.36	0.37	0.36	0.34	0.31	0.27	0.27	0.24	0.42
Composition of input materials (green waste with/without org. kitchen waste)	0.17	0.11	0.08	0.02	0.09	0.07	0.10	0.08	0.13	0.08	0.10
Duration of the treatment process	-0.23	-0.18	-0.14	-0.08	-0.18	-0.13	-0.17	-0.13	-0.22	-0.13	-0.18
r^2 of the model[c]	0.25	0.34	0.32	0.31	0.30	0.30	0.30	0.20	0.23	0.12	0.32
Individual PCB/Σ10PCB											
Particle size (>20 mm/≤20mm)	0.021	0.005	0.005	0.013	-0.001	-0.005	-0.007	-0.016	-0.003	-0.012	na
Organic matter content[b]	0.001	>0	0.001	>0	>0	>0	-0.001	-0.001	<0	-0.001	na
Maturity (NO_3^-/NH_4^+)	-0.019	-0.005	-0.006	-0.026	0.009	0.007	0.010	0.009	0.003	0.018	na
r^2 of the model[c]	0.16	0.15	0.31	0.14	0.08	0.02	0.31	0.24	0.11	0.35	na

a) positive numbers indicate higher concentrations in first term named, or positive correlations with increasing continuous coefficient, negative numbers indicate lower concentrations in first term named, or negative correlations with increasing continuous coefficient

b) >0: coefficient >0 but <0.001, <0: coefficient <0 but >-0.001

c) r^2 is the fraction of explained variation by the model. It varies between 0 and 1 with the higher the value the more successful is the linear model in explaining the variation in the responses

Table 7: *p* Values and coefficients in the final linear model influencing enantiomeric fractions of atropisomeric PCB in compost and digestate.

	EF PCB 95	EF PCB 132	EF PCB 149	EF PCB 95[a]	EF PCB 132[a]	EF PCB 149[a]
Treatment process (anaerobic/aerobic)	++		--	-0.001	<0[b]	0.001
Season of input material collection (autumn/remaining year)[b]				-0.001	-0.002	0.003
Season of input material collection ((summer/spring)/remaining year)			++	0.002	0.001	-0.003
Duration of the treatment process				-0.001	0.002	-0.001
r^2 of the model[c]				0.20	0.07	0.20

++ first term named/with increasing continuous coefficient: significantly higher concentration on 95% level, + first term named/with increasing continuous coefficient: significantly higher concentration on 90% level

-- first term named/with increasing continuous coefficient: significantly lower concentration on 95% level, - first term named/with increasing continuous coefficient: significantly lower concentration on 90% level

a) positive numbers indicate higher concentrations in first term named or positive correlations with increasing continuous coefficient, negative number indicate lower concentrations in first term named or negative correlations with increasing continuous coefficient.

b) <0: coefficient <0 but >-0.001

c) r^2 is the fraction of explained variation by the model. It varies between 0 and 1 with the higher the value the more successful is the linear model in explaining the variation in the responses

Table 8: Coefficients of variables kept in the final linear model influencing PAH and relative PAH concentrations in compost and digestate.

PAH Concentration	NAP	ACY	ACE	FLU	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IPY	BPE	Σ15PAH	CPHE	RET	PER	CPYR	COR
Treatment process (anaerobic/aerobic)	0.49	0.38	0.74	0.62	0.52	0.56	0.32	0.37	0.18	0.15	0.11	0.10	0.10	0.06	0.03	0.29	0.30	-0.05	0.09	0.10	-0.01
Season of input material collection (autumn/remaining year)	-0.30	-0.35	-0.38	-0.34	-0.17	-0.30	-0.19	-0.27	-0.26	-0.21	-0.24	-0.28	-0.27	-0.23	-0.15	-0.25	-0.32	-0.10	-0.08	-0.21	-0.06
Season of input material collection ((summer/spring)/ remaining year)	0.02	0.17	0.33	0.25	0.11	0.16	0.11	0.21	0.19	0.18	0.20	0.20	0.19	0.23	0.10	0.18	0.16	-0.04	-0.17	0.14	0.02
Particle size (>20 mm /≤20mm)	0.18	0.52	0.19	0.41	0.22	0.42	0.22	0.34	0.45	0.36	0.33	0.33	0.42	0.36	0.34	0.31	0.32	0.05	0.60	0.39	0.38
Maturity (NO_3^-/NH_4^+)	-0.01	-0.29	-1.45	-1.41	-1.36	-0.98	-0.82	-0.96	-0.35	-0.11	-0.11	-0.19	-0.36	-0.23	-0.19	-0.56	-1.31	-0.60	-0.30	-0.31	-0.13
r^2 of the model[c]	0.34	0.33	0.44	0.40	0.53	0.43	0.45	0.50	0.23	0.19	0.15	0.16	0.21	0.18	0.13	0.40	0.42	0.17	0.25	0.19	0.16
Individual PAH/Σ20PAH																					
Treatment process (anaerobic/aerobic)[b]	0.002	>0	0.007	0.006	0.028	0.003	0.009	0.013	-0.006	-0.008	-0.009	-0.005	-0.007	-0.009	-0.009	na	0.001	-0.008	-0.002	>0	-0.005
Maturity (NO_3^-/NH_4^+)	0.009	>0	-0.010	-0.011	-0.071	-0.004	-0.050	-0.042	0.016	0.044	0.035	0.013	0.012	0.019	0.025	na	-0.004	-0.005	0.006	0.002	0.017
r^2 of the model[c]	0.11	0.09	0.29	0.27	0.45	0.29	0.29	0.37	0.21	0.50	0.43	0.32	0.29	0.27	0.49	na	0.23	0.07	0.17	0.36	0.45

a) positive numbers indicate higher concentrations in first term named or positive correlations with increasing continuous coefficient, negative number indicate lower concentrations in first term named or negative correlations with increasing continuous coefficient.

b) >0: coefficient >0 but <0.001

c) r^2 is the fraction of explained variation by the model. It varies between 0 and 1 with the higher the value the more successful is the linear model in explaining the variation in the responses

Table 9: Significant variables influencing characteristic PAH ratios in compost and digeate and corresponding coefficients.

	FLT/ (FLT&PYR)	BaA/ (BaA&CHR)	IPY/ (IPY&BPE)	ComPAH/ 15PAH	1,7-/(1,7-& 2,6DmPHE)	FLT/ (FLT&PYR)[a]	BaA/ (BaA&CHR)[a]	IPY/ (IPY&BPE)[a]	ComPAH/ 15PAH[a]	1,7-/(1,7-& 2,6DmPHE)[a]
Treatment process (anaerobic/aerobic)				--		-0.013	0.007	0.005	-0.056	-0.029
Season of input material collection (autumn/remaining year)	++		--			0.020	-0.011	-0.018	0.013	0.001
Season of input material collection ((summer/spring)/remaining year)	--		++			-0.024	0.002	0.030	-0.005	-0.012
Particle size (>20 mm /≤20mm)	-	+				-0.027	0.019	0.001	0.004	-0.019
Maturity (NO_3^-/NH_4^+)	+	--		++	--	0.030	-0.062	-0.005	0.083	0.010
r^2 of the model[b]						0.19	0.31	0.38	0.37	0.29

++ first term named/with increasing continuous coefficient: significantly higher concentration on 95% level, + first term named/with increasing continuous coefficient: significantly higher concentration on 90% level

-- first term named/with increasing continuous coefficient: significantly lower concentration on 95% level, - first term named/with increasing continuous coefficient: significantly lower concentration on 90% level

a) positive numbers indicate higher concentrations in first term named or positive correlations with increasing continuous coefficient, negative number indicate lower concentrations in first term named or negative correlations with increasing continuous coefficient.

b) r^2 is the fraction of explained variation by the model. It varies between 0 and 1 with the higher the value the more successful is the linear model in explaining the variation in the responses

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Organic pollutants in Swiss compost and digestate; 2. Polychlorinated Dibenzo-p-dioxins, and -furans, dioxin-like polychlorinated biphenyls, brominated flame retardants, perfluorinated alkyl substances, pesticides, and other compounds

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6.1 Manuscript 2: Text

Abstract

Compost and digestate are important recycling fertilizers, having beneficial effects on soil parameters. However, they can contain significant amounts of organic pollutants. Here, the first comprehensive data set on dibenzo-*p*-dioxins and –furans (PCDD/F), dioxin-like polychlorinated biphenyls (DL-PCB), brominated flame retardants, perfluorinated alkyl substances (PFAS), pesticides, phthalates, nonylphenol and chlorinated paraffins (CP) in source-separated compost and digestate from Switzerland is presented (n=3-18). The median Σ17PCDD/F and Σ12DL-PCB concentrations were at 3.2 ng I-TEQ/kg$_{\text{dry weight (dw)}}$ and 3.0 ng WHO-TEQ/kg$_{\text{dw}}$, respectively. Brominated diphenyl ether 209 (BDE 209) accounted for 72% of the total polyBDE content (10 μg/kg$_{\text{dw}}$). Hexabromocyclododecane and tetrabromobisphenol A levels were at 100 and 0.51 μg/kg$_{\text{dw}}$, respectively. PFAS were identified for the first time in compost and digestate (median concentration 6.3 μg/kg$_{\text{dw}}$, Σ21compounds). Out of 269 pesticides looked for, 30 fungicides, 14 herbicides, eight insecticides and one acaricide were detected. Di(2-ethylhexyl)phthalate median concentration accounted for 280 μg/kg$_{\text{dw}}$ and nonylphenol was below detection limit of 1mg/kg$_{\text{dw}}$. The sum of short and medium chain CP was between 90 and 390 μg/kg$_{\text{dw}}$. The concentrations observed were at or above levels found in soils, which are the main recipient of compost and digestate. Where actually applied, compost can contribute considerably to the total input of organic pollutants to soil. However, on a total Swiss agricultural area base, loads seem to be limited.

Introduction

Composting and digestion (i.e., aerobic and anaerobic degradation of organic wastes) are important waste management strategies in Europe (*1*). The resulting compost and digestate can be used as soil conditioner and fertilizers, recycling nutrients back to agriculture and horticulture. However, if the compost and digestate contain non-degraded residues of pollutants these are introduced to soil. Little is known about organic pollutants and pesticides in source-separated compost (i.e., compost solely derived from crude organic kitchen waste and green waste; for reviews see (*2,3*). Data on digestate is completely lacking. Emerging organic pollutants, such as brominated flame retardants (BFR), perfluorinated alkyl substances (PFAS) and chlorinated paraffins (CP) have not yet been systematically investigated in recycling fertilizers. These contaminants need to be included in inventory studies, since they have reached similar production volumes as the “classical” persistent organic pollutants (POPs) and exhibit some similar properties, i.e., ubiquitous occurrence, toxicity, persistence, carcinogenic and/or endocrine disrupting effects (*4-7*). In this study polychlorinated dibenzo-*p*-dioxins, and –furans (PCDD/F), dioxin-like polychlorinated biphenyls (DL-PCB), BFR (polybrominated diphenyl ethers (PBDE); hexabromocyclododecane (HBCD); tetrabromobisphenol A (TBBPA)), PFAS, and about 270 pesticides were analysed in 13 compost and five digestate samples from commercial plants in Switzerland. Additionally, phthalates and nonylphenol were determined in six, and short and medium chain CP (SCCP and MCCP) in three samples. The 18 samples were part of an extended inventory study on compost where polycyclic aromatic hydrocarbons (Σ16PAHs defined by the US EPA and selected source-diagnostic compounds), PCBs (seven Institute for Reference Material and Methods (IRMM) congeners i.e., PCB 28, 52, 101, 118, 138, 153, 180 (Σ7PCBs), and four chiral PCBs), heavy metals and nutrients were determined. Respective results are discussed in a companion paper (*1*).

The aim of this paper is (i) to provide a comprehensive and state-of-the-art overview on the presence of hazardous organic pollutants and pesticides, including emerging contaminants, in source-separated compost and digestate, (ii) to assess variables which determine their concentrations, (iii) to compare the organic pollutant contents in compost and digestate with recipient soils, and (iv) to compare fluxes to soil by compost application to other inputs.

Materials and Methods

Experimental design, sampling and sample preparation

Samples were selected to account for variables that may influence organic pollutant concentrations in compost and digestate (*2*), namely, treatment processes (composting/digestion), origin (urban/rural) and composition of input material (green waste with/without crude organic kitchen waste), and season of collection (spring/summer, autumn, winter). However, it was not possible to cover every combination of these variables due to limited resources.

Sampling procedure was described in Brändli et al. (*8*). Samples were either air-dried at room temperature for ten to 30 days in a climate chamber (for PCDD/F, DL-PCB and BFR analysis), dried at 40 ^{o}C for seven days (pesticides), frozen at -20 ^{o}C (phthalates), lyophilized (CP) or dried chemically (PFAS,(*8*). Samples dried at ambient temperature and at 40 ^{o}C were stored at room temperature in the dark, whereas lyophilized and chemically dried material was stored at 4 ^{o}C. Sub-samples of each type were shipped to the different partner laboratories for analysis.

Analytical procedure

PCDD/F, DL-PCB and BFR analysis was performed as in Zennegg et al. (*9*). PFAS extraction was carried out according to Powley et al. (*10*) with the following modifications: 7.5 g of chemically dried compost (2.5 g compost and 5 g Na_2SO_4) were spiked with perfluoro-3,7-di-methyl-octanoic acid used as internal standard for quantification. NaOH and HCl were dissolved in methanol. Before injection, the recovery standard 3,5-bis(trifluoromethyl)phenyl acetic acid was added to the extract. Liquid chromatography-mass spectrometer (LC-MS) separation and detection was described in Berger and Haukås (*11*). Two different multiresidue methods (one with LC-MS/MS and the other with gas chromatograph (GC) separation and electron capture detection or nitrogen phosphorous detection) were used to screen samples for 269 pesticides (*12,13*). Phthalate analysis was outlined in Herrchen et al. (*14*) (GC-MS) and nonylphenol was determined according to Hecht et al. (*15*) (LC-MS). CP were analysed and quantified as in Hüttig et al. (*16*) and Reth et al. (GC-MS) (*17*). Dry matter content was determined at 105 °C.

Data Processing and Statistics

For median calculation, only samples in which a compound was detected were taken into account due to low number of samples. Therefore n can differ from the number of samples. After basic evaluation of the dataset (i.e., median, comparison with literature values and soil data), the variables 'treatment process', 'composition of input material', 'origin of input material' and 'season of input material collection' were assessed by the Mann-Whitney-U Test (Statistica 6.1 StatSoft, Inc., Tulsa, USA . This test does not require normal distribution of the data and is robust to outliers. The level of significance was 0.025.

To account for the treatment process, digestates originating from urban areas and containing organic kitchen waste in the input material were tested against composts derived from the same kind of input material. Since only two samples (no. 17 and 35, see Supporting information, Table 1) of green waste composts from urban areas were available, the effects of the origin of input material (urban/rural) and of the input material composition (with/without organic kitchen waste) could not be evaluated separately. Hence, urban composts and digestates containing organic kitchen waste (n=13) were tested against rural green waste composts (n=5) only. Relative contributions of individual compounds to their respective sums were assessed with principal component analysis (PCA). Organic pollutant and pesticide contents were tested for (linear) correlation with the duration of the composting process and organic carbon content. Correlations between different organic pollutant classes as well as between heavy metals and organic pollutants were also assessed. The level of significance for all correlations was 0.05.

Mass loads of organic pollutants to soil

Input of organic pollutants to Swiss agriculture by compost application and time to reach Swiss guide or limit values for soil were determined as in Brändli et al. (*1*). Aerial deposition rates and contents in manure and sludge were obtained from the Swiss or European literature (Supporting information, Table 2).

Results and Discussion

Organic pollutant concentrations measured in Swiss compost and digestate are first compared with literature values where available. Thereafter, the observed contents are discussed in relation to the hypothesized key determinants and compared with typical concentrations in the soil as the major recipient of these recycling fertilizers. Finally, input via compost application to agricultural land is compared with other inputs (i.e., aerial deposition, input via manure and sewage sludge application) on a national and local scale. Common to all compound classes is that correlation was found neither between the contents of organic matter and organic pollutants, nor between the content of heavy metals and organic pollutants. For the remaining results it is referred to the following section.

PCDD/F

Median Σ17PCDD/F (sum of the 17 2,3,7,8-chlorosubstituted PCDD/F) concentration in composts and digestates was 3.2 ng I-TEQ/kg$_{\text{dry weight (dw)}}$, ranging from 0.52 to 21 ng I-TEQ/kg$_{\text{dw}}$ (Figure 1, n=18, Supporting information, Table 1). One sample was above the Swiss guide value for compost (20 ng I-TEQ/kg$_{\text{dw}}$, (*18*)). The median literature value for compost was 9.3 ng I-TEQ/kg$_{\text{dw}}$ (n=185, (*2*)), which is almost at the 90% level of this study's dataset (Figure 1). Median concentrations of the sum of all tetra- to octa-chlorinated PCDD/F in this work were 466 ng/kg$_{\text{dw}}$ and 102 ng/kg$_{\text{dw}}$, respectively. Compared to literature (*2*), the concentrations of the higher chlorinated PCDD/Fs were lower in Swiss compost, whereas lower chlorinated compounds concentrations were in the same range (Supporting information, Figure 1 and 2). This might be explained by the banning of pentachlorophenol (PCP) for wood preservation, which was often contaminated with highly chlorinated PCCD/F, by decreasing emission of higher chlorinated PCDD/F compared to the early 90's when most of the literature data was collected, or by different emission patterns between countries, since most literature data originated from Germany.

Σ17PCDD/F concentrations were not significantly different in digestate and compost. Concentrations varied slightly more in rural green waste composts compared to urban samples containing organic kitchen waste but the median Σ17PCDD/F concentration of the latter was slightly higher 3.3 versus 2.6 ng I-TEQ/kg$_{\text{dw}}$), which is in line with the literature (*2*).

PCA revealed that the ratios of individual 17 toxic congeners to their sum, as well as the ratios of the sum of tetra, penta, hexa, hepta, and octa PCDD/Fs to the total sum, was different for sample no. 1, 17 and 35 (Supporting information, Figure 3). Sample no. 1 had higher relative octaCDD (OCDD) content, which might be due to OCDD-formation during composting from precursor compounds (e.g., PCP) as described by Oeberg (*19*). Unfortunately, PCP was not included in the pesticide screening. Other precursor molecules are also possible. However, the mechanism of OCDD-formation during composting seems controversial (*20*). Furthermore, there was no indication (e.g., different process, input material) of why OCDD should be formed in sample no. 1 only. Sample no. 17 and 35, originating from the same plant, had higher relative HexaCDF contents, as well as higher absolute concentrations. In this plant, small amounts of wood ash were composted which originated from a cogeneration plant burning native wood for energy production. However, PCDD/F levels of bottom wood ash was found to be low (*21*) and can therefore not account for the relatively high values. The longer the composting process lasted, the higher were the PCDD/F concentrations. This can be attributed to the relative persistence of PCDD/F compared to organic matter. However, for neither of the congeners nor for any of their sums the increase in concentration was significant.

Σ17PCDD/F contents in Swiss agricultural soil and permanent grassland were at 1.4 ng I-TEQ/kg$_{\text{dw}}$ (*22*), which is slightly lower than data for compost and digestate presented above. Atmospheric deposition was the most important input pathway for Σ17PCDD/Fs to the total agricultural surface of Switzerland (24 g I-TEQ/y, Figure 2a). The total loads of sewage sludge and compost application were lower by almost two orders of magnitude. However, considering surface specific loads (i.e., loads per hectare based on a standard fertilization), input by compost accounted for more than the double compared to other inputs (Figure 2a). Time to reach the Swiss trigger value for soil (5 ng I-TEQ/kg$_{\text{dw}}$

for Σ17PCDD/F (*23*)), solely by compost application and aerial deposition (accounting for 0.04% of the total surface specific load) in absence of any removal process was estimated to be 112 years (with the starting level in soil 1.4 ng I-TEQ/kg$_{dw}$ (*22*), for deposition rate see Supporting information Table 2).

DL-PCB

Median concentration of the Σ12DL-PCB (Sum of PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) in composts and digestates was 3.0 ng WHO-TEQ/kg$_{dw}$, ranging from 0.4 to 6.8 ng WHO-TEQ/kg$_{dw}$ (Figure 1, n=18, Supporting information, Table 1). Kerst et al. (*24*) reported comparable median concentration in German compost (n=22). Analogous to PCDD/Fs and the seven IRMM PCB (see (*1*)), concentrations of DL-PCB in compost and digestate were similar, indicating that composting and digestion followed by aerobic treatment of the digestate had similar capacity to degrade DL-PCB. This was also indicated by results from Brändli et al (*25*). However, enhanced reduction of higher chlorinated PCBs in anaerobic conditions have also been reported (*26*). Median values for all congeners were higher in urban samples containing organic kitchen waste in the input material compared to rural green waste compost. However, the difference was significant for PCB 126 only. In previous reports, PCB levels were found to be higher in urban composts, whereas the type of input material was not a determinant of their concentrations (*1,2*). Consequently, the difference in DL-PCB concentration is rather attributed to the different origin of the input material than to its composition. The Σ12DL-PCB correlated well with the Σ7PCB (see (*1*) for details) except for sample no. 76 (green waste, rural). In this sample the Σ7PCB was much higher compared to the Σ12DL-PCBs (Supporting information, Table 1). It is assumed that this compost was subject to PCB input sources different from aerial deposition, e.g., products containing PCBs in Aroclor-like mixtures, since these contained only small portion of certain DL-PCB congeners (*27*). Also, PCA of DL-PCBs singled out sample no. 76 due to lower contribution of PCB 105, 118 and 126 and higher ratios of PCB 156, 176 and 189 to Σ12DL-PCB (Supporting information, Table 1, Figure 4). Lower PCB 156 and 176 and higher PCB 126 to Σ12DL-PCB ratios support the hypothesis of input by Aroclor-like mixtures, but the pattern of PCB 105, 118, and 189 does not agree. No correlation was found between DL-PCB concentrations and the duration of the composting process.

No Swiss soil data for (Σ12)DL-PCB could be found in the literature. Concentration in Spanish forest soils were in the same range as compost (between 1.9 and 8.4 ng WHO-TEQ/kg$_{dw}$ (*28*)). Input of Σ12DL-PCB to the total Swiss agricultural surface was dominated by aerial deposition (mean: 9.4 g WHO-TEQ/y). Compost and manure application accounted for more than one order of magnitude less. As for PCDD/Fs, surface specific loads to soil by compost application can outweigh input by aerial deposition and manure application (Figure 2b). However, aerial deposition and sewage sludge data on DL-PCB are sparse and their interpretation needs caution. Since DL-PCB and PCDD/F concentrations in compost were in the same range (assuming WHO-TEQ equals I-TEQ), time for DL-PCB accumulation in soils to a certain level would be similar for both compound classes. Therefore, it would be useful to include DL-PCBs in studies and legislation on PCDD/Fs.

Brominated flame retardants

Median PBDE concentrations (Sum of BDE 28, 47, 99, 100, 153, 154, 183, 209, Σ8BDE) in composts and digestates was 10 μg/kg$_{dw}$ (range: 0.74-35 μg/kg$_{dw}$, Figure 1, n=18, Supporting information, Table 1). The dominating compound was decaBDE, i.e., BDE 209 (median 7.3 μg/kg$_{dw}$). It correlated significantly with the sum of the remaining PBDEs (r^2=0.58, p=0.0003). Marb et al. (*29*) reported a median value of 12 μg/kg$_{dw}$ for the sum of tri- to heptaBDE in compost (n=12). Unfortunately, compound specific comparison is not possible, since only the total sum was reported. Median concentrations of pentaBDE and octaBDE in Swiss composts and digestates, calculated according to Morf et al. (*30*), were 1.9 $\mu g/kg_{dw}$, and 0.2 $\mu g/kg_{dw}$, respectively. This is in line with estimated diffusive emission patterns in Switzerland (emission: 1.9 t/y and 0.37 t/y, respectively (*31*)). DecaBDE emission data (2.1 t/y (*31*)) was in the same range as pentaBDE, but respective concentrations in compost were much higher. This might reflect increasing production of decaBDE in the beginning of the third millennium (*32*). There was a weak correlation between Σ8BDE and Σ12DL-PCBs (r^2=0.35, p=0.01) pointing at similar input pathways to compost, e.g., aerial deposition.

Octa- and decaBDE levels were slightly higher in digestate than in compost. As for Σ12DL-PCBs, higher Σ8BDE concentrations were found in urban compost and digestates containing organic kitchen waste compared to rural green waste compost (11 versus 5.2 $\mu g/kg_{dw}$). This may reflect higher PBDE concentrations in urban areas (*33*) or higher input via organic kitchen waste. However, the difference was significant for BDE 183 only. PCA revealed a considerably different BDE pattern in sample no. 28 (Supporting information, Figure 5), which had a high concentration of BDE183 relative to Σ8BDE. This may be due to contamination by commercially produced octaBDE, in which BDE183 is the major congener (*34*). No correlation was found between any of the BDE congeners and the duration of the composting process.

PBDE concentrations in compost were higher than in Swedish soil (pentaBDE: 122 ng/kg_{dw}, octaBDE: below quantification limit, decaBDE: 480 ng/kg_{dw} (*35*)), but congener patterns were similar (no data for Switzerland available).

Even though data are limited, it is suggested that total and surface specific loads of PBDE to soil by compost application is low compared to other inputs (Figure 2c). This contrasts with the findings for PCDD/F, PCB and PAH (see above and (*1*)). A possible explanation is additional input sources of PBDE to sewage sludge (e.g., leaching from building materials via surface runoff), whereas for the other compounds aerial deposition plays the most important role. However, since PBDE are still released to the environment, increasing levels in most environmental compartments, including compost and soil may be anticipated.

Median HBCD and TBBPA concentrations in compost were 100 and 0.51 $\mu g/kg_{dw}$, respectively (Figure 1, n=18, Supporting information, Table 1). Even though European market demand in 2001 of all three classes of BFR were in the same range (PBDE: 8360 t/y, HBCD: 9500 t/y, TBBPA: 11600 t/y, (*32*)), compost contained significantly more HBCD than TPPBA. This profile has been observed in sewage sludge previously (*36*) and is explained by the different ways that HBCD and TBBPA are incorporated in products (HBCD as additive, whereas TBBPA is manly covalently bound (*30*)). Concentrations of HBCD and TBBPA were slightly higher in digestate (170 and 1.0 $\mu g/kg_{dw}$, respectively) than in compost (47 and 0.5 $\mu g/kg_{dw}$, respectively), contrasting with a laboratory study where HBCD was found to degrade faster under anaerobic than under aerobic conditions (*37*). However, higher concentrations in the digestate input material might have caused this difference as well. Similar to PBDEs, urban compost containing kitchen waste had significantly higher TBBPA concentrations than rural green waste compost (0.63 versus 0.11 $\mu g/kg_{dw}$), whereas for HBCD no significant difference was identified. No correlation was found between HBCD or TBBPA concentrations and the duration of the composting process. We are not aware of any soil data on HBCD and TBBPA for comparison.

As for PCDD/Fs, DL-PCBs (see above) and PAHs (*1*), aerial deposition dominated the input of HBCD to total agricultural soil. Surface specific load of HBCD by compost application was estimated to be between input by sewage sludge (2.0 g/ha/y) and aerial deposition (0.3 g/ha/y, Figure 2d) as found for PBDEs. Data for TBBPA input estimation was not available.

PFAS

Median PFAS concentration (Sum of 6:2 fluorotelomer sulfonate (6:2 FTS), saturated/unsaturated fluorotelomer carboxylates (FT(U)CA), perfluorinated sulfonates (PFS), perfluorinated carboxylates (PFCA), fluorooctane sulfonamides (FOSA), fluorooctane sulfonamidoethanols (FOSE)) was 6.3 $\mu g/kg_{dw}$, ranging from 3.4 to 35 $\mu g/kg_{dw}$ (Figure 1, n=18, and Supporting information, Table 1). 6:2 FTS, which is the degradation product of recent replacement compounds for perfluorooctane sulfonate (PFOS) in, e.g., fire fighting foams, was detected in nine out of 18 samples (median 1.2 $\mu g/kg_{dw}$, n=9). Other FTS and FT(U)CA (degradation products of fluorotelomer alcohols) were not found. Except for perfluorobutane sulfonate (PFBS, another successor of PFOS), all analysed PFS were detected. Their sum concentration varied between 1.0 and 24 $\mu g/kg_{dw}$ with a median at 2.3 $\mu g/kg_{dw}$ (n=18). Perfluorinated hexa- to dodecanoates were also found in compost (median concentration of the Sum of PFCA: 2.8 $\mu g/kg_{dw}$, n=18). Even carbon number PFCA were found in higher concentrations than their odd-numbered homologues, which might be an indication for near-source contamination with input from PFCA manufactured both by telomerisation and electrochemical fluorination. The opposite (odd C number > even C number) was found in Arctic biota (*38*), indicating that degradation of fluorotelomer alcohols or other precursor compounds could be the reason for the altered pattern.

No difference in PFAS concentration was found between digestate and compost and between urban organic kitchen waste samples compared to rural green waste composts. No sample was singled out in PCA of the relative contribution of the sums of 6:2 FTS, PFS, PFCA, and perfluorooctane sulfonamide to the total sum (Supporting information, Figure 6). This may indicate a uniform distribution of these compounds. As for PCDD/Fs, weak but significant positive correlations of PFS (r^2=0.27, p=0.03) with the duration of the composting process were observed.

No data on PFAS in compost and soil could be found. The here presented PFS (perfluorohexane sulfonate, PFOS and perfluorodecane sulfonate) and PFCA (perfluorooctanoate to perfluorododecanoate) concentrations in compost were between concentrations in sludge and surface sediment from the USA (*39*). The total and surface specific loads for PFAS seemed to be lower for compost than for sewage sludge application (Figure 2e-f). However, data is sparse or nonexistent (deposition data, concentrations in manure) and no final conclusion can be drawn.

Pesticides

Out of the 269 pesticides (86 fungicides, 86 herbicides, 92 insecticides, five acaricides, one nematicide) that were looked for, 30 fungicides, 14 herbicides, eight insecticides, and one acaricide were detected in compost and digestate (Supporting information Table 1 & 3 and Figure 7). The consumption data on pesticide use available for Switzerland (*40*) was not reflected in compost. The pesticides half-lives in soil (*41*) seemed to be related to their occurrence (i.e., compounds with longer half-lives were detected more often).

Fungicides dominated over the other pesticides not only in terms of incidence of detection (see above), but also of concentrations (median total concentration of fungicides: 42.4 $\mu g/kg_{dw}$, n=18). Highest median concentrations were found for imazalil (9.0 $\mu g/kg_{dw}$, n=13) and thiabendazole (5.3 $\mu g/kg_{dw}$, n=14, Supporting information, Figure 7). These typical post-harvest fungicides are often found on tropical fruits (*42*). The median thiabendazole concentration in Swiss compost was slightly lower than in the literature (7 $\mu g/kg_{dw}$, n= 23, (*2*)). Triazoles dominated among the fungicides (19 analysed, 13 detected, median of the sum of triazoles: 21.6 $\mu g/kg_{dw}$, n=18). Difenoconazole, fenbuconazole, propiconazole, and tebiconazole were detected in all compost samples. These compounds are widely used in viticulture, orchards and horticulture in Switzerland and other countries. They are frequently detected in fruit and vegetables and some of them exhibit half-lives of more than 40 days in soil (*41*). Compost and digestate did not differ in fungicide concentrations. The sum of all fungicides was significantly higher in urban composts and digestates containing organic kitchen waste (median: 61 $\mu g/kg_{dw}$) compared to rural green waste compost (median: 27 $\mu g/kg_{dw}$). Rather than by the origin of the input material, this is explained by higher contamination of organic kitchen waste. In general, numbers and concentrations of fungicides detected in compost decreased with the duration of the composting process. However, respective correlations were weak and not significant (p=0.11 and 0.15, respectively). Urban samples containing organic kitchen waste exhibited significantly higher median fungicide concentration in winter (90 $\mu g/kg_{dw}$, n=4) compared to summer (64 $\mu g/kg_{dw}$, n=6, p=0.011). This is explained by the higher consumption of fungicide-treated (especially imazalil and thiabendazole, see above) tropical fruits in winter.

Median herbicide concentration was 5.8 $\mu g/kg_{dw}$ (n=13). Three herbicides (or herbicide metabolites, respectively) were detected in more than four compost samples (oxadiazon, median: 1.6 $\mu g/kg_{dw}$, n=8; terbuthylazine-2-hydroxy, median: 1.1 $\mu g/kg_{dw}$, n=8; and oryzalin, median: 2.1 $\mu g/kg_{dw}$, n=5). Oxadiazon is not registered in Switzerland, whereas the others are listed in the Swiss phytosanitary product index (*43*). The lower abundance of herbicides compared to fungicides in compost can be explained by the fact that herbicides are mainly used at the beginning of the growing season in horticulture and should be mostly degraded by the time of harvest. In contrast, fungicides are applied later during the growth season, or for post-harvest treatment. Other agricultural residues that might contain herbicides (e.g., straw, grass) hardly end up in Swiss commercial composting plants. There was no difference in herbicide concentration in compost and digestate. Median herbicide concentrations in urban samples with organic kitchen waste were significantly higher (8.5 $\mu g/kg_{dw}$, n=9) than in rural green waste compost (1.1 $\mu g/kg_{dw}$ n=3). Herbicide application is banned in traffic areas in Switzerland, and since it can be assumed that herbicide concentrations in kitchen waste are low (see above), it is concluded that urban green waste is more contaminated with herbicides than rural one (probably due to higher application rates in, e.g., private gardens and public green areas).

Median concentration of the sum of all insecticides was 4.1 $\mu g/kg_{dw}$ (n=18). The only insecticide detected in several composts was propoxur (median 4.2 $\mu g/kg_{dw}$, n=12). Propoxur is not used for agricultural purposes, but as biocide in numerous commercial products to control insect pests in food storage areas, houses, animal shelters etc. The important contribution of propoxur to the total sum of insecticides point to a high consumption, since it is neither particularly hydrophobic ($\log K_{ow}$ 1.56, (*41*) which is at the lower end of all the compounds detected), nor very persistent (readily degradable (*41*)). In contrast to former studies (*3*), organochlorine insecticides were not detected in composts and digestates. No Swiss data on pesticides in soil are available. Any comparison with soil data from other countries is problematic, since the use of pesticides varies considerably between them. Information on deposition rates obtained from Bucheli et al. (*44*) showed that total and surface specific loads of fungicides by compost application were at least a factor 20 below aerial deposition, and several orders of magnitudes lower than input from direct application (Swiss phytosanitary product index). For herbicides, surface specific loads of aerial deposition and compost application differed by a factor of 1500. However, as for fungicides, application on agricultural crops is considered to be the far most important input pathway.

Phthalates, nonylphenol and chlorinated paraffins

Median di(2-ethylhexyl)phthalate (DEHP) concentration was 280 $\mu g/kg_{dw}$ (n=6), corresponding well with literature values (300 $\mu g/kg_{dw}$, (*2*)). This is clearly below the limit of the Danish Statutory Order (50 mg/kg_{dw}, (*45*)). The highest value (1990 $\mu g/kg_{dw}$) was detected in an urban digestate sample containing organic kitchen waste, as well as fruit and vegetable residues from grocery stores, in which also dibutylphthalate (DBP) was detected (105 $\mu g/kg_{dw}$). These elevated phthalate levels might be due to plastic residues in the input material originating from fruit and vegetable wrapping. DEHP concentrations in agricultural soils were observed to be in the same range as concentrations in compost (300-700 $\mu g/kg_{dw}$, (*46*)). Total and surface specific loads of DEHP to soil by compost application were estimated to be below the input by sewage sludge or manure application (Figure 2g). Even though detected at considerable concentrations in German apples and tomatoes (*47*), nonylphenol was not detected in compost. Possible reasons are the relatively high detection limit (1 mg/kg_{dw}) and/or rapid degradation during composting (*48*).

CP were analysed and detected in three samples. Concentrations were between 57-140 $\mu g/kg_{dw}$ for SCCP (C_{10}-C_{13}) and 29-245 $\mu g/kg_{dw}$ for MCCP (C_{14}-C_{17}). These concentrations were lower than the qualitative concentrations in Swedish source-separated organic waste (*49*) and values in sewage sludge (*50*), but in the same range as Swiss soils (*51*). This resulted in total and surface specific loads of SCCP and MCCP to soil of 5 and 11%, respectively, by compost compared to sewage sludge application.

Synopsis and Recommendation

This paper presents the most comprehensive dataset on organic priority pollutants in compost, and – for the first time – digestate. Several of the investigated compounds have not been analysed previously, and most of them could be quantified in concentrations at or above those found in background soils. On a national scale, input of organic contaminants to agricultural soils by compost application seemed to be limited. However, similar to PAHs (*1*), loads of PCDD/Fs and DL-PCBs to actually treated areas, could be of concern. This seemingly negative characteristic of compost application needs to be counterbalanced with its apparent and well-documented beneficial aspects, such as soil improving properties and the sustainable management of natural resources. Further research is needed to appoint relevant sources of organic pollutants in compost, to identify possible stable degradation products and to assess to what extent they are biologically available.

Acknowledgements:

The Federal Office for the Environment and the Swiss Federal Office of Energy are acknowledged for financial support and the European Union (PERFORCE project NEST-508967) for supporting PFAS analyses. Thanks due to Henrik Kylin for reviewing this manuscript.

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6.2 Manuscript 2: Figures

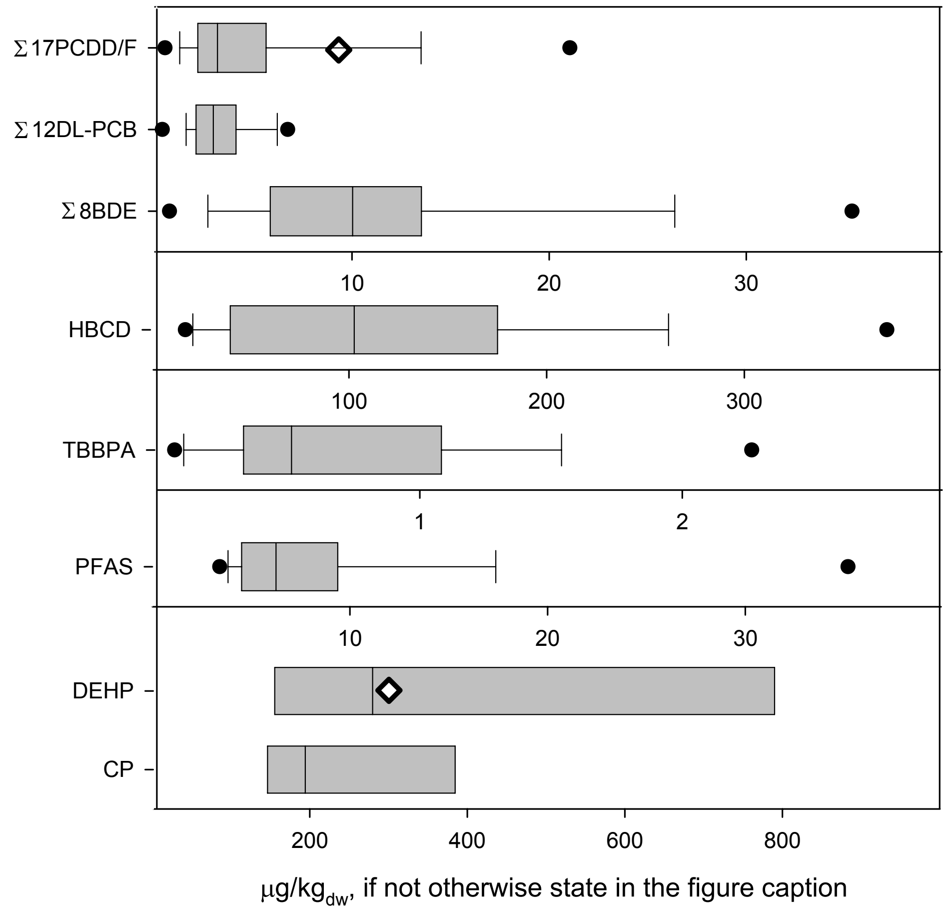

Figure 1: Concentrations of organic pollutants in compost and digestate (line: median; box: 25th and 75th percentile; lines with whiskers 10th and 90th percentile, dots: outliers, diamond: median literature value (*2*); where missing: not available), Σ17PCDD/Fs (sum of the 17 2,3,7,8-chlorosubstituted PCDD/Fs in ng I-TEQ/kg$_{\text{dry weight (dw)}}$, n=18), Σ12DL-PCBs (sum of PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189 in ng WHO-TEQ/kg$_{dw}$, n=18), Σ8BDE (sum of PBDE 28, 47, 99, 100, 153, 154, 183, 209, n=18), HBCD (hexabromocyclododecane, n=18), TBBPA (tetrabromobisphenol A, n=18), PFAS (sum of 21 perfluorinated alkyl substances, n=18), DEHP (di(2-ethylhexyl)phthalate, n=6) and CP (sum of short and medium chain chlorinated paraffins, n=3). For IRMM PCBs and PAHs see (*1*).

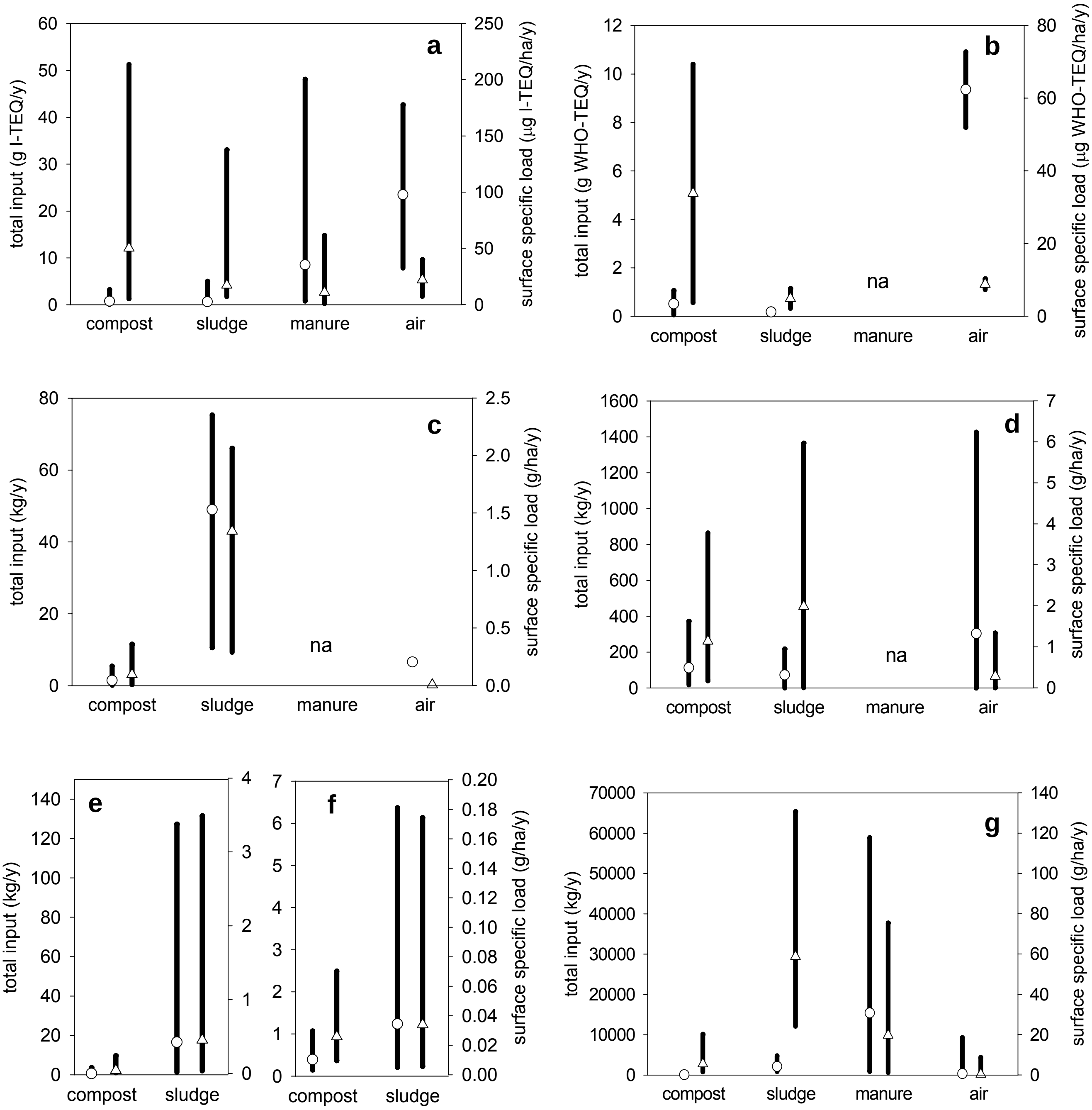

Figure 2: Average annual loads of organic pollutants from different sources: application of compost, sewage sludge (sludge), farmyard manure (manure) and atmospheric deposition (air) into agricultural soil into agricultural soil: total loads to the Swiss agricultural area (○), surface specific loads (△), bars represent minimum and maximum values, na: not available. a) Σ17PCDD/Fs (sum of the 17 2,3,7,8-chlorosubstituted PCDD/Fs), b) Σ12DL-PCBs (sum of PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189), c) Σ8BDE (sum of PBDE 28, 47, 99, 100, 153, 154, 183, 209), d) hexabromocyclododecane, e) perfluorohexane sulfonate, f) perfluorooctanoate to perfluorododecanoate g) di(2-ethylhexyl)phthalate For assumptions/calculations, see text, for IRMM PCB and PAH see (*1*). na: not available.

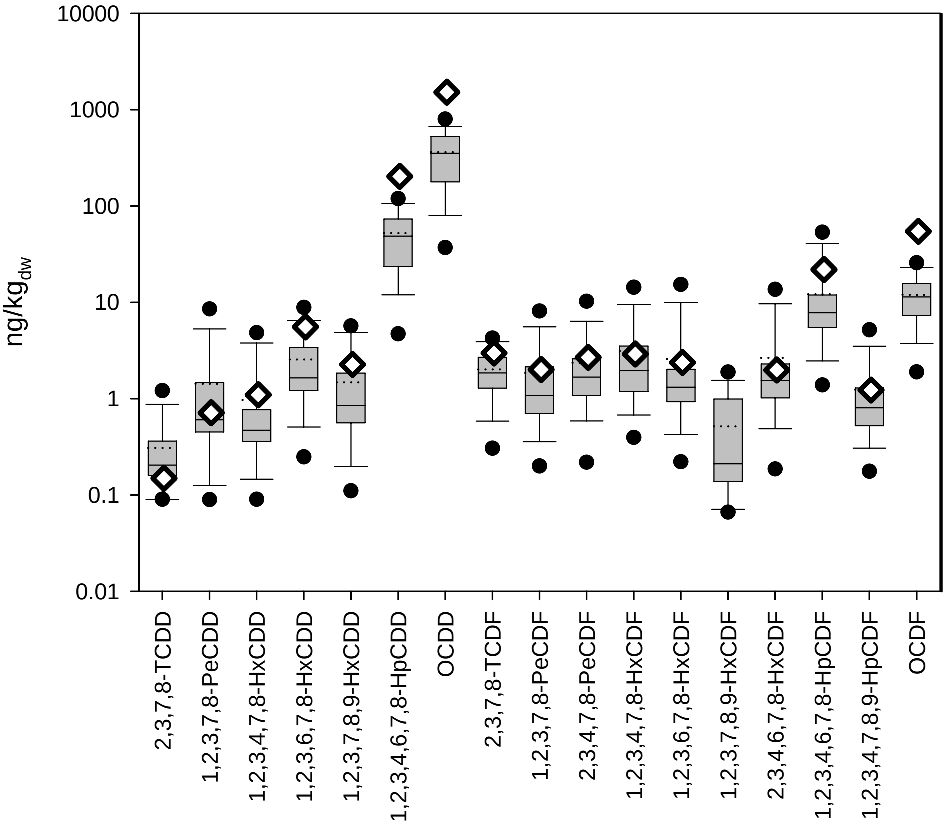

Figure 1: PCDD/F single compounds concentrations in Swiss compost and digestate (line: median, dotted line: mean, box: 25 and 75 percentile, whiskers: 10 and 90 percentile, circles: outliers) and corresponding literature values (diamonds).

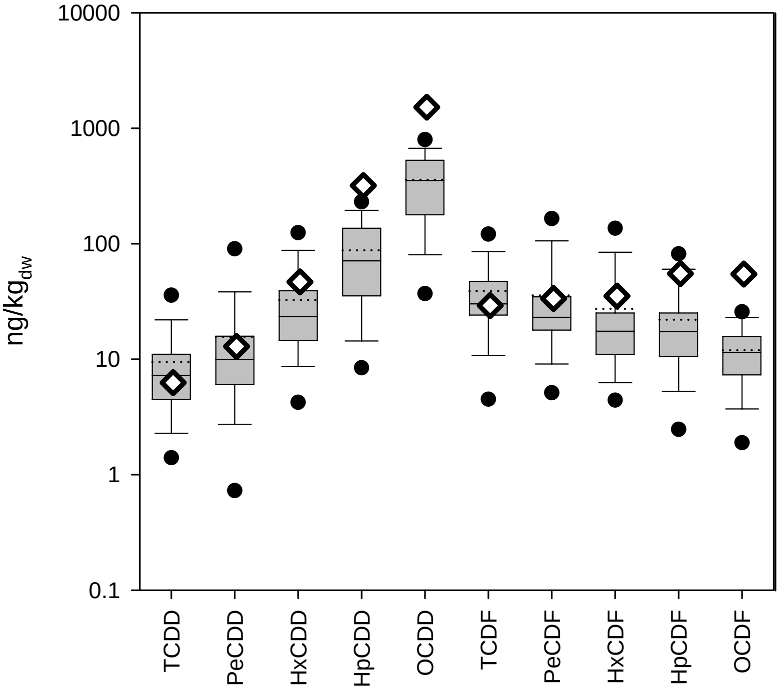

Figure 2: sum all tetra, penta, hexa, hepta, octa PCDD/F in Swiss compost and digestate (line: median, dotted line: mean, box: 25 and 75 percentile, whiskers: 10 and 90 percentile, circles: outliers) and corresponding literature values (diamonds).

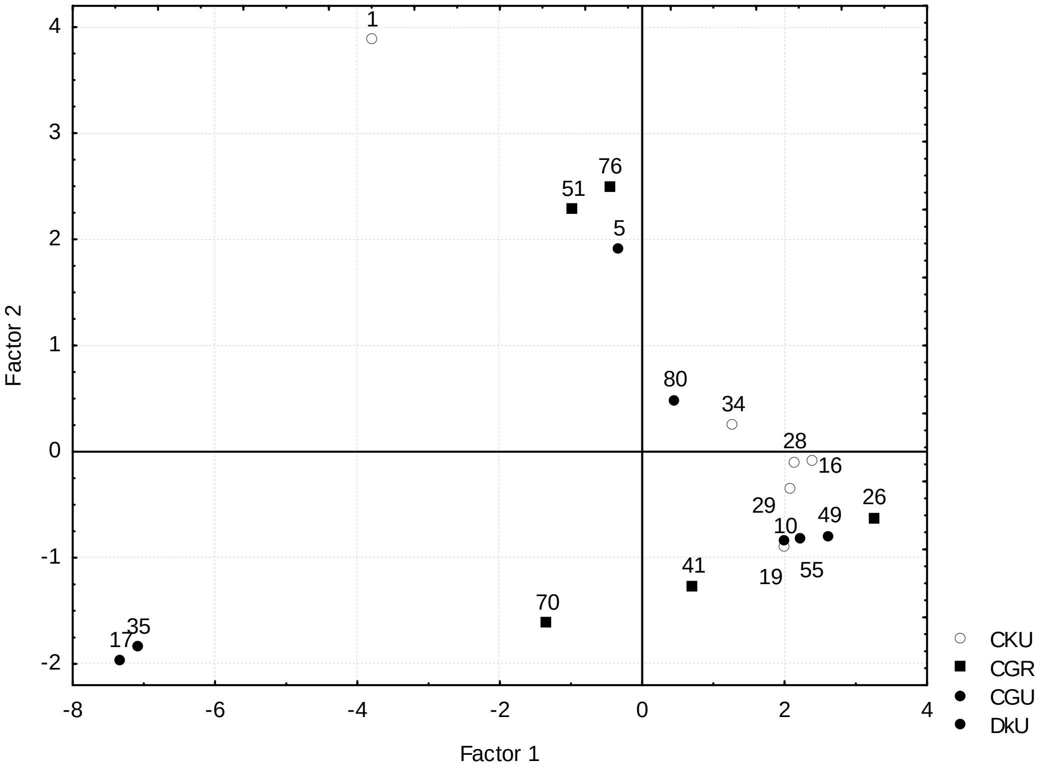

Figure 3: Factor 1 and 2 of the PCA of the PCDD/F ratios (sums of tetra to octa PCDD/Fs to the total sum) in Swiss compost and digestate (CKU: compost containing kitchen waste originating from urban areas, CGR: compost derived from greenwaste originating from rural aeras, CGU: compost derived from greenwaste originating from urban areas, DKU: digestate containing kitchen waste originating from urban areas).

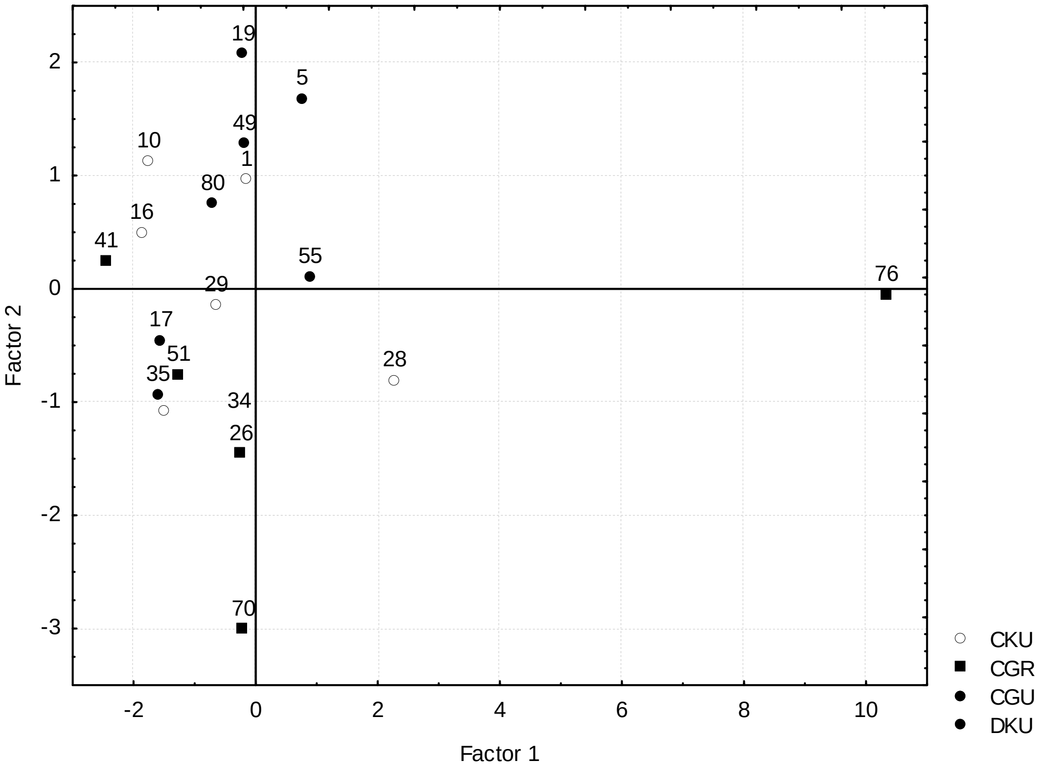

Figure 4: Factor 1 and 2 of the PCA of the dioxin-like PCB ratios (single congeners/total sum) in Swiss compost and digestate (CKU: compost containing kitchen waste originating from urban areas, CGR: compost derived from greenwaste originating from rural aeras, CGU: compost derived from greenwaste originating from urban areas, DKU: digestate containing kitchen waste originating from urban areas).

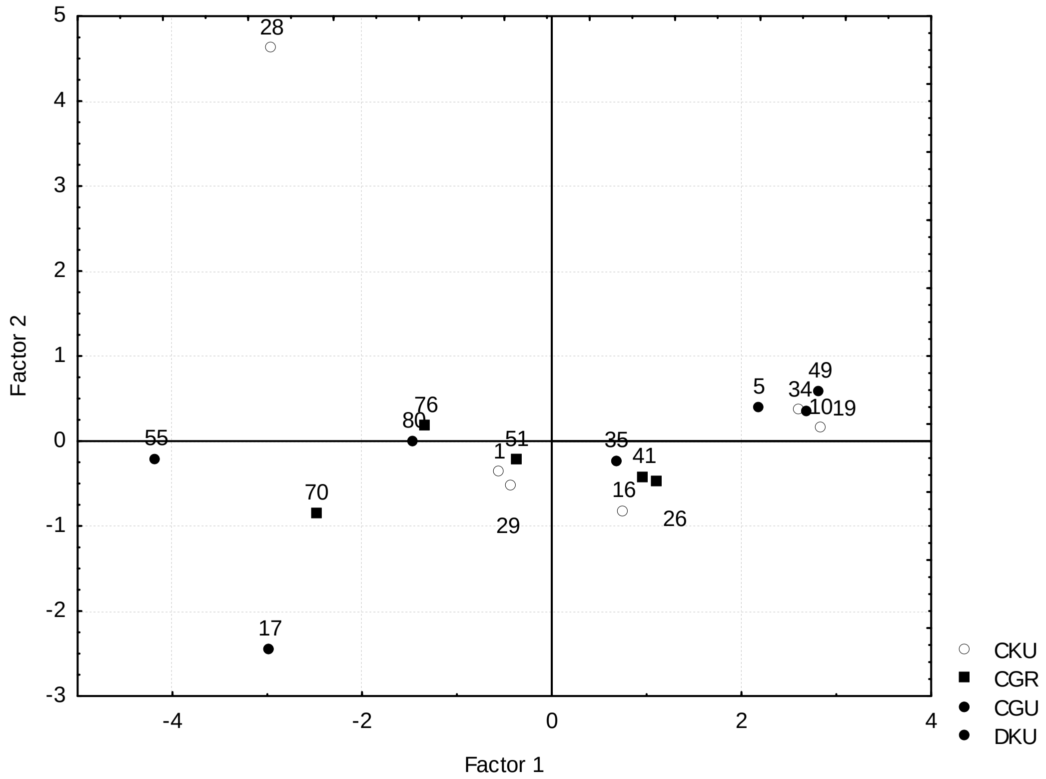

Figure 5: Factor 1 and 2 of the PCA of the polybrominated diphenyl ether ratios (single compound/total sum) in Swiss compost and digestate (CKU: compost containing kitchen waste originating from urban areas, CGR: compost derived from greenwaste originating from rural aeras, CGU: compost derived from greenwaste originating from urban areas, DKU: digestate containing kitchen waste originating from urban areas).

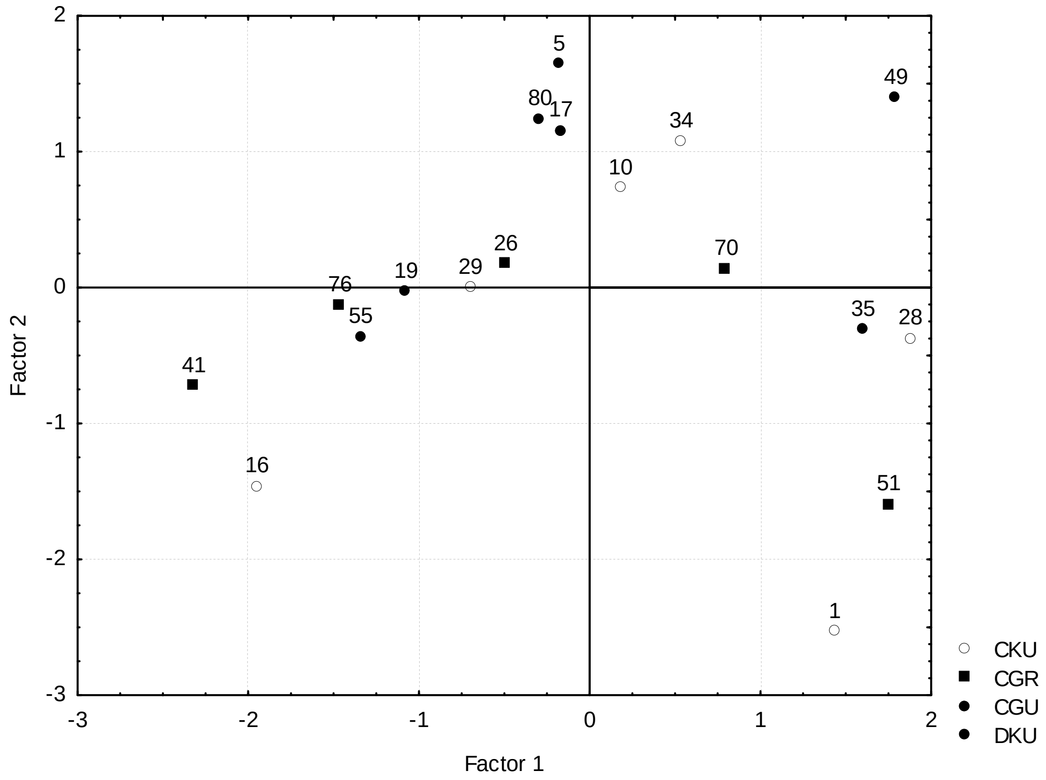

Figure 6: Factor 1 and 2 of the PCA of the polyfluorinated alkyl substances ratios (6:2 fluorotelomer sulfonate, perfluorinated sulfonates, perfluorinated carboxylates, and perfluorooctane sulfonamide to the total sum) of in Swiss compost and digestate (CKU: compost containing kitchen waste originating from urban areas, CGR: compost derived from greenwaste originating from rural aeras, CGU: compost derived from greenwaste originating from urban areas, DKU: digestate containing kitchen waste originating from urban areas).

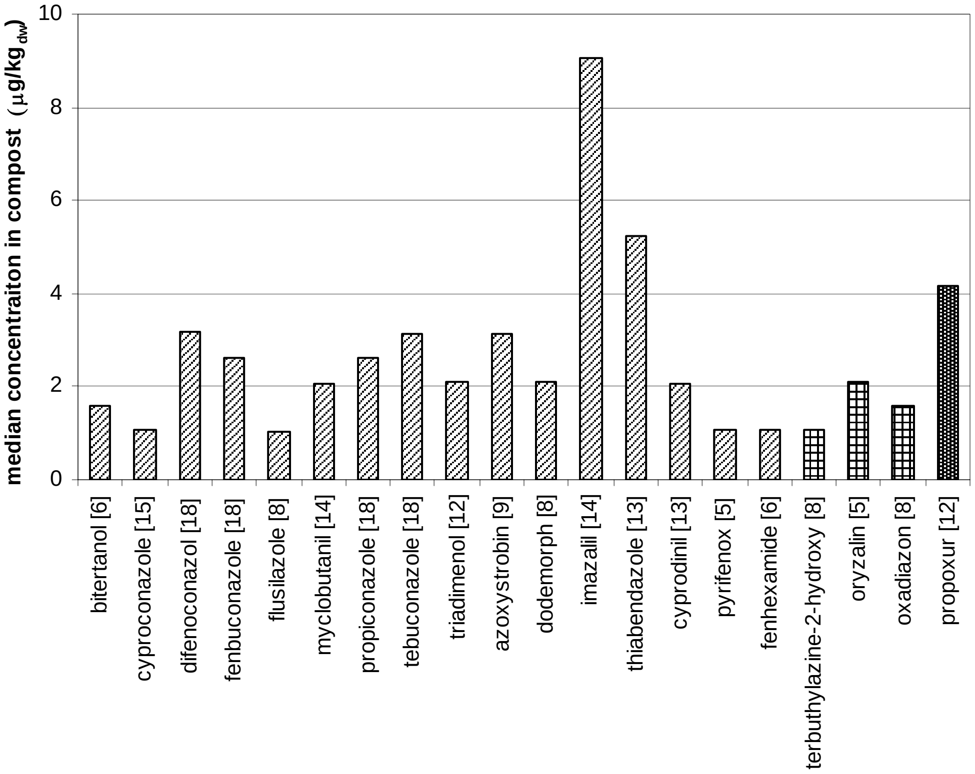

Figure 7: Median pesticide concentrations in Swiss compost and digestate for compounds detected more than four times (fungicide ▨, herbicide ▩ and insecticide ▦). Median calculations were based on the number of detections out of 18, which are represented in brackets. Note that the first nine compounds are triazoles.

Table 1: Organic pollutant contents of compost and digestate samples in Switzerland

Sample No.	1	5	10	16	17	19	26	28	29
Product[a]	Com	Dig	Com	Com	Com	Dig	Com	Com	Com
Plant type and number[b]	CKU1	DKU1	CKU2	CKU4	CGU4	DKU2	CGR04	CKU02	CKU01
Input material[c]	kw, gw, iw	kw, gw, iw	kw, gw	kw, gw	gw	kw, gw	gw	kw, gw	kw,gw, iw
Origin of input material[d]	urban	urban	urban	urban	urban	urban	rural	urban	urban
Season[e]	winter	winter	winter	autumn	winter	winter	autumn	summer	summer
Plant type[f]	twl	tad	ab	twh	tbw	tad	twh	ab	twl
Process duration (d)[f]	53	42	77	210	127	105	203	55	50
Water content [% ww]	50	49	45	47	53	45	40	45	49
Org matter content [% dw]	62	46	57	41	40	42	27	51	51
PCDD/F (ng/kg$_{dw}$)									
2,3,7,8-TCDD	0.17	0.14	0.21	0.85	1.2	0.26	0.18	0.22	0.20
1,2,3,7,8-PeCDD	0.33	0.54	0.95	0.83	8.8	1.6	0.58	0.49	0.61
1,2,3,4,7,8-HxCDD	0.22	0.44	0.47	0.69	5.0	0.66	0.41	0.45	0.47
1,2,3,6,7,8-HxCDD	1.0	1.3	2.3	2.8	9.1	3.8	1.3	1.3	1.5
1,2,3,7,8,9-HxCDD	0.37	0.74	1.1	1.5	5.9	1.8	0.87	0.82	0.83
1,2,3,4,6,7,8-HpCDD	13	24	65	70	120	110	39	33	44
OCDD	85	210	410	510	820	660	360	290	310
2,3,7,8-TCDF	1.2	2.0	2.2	2.0	4.4	3.9	1.3	1.9	1.6
1,2,3,7,8-PeCDF	0.76	1.4	1.9	1.6	8.4	3.1	1.0	0.75	0.88
2,3,4,7,8-PeCDF	0.75	1.5	1.7	1.9	11	2.8	1.1	0.96	1.4
1,2,3,4,7,8-HxCDF	1.5	2.4	2.9	3.3	15	4.8	1.0	2.2	1.6
1,2,3,6,7,8-HxCDF	0.66	1.1	1.2	1.7	16	1.9	1.0	1.4	1.3
1,2,3,7,8,9-HxCDF	0.14	0.20	1.2	0.21	1.2	1.9	0.21	0.12	0.22
2,3,4,6,7,8-HxCDF	0.76	1.1	1.4	1.7	14	2.3	1.2	1.6	1.7
1,2,3,4,6,7,8-HpCDF	4.9	6.4	7.5	10	55	12	7.6	5.8	8.0
1,2,3,4,7,8,9-HpCDF	0.32	0.63	0.87	0.96	5.3	1.4	0.77	0.84	0.68
OCDF	6.6	11	12	15	27	19	10	7.6	11
Σ17PCDD/Fs (I-TEQ)	1.6	2.7	3.9	5.0	21	6.6	2.6	2.7	3.0
Sum TCDD	3.8	4.7	9.6	9.5	37	11	5.5	6.6	11
Sum PeCDD	6.4	9.7	9.9	17	93	16	6.3	5.4	13
Sum HxCDD	11	16	25	40	130	39	17	16	26
Sum HpCDD	24	47	120	140	240	190	65	44	77
Sum TCDF	27	31	36	37	120	57	20	28	34
Sum PeCDF	12	20	23	31	170	36	20	24	27
Sum HxCDF	9.4	11	16	22	140	25	16	17	18
Sum HpCDF	8.3	12	20	19	84	33	14	11	17
DL-PCB (µg/kg$_{dw}$)									
PCB 77	0.067	0.12	0.25	0.29	0.21	0.23	0.058	0.071	0.097
PCB 81	0.0024	0.0041	0.0082	0.0088	0.0073	0.0076	0.0018	0.0030	0.0037
PCB 105	0.77	2.2	2.6	2.5	2.3	3.9	0.65	0.75	1.2
PCB 114	0.034	0.090	0.098	0.12	0.11	0.18	0.032	0.035	0.060
PCB 118	2.1	5.0	5.8	5.6	5.5	9.1	1.6	2.1	3.0
PCB 123	0.15	0.37	0.40	0.49	0.43	0.67	0.060	0.15	0.13
PCB 126	0.012	0.024	0.035	0.047	0.043	0.044	0.013	0.015	0.018
PCB 156	0.36	0.97	0.73	0.88	0.81	1.5	0.28	0.57	0.50
PCB 157	0.07	0.18	0.18	0.18	0.19	0.28	0.060	0.090	0.10
PCB 167	0.16	0.40	0.29	0.40	0.36	0.64	0.14	0.27	0.24
PCB 169	0.0011	0.0024	0.0025	0.0029	0.0049	0.0037	0.0012	0.0016	0.0018
PCB 189	0.039	0.12	0.060	0.075	0.066	0.14	0.039	0.10	0.053
Σ12PCB (WHO-TEQ)	1.8	3.9	5.0	6.3	5.8	6.8	1.7	2.2	2.6
BFR (µg/kg$_{dw}$)									
BDE 28	0.013	0.023	0.030	0.052	0.13	0.031	0.015	0.013	0.022
BDE 47	0.59	0.63	0.84	1.5	1.3	1.3	0.45	0.56	1.0

BDE 99	0.78	0.69	0.84	0.64	0.87	1.3	0.32	0.76	1.3
BDE 100	0.17	0.15	0.18	0.29	0.28	0.32	0.11	0.15	0.29
BDE 153	0.067	0.10	0.074	0.10	0.13	0.16	0.040	0.29	0.11
BDE 154	0.080	0.082	0.090	0.15	0.16	0.17	0.032	0.12	0.10
BDE 183	0.049	0.087	0.056	0.11	0.11	0.11	0.038	1.2	0.042
BDE 209	5.2	10	14	12	6.9	22	4.2	4.8	8.3
HBCD	21	170	190	26	47	110	230	140	35
TBBPA	1.4	1.5	0.51	2.3	1.4	0.63	0.065	0.52	0.57

PFAS ($\mu g/kg_{dw}$)[6]

6:2 FTS	1.4	nd	nd	1.5	nd	nd	nd	1.4	nd
PFHxS	0.070	0.13	0.080	2.2	0.33	0.39	0.090	nd	0.17
PFOS	1.2	2.1	1.4	21	3.6	8.2	2.1	1.0	2.1
PFDcS	nd	0.070	nd	0.31	nd	0.050	nd	nd	nd
PFHxA	0.30	0.68	0.24	2.1	0.97	1.1	0.19	0.33	0.71
PFHpA	nd	0.19	nd	0.81	0.49	0.60	0.50	0.36	nd
PFOA	0.67	1.3	1	3.6	1.6	2.5	1.2	0.77	1.0
PFNA	0.28	0.27	0.29	0.91	0.36	0.60	0.23	nd	0.21
PFDcA	nd	0.66	0.39	1.7	0.85	1.4	nd	0.50	nd
PFUnA	nd	nd	nd	0.31	0.26	0.29	nd	nd	nd
PFDoA	nd	nd	nd	0.37	0.24	0.16	nd	0.20	nd
PFOSA	nd	0.37	nd	0.20	0.34	0.23	nd	0.26	nd

Pesticides ($\mu g/kg_{dw}$)

atrazine-2-hydroxy	nd	nd	nd	nd	nd	nd	nd	1.1	1.0
azaconazole	nd	nd	nd	nd	nd	nd	nd	nd	6.3
azoxystrobin	6.4	nd	7.5	nd	nd	nd	nd	2.1	3.1
bitertanol	nd	nd	nd	nd	nd	nd	nd	2.1	1.0
bromacil	nd	nd	nd	nd	nd	nd	nd	2.1	nd
buprofezin	nd	1.1	1.1	nd	nd	nd	nd	nd	nd
carbendazim	nd	1.1	nd	nd	nd	nd	nd	nd	nd
cyproconazole	nd	1.1	1.1	3.2	1.1	1.1	1.1	nd	3.1
cyprodinil	1.1	7.4	2.1	1.1	nd	nd	nd	1.1	1.0
difenoconazole	2.2	2.1	3.2	3.2	2.1	2.1	4.2	3.2	3.1
diuron	nd	1.1	nd	5.3	nd	nd	nd	nd	nd
dimethomorph	nd	nd	17	nd	nd	nd	nd	1.1	
dodemorph	nd	nd	nd	nd	nd	nd	nd	2.1	2.1
epoxiconazole	nd	nd	nd	nd	nd	nd	nd	nd	nd
etaconazole	nd	nd	nd	nd	nd	nd	nd	nd	nd
fenbuconazole	1.1	2.1	2.1	5.3	3.2	2.1	2.1	3.2	2.1
fenhexamide	nd	6.3	nd	nd	nd	nd	nd	1.1	1.0
fenoxycarb	nd	nd	nd	nd	nd	nd	nd	nd	nd
fenpropathrin	nd	nd	nd	nd	nd	nd	nd	nd	nd
fenpropimorph	nd	2.1	nd	nd	nd	nd	nd	nd	nd
fenpyroximat	nd	nd	nd	nd	nd	nd	nd	nd	nd
flusilazole	na	na	na	na	na	na	1.1	nd	nd
flutolanil	na	na	na	na	na	na	nd	nd	nd
imazalil	8.6	79	99	17	9.5	8.5	nd	24	5.2
mecoprop	nd	3.2	nd	nd	nd	nd	nd	nd	nd
metamitron	nd	nd	nd	nd	nd	nd	nd	nd	nd
methabenzthiazuron	nd	nd	nd	nd	nd	nd	nd	nd	nd
metolcarb	nd	nd	nd	nd	nd	nd	nd	nd	1.0
myclobutanil	nd	1.1	2.1	6.3	2.1	2.1	nd	1.1	1.0
oryzalin	nd	nd	nd	nd	nd	nd	nd	3.2	nd
oxadiazon	nd	1.1	2.1	1.1	nd	nd	nd	3.2	nd
oxadixyl	nd	nd	nd	nd	nd	nd	nd	nd	nd
prochloraz	nd	3.2	nd	nd	nd	nd	nd	nd	nd
propiconazole	1.1	5.3	2.1	1.1	1.1	4.3	2.1	5.3	3.1
propoxur	nd	nd	nd	nd	nd	nd	7.4	4.2	5.2
propyzamide	nd	1.1	nd	nd	nd	nd	nd	nd	nd
pyridaben	nd	nd	nd	nd	nd	nd	nd	nd	nd
pyrifenox	nd	nd	nd	nd	nd	nd	nd	1.1	nd
pyrimethanil	nd	6.3	nd	nd	nd	nd	nd	nd	nd
pyriproxyfen	nd	nd	nd	nd	nd	nd	nd	nd	nd
simazin	nd	nd	nd	3.2	nd	nd	nd	nd	nd

spiroxamine	nd	3.2	nd	nd	nd	nd	nd	nd	nd
tebuconazole	2.2	5.3	8.6	3.2	1.1	5.3	1.1	3.2	3.1
tebufenpyrad	nd	nd	nd	nd	1.1	nd	nd	nd	nd
terbumeton	nd	nd	nd	nd	nd	nd	nd	1.1	nd
terbuthylazine-2-hydroxy	nd	1.1	1.1	1.1	1.1	nd	nd	1.1	nd
terbutryn	nd	1.1	nd	nd	nd	nd	nd	nd	nd
tetraconazole	nd	nd	nd	nd	nd	nd	nd	nd	nd
thiabendazole	2.2	23	23	5.3	2.1	4.3	nd	13	2.1
thiophanate ethyl	nd	nd	nd	nd	nd	nd	nd	nd	nd
triadimefon	nd	nd	nd	nd	nd	nd	nd	nd	nd
triadimenol	nd	nd	nd	nd	nd	nd	1.1	3.2	2.1
triasulfuron	nd	nd	nd	nd	nd	nd	nd	nd	nd
Phthalates (µg/kg$_{dw}$)									
DEHP	270	1980	150	390	160	300	na	na	na
DBP	nd	110	nd	nd	nd	nd	na	na	na
Nonylphenol (µg/kg$_{dw}$)	nd	nd	nd	nd	nd	nd	na	na	na
CP (µg/kg$_{dw}$)									
SCCP									
C10Cl5	nd	na	nd	nd	na	na	na	na	na
C10Cl6	1.1	na	1.3	1.0	na	na	na	na	na
C10Cl7	4.5	na	5.7	1.9	na	na	na	na	na
C10Cl8	2.1	na	4.9	1.0	na	na	na	na	na
C10Cl9	0.79	na	0.78	0.53	na	na	na	na	na
C10Cl10	0.02	na	0.66	nd	na	na	na	na	na
C10Cl11	nd	na	nd	nd	na	na	na	na	na
C11Cl5	1.3	na	2.4	nd	na	na	na	na	na
C11Cl6	28	na	4.8	2.5	na	na	na	na	na
C11Cl7	16	na	20	8.7	na	na	na	na	na
C11Cl8	11	na	17	3.7	na	na	na	na	na
C11Cl9	3.1	na	6.2	1.2	na	na	na	na	na
C11Cl10	0.85	na	2.2	0.52	na	na	na	na	na
C12Cl5	2.4	na	nd	nd	na	na	na	na	na
C12Cl6	2.8	na	3.3	3.8	na	na	na	na	na
C12Cl7	7.6	na	9.8	5.6	na	na	na	na	na
C12Cl8	10	na	15	4.7	na	na	na	na	na
C12Cl9	5.2	na	11	1.7	na	na	na	na	na
C12Cl10	1.2	na	4.3	1.3	na	na	na	na	na
C13Cl5	2.2	na	2.5	2.6	na	na	na	na	na
C13Cl6	2.5	na	3.3	4.2	na	na	na	na	na
C13Cl7	5.4	na	8.1	5.6	na	na	na	na	na
C13Cl8	4.5	na	9.9	3.9	na	na	na	na	na
C13Cl9	2.7	na	5.4	1.6	na	na	na	na	na
C13Cl10	0.78	na	1.8	0.51	na	na	na	na	na
MCCP									
C14Cl5	nd	na	nd	nd	na	na	na	na	na
C14Cl6	3.0	na	12	15	na	na	na	na	na
C14Cl7	7.4	na	51	39	na	na	na	na	na
C14Cl8	9.8	na	79	43	na	na	na	na	na
C14Cl9	6.2	na	50	23	na	na	na	na	na
C14Cl10	nd	na	17	nd	na	na	na	na	na
C15Cl5	nd	na	0.46	0.50					
C15Cl6	0.57	na	2.5	2.2	na	na	na	na	na
C15Cl7	0.85	na	6.5	3.5	na	na	na	na	na
C15Cl8	0.48	na	5.8	2.0	na	na	na	na	na
C15Cl9	nd	na	2.9	0.69	na	na	na	na	na
C15Cl10	nd	na	0.62	nd	na	na	na	na	na

C16Cl5	nd	na	0.48	nd	na	na	na	na	na
C16Cl6	nd	na	1.2	1.2	na	na	na	na	na
C16Cl7	0.36	na	3.0	2.3	na	na	na	na	na
C16Cl8	0.24	na	3.3	1.7	na	na	na	na	na
C16Cl9	nd	na	1.8	0.65	na	na	na	na	na
C16Cl10	nd	na	0.63	nd	na	na	na	na	na
C17Cl5	nd	na	nd	nd	na	na	na	na	na
C17Cl6	nd	na	1.0	0.83	na	na	na	na	na
C17Cl7	nd	na	1.6	1.0	na	na	na	na	na
C17Cl8	0.13	na	2.1	0.92	na	na	na	na	na
C17Cl9	nd	na	1.2	0.35	na	na	na	na	na
C17Cl10	nd	na	0.41	nd	na	na	na	na	na

a) Com: compost, Dig: digestate, all digestate samples were submitted to subsequent aerobic treatment except for samples 80
b) plant code: C: compost, K: organic kitchen waste and green waste as input materials, G: pure green waste compost, U: urban area of input material collection, R: rural area of input material collection
c) kw: kitchen waste, gw: green waste, iw: industrial waste including paper sludge, coffee ground, tea leaves, residues from potato chips production, biodegradable plastics, edible oil, cacao
d) characterisation of the area where the input material was collected
e) season of input material collection
f) plant type: ab: aerated boxes, tad: thermophilic aerobic digestion, tbw: table windrows, twh: triangle windrows higher than 2 meters, twl: triangle windrows lower than 2 meters
g) duration of the degradation process in days

6 FTS: fluorotelomer sulfonate, PFHxS: perfluorohexane sulfonate, PFOS: perfluorooctane sulfonate, PFDcS: perfluorodecane sulfonate, PFHxA: perfluorohexanoate, PFHpA: perfluoroheptanoate, PFOA: perfluorooctanoate, PFNA: perfluorononanoate, PFDcA: perfluorodecanoate, PFUnA: perfluoroundecanoate, PFDcA: perfluorododecanoate, PFOSA: perfluorooctane sulphonamide, na: not available, nd: not detected, ww: wet weight, dw: dry weight

PFAS below detection limit not listed, dedection limit for 6:2 fluorotelomer unsaturated carboxylate (FTUCA): 0.37µg/kg dw, 8:2 FTUCA: 0.4 µg/kg, 6:2 fluorotelomer carboxylate (FTCA): 0.37µg/kg, 8:2 FTCA: 0.4 µg/kg, perfluorobutane sulfonate: 0.33 µg/kg, n-Methyl-heptadecafluorooctane sulphonamide: <0.18 µg/kg dw, n-Ethyl-heptadecafluorooctane sulfonamide: <0.14 µg/kg dw, n-Methyl-heptadecafluorooctane sulfonamidoethanol: <0.14 µg/kg dw, n-Ethyl-heptadecafluorooctane sulfonamidoethanol: <0.28 µg/kg dw

Table 1: (cont.) Organic pollutant contents of compost and digestate samples in Switzerland

Sample No.	34	35	41	49	51	55	70	76	80
Product[a]	Com	Com	Com	Dig	Com	Dig	Com	Com	Dig
Plant code and number[b]	CKU04	CGU04	CGR02	DKU01	CGR04	DKU02	CGR03	CGR01	DKU03
Input material[c]	kw, gw, iw	gw	gw	kw, gw, iw	gw	kw, gw	gw	gw	kw, gw
Origin of input material[d]	urban	urban	rural	urban	rural	urban	rural	rural	urban
Season[e]	summer	summer	summer	summer	summer	summer	autumn	winter	summer
Plant type[f]	tbw	twh	twh	tad	twh	tad	twh	twl	tad
Process duration (d)[g]	91	96	70	20	105	126	72	21	16
Water content [% ww]	37	43	51	44	32	34	53	39	52
Org. matter content [% dw]	36	45	33	51	39	47	29	24	29
PCDD/F (ng/kg$_{dw}$)									
2,3,7,8-TCDD	0.17	0.49	0.32	0.21	0.09	0.09	0.49	0.10	0.17
1,2,3,7,8-PeCDD	0.72	4.93	1.4	0.60	0.09	0.24	2.5	0.13	0.58
1,2,3,4,7,8-HxCDD	0.68	3.66	1.0	0.52	0.09	0.15	2.0	0.20	0.47
1,2,3,6,7,8-HxCDD	2.4	6.2	3.3	1.8	0.25	0.92	5.0	0.53	1.3
1,2,3,7,8,9-HxCDD	1.0	4.8	1.9	0.62	0.11	0.37	3.1	0.21	0.74
1,2,3,4,6,7,8-HpCDD	68	74	73	53	4.7	24	99	13	22
OCDD	520	560	450	350	37	140	590	100	190
2,3,7,8-TCDF	1.8	3.5	2.5	1.5	0.31	0.62	3.4	1.1	1.4
1,2,3,7,8-PeCDF	0.99	5.3	1.8	1.2	0.20	0.37	3.1	0.51	0.56
2,3,4,7,8-PeCDF	2.0	5.9	2.5	1.7	0.22	0.63	4.2	1.7	1.2
1,2,3,4,7,8-HxCDF	1.6	8.9	2.4	1.2	0.39	0.71	4.2	1.7	0.95
1,2,3,6,7,8-HxCDF	1.4	9.4	2.4	1.5	0.22	0.45	4.0	0.54	1.0
1,2,3,7,8,9-HxCDF	0.38	1.5	0.42	0.21	0.066	0.071	0.93	0.13	0.19
2,3,4,6,7,8-HxCDF	1.4	9.2	2.5	1.8	0.19	0.52	5.0	0.56	1.1
1,2,3,4,6,7,8-HpCDF	9.7	40	12	9.2	1.4	2.9	21	2.6	5.67
1,2,3,4,7,8,9-HpCDF	1.2	3.3	1.3	0.56	0.18	0.47	2.8	0.45	0.54
OCDF	14	23	13	11	1.9	5.0	18	3.9	8.1
Σ17PCDD/Fs (I-TEQ)	4.0	13	5.3	3.3	0.5	1.3	8.6	1.8	2.3
Sum TCDD	7.9	20	13	5.0	1.4	3.1	16	2.4	5.1
Sum PeCDD	10	33	15	14	0.7	2.9	23	3.0	6.4
Sum HxCDD	25	84	37	22	4.2	10	63	9.1	18
Sum HpCDD	120	140	15	89	8.4	39	170	23	42
Sum TCDF	30	81	44	28	4.5	11	72	15	25
Sum PeCDF	28	99	34	22	5.1	9.5	53	18	18
Sum HxCDF	23	79	26	20	4.4	6.5	42	12	11
Sum HpCDF	19	58	23	18	2.5	6.4	37	5.6	12
DL-PCB (µg/kg$_{dw}$)									
PCB 77	0.12	0.13	0.22	0.14	0.011	0.047	0.061	0.047	0.14
PCB 81	0.0040	0.0050	0.0085	0.0046	0.00048	0.0018	0.0022	0.0013	0.0049
PCB 105	1.2	1.6	1.7	1.9	0.14	0.77	0.62	0.95	1.8
PCB 114	0.054	0.072	0.090	0.089	0.0080	0.036	0.027	0.041	0.098
PCB 118	2.8	3.7	3.8	4.5	0.36	1.9	1.5	3.7	4.3
PCB 123	0.10	0.15	0.20	0.34	0.026	0.13	0.055	0.19	0.21
PCB 126	0.023	0.026	0.019	0.025	0.0028	0.018	0.013	0.0089	0.023
PCB 156	0.42	0.52	0.6	0.79	0.057	0.43	0.29	2.2	0.70
PCB 157	0.091	0.11	0.12	0.16	0.011	0.072	0.057	0.26	0.14
PCB 167	0.19	0.24	0.25	0.33	0.030	0.19	0.14	1.0	0.32
PCB 169	0.0015	0.0027	0.0016	0.0023	0.00034	0.00093	0.0016	0.0014	0.0018
PCB 189	0.038	0.049	0.057	0.077	0.0069	0.057	0.040	0.44	0.078
Σ12PCB (WHO-TEQ)	3.0	3.5	2.9	3.7	0.38	2.4	1.8	2.7	3.4
BFR (µg/kg$_{dw}$)									
BDE 28	0.018	0.022	0.013	0.027	0.0031	0.0079	0.031	0.0073	0.031
BDE 47	0.63	1.1	0.58	1.4	0.068	0.36	1.2	0.36	0.63

BDE 99	0.51	1.2	0.46	2.0	0.070	0.50	1.3	0.51	0.66
BDE 100	0.13	0.27	0.13	0.43	0.015	0.10	0.36	0.091	0.13
BDE 153	0.067	0.11	0.048	0.25	0.0079	0.063	0.16	0.069	0.11
BDE 154	0.051	0.095	0.046	0.22	0.007	0.043	0.19	0.035	0.064
BDE 183	0.14	0.071	0.037	0.13	0.019	0.081	0.060	0.046	0.19
BDE 209	9.0	10	5.2	31	0.55	1.7	7.8	2.6	4.3
HBCD	17	45	100	98	22	180	67	140	370
TBBPA	0.22	0.50	0.11	1.0	0.36	0.44	0.10	0.38	0.98

PFAS (μg/kg$_{dw}$)[6]

6:2 FTS	0.46	1.2	nd	0.48	1.5	0.36	0.97	nd	nd
PFHxS	0.41	0.080	0.16	0.11	0.10	0.35	0.16	0.14	0.12
PFOS	4.0	1.8	4.0	2.1	1.3	3.7	2.5	6.0	1.9
PFDcS	0.050	nd	nd	0.10	nd	0.070	nd	0.080	nd
PFHxA	1.3	0.44	0.46	1.1	0.42	0.69	1.3	1.0	0.67
PFHpA	0.69	0.47	nd	0.42	0.32	0.25	0.38	0.63	0.32
PFOA	2.8	1.4	1.1	2.2	1.2	1.3	1.2	1.7	1.1
PFNA	0.56	0.34	0.23	0.74	nd	0.31	0.40	nd	0.26
PFDcA	0.84	0.70	nd	1.3	nd	nd	0.42	0.48	nd
PFUnA	nd	nd	nd	0.25	nd	nd	nd	nd	nd
PFDoA	0.55	nd	nd	nd	0.16	nd	nd	0.24	nd
PFOSA	0.33	nd	0.20	nd	nd	0.3	0.19	0.28	0.22

Pesticides (μg/kg$_{dw}$)

atrazine-2-hydroxy	nd	nd	nd	nd	nd	nd	nd	nd	nd
azaconazole	1.0	nd	nd	nd	nd	nd	nd	nd	nd
azoxystrobin	3.1	3.2	nd	nd	2.1	nd	nd	1.0	5.1
bitertanol	nd	2.1	nd	2.1	nd	1.0	nd	nd	1.0
bromacil	nd	nd	nd	nd	nd	nd	nd	nd	nd
buprofezin	nd	nd	nd	nd	nd	nd	nd	nd	nd
carbendazim	nd	nd	nd	nd	nd	nd	nd	nd	5.1
cyproconazole	3.1	8.4	nd	1.1	1.0	2.1	1.1	1.0	1.0
cyprodinil	1.0	2.1	nd	3.2	6.2	2.1	1.1	nd	4.1
difenoconazole	5.2	6.3	2.1	5.3	4.1	4.1	4.2	2.1	5.1
diuron	nd	nd	nd	nd	nd	nd	nd	nd	1.0
dimethomorph	2.1	1.1	nd	nd	nd	nd	nd	nd	nd
dodemorph	nd	3.2	nd	9.5	1.0	1.0	1.1	nd	26
epoxiconazole	nd	nd	nd	nd	nd	nd	nd	1.0	nd
etaconazole	nd	1.1	nd	nd	1.0	nd	nd	nd	nd
fenbuconazole	7.3	11	16	2.1	1.0	4.1	4.2	2.1	3.1
fenhexamide	nd	1.1	nd	1.1	nd	nd	nd	nd	13
fenoxycarb	nd	1.1	nd	nd	nd	nd	nd	nd	nd
fenpropathrin	nd	nd	nd	nd	nd	nd	1.1	nd	nd
fenpropimorph	nd	1.1	nd	1.1	nd	nd	nd	nd	3.1
fenpyroximat	nd	nd	nd	nd	nd	nd	2.1	nd	nd
flusilazole	1.0	1.1	nd	1.1	1.0	1.0	nd	1.0	2.0
flutolanil	nd	1.1	nd	1.1	nd	1.0	nd	nd	nd
imazalil	3.1	7.4	nd	12	nd	8.3	2.1	nd	103
mecoprop	nd	nd	nd	nd	nd	nd	nd	nd	nd
metamitron	nd	9.5	nd	nd	nd	nd	nd	nd	nd
methabenzthiazuron	nd	nd	nd	nd	nd	nd	nd	nd	1.0
metolcarb	nd	nd	nd	nd	nd	nd	nd	nd	nd
myclobutanil	3.1	1.1	2.1	1.1	nd	3.1	1.1	nd	2.1
oryzalin	11	2.1	nd	nd	nd	1.0	nd	nd	1.0
oxadiazon	10	2.1	nd	nd	nd	1.0	nd	nd	1.0
oxadixyl	15	18	nd	nd	nd	nd	nd	nd	nd
prochloraz	nd	nd	nd	nd	nd	nd	nd	nd	3.1
propiconazole	2.1	5.3	3.1	5.3	2.1	6.2	2.1	2.1	10
propoxur	4.2	3.2	4.2	4.2	4.1	4.1	4.2	4.1	5.1
propyzamide	nd	nd	nd	nd	nd	nd	nd	nd	4.1
pyridaben	nd	nd	nd	nd	nd	nd	2.1	nd	nd
pyrifenox	2.1	1.1	nd	nd	1.0	nd	1.1	nd	nd
pyrimethanil	nd	nd	nd	nd	nd	nd	nd	nd	nd
pyriproxyfen	nd	nd	nd	nd	nd	nd	1.1	nd	nd
simazin	nd	nd	nd	nd	nd	nd	nd	nd	nd

spiroxamine	nd	nd	nd	2.1	nd	nd	nd	nd	6.1
tebuconazole	2.1	2.1	3.1	5.3	2.1	5.2	8.4	1.0	4.1
tebufenpyrad	nd	nd	nd	nd	nd	nd	nd	nd	nd
terbumeton	nd	nd	nd	nd	nd	nd	nd	nd	nd
terbuthylazine-2-hydroxy	1.0	1.1	nd	nd	nd	nd	1.1	nd	nd
terbutryn	nd	nd	nd	1.1	nd	nd	nd	nd	1.0
tetraconazole	nd	nd	nd	nd	nd	nd	nd	nd	1.0
thiabendazole	2.1	3.2	nd	7.4	nd	7.2	nd	nd	19
thiophanate ethyl	nd	nd	nd	nd	12	nd	nd	nd	nd
triadimefon	nd	nd	nd	1.1	nd	1.0	nd	nd	3.1
triadimenol	2.1	2.1	1.0	16	1.0	13	2.1	2.1	23
triasulfuron	nd	4.2	nd	nd	nd	nd	nd	nd	nd
Phthalates (μg/kg$_{dw}$)	na	na	na	na	na	na	na	na	na
Nonylphenol (μg/kg$_{dw}$)	na	na	na	na	na	na	na	na	na
CP (μg/kg$_{dw}$)	na	na	na	na	na	na	na	na	na

a) Com: compost, Dig: digestate, all digestate samples were submitted to subsequent aerobic treatment except for samples 80
b) plant code: C: compost, K: organic kitchen waste and green waste as input materials, G: pure green waste compost, U: urban area of input material collection, R: rural area of input material collection
c) kw: kitchen waste, gw: green waste, iw: industrial waste including paper sludge, coffee ground, tea leaves, residues from potato chips production, biodegradable plastics, edible oil, cacao
d) characterisation of the area where the input material was collected
e) season of input material collection
f) plant type: ab: aerated boxes, tad: thermophilic aerobic digestion, tbw: table windrows, twh: triangle windrows higher than 2 meters, twl: triangle windrows lower than 2 meters
g) duration of the degradation process in days

6 FTS: fluorotelomer sulfonate, PFHxS: perfluorohexane sulfonate, PFOS: perfluorooctane sulfonate, PFDcS: perfluorodecane sulfonate, PFHxA: perfluorohexanoate, PFHpA: perfluoroheptanoate, PFOA: perfluorooctanoate, PFNA: perfluorononanoate, PFDcA: perfluorodecanoate, PFUnA: perfluoroundecanoate, PFDcA: perfluorododecanoate, PFOSA: perfluorooctane sulphonamide, na: not available, nd: not detected, ww: wet weight, dw: dry weight

PFAS below detection limit not listed, dedection limit for 6:2 fluorotelomer unsaturated carboxylate (FTUCA): 0.37μg/kg dw, 8:2 FTUCA: 0.4 μg/kg, 6:2 fluorotelomer carboxylate (FTCA): 0.37μg/kg, 8:2 FTCA: 0.4 μg/kg, perfluorobutane sulfonate: 0.33 μg/kg, n-Methyl-heptadecafluorooctane sulphonamide: <0.18 μg/kg dw, n-Ethyl-heptadecafluorooctane sulfonamide: <0.14 μg/kg dw, n-Methyl-heptadecafluorooctane sulfonamidoethanol: <0.14 μg/kg dw, n-Ethyl-heptadecafluorooctane sulfonamidoethanol: <0.28 μg/kg dw

Table 2: Aerial deposition rates of organic pollutants and their content in manure and sewage sludge

	deposition rate (min, max)	reference	manure (min, max)	reference	sewage sludge (min, max)	reference
Σ17PCDD/F	22 μg I-TEQ/ha/y (7, 40)	(*1*,*2*)	3.77 ng I-TEQ/kg$_{dw}$ (0.36, 21)	(*3*)	15 ng I-TEQ/kg$_{dw}$ (6.1, 120^{a})	(*4*)
DL-PCB	9 μg WHO-TEQ/ha/y (7;10)	(*2*)	na		4.2 ng WHO-TEQ/kg$_{dw}$ (1.9, 6.6)	(*5*)
ΣBDE	6.2 mg/ha/y (only one datapoint)	(*6*)	na		1170 μg/kg$_{dw}$ (250, 1800)	(*7*)
HBCD	284 mg/ha/y (0.073-1340)	(*8*)	na		1730 μg/kg$_{dw}$ (1, 5200)	(*9*)
PFS	na		na		395 μg/kg$_{dw}$ (31, 3040)	(*10*)
PFCA	na		na		30 μg/kg$_{dw}$ (5, 150)	(*10*)
DEHP	0.19 g/ha/y (0-2.5)	(*11*)	6.8 mg/kg$_{dw}$ (0.41, 26)	(*12*,*13*)	51 mg/kg$_{dw}$ (21, 110)	(*14*)

na: not available

a) highest value not taken into account

Table 3: Pesticides analysed and detected in Swiss compost and digestate

Pesticides analysed		detection[a]	Pesticides analysed		detection[a]
Acephate	Insecticide	2	Haloxyfop-methyl	Herbicide	2
Acetamiprid	Insecticide	2	Hexachlorbenzene	Fungicide	2
Acetochlor	Herbicide	2	Hexaconazole	Fungicide	2
Alachlor	Herbicide	2	Hexaflumuron	Insecticide	2
Aldicarb	Insecticide	2	Hexythiazox	Insecticide	2
Aldicarb sulfoxide	Insecticide	2	Imazalil	Fungicide	1
Aldoxycarb	Insecticide	2	Imidacloprid	Insecticide	2
alpha Endosulfan	Insecticide	2	Indoxacarb	Insecticide	2
Amidosulfuron	Herbicide	2	Iodosulfuron	Herbicide	2
Amitrole	Herbicide	2	Ioxynil	Herbicide	2
Anilazine	Fungicide	2	Iprodione	Fungicide	2
Asulam	Herbicide	2	Iprovalicarb	Fungicide	2
Atrazine	Herbicide	2	Isazophos	Insecticide	2
Atrazine-2-hydroxy	Herbicide	1	Isoproturon	Herbicide	2
Atrazine-desethyl	Herbicide	2	Kresoxym methyl	Fungicide	2
Atrazine-desisopropyl	Herbicide	2	Lenacil	Herbicide	2
Azaconazole	Fungicide	1	Lindane and isomers	Insecticide	2
Azamethiphos	Insecticide	2	Linuron	Herbicide	2
Azinphos methyl	Insecticide	2	Lufenuron	Insecticide	2
Aziprotryne	Herbicide	2	Malathion	Insecticide	2
Azoxystrobin	Fungicide	1	MCPA	Herbicide	2
Benalaxyl	Fungicide	2	MCPB	Herbicide	2
Bendiocarb	Insecticide	2	Mecarbam	Insecticide	2
Benfuracarb	Insecticide	2	Mecoprop	Herbicide	1
Benodanil	Fungicide	2	Mepanipyrim	Fungicide	2
Benomyl	Fungicide	2	Metalaxyl	Fungicide	1
Bentazone	Herbicide	2	Metamitron	Herbicide	2
Benthiavalicarb isopropyl	Fungicide	2	Metconazole	Fungicide	2
Benzoximate	Acaricide	2	Methabenzthiazuron	Herbicide	1
beta Endosulfan	Insecticide	2	Methidathion	Insecticide	2
Bifenox	Herbicide	2	Methiocarb	Insecticide	2
Bitertanol	Fungicide	1	Methomyl	Insecticide	2
Boscalid	Fungicide	2	Methoxyfenozide	Insecticide	2
Bromacil	Herbicide	1	Metobromuron	Herbicide	2
Bromophos ethyl	Insecticide	2	Metolachlor	Herbicide	2
Bromopropylate	Insecticide	2	Metolcarb	Insecticide	1
Bromuconazole	Fungicide	2	Metoxuron	Herbicide	2
Bupirimate	Fungicide	2	Metribuzin	Herbicide	2
Buprofezin	Insecticide	1	Metsulfuron-methyl	Herbicide	2
Butocarboxim	Insecticide	2	Mevinphos	Insecticide	2
Captan	Fungicide	2	Monocrotophos	Insecticide	2
Carbaryl	Insecticide	2	Monolinuron	Herbicide	2
Carbendazim	Fungicide	1	Monuron	Herbicide	2
Carbofuran	Insecticide	2	Myclobutanil	Fungicide	1
Carboxin	Fungicide	2	Napropamid	Herbicide	2
Chlorbromuron	Herbicide	2	Norflurazon	Herbicide	2
Chlorfenapyr	Insecticide	2	Nuarimol	Fungicide	2
Chlorfenvinphos	Insecticide	2	Omethoate	Insecticide	2
Chlorfluazuron	Insecticide	2	Orbencarb	Herbicide	2
Chloridazon	Herbicide	2	Orthosulfamuron	herbicide	2
Chlorothalonil	Fungicide	2	Oryzalin	Herbicide	1
Chlorotoluron	Herbicide	2	Oxadiazon	Herbicide	1
Chloroxuron	Herbicide	2	Oxadixyl	Fungicide	1
Chlorpropham	Herbicide	2	Oxamyl	Insecticide	2
Chlorpyrifos	Insecticide	2	Parathion	Insecticide	2
Chlorpyrifos methyl	Insecticide	2	Parathion methyl	Insecticide	2
Chlozolinate	Fungicide	2	Penconazole	Fungicide	2
Clofentezine	acaricide	2	Pencycuron	Fungicide	2
Clopyralid	Herbicide	2	Pendimethalin	Herbicide	2
Cyanazin	Herbicide	2	Phenmedipham	Herbicide	2

Cycloxydim	Herbicide	2
Cymoxanil	Fungicide	2
Cyproconazole	Fungicide	1
Cyprodinil	Fungicide	1
DDT and isomers	Insecticide	2
Demeton-S-methyl	Insecticide	2
Diafenthiuron	Insecticide	2
Diazinon	Insecticide	2
Dichlofenthion	Insecticide	2
Dichlofluanid	Fungicide	2
Dichlorprop-methyl ester	Herbicide	2
Dichlorprop-P	Herbicide	2
Diclobutrazol	Fungicide	2
Dicofol	Insecticide	2
Dicrotophos	Insecticide	2
Diethofencarb	Fungicide	2
Difenoconazol	Fungicide	1
Difenoxuron	Herbicide	2
Diflubenzuron	Insecticide	2
Dimefuron	Herbicide	2
Dimethachlor	Herbicide	2
Dimethenamid	Herbicide	2
Dimethoate	Insecticide	2
Dimethomorph	Fungicide	1
Dimetilan	Insecticide	2
Diniconazole	Fungicide	2
Dinocap	Fungicide	2
Dinoseb	Herbicide	2
Dinoterb	Herbicide	2
Dioxacarb	Insecticide	2
Diphenylamine	Fungicide	2
Disulfoton	Insecticide	2
Diuron	Herbicide	1
Dodemorph	Fungicide	1
Endosulfan sulfate	Insecticide	2
Epoxiconazole	Fungicide	1
Etaconazole	Fungicide	1
Ethiofencarb	Insecticide	2
Ethion	Insecticide	2
Ethoxyquin	Fungicide	2
Ethoxysulfuron	herbicide	2
Etrimfos	Insecticide	2
Fenamidone	Fungicide	2
Fenamiphos	nematicide	2
Fenarimol	Fungicide	2
Fenazaquin	Acaricide	2
Fenbuconazole	Fungicide	1
Fenhexamide	Fungicide	1
Fenitrothion	Insecticide	2
Fenoxycarb	Insecticide	1
Fenpiclonil	Fungicide	2
Fenpropathrin	Fungicide	1
Fenpropidin	Fungicide	2
Fenpropimorph	Insecticide	1
Fenpyroximat	Acaricide	1
Fenthion	Insecticide	2
Fenuron	Herbicide	2
Fipronil	Insecticide	2
Fluazifop-butyl	Herbicide	2
Fluazinam	Fungicide	2
Flucycloxuron	Acaricide	2
Fludioxonil	Fungicide	2
Phenthoate	Insecticide	2
Phosalone	Insecticide	2
Phosphamidon	Insecticide	2
Pirimicarb	Insecticide	2
Pirimiphos methyl	Insecticide	2
Prochloraz	Fungicide	1
Procymidone	Fungicide	2
Promecarb	Insecticide	2
Prometryn	Herbicide	2
Propachlor	Herbicide	2
Propamocarb	Fungicide	2
Propanil	Herbicide	2
Propaquizafop	Herbicide	2
Propazine	Herbicide	2
Propetamphos	Insecticide	2
Propham	Herbicide	2
Propiconazole	Fungicide	1
Propoxur	Insecticide	1
Propyzamide	Herbicide	1
Prosulfocarb	Herbicide	2
Pymetrozine	Insecticide	2
Pyridaben	Insecticide	1
Pyridate	Herbicide	2
Pyrifenox	Fungicide	1
Pyrimethanil	Fungicide	1
Pyriproxyfen	Insecticide	1
Quinalphos	Insecticide	2
Quintozene	Fungicide	2
Quizalofop-P-Ethyl	Herbicide	2
Simazin	Herbicide	1
Simazin-2-hydroxy	Herbicide	2
Soufre	Fungicide	2
Spinosad	Insecticide	2
Spirodiclofen	Insecticide	2
Spiroxamine	Fungicide	1
Tebuconazole	Fungicide	1
Tebufenozide	Insecticide	2
Tebufenpyrad	Insecticide	1
Tebutam	Herbicide	2
Teflubenzuron	Insecticide	2
Tepraloxydim	Herbicide	2
Terbacil	Herbicide	2
Terbufos	Insecticide	2
Terbumeton	Herbicide	1
Terbuthylazine-2-hydroxy	Herbicide	1
Terbuthylazine-desethyl	Herbicide	2
Terbutryn	Herbicide	1
Tetraconazole	Fungicide	1
Thiabendazole	Fungicide	1
Thiacloprid	Insecticide	2
Thiamethoxam	Insecticide	2
Thifensulfuron-methyl	Herbicide	2
Thiobencarb	Herbicide	2
Thiocyclam	Insecticide	2
Thiodicarb	Insecticide	2
Thiofanox	Insecticide	2
Thiometon	Insecticide	2
Thiophanate ethyl	Fungicide	1
Thiophanate methyl	Fungicide	2
Tolclofos-methyl	Fungicide	2
Tolylfluanid	Fungicide	2
Triadimefon	Fungicide	1

Flufenoxuron	Insecticide	2
Fluquinconazole	Fungicide	2
Fluroxypyr	herbicide	2
Flurprimidol	Fungicide	2
Flusilazole	Fungicide	1
Flutolanil	Fungicide	1
Flutriafol	Fungicide	2
Folpet	Fungicide	2
Foramsulfuron	Herbicide	2
Formothion	Insecticide	2
Fuberidazole	Fungicide	2
Furalaxyl	Fungicide	2
Furathiocarb	Insecticide	2
Triadimenol	Fungicide	1
Triasulfuron	Herbicide	1
Triclopyr	Herbicide	2
Tricyclazole	Fungicide	2
Tridemorph	Fungicide	2
Trifloxystrobin	Fungicide	2
Triflumizole	Fungicide	2
Triflumuron	Insecticide	2
Trifluralin	Herbicide	2
Triforine	Fungicide	2
Vamidothion	Insecticide	2
Vinclozolin	Fungicide	2

a) 1: detected at least once in compost and/or digestate, 2: not detected in compost and/or digestate

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7 Manuscript 3

Fate of PCBs, PAHs and their source characteristic ratios during composting and digestion of source-separated organic waste in full-scale plants

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Environmental Pollution, submitted.

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7.1 Manuscript 3: Text

Abstract

Composting and digestion are important waste management strategies. However, the resulting products can contain significant amounts of organic pollutants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). In this study we followed the concentration changes of PCBs and PAHs during composting and digestion on field-scale for the first time. Concentrations of low-chlorinated PCBs increased during composting (about 30%), whereas a slight decrease was observed for the higher-chlorinated congeners (about 10%). Enantiomeric fractions of atropisomeric PCBs were essentially racemic and stable over time. Levels of low-molecular-weight PAHs declined during composting (50-90% reduction), whereas high-molecular-weight compounds were stable. The PCBs and PAHs concentrations did not seem to vary during digestion. Source apportionment by applying characteristic PAH ratios and molecular markers in input material did not give any clear results. Some of these parameters changed considerably during composting. Hence, their diagnostic potential for finished compost must be questioned.

Capsule

During field scale composting, low molecular weight PCBs and PAHs increased and decreased, respectively, whereas high molecular weight compounds remained stable.

Introduction

Composting (aerobic treatment) and digestion (anaerobic treatment combined with biogas production) of organic waste are important in current waste management strategies. In the 25 European Union member states, 31.5 $*10^6$ t of biodegradable waste is composted annually (European Communities, 2005). Most of the compost produced is applied to agricultural fields or used in horticulture and landscaping whereby nutrients are recycled according to the sustainability principle. Compost can contain pollutants such as heavy metals and a wide range of organic contaminants (Buyuksonmez et al., 2000, Hogg et al., 2002, Brändli et al., 2005, Brändli et al., 2006c), which enter compost most probably via aerial deposition on green waste, accidental (i.e., improper separation of input materials, e.g., plastic debris) or deliberate input (e.g., pesticide application to fruits and vegetables). However, during composting and/or digestion, microbial activities may enhance degradation of organic pollutants. In lab studies, some compounds (e.g., low molecular weight (LMW) polycyclic aromatic hydrocarbons (PAHs)) were observed to decrease during composting, whereas other compounds (e.g., polychlorinated biphenyls (PCBs), high molecular weight (HMW) PAHs) remained stable (van Raaij et al., 1996, Vergé-Leviel, 2001). Composting of PCB- and PAH-contaminated soils and sediments was also applied successfully as remediation strategy (Michel et al., 2001). However, conditions (e.g. availability of the pollutants, nutrients, temperature) need to be appropriate for it to work successfully (Semple et al., 2001).

Extrapolation of (simplified, small scale) laboratory-derived findings to (complex, large scale) environmental systems is always difficult. Up to now, the fate of organic pollutants during composting and digestion of green waste (originating from private gardens and public green areas), and organic kitchen waste (crude organic leftovers from vegetable production and from private kitchens) - so-called “source-separated” organic waste - has not been investigated on full-scale. It needs to be elucidated to take appropriate measures either during the degradation process or when selecting the input materials to reduce organic pollutants contents in compost, especially for PAHs (Brändli et al., 2006b).

We followed the concentrations of two important organic pollutant classes, PCBs and PAHs during open windrow composting of three different materials: i) pure green waste (CG), ii) a mixture of green and organic kitchen waste (CK) and iii) digested green- and kitchen waste (digestate, CDK). Organic pollutant concentrations were also determined during digestion of green- and kitchen waste (DK). To assess whether biological processes drive the possible elimination of PCBs, enantiomeric fractions (EFs) of three atropisometric compounds were determined. Shifts of EFs serve as a marker for biodegradation (Harner et al., 2000). Characteristic PAH ratios and molecular markers are frequently used for source apportionment of PAHs (Supplementary Information, Table 1). However, these ratios can be altered from emission to the recipient matrix (Zhang et al., 2005). Possible variations thereof during composting have not yet been assessed. Here, we investigated to what extent such changes take place and singled out the most robust of these source diagnostic parameters.

Materials and Methods

Experimental design, sampling and sample preparation

This study focuses on open windrow composting and combined thermophilic digestion-composting systems since they are most commonly used in Switzerland (Hügi and Kettler, 2004) and suitable for sampling. Two composting plants were selected, one processing green waste and the other treating a mixture of green and organic kitchen waste. Additionally, we followed organic pollutant concentrations during aerobic stabilisation of digestate, i.e. composting of output material from the digestion process (for description of the process see Supplementary information Text 1). All three windrows were covered with air-permeable fabric, irrigated with fresh water if necessary, and turned regularly. The personnel at the plants recorded the temperature evolution of the windrows (see Supplementary Information, Table 2-4). Aerobic conditions were controlled in CK and CDK by methane measurements.

Sampling periods considered the four phases of composting: mesophilic, thermophilic, cooling and maturation stage (Semple et al., 2001). These phases are of augmenting duration and consequently sampling intervals were increased accordingly (day 0, 3, 7, 14, 28, 56, 112; for a detailed description on sampling and an illustrative picture thereof see Supplementary information Text 2, and Figure 1, respectively). To verify and backup field degradation studies, the input material obtained from the plants was additionally composted on a laboratory scale in vessels of 230 litres (see Supplementary information Figure 2, CG_{lab}, CK_{lab}). The material was thoroughly mixed twice a week for aeration and ambient air temperature kept at 30^{o}C. If necessary, fresh water was added (for temperature protocols, see Supplementary information, Figure 3). For description of the digestion process and respective sampling see Supplementary information Text 1 and Figure 4.

Analytical procedure

During composting non-extractable residues (NER) may be formed (Semple et al., 2001). Since the use of isotope-labelled probe organic compounds is not feasible in field studies and native organic pollutants might be ‘bound’ differently to the organic material, it is essential to achieve maximal extraction by applying harsh techniques. Details of such an optimized extraction for compost, digestate and presswater are given in Brändli et al. (2006a) and Brändli et al. (2006b). Compounds analysed in this study were: naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IPY), dibenzo[*a,h*]anthracene (DBA), benzo[*ghi*]perylene (BPE), 4-H-cyclopenta[*def*]PHE (CPHE), retene (RET), cyclopenta[*cd*]PYR (CPYR), perylene (PER), coronene (COR), the ratio of methylPHE and –ANT to PHE (MPHE&ANT)/PHE), the ratio of methylFLT and -PYR to PYR (MFLT&PYR)/PYR), the ratio of 1,7- to 1,7- and 2,6-dimethylPHE (1,7-/(1,7-&2,6-)DmPHE, PCBs (28, 52, 95, 101, 118, 149, 132, 153, 138, 174, 180) and EFs of PCB 95, 149, 132. For details see Bucheli et al. (2004), Bucheli and Brändli (2006) and Brändli et al. (2006b). PAHs were found not to be homogenously distributed in compost (sample size: 5 $g_{dry\ weight\ (dw)}$ milled to <2 mm (Brändli et al., 2006a)). Therefore, chemically dried material was cut to <1 mm and the amount of sample extracted was tripled (about 15 g_{dw}) in this study. Extraction was performed with an Accelerated Solvent Extractor 300 (Dionex Corporation, Sunnyvale, CA, USA) applying the same conditions as in Brändli et al. (2006a), but using only a third of the extract for subsequent analysis. PAH extraction and analysis was carried out twice and if variation was higher than method precision (Brändli et al., 2006a) two additional samples were analysed. Outliers were removed by the Grubbs outlier test (Grubbs, 1969) and mean values calculated. Organic matter, crude ash, heavy metals and nutrients were determined according to the Swiss reference methods for fertilizer and manure (Eidgenössische landwirtschaftliche Forschungsanstalten, 2004).

Data processing

To follow possible alteration of organic pollutants during organic matter degradation, either quantification of mass reduction or normalization of the concentrations measured to a conservative tracer is feasible. The latter approach was chosen, since mass reduction is difficult to quantify under real-world conditions. Crude ash turned out to be the most reliable reference parameter as compared to other potentially suitable candidates such as heavy metals and can be assumed to be stable since no leaching of soluable crude ash constituents was observed during composting. The concentrations measured were converted to μg/kg crude ash as follows:

$$c_{i,norm} = \frac{c_{i,meas}}{c_{ash}} * 1000$$

where $c_{i,norm}$ denotes the normalized concentration of the compound *i* (μg/kg$_{\text{crude ash}}$), $c_{i,meas}$ is the quantified concentration of the compound *i* (μg/kg$_{\text{dw}}$), and c_{ash} is the crude ash content (g$_{\text{crude ash}}$/kg$_{\text{dw}}$) in the very same sample. Accumulation factors were used to characterize the fate of the compounds in the substrate. They were calculated as follows:

$$accumulation\_factor = \frac{c_{i,norm,day\_x}}{c_{i,norm,day\_0}}$$

where $c_{i,norm,\ day\_x}$ denotes the normalized concentration of the compound *i* (μg/kg$_{\text{crude ash}}$) on day x (x = 3, 7, 14, 28, 56, 112) and $c_{i,norm,\ day\_0}$ is the normalized concentration of the compound *i* (μg/kg$_{\text{crude ash}}$) on day 0. Accumulation factors smaller than one point to loss (or sequestration) of a compound and constant factors at persistency.

Since in the digestion process input material is mixed with recycled presswater, digestate and fresh water (see Supplementary information, Text 1), normalized concentrations cannot be followed in the same way. A mass balance in the fermenter was calculated instead, based on the assumption of stable crude ash (input = output = 7800 kg ash) and an output ratio of presswater to digestate of 2:1 (wet weight, for calculation see Supplementary information, Figure 4). Accumulation factors were determined on this mass balance basis (amount of organic pollutant in the output/amount of the organic pollutant in the input).

To account for altered characteristic PAH ratios between emission and input material of compost, rectification factors as defined by Zhang et al. (2005) for air particles were applied. Ratios determined in input material for compost in the form x/(x+y) were converted to sources ratios as follows:

$$r_{\text{source}} = r_{\text{input material}}/(RF_{\text{Zhang}} + r_{\text{input material}} - RF_{\text{Zhang}} * r_{\text{input material}})$$

where r_{source} is the characteristic PAH ratio at the emission source, $r_{\text{input material}}$ is the PAH ratio in compost input material and RF_{Zhang} is the rectification factor (for ANT/PHE 2.16, for FLT/PYR 1.68, for BaA/CHR 0.59, for IPY/BPE 0.92). BaP/BPE ratios were converted by dividing the BaP/BPE$_{\text{input material}}$ by $RF_{\text{ZhangBaP/BPE}}$ (0.60).

Results and Discussions

Before results are presented, uncertainties due to sampling, sample preparation and analysis are discussed. Then, initial organic pollutant concentrations measured in input material of full-scale composting plants (CG, CK, CDK) are compared to those measured at the end of the composting process (in μg/kg$_{\text{dw}}$). Thereafter, respective accumulation factors (based on crude ash) and their evolution during composting are presented and compared with the lab studies (CG$_{\text{lab}}$, CK$_{\text{lab}}$). Possible processes leading to the observed changes are discussed and own results compared with studies from the literature (mostly lab studies). Finally, accumulation factors during digestions are presented. For description of the process parameter (i.e. temperature evolution, organic matter degradation) during composting it is referred to Supplementary information, Text 3

Sampling and analytical uncertainties

Sampling and sample preparation are crucial steps of any field study campaign. The uncertainties associated with the PCB and PAH data presented here result largely/mainly from errors during sampling, sample preparation and analysis. The latter was quantified earlier (Brändli et al., 2006a) and accounted for some 6 to 17% for single PCBs and 12 to 34% for single PAHs. For specific challenges arising from the heterogeneity of the compost matrix and the physical-chemical nature of the target analytes that are prone to evaporation and/or (cross-)contamination, and respective (counter-)measures taken during sample preparation see (Brändli et al., 2006a). Although our sampling strategy was particularly adapted to compost windrows (see Supplementary information Text 2), it was not designed to quantifying sampling errors separately (since all sub-samples were merged to yield one final sample at a time). However, such experiments were conducted earlier by Breuer et al. (1997), who found total errors, i.e., combined sampling and analytical errors, related to compost field study data to be in the order of 30% for PCBs and PAHs. We therefore have to keep in mind that apparent PCB and PAH concentrations reported here are probably associated with errors of this order.

PCB

Composting

Initial Σ11PCBs concentrations (Sum of PCB 28, 52, 95, 101, 118, 149, 132, 153, 138, 174, 180) were similar in all three composting studies (CG 18 $\mu g/kg_{dw}$, CK 16 $\mu g/kg_{dw}$, CDK 29 $\mu g/kg_{dw}$, Supplementary information Table 5-7). Final concentrations were 28 $\mu g/kg_{dw}$, 22 $\mu g/kg_{dw}$ and 48 $\mu g/kg_{dw}$, respectively. In general these concentrations are on the lower end compared to respective concentrations from corresponding categories by Brändli et al. (2006b), and numbers found in the literature (Brändli et al., 2005). Accumulation factors after 112 days (Σ11PCBs) were 1.12 in CG, 1.16 in CK and 1.18 in CDK, indicating sampling artifacts. However, the error was within the variation discussed above. Factors of the tetra- and penta-chlorinated PCBs (52-118) ranged from 1.1 to 1.5, whereas for the two hepta-chlorinated compounds (174 and 180), they were in general lower than one (Figure 1). Values of the hexa-chlorinated compounds (149, 132, 153, 138) varied between 1.1 to 1.2. Similar results were found in the lab studies (Supplementary information Tables 8 & 9 and Figures 8 & 9). In the final compost (day 112), accumulation factors correlated significantly negative (for all five degradation studies, except CK_{lab}) with octanol-water partition coefficients (log K_{ow}) (Oberg, 2001), Supplementary information Table 10). Only in CK there was a significant correlation of the accumulation factor at day 112 with vapour pressures.

EFs of PCB 149 and 132 were between 0.497 and 0.503 in all three input materials. For PCB 95, the EF was 0.507 in CDK, 0.491 in CG, and 0.512 in CK (Supplementary information Table 5-7). These close-to-racemic EFs remained stable at their respective initial numbers over the lab- and field-composting studies (Figure 1). Accumulation factors of PCBs peaked at day 14 (CDK, CK) or 56 (CG) (Supplementary Information, Figure 5-7). A similar increase was observed in the laboratory studies (CG_{lab} day 7, CK_{lab} day 3, Supplementary Information, Figure 8&9). This correlation of temporal development in all studies indicates that the entire process of obtaining field data, including the sampling, generates relevant data.

The fate of PCBs did not seem to be different in composting of non-treated (CG and CK) compared to previously anaerobically treated organic waste (CDK). This could have been hypothesised due to possibly altered structure of organic matter that may have changed the availability of the pollutants.

Four major processes can influence PCB levels during composting: i) evaporation, ii), sequestration, i.e., formation of NER, iii) transformation, and iv) contamination, either during composting or sample preparation. In general it is difficult to differentiate between these four processes. Additionally, they may be superimposed and mask each other.

i) Evaporation: Evaporation is unlikely to be the driving process for the decreasing levels of HMW PCBs during composting, since it would have affected (possibly even in a more pronounced way) LMW PCBs as well. However, volatilization could have been superimposed by other processes (e.g., formation of LMW PCBs; see below). ii) Sequestration: Sequestration may explain the decreasing concentrations of particularly HMW PCBs. Formation of small amount of NER during composting of labelled PCBs in the lab have been observed previously (van Raaij et al., 1996, Vergé-Leviel, 2001). The varying accumulation factors during the composting process (e.g., peak at day 14 for CK and CDK and day 56 for CG) might reflect different extractability during the process. Such variations were reported in a field study of municipal solid waste composting (e.g., an accumulation factor of 2.8 on day 16 for PCB 52, and of 1.7 on day 37, calculated for the data of (Dahosch, 1998)) and in a lab study with ^{14}C-labelled PCB 77 (80% of the applied activity extracted on day 35, 95% on day 50 and 70% on day 68 (van Raaij et al., 1996)). Formation of natural organic matter glassy-rubbery transition at temperatures in the range of 50 to 70 ^{o}C have been observed for many natural organic materials (Delapp et al., 2004). Is seems likely that formation of such a glassy-rubbery transition can take place in composts and that this may alter sorption properties and extractability of various contaminants. iii) Transformation: Transformation processes can either be abiotic or biotic. A shift of EFs could identify biological processes. If a shift in EF occurs biodegradation has taken place, but biodegradation may also take place without shift in EF (Pakdeesusuk et al., 2003). Dechlorination of higher chlorinated PCBs during composting could explain the increase and decrease of the LMW and HMW congeners, respectively. However, with the number of congeners analysed in this study, it is impossible to perform any PCBs mass balance to quantitatively verify the occurrence and extent of this possible transformation process. Additionally, anaerobic environments seem to be a prerequisite for reductive dechlorination, whereas one aims at aerobic conditions during composting. Non-detectable methane concentration in CK and CDK assured such conditions at all times. Under aerobic conditions, PCBs are expected to degrade oxidatively, leading to the formation of hydroxy-PCBs (Borja et al., 2005). Such metabolites have not yet been investigated in compost. iv) Contamination: Contamination during composting and/or analysis could account for the increasing levels of LMW PCBs. However, that such contaminations with predominantly LMW PCBs consistently occurred on two sites is rather unlikely and analytical method blank levels were low.

An increase of the less and a decrease of the higher chlorinated PCBs were observed previously in a field-scale study on the concentration changes of PCBs (at the mg/kg concentration level) during municipal solid waste composting (Dahosch, 1998). However, preferential loss of the lower chlorinated congeners was observed during composting of PCB contaminated soil (mg/kg concentration level (Michel et al., 2001). At a more comparable concentration range stable concentrations were reported by Lazzari et al. (2000). In summary, from the data generated here and earlier, no generally valid picture about the evolution of PCB concentrations during composting can be derived. However, our field data obtained from full-scale plants consistently pointed to no overall degradation, but a concomitant shift from HMW to LMW congeners.

Digestion

Initial Σ11PCBs concentration in the input material was 23 μg/kg$_{dw}$. In the output (calculated mixture of presswater and digestate, see Supplementary information, Figure 4 and Table 11 for details), it accounted for 33 μg/kg$_{dw}$. Based on crude ash, this results in an accumulation factor of 1.3 (Supplementary information, Figure 10a). This apparent increase, which was similar for all congeners, together with high accumulation factors of PAHs and heavy metals (up to 3.2 for ACE and 2.0 for Pb, see below) point rather to sampling errors than to PCB formation during digestion. It seems likely that that residence time in the fermenter was not determined correctly. Additionally, the calculated mass loss during digestion was lower (9.6% based on dw, Supplementary information, Figure 4) than the normal degradation rate of 13% (Personal communication, M. Leisner, Kogas AG). According to the literature, dechlorination of PCBs was expected under anaerobic conditions (Borja et al., 2005). This was observed previously in a screening study, where organic waste was treated anaerobically and aerobically (Nilsson, 2000).

PAH

Composting

The Σ15PAH concentrations (Σ16 EPA PAHs, DBA was excluded due to low recoveries) in the input material were 3320 $\mu g/kg_{dw}$ in CG, 410 $\mu g/kg_{dw}$ in CK and 1450 $\mu g/kg_{dw}$ in CDK. To obtain respective concentrations in finished compost, several outliers were removed (due to high values and elevated standard deviation) and values of day 56 taken instead of day 112 for several compounds (CG: ANT to BPE; CK: ACE to PYR). Apparently, measures taken were not sufficient to deal with the heterogeneous distribution of PAHs in these cases. The resulting end concentrations were 2080 $\mu g/kg_{dw}$ (CG), 360 $\mu g/kg_{dw}$ (CK) and 620 $\mu g/kg_{dw}$ (CDK), respectively. Such values are lower than median PAH concentrations in corresponding categories of Swiss compost and digestate and values in the literature (Brändli et al., 2005, Brändli et al., 2006b).

Overall, accumulation factors after 112 days (Σ15PAHs) were 0.47 (CG), 0.76 (CK) and 0.31 (CDK). LMW PAHs (NAP-PYR) were generally reduced during full-scale composting, whereas HMW compounds (BbF-BPE) were either stable (CK and CDK) or increased (CG, Figure 2). These findings were confirmed by the laboratory studies (Supplementary Information, Table 8&9). There was, opposite to the PCBs, a significant positive correlation between logK_{ow} of all 15 PAHs except IPY but with PER, COR (Mackay et al., 1992) and the accumulation factors of day 112 in all five degradation studies (Supplementary information, Table 10). Correlations with vapour pressures were significant in the beginning of the experiments. In CK and CDK, accumulation factors of LMW PAH decreased in general continuously over 112 days whereas HMW congeners remained more or less stable (Supplementary information, Figure 12&13). In both CG and laboratory studies CG_{lab}, increases in PAH accumulation factors during composting could be observed (CG: between day 3 and 7 for ACE to CHR, CG_{lab}: between day 0 and 3 for FLT to BPE, Supplementary information Figure 11, 14). Interestingly, LMW PAH (NAP-ANT) concentrations increased again between day 14 and 28 in the laboratory study (CG_{lab}), whereas HMW PAHs (BbF-BPE) increase took place later between day 28 and 56. The considerable increase at day 14 in Ck_{lab} is attributed to sampling artefacts. As for the PCBs, the fate of PAHs did not seem to differ between composting of organic waste compared to already anaerobically treated material.

The same four processes as discussed above (evaporation, sequestration, transformation and contamination) and superimposition thereof can be responsible for the observed changes of accumulation factors. Evaporation is a likely process responsible for the decreasing levels of the LMW PAHs, especially in the beginning of the process, when temperatures are high (up to 70 ^{o}C, Supplementary information, Table 2-4 and Figure 3) and windrows turned more frequently. The significant negative correlations of the accumulations factors and the vapour pressures in the beginning of the processes also indicate evaporation as the driving process. It was observed earlier that even at 40 °C NAP recoveries were considerably reduced during drying (Berset et al., 1999). Sequestration did not seem to play an important role in the present study, since accumulation factors of HMW PAHs were not reduced significantly. However, it has been reported that this process is more important for PAHs than for PCBs (van Raaij et al., 1996, Vergé-Leviel, 2001, Doick et al., 2005) and considerable formation of NER was observed from laboratory composting studies with isotope-labelled probe PAHs, in which 9-70% of the initially applied amount was extracted at the end of the process (van Raaij et al., 1996, Vergé-Leviel, 2001, Hartlieb et al., 2003). In contrast to the present study, the HMW PAHs were more affected due to their higher hydrophobicity (van Raaij et al., 1996, Vergé-Leviel, 2001). Still, sequestration may account for increased accumulation factors during composting (e.g., CG: between day 3 and 7 for ACE to CHR). Such variations in extractability were observed previously (van Raaij et al., 1996, Hund et al., 1999) and for discussion see the PCB section. Transformation and mineralization of (LMW) PAHs was observed to occur in most cases delayed in the maturation phase of composting (Vergé-Leviel, 2001). During this period of the process, PAH concentrations were not significantly reduced(Martens, 1982, Hartlieb et al., 2003) (Supplementary information, Figure 11-15). However, both increasing hydrophobicity/sequestration and decreasing degradability can cause the observed correlation of $\log K_{ow}$ and the accumulation factors at the end of the process (Mackay et al., 1992). Contamination could account for the increasing PAH levels observed in CG and may have been caused by, e.g., soot, liquid fossil fuel or lubricant oil emitted by the windrow turner. However, this is ulikely since i) similar machines were used on the other composting plant and ii) increases were most pronounced in the end of the process, when the windrow was turned less frequently (Supplementary information, Table 2). However, other unknown contamination pathways are still possible. In summary, the findings of this study (reduction of LMW PAHs and stable HMW compounds during composting) are confirmed by previous laboratory and field studies on other input materials (Martens, 1982, Joyce et al., 1998, Dahosch, 1998, Loser et al., 1999, Potter et al., 1999a, Potter et al., 1999b).

Digestion

Σ15PAHs concentration was 2460 $\mu g/kg_{dw}$, and 3280 $\mu g/kg_{dw}$ in the input and output material, respectively. This resulted in an accumulation factor of 2.3. All compounds, but especially the light LMW PAH (NAP-ANT), exhibited factors that were considerably above one. (Supplementary Information, Figure 10b). This would indicate PAH formation during digestion, which is improbable. Rather, the increases are attributed to sampling artefacts as discussed above.

Characteristic PAH ratios and molecular markers

In a first step, characteristic PAH ratios in input material and respective converted ratios (Zhang et al., 2005) are compared with the indicative values from the literature for source apportionment (Supplementary information Table 1). To qualify for source identification in finished compost and digestate, ratios need to remain stable or show consistent changes (i.e. which can be accounted for) during the organic matter degradation processes. In a second step, such suitable markers in finished compost and digestate are appointed.

Input material

Characteristic PAH ratios discriminating between pyrogenic and petrogenic sources all, except for ANT/(ANT&PHE), pointed to a pyrogenic origin of PAHs both in the input material and after conversion (Supplementary Information, Table 1). This is in line with earlier findings (Brändli et al., 2005, Brändli et al., 2006b) and the PAH emission situation in Switzerland. The applicability of the ANT/(ANT&PHE) ratio has been questioned previously (Yunker et al., 2002, Bucheli et al., 2004) and is therefore not discussed further here.

Ratios distinguishing between combustion of liquid fossil fuel and of grass/wood/coal were contradictory (Supplementary Information, Table 1). FLT/(FLT&PYR) ratios pointed at grass/coal/wood combustion before conversion and to liquid fossil fuel combustion thereafter. The latter may be more appropriate for the situation in Switzerland. IPY/(IPY&BPE) indicated grass/coal/wood combustion before and even more after conversion, whereas RET/(RET&CHR) ratios were in the petrogenic range (no conversion factors available). Based on these findings, 1,7-/(1,7-&2,6-)DmPHE ratios of 0.57-0.59 are rather attributed to mixed combustion than to petrogenic origin of PAHs. Overall, PAHs in input material may originate from both, liquid fossil fuel and grass/wood/coal combustion.

On the one hand, BaP/BPE ratios indicated before, and even more pronounced after conversion, traffic as the sole source of PAHs in input material for compost. On the other hand, 1,7-/(1,7-&2,6-)DmPHE ratios were all above 0.45, which was suggested to be characteristic for ‘non-traffic’ PAHs. This contradiction may indicate that one of the two ratios is not suitable for source apportionment or that (other) conversion factors are required. PER/Σ15PAH ratios pointed at predominantly pyrogenic rather than diagenetic origin of PAHs, which is confirmed by ratios distinguishing between petrogenic and pyrogenic sources (see above). The remaining molecular markers (CPHE, CPYR and COR) were, similar to Σ15PAHs, highest in the input material of CG, compared to CK and CDK. Opposite the Σ15PAH, COR concentration was higher in CK than in CDK, which could point to some additional PAH input from traffic sources in CK. However, 1,7-/(1,7-&2,6-)DmPHE and BaP/BPE pointed to more traffic PAH in CDK than in CK.

Development during composting

BaA/(BaA&BPE), FLT/(FLT&PYR), IPY/(IPY&BPE), BaP/BPE and 1,7-/(1,7-&2,6-)DmPHE ratios varied little during composting (Figure 3, Supplementary information Figure 16-20), suggesting them as suitable PAH source apportionment ratios in finished compost. However, the processes between emission and input material still need to be accounted for (see above). Since the Σ15PAHs decreased more compared to the sum of (the heavier) combustion PAHs, (ComPAHs: Sum of FLT, PYR, BaA, CHR, BbF, BkF, BaP, IPY, BPE), ComPAH/Σ15PAH ratios increased during composting in CG, CDK, CG_{lab} and CK_{lab}. In CK it decreased slightly. This renders the application of a conversion factor difficult for the composting process. Also ambiguous was (MFLT&PYR)/PYR, which increased considerably in CDK, whereas in the remaining studies it was stable. (MPHE&ANT)/PHE and RET/(RET&CHR) were unfit in this study because they changed inconsistently in the different studies (Figure 3).

Concentration changes of all molecular markers (CPYR, CPHE, PER, COR) evolved similarly as the corresponding 15 PAHs: the LMW substances CPHE and CPYR generaly decreased, whereas the HMW PER and COR were more or less stable (Figure 3). PER (and also RET, see above) can be formed during organic matter degradation (Wakeham et al., 1980), which might explain their significant concentration increases in CG. However, standard variations were high, which can also point to sample heterogeneity. It might be useful to normalise these marker substances for source apportionment. However, as seen before for ComPAH/Σ15PAH normalization to Σ15PAH is questionable. Further research is required to appoint appropriate single compounds for normalization.

Development during digestion

Stable ratios during digestion were BaA/(BaA&CHR), FLT/(FLT&PYR), IPY/(IPY&BPE), 1,7-/(1,7-&2,6-)DmPHE and BaP/BPE (Supplementary Information Figure 10c). These five characteristic PAH ratios were also found to remain stable during composting and could be suggested as suitable markers for digestate. However, these results have to be interpreted with caution due to the difficulties in sampling mentioned above.

Conclusion

Concentrations of LMW PCBs increased during full-scale composting, whereas HMW congeners were slightly reduced. Identification of the processes responsible for these alterations remained difficult. Further research is needed, possibly by analysing metabolites such as hydroxy PCBs (Flanagan and May, 1993) pointing to specific degradation mechanisms, establishing a PCB mass balance and/or by accounting for losses (i.e. evaporation, sequestration by sequential extraction etc.) during composting. Although increasing during composting, the total PCB input to agricultural land by compost application may be low, compared to other input pathways due to overall low PCB concentrations in this matrix (Brändli et al., 2006b).

HMW PAHs remained stable during composting, whereas LMW compounds decreased. Due to the relatively high concentrations, inputs of PAHs to soil by compost application may be considerable compared to other inputs (Brändli et al., 2006b). It might therefore be useful to identify parameters to enhance PAH removal during composting. Such an approach was suggested by Ulbricht (2001) for contaminated wood. Another, and probably more promising, approach would be to single out particularly contaminated input materials.

Characteristic PAH ratios pointed to a pyrogenic origin of PAHs in input material, which is reasonable for the situation in Switzerland. However, differentiation between various fuels was not possible. Application of conversion factors to account for environmental processes between emission and recipient matrix as suggested by Zhang et al. (2005) seems conceptually correct, but too simplistic if applied to our data from input material. Only few characteristic ratios were stable during composting, which reduces the set of applicable markers for source apportionment in finished compost considerably.

Acknowledgments:

The Federal Office for the Environment and the Swiss Federal Office of Energy are acknowledged for financial support, personnel from the plants Oensingen, Fehraltorf and Oetwil am See for good collaboration and Ernst Brack and his team for regularly turning the thermo composters. Martina Kobližková and Franziska Blum are thanked for their help with analyses. Thanks due to Henrik Kylin for reviewing this manuscript.

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7.2 Manuscript 3: Figures

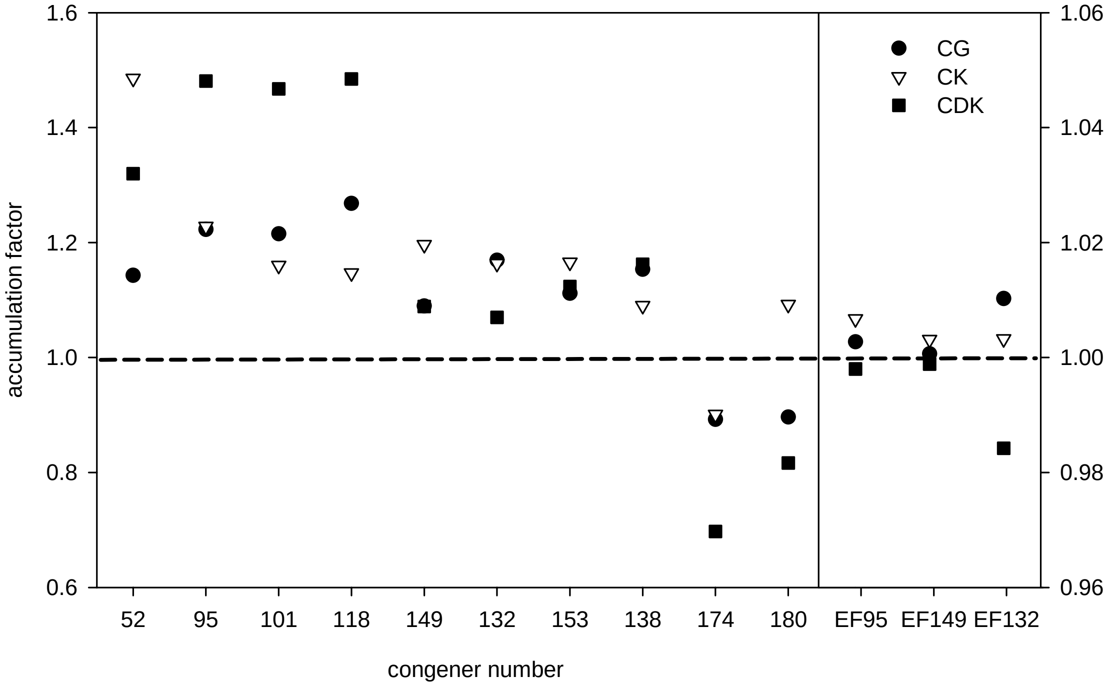

Figure 1: Accumulation factors for PCB and for enantiomeric fractions (EFs) of PCB 95, 149, 132 during composting of green waste (CG), green waste and organic kitchen waste (CK) and digestate (CDK). Dashed line indicates conservative behaviour of target analytes.

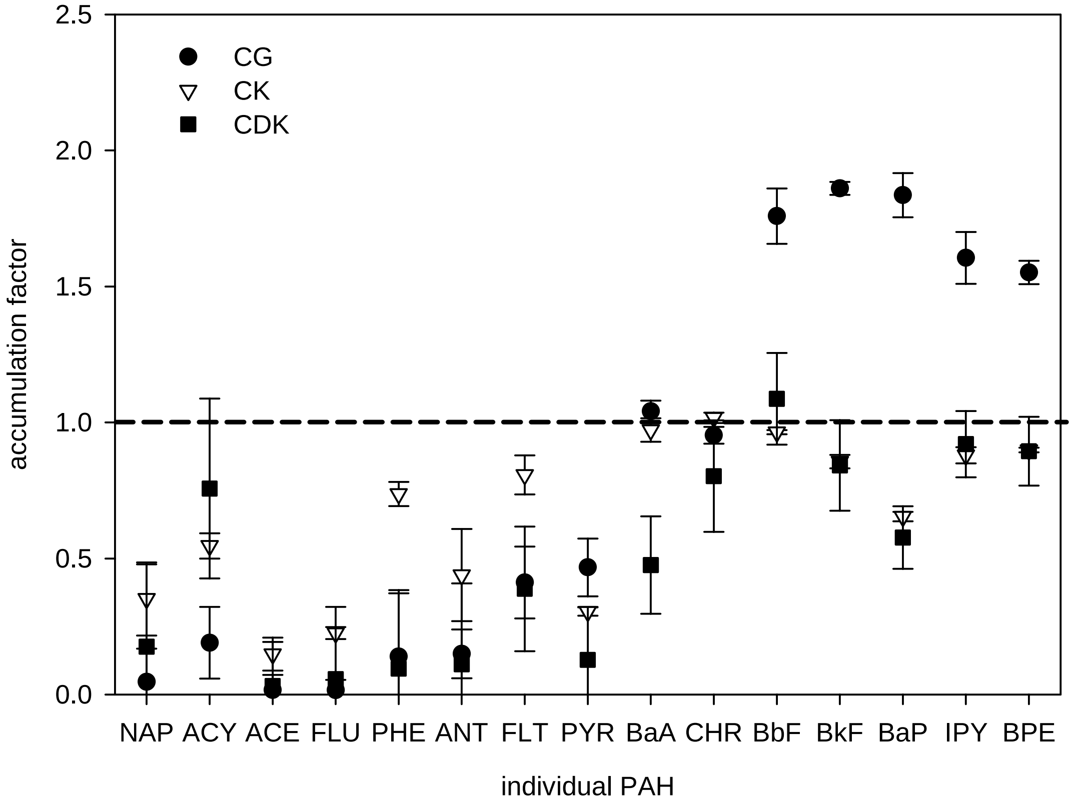

Figure 2: Accumulation factors of PAH during composting of green waste (CG), green waste and organic kitchen waste (CK) and digestate (CDK). Dashed line indicates conservative behaviour of target analytes. NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[*1,2,3-cd*]pyrene, and BPE: benzo[*ghi*]perylene.

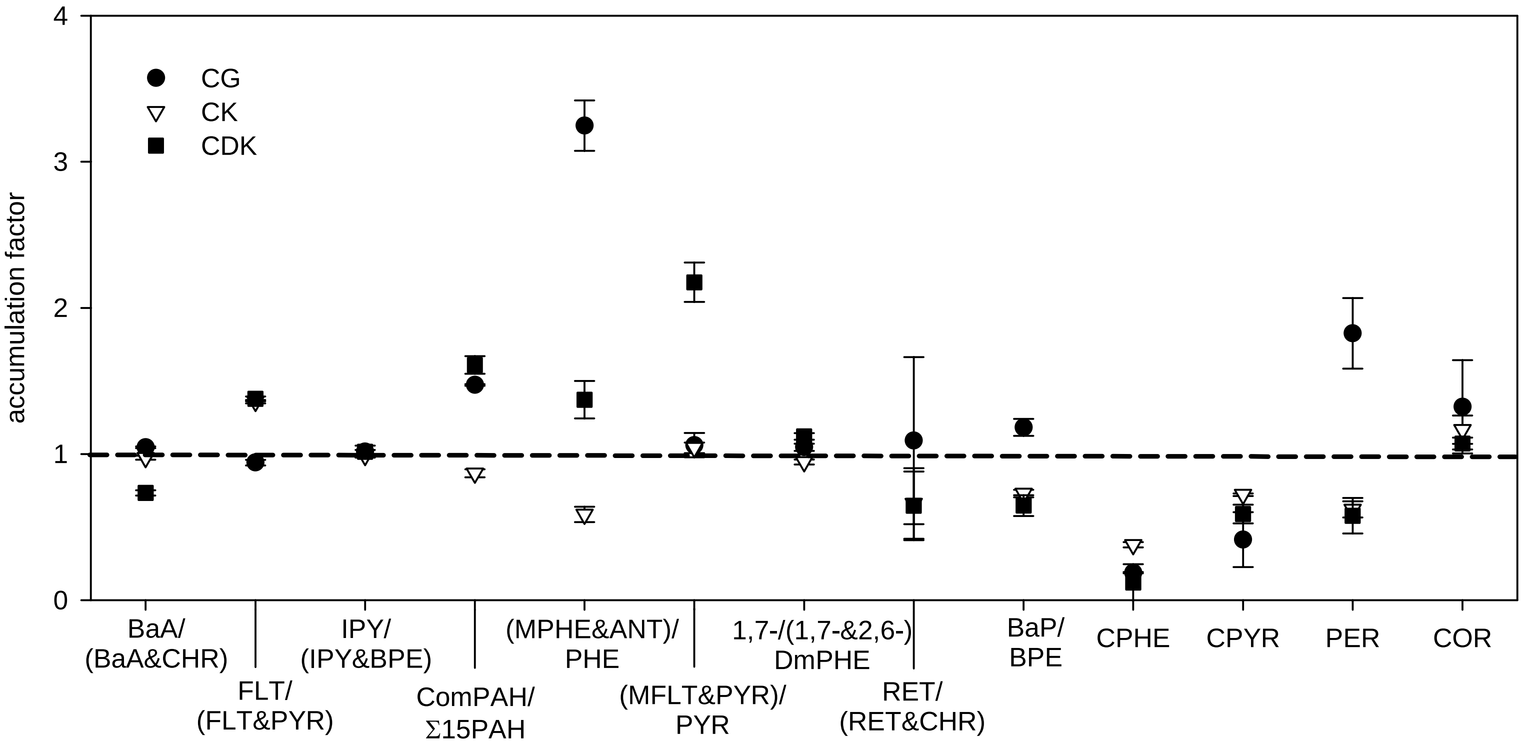

Figure 3: Accumulation factors for characteristic PAH ratios and molecular markers during composting of green waste (CG), green waste and organic kitchen waste (CK) and digestate (CDK). Dashed line indicates conservative behaviour of target analytes. BaA. benzo[*a*]anthracene, CHR: chrysene, FLT: fluoranthene, PYR: pyrene, ComPAH: Sum of FLT, PYR, BaA, CHR, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene (BaP), indeno[*1,2,3-cd*]pyrene (IPY), benzo[*ghi*]perylene (BPE), Σ15PAH: Sum of 16 PAH defined by the US EPA, except dibenzo[*a,h*]anthracene, (MPHE&ANT)/PHE: ratio of methylPHE and –ANT to PHE, (MFLT&PYR)/PYR: ratio of methylFLT and -PYR to PYR, 1,7-/(1,7-&2,6-)DmPHE: ratio of 1,7- to 1,7- and 2,6-dimethylPHE, RET: retene, CPHE: 4-H-cyclopenta[*def*]PHE, CPYR: cyclopenta[*cd*]PYR, PER: perylene, COR: coronene.

7.3 Manuscript 3: Supplementary Information

Text 1

Description of the digestion process and respective sampling

Thermophilic digestion is a continuous process producing methane, carbon dioxide, digestate and presswater (for a schematic overview see Supplementary Information, Figure 4). In the here presented case (which is representative for Switzerland) input material is mixed with fresh water, recycled presswater and inoculated with recycled material at a given ratio (39:18:18:26, w/w) to achieve a pumpable mixture and to initiate the digestion process. Residence time in the fermenter (740 m^3) is about 12 days at 55 ^oC. Thereafter, the liquid fraction (presswater) is separated from the solids. The latter are stabilised (i.e. composted, see below). Since the fermenter is closed and under pressure, only input and output material (equal to the input material of the composting study CDK) could be sampled. It was attempted to keep track of a specific batch (1/12 of the total material in the tank), which was possible since there is no complete mixing in the tank, but the material is forwarded by the Archimedes spiral. Sampling was performed as follows (for sampling locations see Supplementary Information, Figure 4): Input material was sampled at day 0 from every shovel of the front loader filling the feeding tank (54 m^3, which continuously loads the fermenter over 24 hours). Mixing and volume reduction of the gathered composite sample was performed as for compost samples (see below). Material for inoculation could not be sampled directly (no access to the fermenters output pipe). Instead the solid fraction (digestate) was sampled continuously over half a day after presswater had been separated and the corresponding ‘input presswaster’ (50 litres) was sampled from its storage tank at the same time. After 12 days, presswater was sampled again from its storage tank, since there was no access to the outlet of the solid-liquid separator. Digestate ‘output’ was sampled directly from the windrow of composting study CDK.

Text 2

Compost sampling

Before each sampling, the windrows were turned at least twice. The sampling techniques judged as most suitable were different for organic waste composting and digestate stabilization. For windrow CG and CK, which contained coarse structuring material (e.g., branches up to 50 cm long and 5 cm in diameter which had escaped chopping of the input material), a profile was dug about every three meters and a roughly 20 cm “slice” of material was shovelled aside (see Supplementary Information, Figure 1). This material was mixed thoroughly before a sub-sample of 60 litres of every “slice” was filled in an individual aluminum box (yielding some 10 boxes per windrow; for mixing and volume reduction of the composite sample see Kupper (1995), Kehres and Pohle (1998), and Bundesminister für Land- und Forstwirtschaft (2001). Early stage material (CG: day 0-14, CK: day 0) was cut down by a shredder (Althaus, Ersigen, Switzerland, Model 300 K1), mixed thoroughly and reduced to 120 litres (see above). Samples (60 litres each) from CDK, which consisted of relatively fine structured and homogeneous material, were collected from 8 (top to bottom) drilling cores on each side of the windrow. For each CG, CK, and CDK, respectively, samples were mixed in a concrete mixer, before sub-samples (500g) were taken. They were dried chemically using sodium sulphate (1:2 w/w) and cut down to <1mm with a cutting mill (Model SM 2000 Retsch GmbH & Co. KG, Haan, Germany). Samples were stored at 4 ^{o}C in the dark until analysis.

Text 3

Process parameters

Temperature in CK and CDK rose quickly up to 71 ^{o}C and remained high for about 40 days, whereas in CG temperature was lower (maximum 65 ^{o}C) but remained relatively high for a longer time (80 days, Supplementary information Table 2-4). This can be attributed to the slightly higher water content in CK (54 %) and CDK (65 %) compared to CG (51 %, Supplementary information, Table 5-7), which may have accelerated degradation. In CG, organic matter degradation (normalised to ash content) was 53 % whereas in CDK and CK degradation accounted for 48 % and 36 % respectively. Such temperatures and organic mass reduction numbers are in the expected range (Hügi and Kettler, 2004; Mason and Milke, 2005) and give no indication of a different behaviour during composting of organic wastes with and without previous anaerobic treatment, respectively. Temperatures in the thermo composters used for the laboratory studies evolved quicker than in the corresponding field studies (Supplementary information, Figure 3). Organic matter degradation on the lab scale (48 and 40%, respectively, Supplementary information Table 9&10) was comparable to the full-scale conditions (46-53%, Supplementary information Table 5-7).

Table 1: Characteristic PAH ratios and molecular markers for source apportionment corresponding values in input material for composting and digestion

	petrogenic[a]	**pyrogenic**[a]	**Input material for compost/digestion**[b]	**Input material for compost/dig conv**[c]
ANT/(ANT&PHE)	<0.1 [d]	>0.1 [d]	0.07-0.1	0.03-0.05
BaA/(BaA&CHR)	<0.2 [d]	>0.35 [d]	0.43-0.48	0.56-0.61
FLT/(FLT&PYR)	<0.4 [d]	>0.4 [d]	0.54-0.58	0.42-0.45
IPY/(IPY&BPE)	<0.2 [d]	>0.2 [d]	0.48-0.51	0.50-0.53
ComPAH/Σ16PAH	0.3 [d]	0.7 [d]	0.63-0.85	na [e]
(MPHE&ANT)/PHE	5 [d]	0.5 [d]	0.20-0.40	na [e]
(MFLT&PYR)/PYR	4 [d]	0.3 [d]	0.38-0.48	na [e]
1,7-/(1,7-&2,6-)DmPHE	0.45-0.7 [d,f]	<0.45 or 0.7-0.9 [d]	0.57-0.59	na [e]
	fuel combustion	**grass/coal/wood combustion**		
FLT/(FLT&PYR)	0.4-0.5 [d]	>0.5 [d]	0.54-0.58	0.42-0.45
IPY/(IPY&BPE)	0.2-0.5 [d]	>0.5 [d]	0.48-0.51	0.50-0.53
RET/(RET&CHR)	0.15-0.5 [g]	0.83 [h]/0.96 [g,h]	0.05-0.27	na [e]
1,7-/(1,7-&2,6-)DmPHE	<0.45 [d,i]	0.7-0.9 [d, h]	0.57-0.59	na [e]
	non-traffic	**traffic**		
BaP/BPE	<0.6 [d]	>0.6 [d]	1.04-1.24	1.73-2.06
1,7-/(1,7-&2,6-)DmPHE	>0.45 [d]	<0.45 [d]	0.57-0.59	na [e]
	diagenetic	**pyrogenic**		
PER/16PAH	>0.05 [j]	<0.05 [j]	0.00-0.03	na [e]
Markers				
COR/ Σ15PAH	vehicle exhaust [e]		0.01-0.04	na [e]
CPHE/ Σ15PAH	pyrogenic marker[k]		0.01-0.02	>na [e]
CPYR/ Σ15PAH	wood or traffic marker [l]		0.00-0.01	>na [e]

a) prevalent discrimination levels, b) range (n=3), Dibenzo[*a,h*]anthracene was not determined, instead of Σ16PAHs it is referred to Σ15PAHs c) applying conversion factor for air particles suggested by Zhang et al. (2005), d) characteristic PAH ratios according to Bucheli et al. (2004) and references therein, e) conversion factor not available, f) also mixed combustion sources, g) Yan et al. (2005), h) softwood combustion, i) vehicle emission, j) Venkatesan (1988) , k) Garrigues et al. (1995), l) Hedberg et al. (2002), Simoneit, (2002).

ANT: anthracene, PHE: phenanthrene, BaA: benzo[*a*]anthracene; CHR: chrysene; FLU: fluoranthene, PYR: pyrene, IPY: indeno[*1,2,3-cd*)pyrene, BPE: benzo[*g,h,i*]perylene (BPE), ComPAH (Σ of FLT, PYR, BaA, CHR, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene (BaP), IPY, BPE), M: methylated, Dm: dimethylated, RET: retene, PER: perylene, COR: coronene COR, CPHE: 4-H cyclopenta[*def*]PHE, CPYR: cyclopenta[*cd*]PYR

Table 2: Input material composition, windrow dimensions and protocol providing information on sampling, temperature evolution, turning and irrigation of the windrows for the full-scale composting study CG

Input material composition	35 % trimmings from trees and shrubs, 20 % lawn clippings, approx. 38 % green waste[a], 3-4 % soil, 3-4 % residues from processing of cereals, Compazym®[b]
Windrow dimension:	length: 30 m, width: 2-3 m, height ca. 1.8 m

Date	Day	Sampling	Temperature [^{o}C]	Turning	Irrigation
13.09.2005	0	x		x	
14.09.2005	1		33	x	
16.09.2005	3	x	48	x	
19.09.2005	7	x	56	x	
23.09.2005	10		62	x	x
26.09.2005	13		63	x	
27.09.2005	14	x	63	x	
30.09.2005	17		63	x	
03.10.2005	20		62	x	
05.10.2005	22		65	x	
10.10.2005	27		62	x	
12.10.2005	28	x	62	x	
14.10.2005	31		61	x	
17.10.2005	34		63	x	
20.10.2005	37		65	x	x
21.10.2005	38		60	x	
24.10.2005	41		61	x	
26.10.2005	43		58	x	x
28.10.2005	45		59	x	
31.10.2005	48		55	x	
04.11.2005	52		56	x	
07.11.2005	56	x	55	x	
10.11.2005	58		53	x	
11.11.2005	59		53	x	
14.11.2005	62		50	x	
18.11.2005	66		49	x	
21.11.2005	69		51	x	
25.11.2005	73		48	x	
28.11.2005	76		44	x	
02.12.2005	80		43	x	
05.12.2005	83		40	x	
09.12.2005	87		37	x	
12.12.2005	90		35	x	
16.12.2005	94		31	x	
19.12.2005	97		20	x	
27.12.2005	105		10	x	
30.12.2005	108		9	x	
03.01.2006	112	x	8		

a) Parts of the input material have been stored on heaps over some days leading to anaerobic conditions in the heap.

b) auxiliary agent consisting of enzymes for improvement of compost quality

Table 3: Input material composition, windrow dimensions and protocol providing information on sampling, temperature evolution, turning and irrigation of the windrows for the full-scale composting study CK

Input material composition	50 % green waste, 25% horse manure, 5 % residues from processing of vegetables, 10 % soil, 10 % mature compost
Windrow dimension:	length: 12 m, width: 2.5 m, height ca. 1.7 m

Date	Day	Sampling	Temperature [^{o}C]	Turning	Irrigation
04.10.2005	0	x		x	
05.10.2005	1		42	x	
06.10.2005	2		58	x	
07.10.2005	3	x	55	x	
10.10.2005	6		69	x	
11.10.2005	7	x	70	x	
12.10.2005	8		71	x	
13.10.2005	9		69	x	
14.10.2005	10		67	x	
17.10.2005	13		68	x	
18.10.2005	14	x	66	x	
19.10.2005	15		55	x	
21.10.2005	17		50	x	
24.10.2005	20		58	x	
25.10.2005	21		55	x	
27.10.2005	23		49	x	
31.10.2005	27	x	56	x	
02.11.2005	29		50	x	
04.11.2005	31		48	x	
07.11.2005	34		48	x	
09.11.2005	36		45	x	
14.11.2005	41		46	x	
21.11.2005	48		33	x	
29.11.2005	56	x	17	x	
24.01.2006	112	x			

Table 4: Input material composition, windrow dimensions and protocol providing information on sampling, temperature evolution, turning and irrigation of the windrows for the full-scale composting study CDK

Input material composition	output of the digestion plant (input material for digestion consisted of green waste, kitchen waste and food residues [a])
Windrow dimension:	length: 12 m, width: 2.5 m, height ca. 1.7 m

Date	Day	Sampling	Temperature [°C]	Turning	Irrigation
04.10.2005	0	x			
05.10.2005	1		52	x	
06.10.2005	*2*		62	x	
07.10.2005	3		57	x	
10.10.2005	6	x	67	x	
11.10.2005	7		66	x	
12.10.2005	8	x	64	x	
13.10.2005	9		63	x	
14.10.2005	10		62	x	
17.10.2005	13		65	x	
18.10.2005	14		66	x	
19.10.2005	15	x	56	x	
21.10.2005	17		63	x	
24.10.2005	20		68	x	
25.10.2005	21		58	x	
27.10.2005	23		56	x	
31.10.2005	27		54	x	
02.11.2005	29	x	50	x	
04.11.2005	31		50	x	
07.11.2005	34		50	x	
09.11.2005	36		47	x	
14.11.2005	41			x	
21.11.2005	48		41	x	
29.11.2005	56		35	x	
24.01.2006	112	x			

a) The input material has been chopped and stored on a large heap over several days leading to anaerobic conditions in the heap.

Table 5: PCB concentrations, enantiomeric fractions (EFs) of PCBs, PAH concentrations, characteristic PAH ratios and molecular markers during composting of green waste (CG)

	day 0	day 3	day 7	day 14	day 28	day 56	day 112
water content [% ww][a]	51	45	46	44	38	38	50
ash content [% dw][b]	49	49	47	54	64	66	67
PCBs ($\mu g/kg_{dw}$)							
PCB 28	nd	nd	nd	nd	nd	nd	nd
PCB 52	0.94	1.0	1.2	1.3	1.4	1.7	1.5
PCB 95	1.3	1.3	1.6	1.7	1.7	2.6	2.2
PCB 101	1.9	1.9	2.3	2.4	2.5	3.9	3.2
PCB 118	1.4	1.6	1.9	1.9	2.1	3.5	2.5
PCB 149	2.6	2.6	2.6	2.5	2.3	4.4	3.8
PCB 132	1.4	1.6	1.5	1.4	1.2	2.7	2.2
PCB 153	3.4	3.4	3.6	3.5	3.3	5.9	5.1
PCB 138	2.3	2.5	2.5	2.4	2.3	4.4	3.6
PCB 174	0.82	0.96	0.86	0.73	0.62	1.3	1.0
PCB 180	2.0	1.9	2.0	2.0	1.8	2.9	2.4
Enantiomeric fractions (EF)							
EF PCB 95	0.49	0.49	0.50	0.49	0.49	0.49	0.49
EF PCB 149	0.50	0.49	0.50	0.50	0.50	0.50	0.50
EF PCB 132	0.50	0.50	0.50	0.50	0.51	0.50	0.50
PAHs ($\mu g/kg_{dw}$)[c]	n=2	n=2	n=2	n=2	n=2	n=2	n=4
NAP	68	23	19	11	7.6	5	4.3
ACY	3.4	2.6	1.8	1.5	2.0	1.0	0.89
ACE	210	80	120	110	59	13	4.7
FLU	250	87	140	140	18	9.0	5.5
PHE	650	240	390	400	120	79	120
ANT	55	22	34	39	14	11	27 [d]
FLT	810	250	450	500	410	450	560 [d]
PYR	680	200	380	410	410	430	470 [d]
BaA	160	67	110	120	99	220	290 [d]
CHR	170	84	120	130	100	220	280 [d]
BbF	71	66	71	74	76	170	230 [d]
BkF	38	36	37	42	40	96	130 [d]
BaP	58	59	57	63	64	140	180 [d]
IPY	45	48	49	51	57	96	130 [d]
BPE	49	55	51	58	60	100	140 [d]
CPHE	47	19	27	29	20	12	22 [d]
RET	10	11	11	19	21	21	17
CPYR	4.7	4	3.5	4.1	2.7	2.6	3.2
PER	15	16	16	17	18	38	51 [d]
COR	24	27	24	29	31	42	69 [d]

Characteristic PAH ratios							
(MPHE/ANT)/PHE [-]	0.20	0.21	0.18	0.21	0.45	0.62	0.63
(MFLT/PYR)/PYR [-]	0.32	0.32	0.31	0.31	0.24	0.31	0.34
1,7-/(1,7-&2,6-)DmPHE) [-]	0.57	0.58	0.57	0.58	0.61	0.61	0.59
Heavy metals (mg/kg_{dw})							
Cd	0.14	0.15	0.11	0.22	0.13	0.21	0.12
Co	4.5	5.1	5.1	5.4	6.1	6.1	6.3
Cr	29	29	30	30	25	25	26
Cu	28	25	29	31	32	32	33
Ni	20	22	22	24	20	21	21
Pb	24	23	24	25	31	32	28
Zn	96	91	98	110	120	130	120
Nutrients (g/kg_{dw})							
N	13	13	14	15	15	16	16
P	2.2	2.2	2.3	2.5	2.7	2.9	2.7
K	9.0	8.6	9.4	9.4	10	11	11
Mg	2.9	3.0	3.1	3.2	3.7	3.8	3.8
Ca	36	38	34	36	47	48	53
Further elements (g/kg_{dw})							
Fe	11	12	11	12	14	14	15
Na	2.1	0.52	0.36	2.0	0.27	0.30	0.29
Mn	0.39	0.41	0.44	0.46	0.51	0.53	0.53

a) ww: wet weight

b) dw: dry weight

c) number of analysis

d) outliers, replaced by values of day 56

Table 6: PCB concentrations, enantiomeric fractions (EFs) of PCBs, PAH concentrations, characteristic PAH ratios and molecular markers of green and organic kitchen waste (CK)

	day 0	day 3	day 7	day 14	day 28	day 56	day 112
water content [% ww][a]	54	54	52	47	47	47	48
ash content [% dw][b]	63	64	70	70	71	74	73
PCBs (µg/kg$_{dw}$)							
PCB 28	nd	nd	nd	nd	nd	nd	nd
PCB 52	0.84	0.85	0.78	1.1	0.98	0.97	1.4
PCB 95	1.1	1.2	1.1	1.6	1.4	1.4	1.6
PCB 101	1.7	1.7	1.7	2.5	2.1	2.1	2.3
PCB 118	1.3	1.3	1.3	1.9	1.7	1.7	1.7
PCB 149	2.0	2.2	2.1	2.9	2.4	2.4	2.7
PCB 132	1.1	1.1	1.2	1.5	1.3	1.2	1.5
PCB 153	3.2	3.5	3.4	4.8	4.1	4.1	4.3
PCB 138	2.3	2.4	2.2	3.3	2.7	2.8	2.9
PCB 174	0.74	0.78	0.63	0.88	0.73	0.70	0.77
PCB 180	1.9	2.3	1.9	2.6	2.3	2.2	2.4
Enantiomeric fractions (EF)							
EF PCB 95	0.51	0.516	0.51	0.50	0.51	0.50	0.52
EF PCB 149	0.50	0.50	0.50	0.50	0.50	0.50	0.50
EF PCB 132	0.50	0.51	0.50	0.50	0.50	0.51	0.50
PAHs (µg/kg$_{dw}$)[c]	n=2	n=2	n=4	n=2	n=2	n=2	n=2
NAP	9.8	6.6	4.8	3.5	3.9	3.5	4.0
ACY	0.89	0.55	0.45	0.43	0.45	0.42	0.56
ACE	3.4	3.1	3.1	1.5	0.68	0.59	6.2 [d]
FLU	5.2	4.4	4.3	3.9	1.9	1.4	7.8 [d]
PHE	37	37	41	48	45	31	120 [d]
ANT	4.0	3.2	3.8	3.4	2.8	2.0	5.9 [d]
FLT	69	81	74	79	75	64	110 [d]
PYR	51	61	51	44	32	18	47
BaA	31	37	30	32	43	26	34
CHR	41	50	41	45	63	45	48
BbF	42	50	42	43	56	51	46
BkF	21	25	20	22	27	21	20
BaP	33	37	29	29	37	24	25
IPY	32	35	31	32	40	35	33
BPE	32	36	31	32	40	33	33
CPHE	4.6	4.8	4.6	4.1	2.6	2.0	6.9 [d]
RET	15	7.2	7.2	10	7.9	7.7	10
CPYR	2.5	2.6	2.6	2.1	2.0	2.0	2.1
PER	11	13	10	9.8	12	8.0	7.9
COR	17	18	19	18	19	19	23

Characteristic PAH ratios							
(MPHE/ANT)/PHE [-]	0.40	0.39	0.34	0.34	0.32	0.29	0.23
(MFLT/PYR)/PYR [-]	0.48	0.43	0.42	0.52	0.80	0.75	0.50
1,7-/(1,7-&2,6-)DmPHE) [-]	0.59	0.61	0.61	0.63	0.63	0.69	0.56
Heavy metals (mg/kg$_{dw}$)							
Cd	0.087	0.13	0.13	0.17	0.06	0.18	0.17
Co	4.9	5	4.7	5.1	5.3	5.6	5.4
Cr	48	46	24	27	27	28	28
Cu	210	31	32	35	36	36	35
Ni	31	30	17	18	19	20	19
Pb	27	34	27	26	54	32	29
Zn	89	95	96	99	110	120	110
Nutrients (g/kg$_{dw}$)							
N	9.9	10	9.9	11	11	12	11
P	1.9	2.1	2.0	2.2	2.3	2.4	2.3
K	6.1	6.1	5.5	6.4	6.6	7.1	6.9
Mg	6.7	7.4	7.5	7.4	7.7	8.1	8.0
Ca	33	34	39	37	39	40	41
Further elements (g/kg$_{dw}$)							
Fe	13	13	13	14	14	15	14
Na	2.9	0.74	0.33	0.35	0.36	0.37	0.37
Mn	0.63	0.63	0.62	0.66	0.69	0.71	0.68

a) ww: wet weight
b) dw: dry weight
c) number of analysis
d) outliers, replaced by values of day 56

Table 7: PCB concentrations, enantiomeric fractions (EFs) of PCBs, PAH concentrations, characteristic PAH ratios and molecular markers of digested kitchen waste (CDK)

	day 0	day 3	day 7	day 14	day 28	day 56	day 112
water content [% ww][a]	65	64	64	62	61	62	63
ash content [% dw][b]	41	45	44	52	54	55	57
PCBs (μg/kg$_{dw}$)							
PCB 28	nd	nd	nd	nd	nd	nd	nd
PCB 52	2.4	2.3	2.7	5.5	2.7	3.0	4.3
PCB 95	2.3	2.4	2.4	4.9	2.7	2.7	4.8
PCB 101	3.2	3.4	3.4	7.5	3.8	3.9	6.6
PCB 118	2.5	2.5	2.8	11	2.9	3.1	5.1
PCB 149	3.8	4.2	3.5	5.2	5.1	4.0	5.8
PCB 132	2.3	2.5	2.1	3.1	3.2	2.4	3.4
PCB 153	5.1	5.6	5.0	10.2	6.8	5.6	7.9
PCB 138	3.5	3.9	3.6	7.9	4.9	4.0	5.7
PCB 174	1.3	1.4	1.1	1.3	2.0	1.2	1.2
PCB 180	3.0	3.1	2.9	3.9	4.4	3.0	3.5
Enantiomeric fractions (EF)							
EF PCB 95	0.51	0.51	0.51	0.51	0.50	0.51	0.51
EF PCB 149	0.50	0.50	0.50	0.50	0.50	0.50	0.50
EF PCB 132	0.50	0.50	0.50	0.50	0.50	0.50	0.50
PAHs (μg/kg$_{dw}$)[c]	n=2	n=2	n=2	n=2	n=2	n=2	n=4
NAP	37	28	16	8	7.4	7.7	9.0
ACY	1.0	1.1	1.5	2.0	0.9	1.2	1.1
ACE	130	110	97	23	5.6	4.0	5.7
FLU	110	92	76	36	12	7.5	8.5
PHE	380	370	320	210	90	49	50
ANT	39	34	30	20	8.4	6.6	6.1
FLT	260	270	280	300	190	130	140
PYR	180	180	190	160	47	32	32
BaA	62	63	66	72	60	41	41
CHR	71	72	74	83	78	69	79
BbF	52	54	53	67	63	66	79
BkF	27	27	26	32	30	28	32
BaP	42	42	39	44	31	30	34
IPY	34	35	31	43	39	41	43
BPE	33	33	30	39	35	37	41
CPHE	25	23	22	18	6.5	4.4	4.1
RET	11	8.9	9.7	9.4	8.0	8.6	7.1
CPYR	3.5	3.3	3.7	3.1	2.8	3.0	2.9
PER	15	15	15	15	12	11	12
COR	13	13	10	15	14	18	19

Characteristic PAH ratios							
(MPHE/ANT)/PHE [-]	0.22	0.21	0.23	0.34	0.30	0.36	0.31
(MFLT/PYR)/PYR [-]	0.36	0.32	0.31	0.33	0.61	0.73	0.78
1,7-/(1,7-&2,6-)DmPHE) [-]	0.55	0.54	0.54	0.53	0.59	0.62	0.61
Heavy metals (mg/kg$_{dw}$)							
Cd	0.027	0.083	0.050	0.078	0.022	0.11	0.039
Co	2.9	3.1	3.2	2.9	3.2	3.4	3.5
Cr	36	48	38	18	18	21	21
Cu	32	32	33	34	37	39	38
Ni	23	31	25	12	13	14	15
Pb	60	20	22	19	24	25	23
Zn	77	80	81	82	93	100	96
Nutrients (g/kg$_{dw}$)							
N							
P	14	13	15	15	16	16	15
K	2.6	2.8	2.8	3.5	3.1	3.5	3.2
Mg	10	10	10	11	11	12	12
Ca	6.9	7.0	6.7	7.7	8.0	8.9	8.3
	47	50	50	65	61	63	71
Further elements (g/kg$_{dw}$)							
Fe	8.4	7.7	8.1	9.1	9	9.9	9.9
Na	1.2	2.3	1.4	1.1	1.1	1.2	1.2
Mn	0.33	0.33	0.34	0.37	0.45	0.44	0.45

a) ww: wet weight
b) dw: dry weight
c) number of analysis

Table 8: PCB concentrations, enantiomeric fractions (EFs) of PCBs, PAH concentrations, characteristic PAH ratios and molecular markers of green waste (CG_{lab}) in the laboratory study [d]

	day 3	day 7	day 14	day 28	day 56	day 112
water content [% ww][a]	62	59	55	57	49	33
ash content [% dw][b]	49	54	60	59	62	66
PCBs (µg/kg_{dw})						
PCB 28	nd	nd	nd	nd	nd	nd
PCB 52	1.1	1.9	1.4	1.5	1.3	1.5
PCB 95	1.4	2.8	2.2	1.9	1.8	2.3
PCB 101	2.1	3.9	3.0	2.6	2.5	3.0
PCB 118	1.6	3.2	2.0	2.1	2.1	2.5
PCB 149	2.2	3.7	3.9	2.7	2.8	3.2
PCB 132	1.3	2.4	2.3	1.5	1.6	1.8
PCB 153	2.9	5.0	4.4	3.7	4.0	4.6
PCB 138	2.0	3.9	3.1	2.6	2.8	3.3
PCB 174	0.59	0.91	1.1	0.74	1.0	1.0
PCB 180	1.3	2.2	2.1	1.6	2.3	2.5
Enantiomeric fractions (EF)						
EF PCB 95	0.50	0.50	0.50	0.50	0.50	0.50
EF PCB 149	0.50	0.50	0.50	0.50	0.50	0.50
EF PCB 132	0.50	0.50	0.50	0.50	0.50	0.49
PAHs (µg/kg_{dw})[c]	n=4	n=2	n=2	n=2	n=2	n=2
NAP	15	7.3	6.4	14	6.4	9.7
ACY	1.9	1.6	0.94	1.4	0.92	1.1
ACE	130	66	8.6	95	3.6	4.5
FLU	130	89	20	78	6.9	8.6
PHE	620	310	140	340	53	58
ANT	49	27	13	32	7.4	8.3
FLT	1100	390	400	320	110	130
PYR	870	300	290	230	70	92
BaA	230	92	110	77	51	65
CHR	320	120	150	95	80	98
BbF	160	89	72	59	79	99
BkF	85	45	39	30	36	46
BaP	120	66	52	42	54	73
IPY	88	62.	44	34	59	71
BPE	88	61	50	34	56	67
CPHE	49	20	14	25	5	6.7
RET	10	8.7	9.3	13	5.1	9.6
CPYR	4.1	3.0	4.3	2.7	2.5	2.1
PER	32	18	14	14	16	19
COR	39	26	35	14	27	29

Characteristic PAH ratios						
(MPHE/ANT)/PHE [-]	0.21	0.19	0.32	0.26	0.32	0.43
(MFLT/PYR)/PYR [-]	0.32	0.29	0.41	0.35	0.45	0.52
1,7-/(1,7-&2,6-)DmPHE) [-]	0.57	0.59	0.61	0.54	0.62	0.62
Heavy metals (mg/kg$_{dw}$)						
Cd	0.15	0.20	0.16	0.22	0.20	0.17
Co	4.8	5.2	5.7	5.5	6.7	6.3
Cr	27	29	37	25	26	26
Cu	28	29	31	33	34	34
Ni	21	23	29	18	22	21
Pb	22	25	30	27	32	31
Zn	96	100	110	120	130	130
Nutrients (g/kg$_{dw}$)						
N	13	14	16	15	17	16
P	2.3	2.4	2.7	2.6	3.1	2.9
K	9.5	9.8	11	11	12	12
Mg	3.1	3.2	3.6	3.6	4.0	3.9
Ca	38	41	46	43	46	50
Further elements (g/kg$_{dw}$)						
Fe	11	12	13	14	15	15
Na	0.29	0.35	0.33	0.36	0.39	0.40
Mn	0.4	0.44	0.49	0.47	0.58	0.54

a) ww: wet weight
b) dw: dry weight
c) number of analysis
d) for day 0, see day 0 CG

Table 9: PCB concentrations, enantiomeric fractions (EFs) of PCBs, PAH concentrations, characteristic PAH ratios and molecular markers of green waste and organic kitchen waste (CK_{lab}) in the laboratory study[d]

	day 3	day 7	day 14	day 28	day 56	day 112
water content [% ww][a]	56	54	52	50	52	43
ash content [% dw][b]	62	68	68	73	71	74
PCBs (µg/kg$_{dw}$)						
PCB 28	nd	nd	nd	nd	nd	nd
PCB 52	1.1	0.90	0.90	0.89	1.1	1.0
PCB 95	1.8	1.2	1.3	1.3	2.1	1.4
PCB 101	2.8	1.9	1.9	2.0	3.1	2.1
PCB 118	2.1	1.6	1.5	1.5	2.0	1.8
PCB 149	4.6	2.2	2.2	2.5	4.3	2.5
PCB 132	2.6	1.2	1.2	1.5	2.2	1.4
PCB 153	6.5	3.6	3.6	4.2	6.5	4.5
PCB 138	4.5	2.5	2.5	2.8	4.2	3.0
PCB 174	1.5	0.67	0.66	0.73	1.3	0.79
PCB 180	3.8	2.0	1.9	2.1	3.9	2.8
Enantiomeric fractions (EF)						
EF PCB 95	0.51	0.51	0.51	0.50	0.51	0.50
EF PCB 149	0.50	0.50	0.50	0.50	0.49	0.48
EF PCB 132	0.50	0.50	0.50	0.49	0.50	0.48
PAHs (µg/kg$_{dw}$)[c]	n=2	n=2	n=4	n=2	n=2	n=2
NAP	6.6	19	5.3	4.6	4.4	4.9
ACY	0.6	0.5	1.3	0.5	0.5	0.5
ACE	3.2	1.2	1.3	0.6	0.5	0.6
FLU	5.0	2.5	2.3	1.2	1.0	1.2
PHE	46	39	30	18	17	20
ANT	3.9	3.1	4.4	1.6	1.5	2.7
FLT	73	72	66	44	44	69
PYR	48	43	47	22	26	46
BaA	28	35	37	20	24	43
CHR	41	47	52	35	40	58
BbF	43	48	97	42	49	65
BkF	20	23	43	17	20	27
BaP	28	33	110	22	27	43
IPY	31	34	94	28	35	44
BPE	32	35	88	28	33	41
CPHE	4.3	3.4	3.9	2.0	2.0	2.8
RET	6.9	5.4	5.6	4.9	4.4	2.9
CPYR	2.6	2.3	4.0	2.2	2.3	1.8
PER	9.7	11	37	8.0	9.8	13

COR	15	16	36	16	17	18
Characteristic PAH ratios						
(MPHE/ANT)/PHE [-]	0.32	0.31	0.37	0.35	0.37	0.45
(MFLT/PYR)/PYR [-]	0.42	0.49	0.59	0.57	0.55	0.46
1,7-/(1,7-&2,6-)DmPHE) [-]	0.62	0.61	0.63	0.64	0.65	0.61
Heavy metals (mg/kg$_{dw}$)						
Cd	0.068	0.10	0.12	0.11	0.12	0.21
Co	4.4	4.9	4.9	5.4	5.3	5.9
Cr	24	24	24	26	28	31
Cu	32	30	33	33	36	37
Ni	16	18	18	19	19	21
Pb	23	30	30	28	31	46
Zn	87	130	100	110	110	120
Nutrients (g/kg$_{dw}$)						
N	10	11	11	10	12	12
P	1.9	2.1	2.2	2.2	2.3	2.5
K	5.9	6.2	6.3	6.5	6.8	7.4
Mg	7.4	7.9	7.0	7.2	7.4	8.1
Ca	34	37	35	38	36	39
Further elements (g/kg$_{dw}$)						
Fe	12	13	13	15	14	15
Na	0.34	0.35	0.35	0.35	0.37	0.40
Mn	0.61	0.65	0.69	0.67	0.69	0.75

a) ww: wet weight
b) dw: dry weight
c) number of analysis
d) for day 0, see day 0 CK

Table 10: Correlation coefficients for linear relationships between accumulation factors of PCBs and PAHs and corresponding log K_{ow} and vapour pressures

	CG	CK	CDK	CG_{lab}	CK_{lab}
PCBs[a] – log K_{ow}					
day 112	-0.73*	-0.84*	-0.83*	-0.71*	0.24
PCBs[a] – vapour pressure					
day 112	0.53	0.85*	0.38	0.32	-0.38
PAHs[b] – log K_{ow}					
day 3	0.76*	0.74*	0.57*	0.86*	0.24
day 7	0.88*	0.60*	0.25	0.88*	0.13
day 14	0.93*	0.64*	0.53*	0.96*	0.76*
day 28	0.91*	0.76*	0.79*	0.70*	0.84*
day 56	0.85*	0.81*	0.75*	0.88*	0.88*
day 112	0.86*[c]	0.80*[d]	0.70*	0.85*	0.82*
PAHs[b] – vapour pressure					
day 3	-0.25	-0.54*	-0.62*	-0.49	-0.55*
day 7	-0.54*	-0.69*	-0.55*	-0.44	0.67*
day 14	-0.57*	-0.59*	-0.38	-0.35	-0.30
day 28	-0.37	-0.40	-0.30	-0.47	-0.19
day 56	-0.32	-0.33	-0.24	-0.26	-0.23
day 112	-0.32	-0.30	-0.01	-0.25	-0.30

a) congeners considered: PCB 52, 95, 101, 118, 149, 132, 153, 138, 174, 180

b) compounds considered: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene , pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, perylene, coronene

c) due to high relative standard variation on day 112, day 56 was considered for ANT-BPE, PER, COR

d) due to high relative standard variation on day 112, day 56 was considered for ACE-PYR

* significant correlation ($p<0.05$)

Table 11: PCB concentrations, enantiomeric fractions (EFs) of PCBs, PAH concentrations, characteristic PAH ratios and molecular markers in samples taken from the digestion plant (DK)[d]

	input material	pw [e] inoc [f]	digestate inoc [f]	pw [e] at day 12
water content [% ww][a]	38	13	36	13
ash content [% dw][b]	36	51	50	51
PCBs (µg/kg_{dw})				
PCB 28	nd	nd	nd	nd
PCB 52	1.3	2.7	2.1	2.9
PCB 95	1.5	3.3	2.3	3.0
PCB 101	2.1	4.4	3.2	4.2
PCB 118	1.7	3.3	2.4	3.2
PCB 149	2.5	5.1	3.4	4.9
PCB 132	1.5	2.8	2.0	2.5
PCB 153	3.4	6.9	4.7	6.7
PCB 138	2.4	4.7	3.2	4.4
PCB 174	0.86	1.3	0.93	1.3
PCB 180	1.8	3.6	2.4	3.6
Enantiomeric fractions (EF)				
EF PCB 95	0.50	0.50	0.50	0.51
EF PCB 149	0.50	0.50	0.50	0.50
EF PCB 132	0.51	0.50	0.50	0.50
PAHs (µg/kg_{dw})[c]	n=2	n=2	n=4	n=2
NAP	17	230	37	210
ACY	1.6	5.3	1.4	5.2
ACE	15	490	93	510
FLU	20	370	73	410
PHE	110	1300	270	1500
ANT	8.2	130	27	150
FLT	130	950	240	1000
PYR	97	650	190	690
BaA	45	220	66	230
CHR	53	260	74	280
BbF	43	220	50	230
BkF	22	110	27	110
BaP	35	170	39	170
IPY	29	150	32	140
BPE	28	150	30	150
CPHE	10	90	23	92
RET	8.1	31	9.5	27
CPYR	4.2	9.8	4	9.6
PER	13	56	14	54
COR	11	66	14	64

Characteristic PAH ratios				
(MPHE/ANT)/PHE [-]	0.35	0.21	0.21	0.20
(MFLT/PYR)/PYR [-]	0.47	0.32	0.35	0.31
1,7-/(1,7-&2,6-)DmPHE) [-]	0.57	0.55	0.56	0.55
Heavy metals (mg/kg$_{dw}$)				
Cd	0.031	0.3	0.19	0.37
Co	3.0	5.9	5.1	6.1
Cr	36	54	33	50
Cu	33	77	26	74
Ni	26	41	25	38
Pb	21	42	23	42
Zn	97	230	94	230
Nutrients (g/kg$_{dw}$)				
N	16	30	13	28
P	2.7	6.8	2.3	6.7
K	12	33	9.2	32
Mg	6.6	11	3.1	11
Ca	34	37	42	37
Further elements (g/kg$_{dw}$)				
Fe	7.2	13	11	13
Na	0.73	3.6	0.36	3.2
Mn	0.32	0.55	0.41	0.59

a) ww: wet weight

b) dw: dry weight

c) number of analysis

d) for digestate (output material of digestion process) see day 0 CDK

e) pw: presswater

f) inoc: inoculation material for the digestion process

Figure 1: Compost sampling for CG (sampling was similar for CK and CDK see text)

Figure 2: Thermo composter (Handy 230, Neudorff, Emmerthal, Germany) for the laboratory studies (CG_{lab} and CK_{lab})

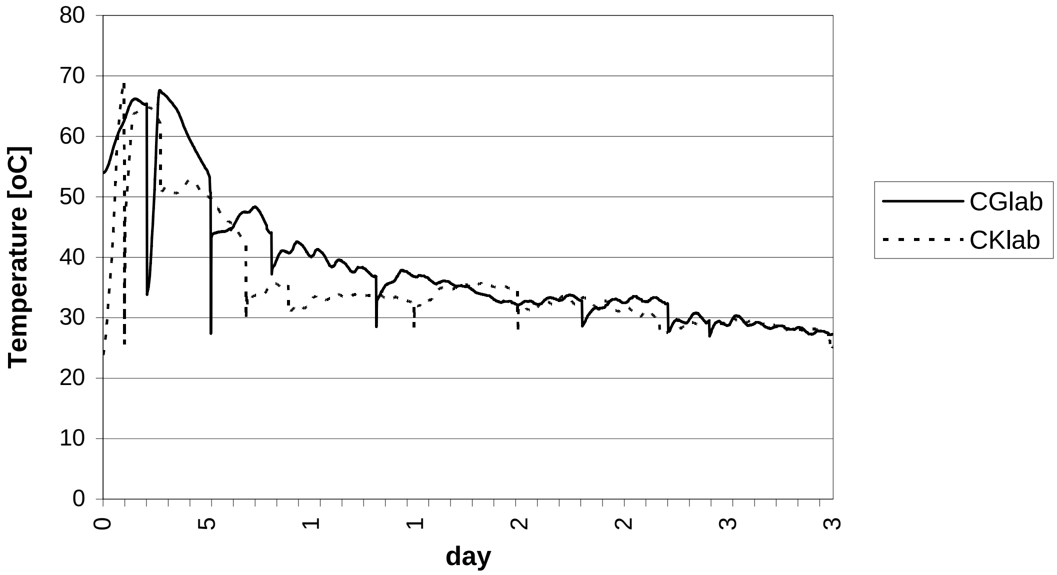

Figure 3: Temperature evolution in the laboratory study CG$_{lab}$ and CK$_{lab}$, (data only shown until day 35, afterwards it remained at 30^{o}C (ambient temperature)

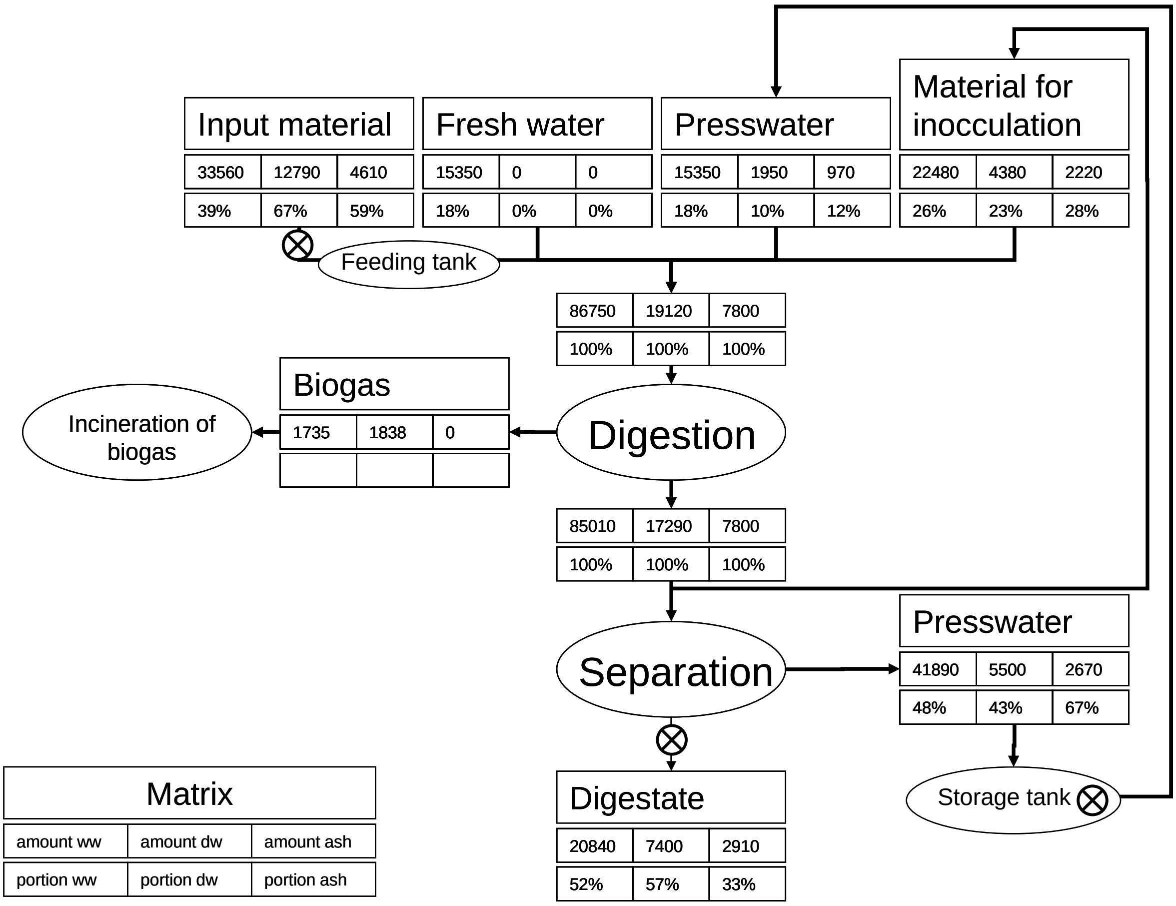

Figure 4: Mass balance of the thermophilic digestion process. The amount of input material, fresh water, presswater and material for inoculation was measured on the plant and the content of crude ash determined in all samples. Stable ash content during digestion and an output ratio of presswater:digestate of 2:1 (ww) were assumed. Note that there is a slight difference in biogas production (in kg) if the calculation is based on ww or dw. ww: wet weight, dw: dry weight; unit: kg; ⊗ sampling location.

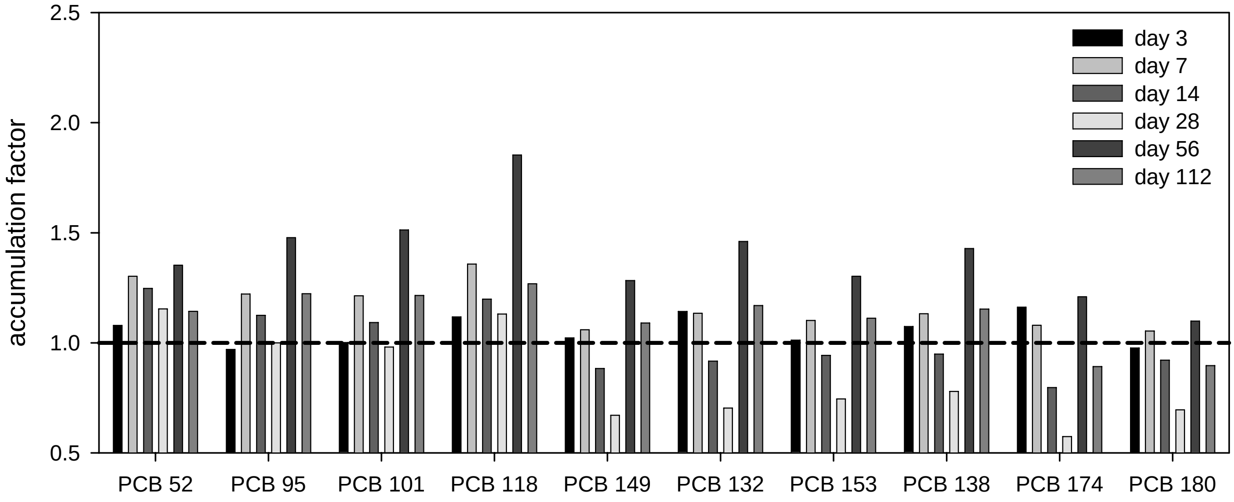

Figure 5: Accumulation factors of PCBs (52, 95, 101, 118, 149, 132, 153, 138, 174, 180) during composting of green waste (CG). Dashed line indicates conservative behaviour of target analytes.

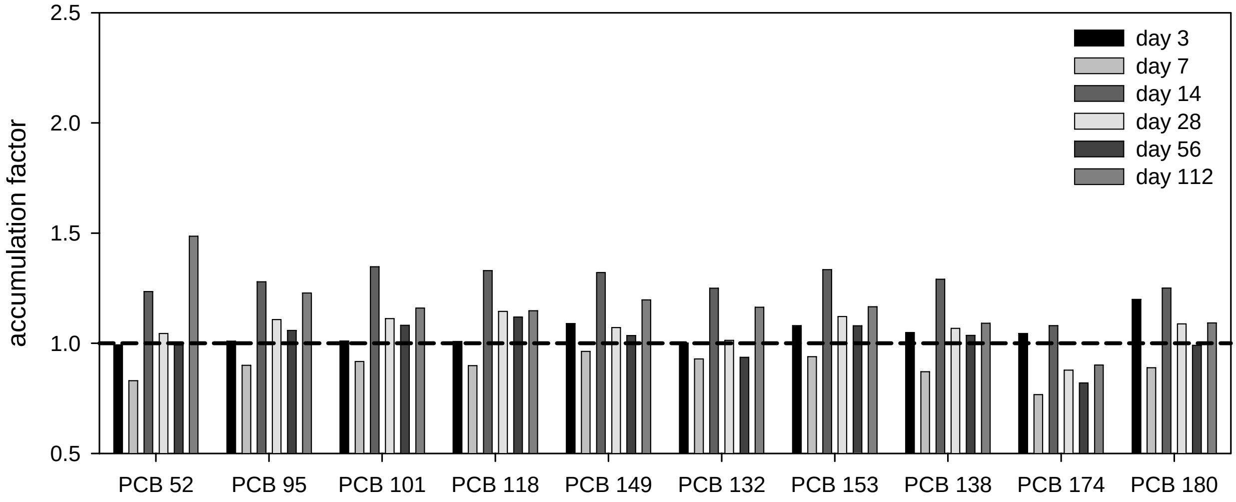

Figure 6: Accumulation factors of PCBs (52, 95, 101, 118, 149, 132, 153, 138, 174, 180) during composting of organic kitchen and green waste (CK). Dashed line indicates conservative behaviour of target analytes.

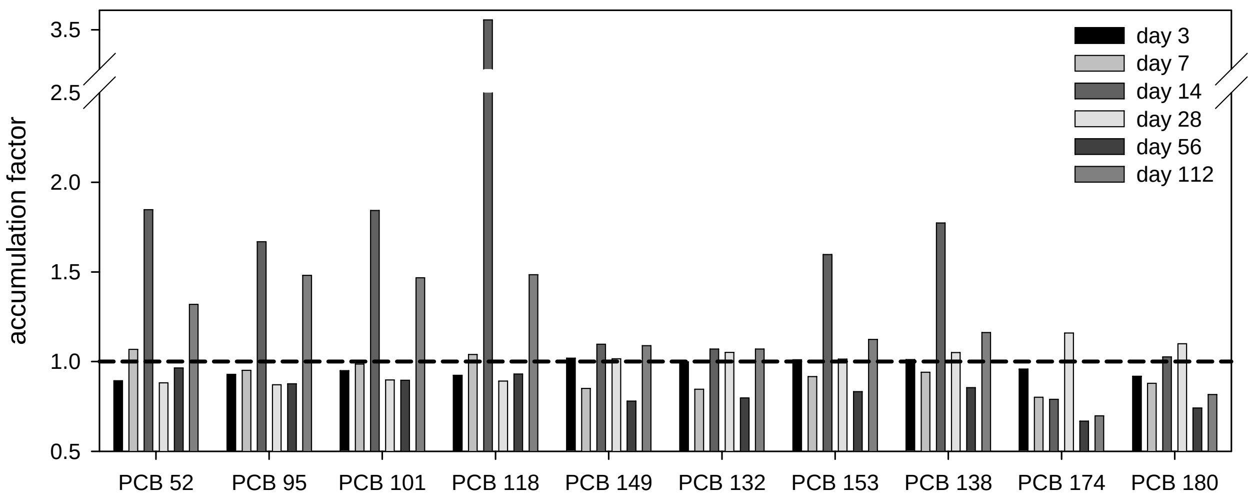

Figure 7: Accumulation factors of PCBs (52, 95, 101, 118, 149, 132, 153, 138, 174, 180) during composting of digestate (CDK). Dashed line indicates conservative behaviour of target analytes.

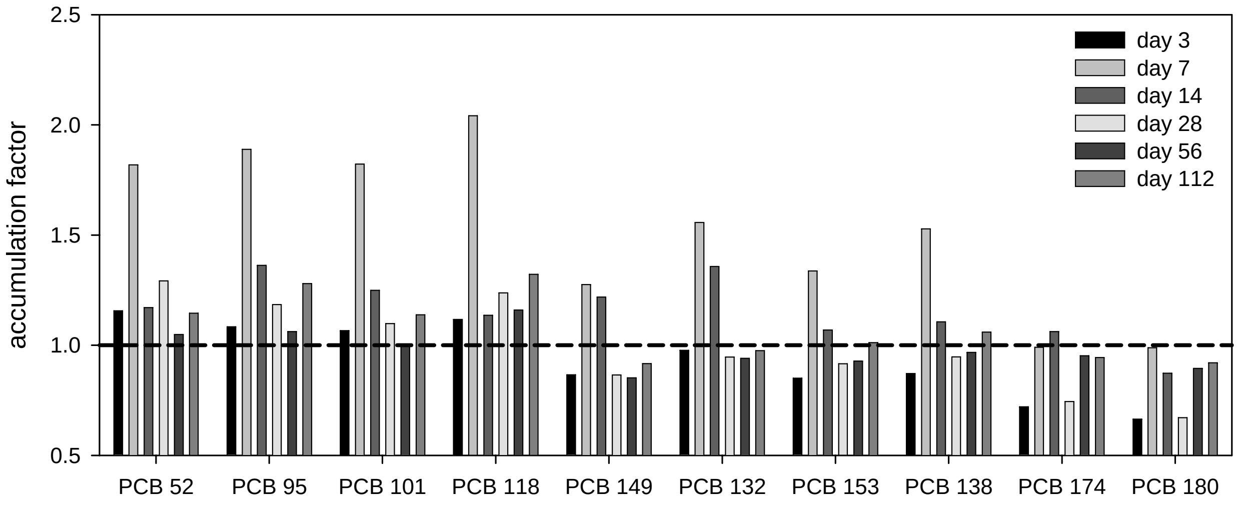

Figure 8: Accumulation factors of PCBs (52, 95, 101, 118, 149, 132, 153, 138, 174, 180) during composting of green waste on laboratory scale (CG_{lab}). Dashed line indicates conservative behaviour of target analytes.

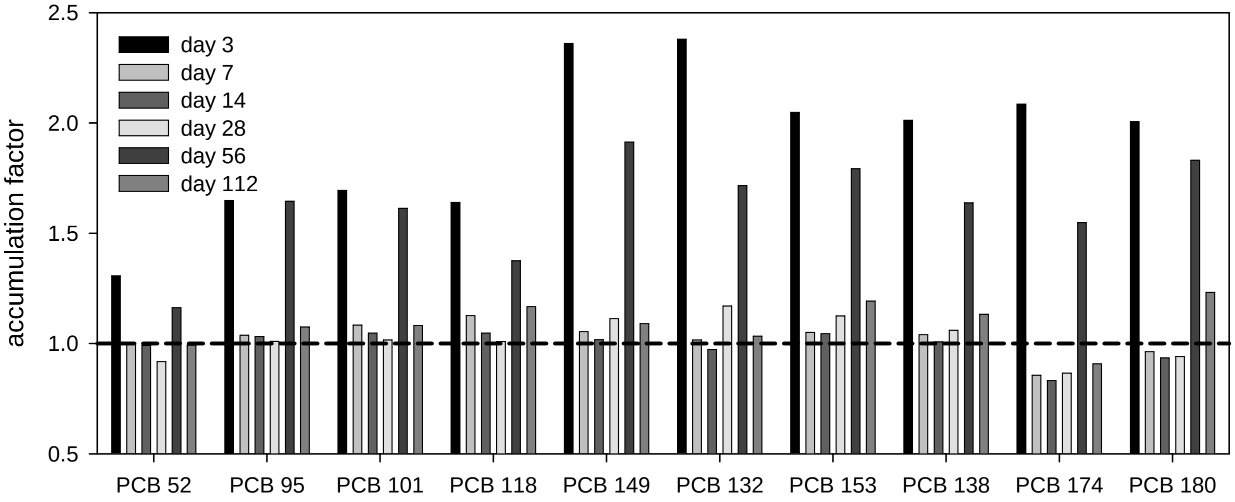

Figure 9: Accumulation factors of PCBs (52, 95, 101, 118, 149, 132, 153, 138, 174, 180) during composting of organic kitchen and green waste on laboratory scale (CK_{lab}). Dashed line indicates conservative behaviour of target analytes.

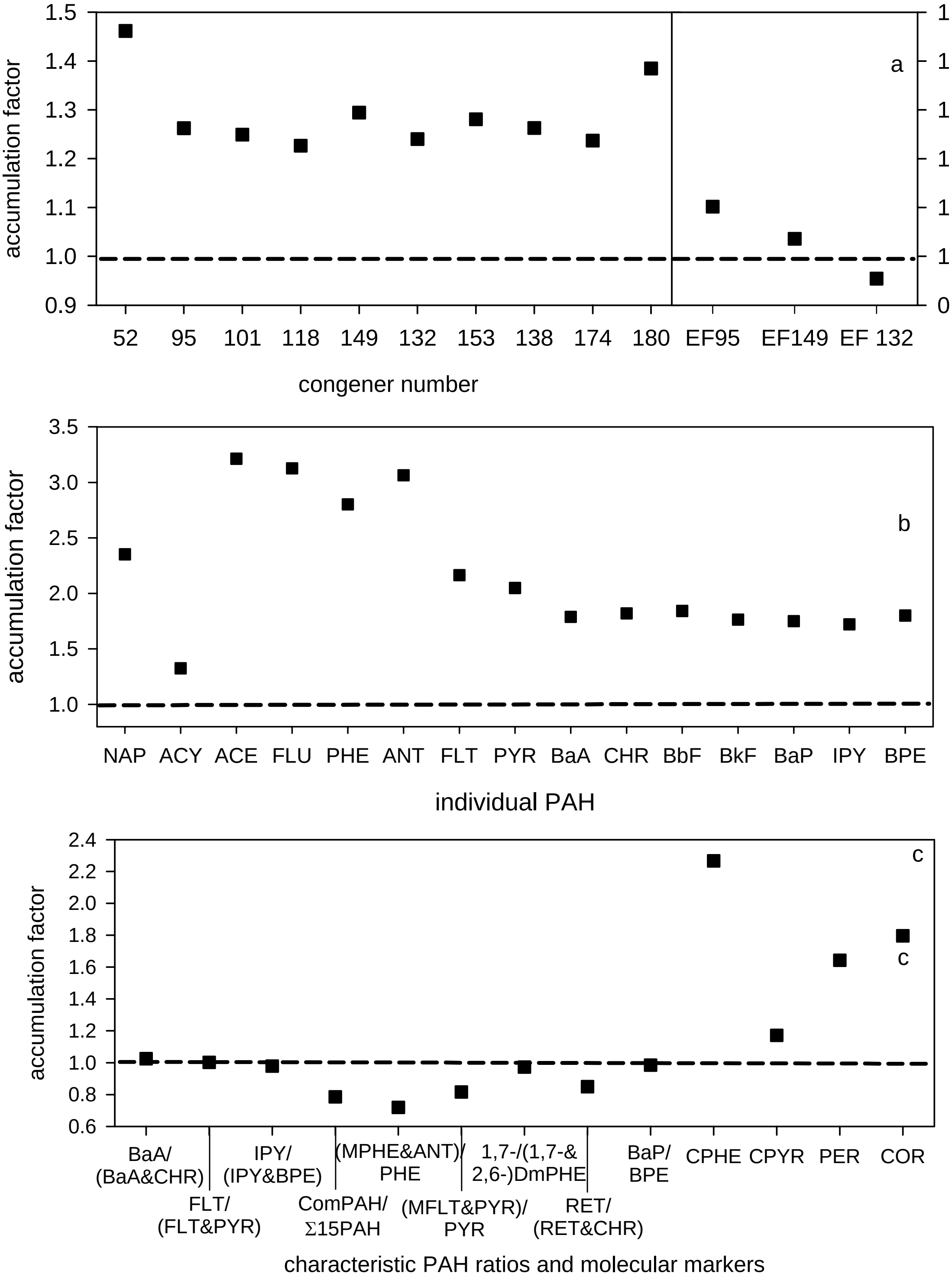

Figure 10: Accumulation factors during digestion of a) PCBs and enantiomeric fractions (EF) of PCBs; b) of PAHs and c) of characteristic PAH ratios and molecular markers. Dashed lines indicate conservative behaviour of target analytes, NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[*1,2,3-cd*]pyrene, BPE: benzo[*ghi*]perylene, ComPAH: Sum of FLT, PYR, BaA, CHR, BbF, BkF, BaP, IPY, BPE, Σ15PAH: Sum of 16 PAHs defined by the US EPA, except dibenzo[*a,h*]anthracene, (MPHE&ANT)/PHE: ratio of methylPHE and –ANT to PHE, (MFLT&PYR)/PYR: ratio of methylFLT and -PYR to PYR, 1,7-/(1,7-&2,6-)DmPHE: ratio of 1,7- to 1,7- and 2,6-dimethylPHE, RET: retene, CPHE: 4-H-cyclopenta[*def*]PHE, CPYR: cyclopenta[*cd*]PYR, PER: perylene, COR: coronene.

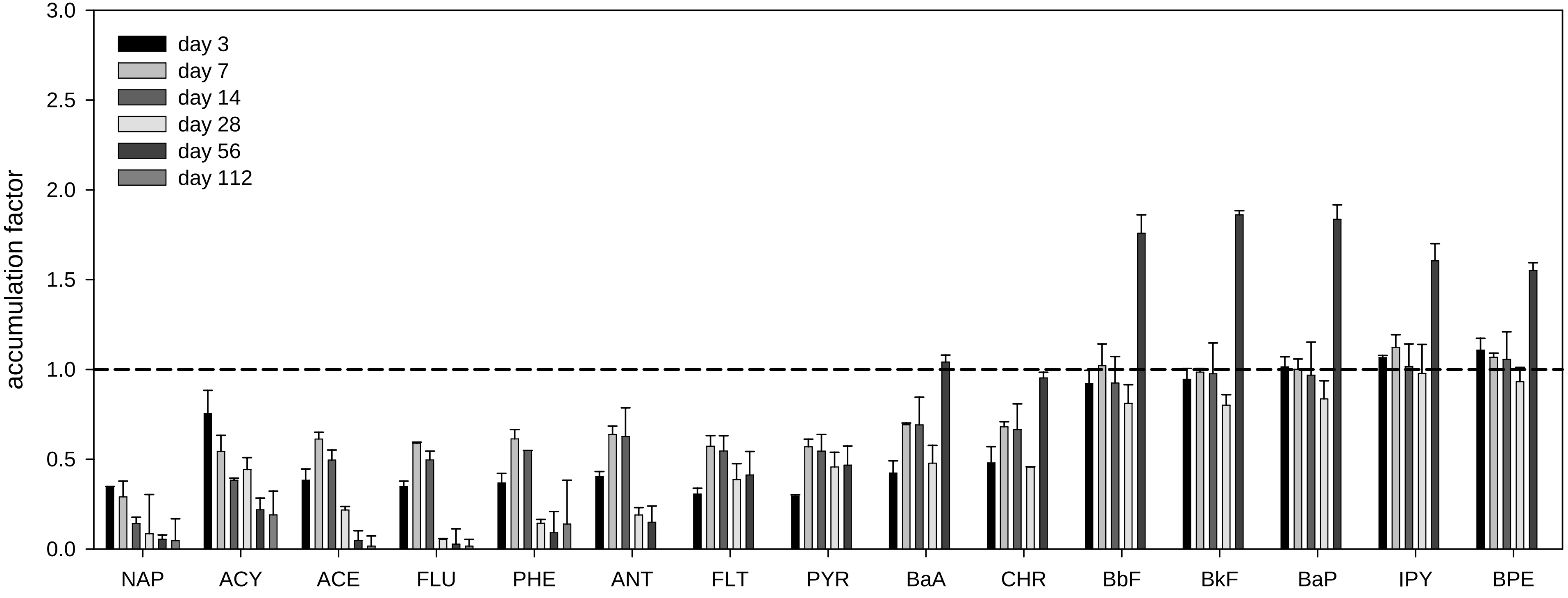

Figure 11: Accumulation factors of PAH during composting of green waste (CG). Outliers (ANT-BPE, day 112) were omitted, note that low molecular weight PAHs (NAP to ANT) exhibit final values below 0.5, whereas the high molecular weight PAHs from (PYR to BPE, except CHR) were above 1. Dashed line indicates conservative behaviour of target analytes.
NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[*1,2,3-cd*]pyrene, BPE: benzo[*ghi*]perylene

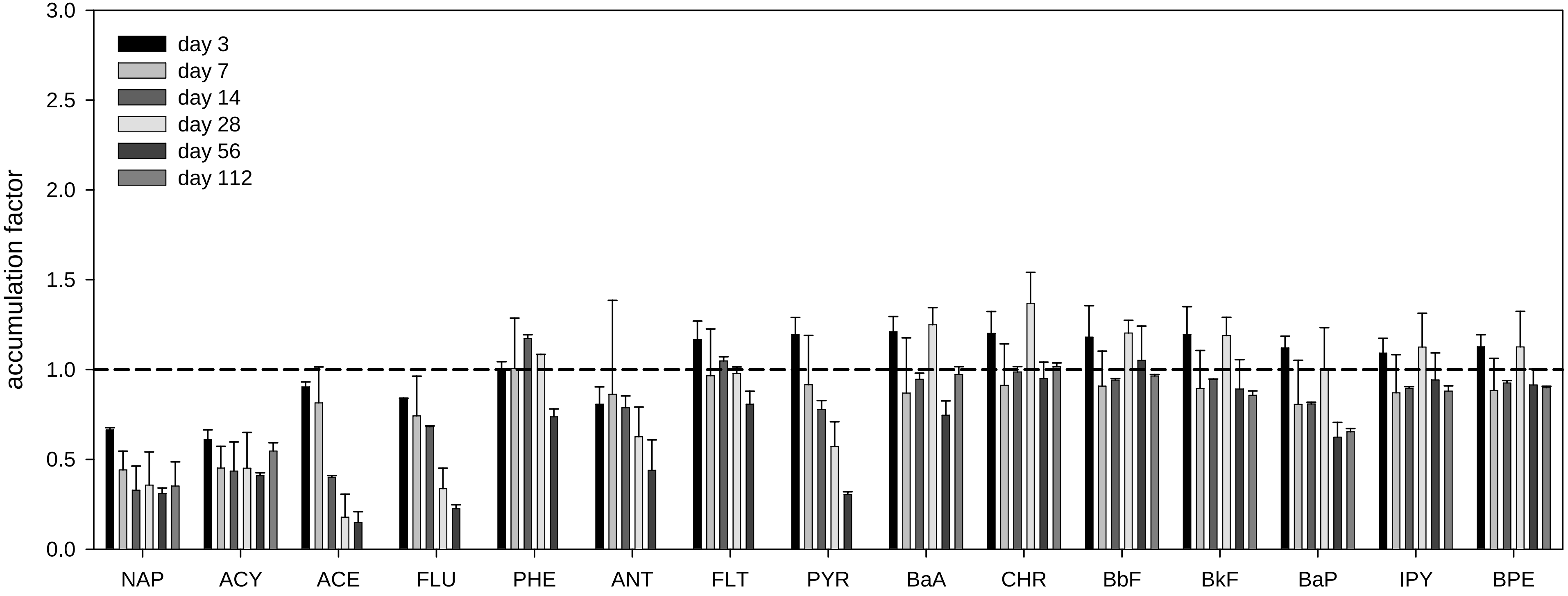

Figure 12: accumulation factors of PAH during composting of organic kitchen and green waste (CK). Outliers (ACE-PYR, day 112) were omitted, note that low molecular weight PAHs (NAP to ANT, except PHE) exhibit final values below 0.6, whereas the high molecular weight PAHs from (BaA to BPE, except BaP) were above 0.8. Dashed line indicates conservative behaviour of target analytes.
NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[*1,2,3-cd*]pyrene, BPE: benzo[*ghi*]perylene)

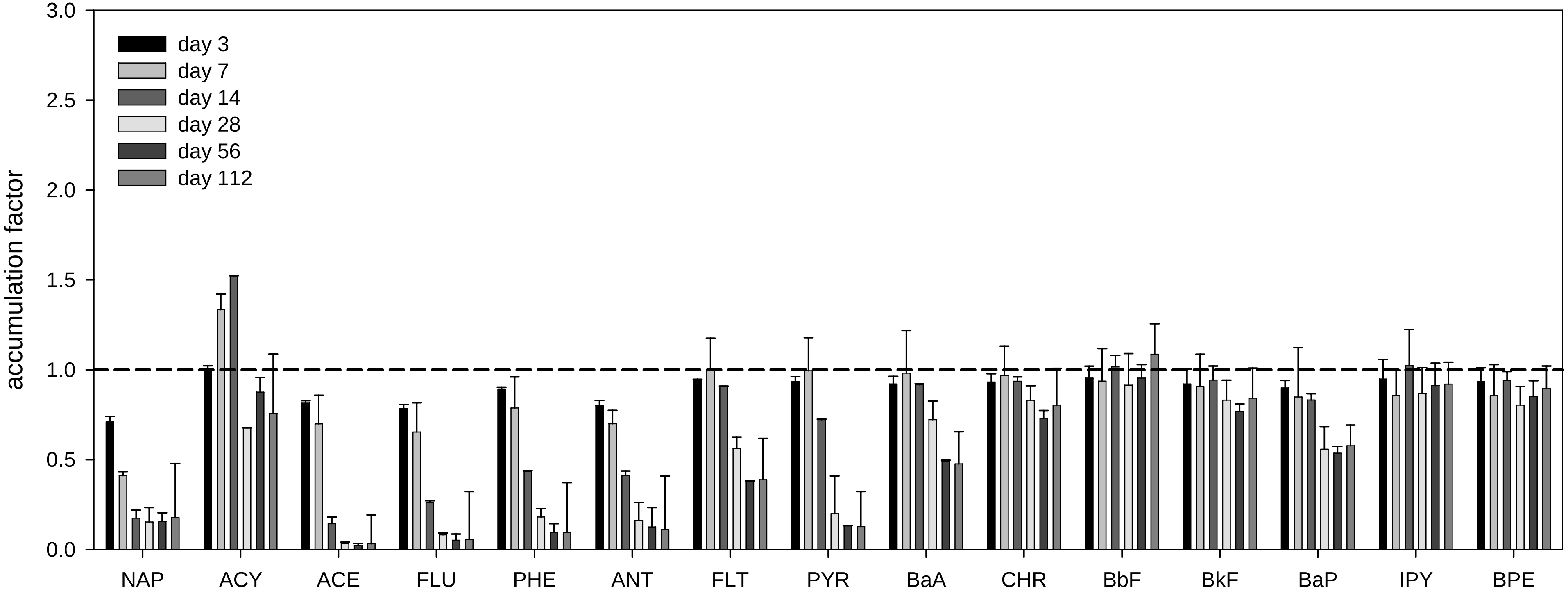

Figure 13: accumulation factors of PAH during composting of digestate (CDK), no outliers removed, note that low molecular weight PAHs (NAP to ANT, except ACY) exhibit final values below 0.2, whereas the high molecular weight PAHs from (BaA to BPE) were above 0.5. The dashed line indicates conservative behaviour of target analytes.

NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[*1,2,3-cd*]pyrene, BPE: benzo[*ghi*]perylene

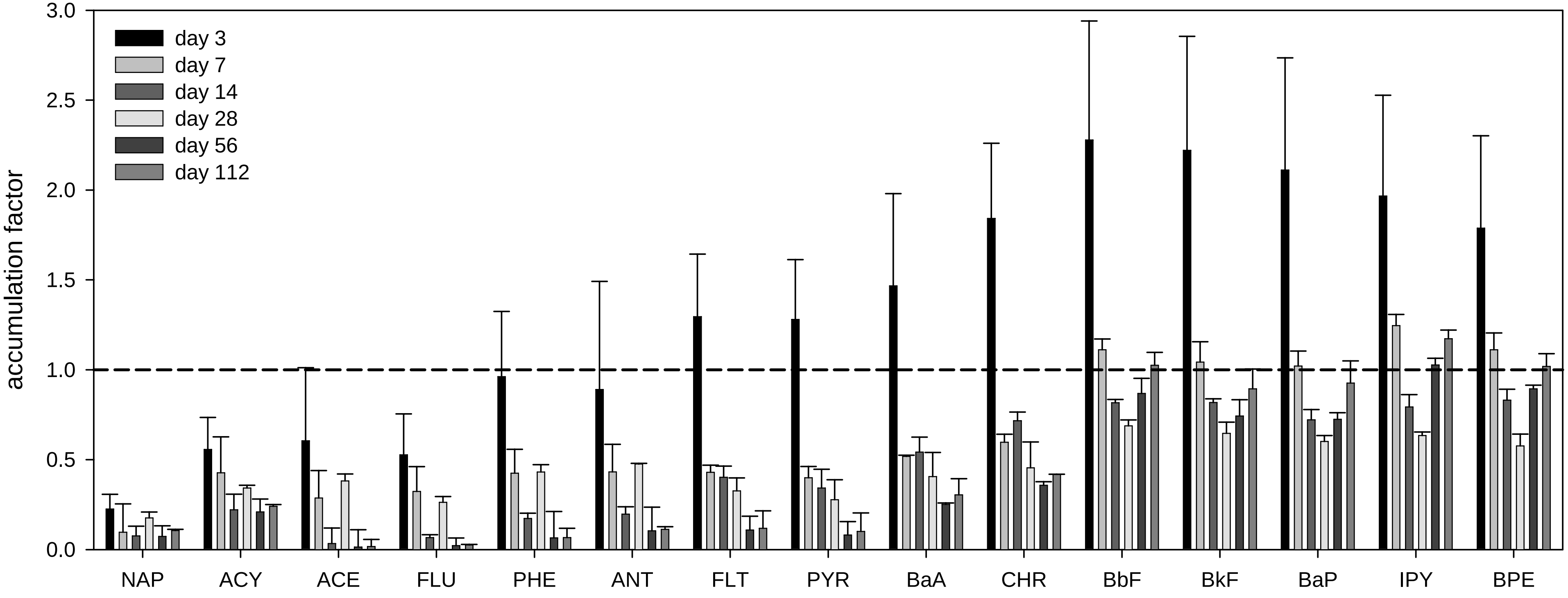

Figure 14: accumulation factors of PAH during composting of green waste on laboratory scale (CG_{lab}), no outliers were removed, note that low molecular weight PAHs (NAP to CHR) exhibit final values below 0.5, whereas the high molecular weight PAHs from (CHR to BPE) were above that value. The dashed line indicates conservative behaviour of target analytes.

NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[*1,2,3-cd*]pyrene, BPE: benzo[*ghi*]perylene

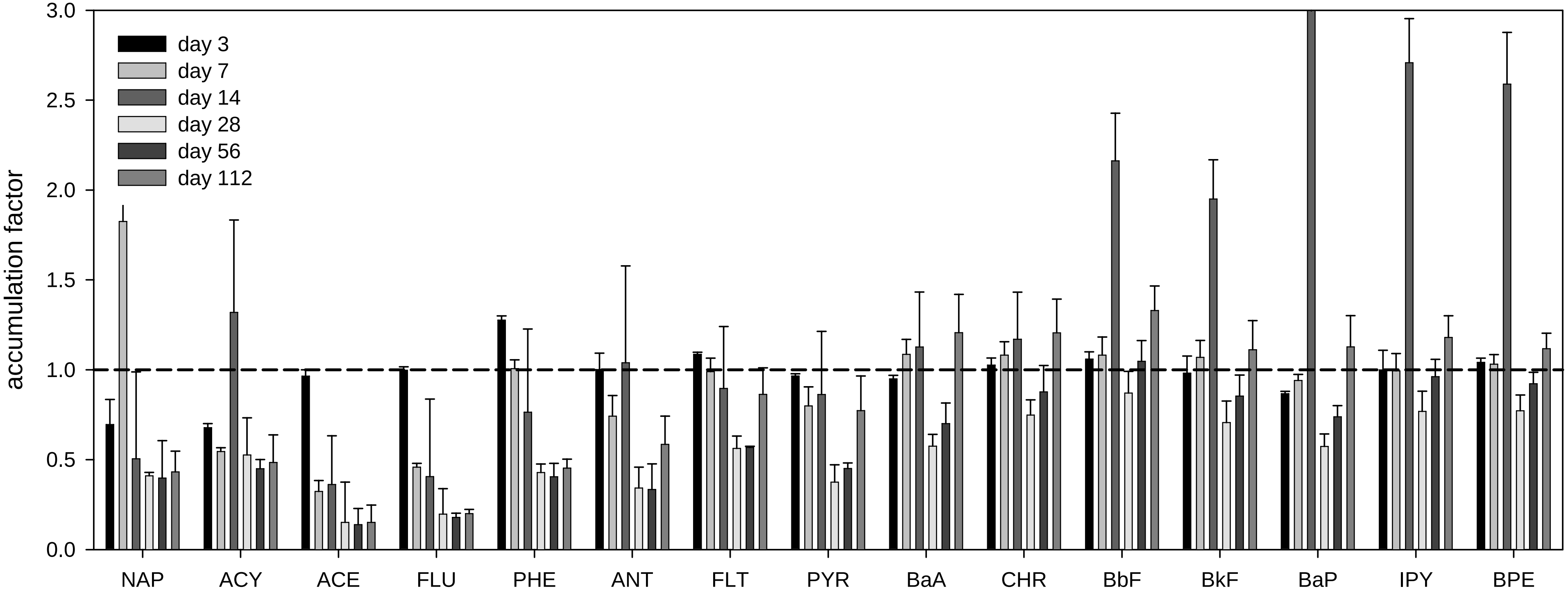

Figure 15: accumulation factors of PAH during composting of organic kitchen and green waste on laboratory scale (CK_{lab}), no outliers were removed, note that low molecular weight PAHs (NAP to PHE) exhibit final values below 0.5, whereas the high molecular weight PAHs from (ANT to BPE) were above that value. The dashed line indicates conservative behaviour of target analytes.
NAP: naphthalene, ACY: acenaphthylene, ACE: acenaphthene, FLU: fluorene, PHE: phenanthrene, ANT: anthracene, FLT: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, IPY: indeno[*1,2,3-cd*]pyrene, BPE: benzo[*ghi*]perylene

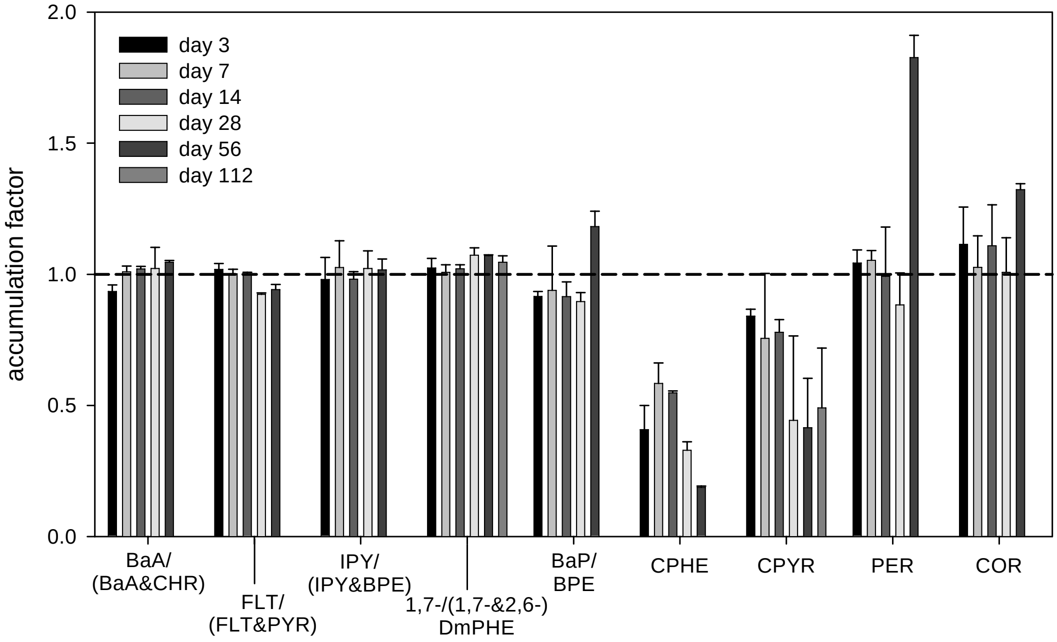

Figure 16: Accumulation factors of stable characteristic PAH ratios and molecular markers during green waste composting (CG). The dashed line indicates conservative behaviour of target analytes. BaA: benzo[*a*]anthracene, CHR: chrysene, FLT: fluoranthene, PYR: pyrene, IPY: indeno[*1,2,3-cd*]pyrene, BPE: benzo[*ghi*]perylene, 1,7-/(1,7-&2,6-)DmPHE: ratio of 1,7- to 1,7- and 2,6-dimethylPHE, BaP: benzo[*a*]pyrene, BPE: benzo[*ghi*]perylene, CPHE: 4-H-cyclopenta[*def*]PHE, CPYR: cylopenta[*cd*]PYR, PER: perylene, COR: coronene.

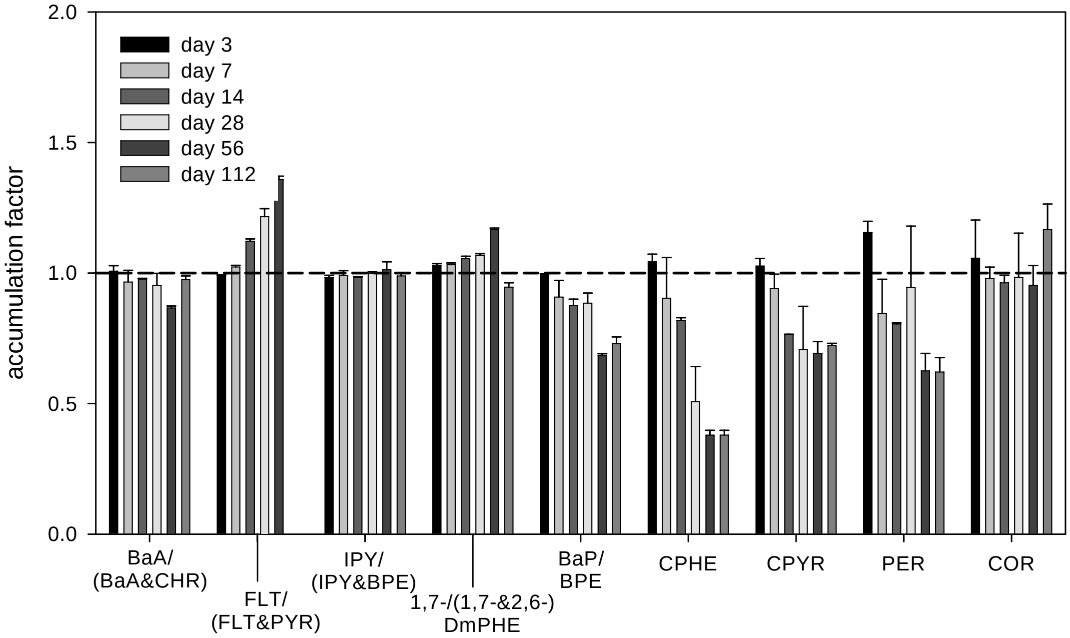

Figure 17: Accumulation factors of stable characteristic PAH ratios and molecular markers during composting of green waste and organic kitchen waste (CK). The dashed line indicates conservative behaviour of target analytes. BaA: benzo[*a*]anthracene, CHR: chrysene, FLT: fluoranthene, PYR: pyrene, IPY: indeno[*1,2,3-cd*]pyrene, BPE: benzo[*ghi*]perylene, 1,7-/(1,7-&2,6-)DmPHE: ratio of 1,7- to 1,7- and 2,6-dimethylPHE, BaP: benzo[*a*]pyrene, BPE: benzo[*ghi*]perylene, CPHE: 4-H-cyclopenta[*def*]PHE, CPYR: cylopenta[*cd*]PYR, PER: perylene, COR: coronene.

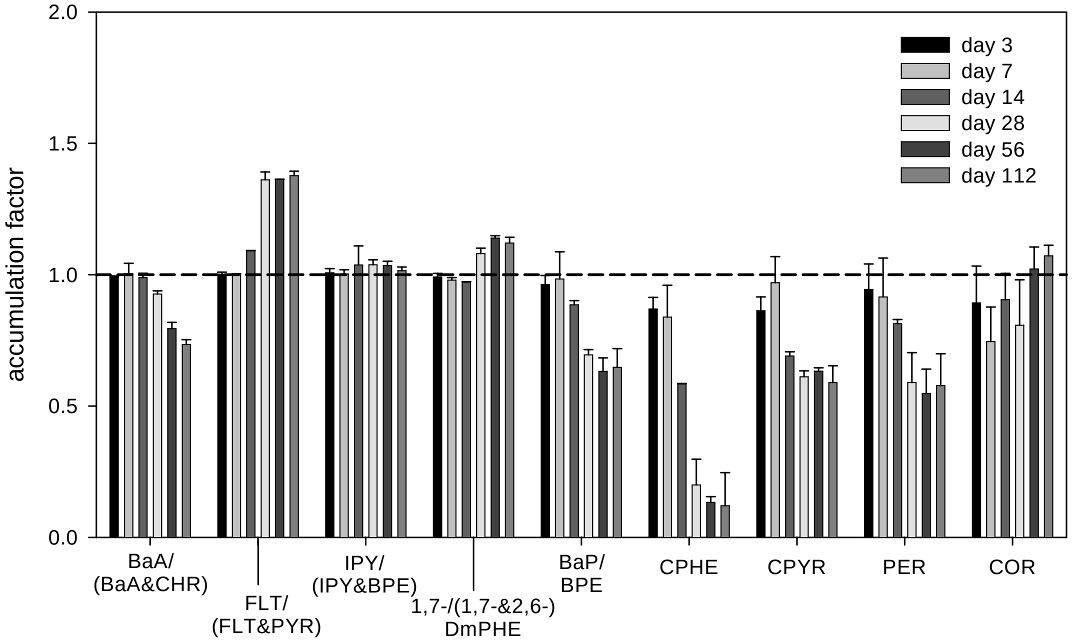

Figure 18: Accumulation factors of stable characteristic PAH ratios and molecular markers during composting of digestate (CDK).The dashed line indicates conservative behaviour of target analytes. BaA: benzo[*a*]anthracene, CHR: chrysene, FLT: fluoranthene, PYR: pyrene, IPY: indeno[*1,2,3-cd*]pyrene, BPE: benzo[*ghi*]perylene, 1,7-/(1,7-&2,6-)DmPHE: ratio of 1,7- to 1,7- and 2,6-dimethylPHE, BaP: benzo[*a*]pyrene, BPE: benzo[*ghi*]perylene, CPHE: 4-H-cyclopenta[*def*]PHE, CPYR: cylopenta[*cd*]PYR, PER: perylene, COR: coronene.

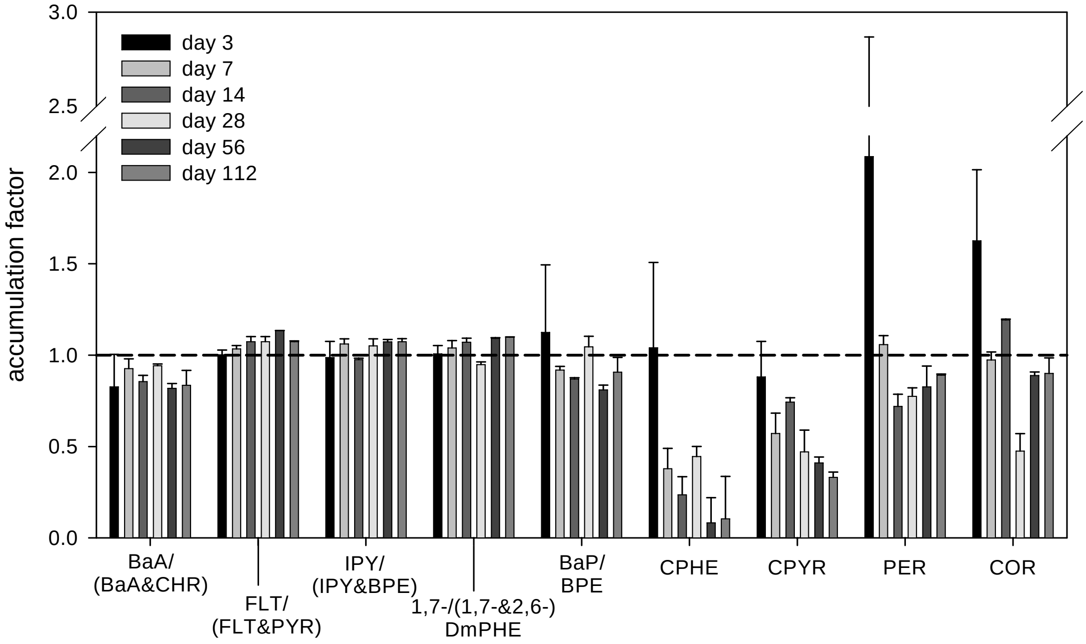

Figure 19: Accumulation factors of stable characteristic PAH ratios and molecular markers during composting of green waste on laboratory scale (CG_{lab}). The dashed line indicates conservative behaviour of target analytes. BaA: benzo[*a*]anthracene, CHR: chrysene, FLT: fluoranthene, PYR: pyrene, IPY: indeno[*1,2,3-cd*]pyrene, BPE: benzo[*ghi*]perylene, 1,7-/(1,7-&2,6-)DmPHE: ratio of 1,7- to 1,7- and 2,6-dimethylPHE, BaP: benzo[*a*]pyrene, BPE: benzo[*ghi*]perylene, CPHE: 4-H-cyclopenta[*def*]PHE, CPYR: cylopenta[*cd*]PYR, PER: perylene, COR: coronene.

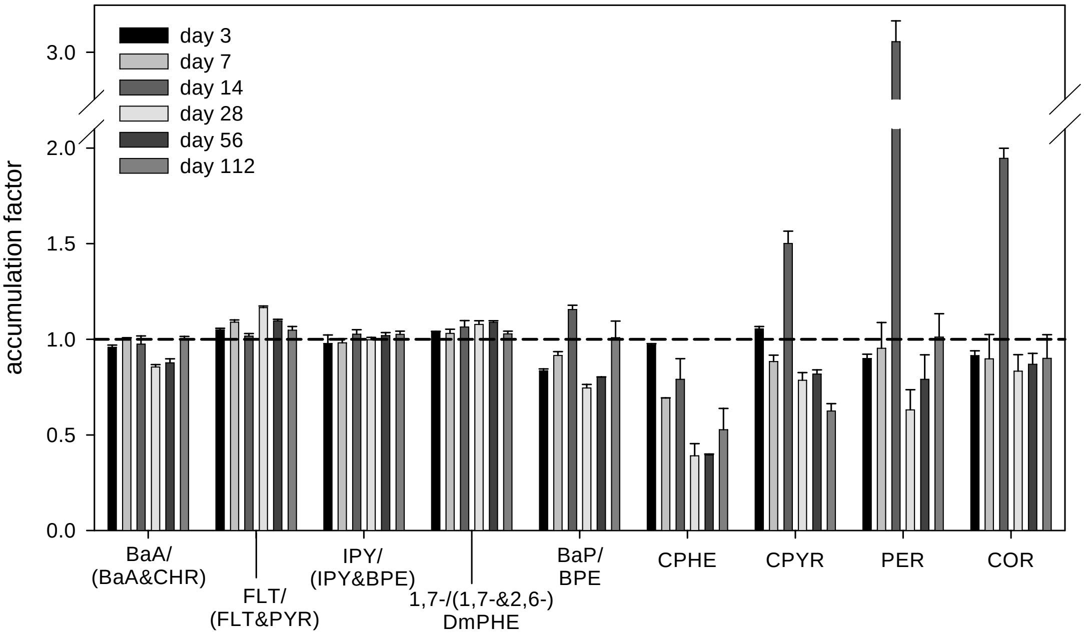

Figure 20: Accumulation factors of stable characteristic PAH ratios and molecular markers during composting of green waste and organic kitchen waste on laboratory scale (CK_{lab}).
The dashed line indicates conservative behaviour of target analytes. BaA: benzo[*a*]anthracene, CHR: chrysene, FLT: fluoranthene, PYR: pyrene, IPY: indeno[*1,2,3-cd*]pyrene, BPE: benzo[*ghi*]perylene, 1,7-/(1,7-&2,6-)DmPHE: ratio of 1,7- to 1,7- and 2,6-dimethylPHE, BaP: benzo[*a*]pyrene, BPE: benzo[*ghi*]perylene, CPHE: 4-H-cyclopenta[*def*]PHE, CPYR: cylopenta[*cd*]PYR, PER: perylene, COR: coronene.

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8 Short Paper 1

Can sources of environmental contamination with PAHs be identified in recipient matrices by concomitant analysis of molecular markers?

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Organohalogen compounds, accepted.

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CAN SOURCES OF ENVIRONMENTAL CONTAMINATION WITH PAHS BE IDENTIFIED IN RECIPIENT MATRICES BY CONCOMITANT ANALYSIS OF MOLECULAR MARKERS?

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Introduction

There is a broad range of molecular markers such as hopanes, phytosterols and methylated polycyclic aromatic hydrocarbon (PAH) available for source apportionment of petrogenic and pyrogenic environmental contamination [1-3]. We selected those that are already part of conventional PAH analysis (or could be easily integrated) and applied them to our soil and compost data to see whether source identification is possible in recipient matrices from monitoring studies in combination with PAH analysis. The inconsistent results motivated us to revisit current source literature and examine prevalent characteristic ratios therein. After that, the suitability of the characteristic ratios and selected makers was re-examined in soil and compost data, taking into account possible alterations due to environmental processes.

Materials and Methods

In a first step, characteristic ratios which can be easily included into conventional PAH analysis and allowing to distinguish between: i) petrogenic and pyrogenic origin, ii) different fuels (e.g. gasoline, grass, coal, wood) and iii) traffic and non-traffic sources of PAHs, were selected and commonly suggested numbers/ranges compiled (Table 1, column 1&2). These ratios were applied to PAH emission data collected from the wider literature, i.e. to different soot particles, oil, gasoline etc. (Table 1, column 3&4, n=175, for references see [4]). Differences between the categories were assessed and the data compared with the earlier suggested characteristic ratios. Secondly, ratios were determined in soil[5] (our own earlier data) and source-separated compost[4]. Additional molecular markers suggested for specific sources, i.e. retene (RET) for wood combustion[6], coronene (COR) for traffic sources[7] and perylene (PER) for digenetic origin[8] of PAHs were included. Less established markers (4-H-cylcopenta(*def*)phenanthrene (cPHE) as pyrogenic marker[9] and cyclopenta(*cd*)pyrene (cPYR) for woodburning[2] and/or vehicle emission[10]) were also assigned. If comparing emission ratios with ratios in recipient matrices (e.g. soil and compost), it has to be considered that they could be altered compared to source data due to environmental fractionation and/or possible degradation. Therefore, as a third step, factors accounting for these processes suggested by Zhang et al.[11] were applied to our soil data converting it back to ratios at the source. Degradation/evaporation during composting as well as processes between emission and aerial deposition of PAHs on input material for compositing (presumably the main input pathway to compost) can alter ratios and molecular markers as well. As a fourth step, results obtained from a full-scale composting study[12] and factors accounting for discriminating processes in air[11] were applied to ratios in compost.

Results and Discussion

Anthracene/(Anthracene&Phenanthrene) (ANT/(ANT&PHE))

Although there was a significant difference between ANT/(ANT&PHE) ratios in sources originating from petrogenic and pyrogenic processes in the literature (Table 1, column 3&4), 41% of the values referring to petrogenic origin were above 0.1, which is the current threshold value. This indicates that the discrimination limit is probably too low, as suggested before[13]. According to the ANT/(ANT&PHE) ratio, 90% of the soil and 50% of the compost samples would be dominated by petrogenic origin of PAHs, which is not plausible for the data from Switzerland. After converting soil ratios back to emission ratios, the “petrogenicity” of the data was even more pronounced. ANT/(ANT&PHE) ratios are likely to increase during composting[12] which would, together with conversion, result in high domination of petrogenic PAHs. Overall, we judge this marker as not applicable to monitoring studies.

Benzo(a)anthracene/(Benzo(a)anthracene&Chrysene) (BaA/(BaA&CHR))

As for ANT/(ANT&PHE), BaA/(BaA&CHR) ratios differed significantly in petrogenic and pyrogenic data from the literature. Again more than 45% of the ratios derived from petrogenic matrices were above 0.35, which is the prevalent range characteristic for combustion (Table 1). Even before conversion, BaA/(BaA&CHR) ratios in soil and compost pointed to combustion as a source for PAHs. After conversion, all ratios were above 0.35. This goes in line with the situation in Switzerland, where pollution of soil and compost due to petrogenic sources is marginal.

Together with the fact that this ratio was more or less stable during composting, it may be more trustworthy then ANT/(ANT&PHE).

Fluoranthene/(Fluoranthene&Pyrene) (FLT/(FLT&PYR))
Ratios of FLT/(FLT&PYR) in matrices originating from combustion were significantly higher than ratios from petrogenic sources (Table 1, Column 3&4). The median of the petrogenic ratios was clearly below the discrimination limit (0.4), suggesting this marker to be suitable for emission source apportionment. The differentiation between fuel and grass/wood/coal combustion could be verified in the literature data. FLT/(FLT&PYR) ratios in soil and compost pointed to grass/wood/coal combustion, whereas conversion shifted them more to fuel combustion, which seems reasonable for the situation in Switzerland. Ratios were slightly higher in compost than in soil, which could point to some PAH input to compost by wood ash. The ratio was stable during composting[12]. In summary, once transformed[11], this ratio seems to preserve its source diagnostic capacity from emission sources to recipient matrices.

Indeno(1,2,3,c,d)pyrene/(Indeno(1,2,3,c,d)pyrene&Benzo(g,h,i)perylene) (IPY/(IPY&BPE))
More than 50% of the petrogenic literature ratios of IPY/(IPY&BPE) were above 0.2 (Table 1, column 3&4), which was suggested to be characteristic for PAHs originating from pyrogenic processes (Table 1, column 1&2). This indicates that the discrimination level may be too low. The median of the IPY/(IPY&BPE) ratios from wood combustion was above 0.5, however almost 70% of the ratios from coal burning were between 0.2 and 0.5, which is supposed to be characteristic for fuel combustion. It is concluded that IPY/(IPY&BPE) differentiated well between wood and fuel but not between coal and fuel combustion. Median IPY/(IPY&BPE) ratios in soil and compost were 0.5, which marks the limit between fuel and grass/wood/coal combustion. After conversion ratios shifted more to the grass/wood/coal combustion, contradicting with the findings of converted FLT/(FLT&PYR) ratios and the situation in Switzerland, where fuel combustion may be an important PAH source. IPY/(IPY&BPE) ratios were stable during composting[12]. To this end, FLT/(FLT&PYR) appears to provide the more plausible source apportionment.

CombustionPAHs/Σ16PAH (ComPAH/16PAH)
ComPAHs (sum of FLT, PYR, BaA, CHR, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(e)pyrene (not included here), BaP, IPY, and BPE)/16PAH ratios of petrogenic literature data were clearly below the prevailing limit (0.3) differentiating for petrogenic origin of PAHs (Table 1, column 3&4). However, most combustion derived ratios were only slightly above 0.3 and most of them were below the prevalent limit identifying combustion (0.7; Table 1, column 1&2). Ratios in soil and compost clearly identified combustion as the source of PAHs, even though this ratio may be increasing during composting[14]. The problem with this marker may be that the lighter PAHs are gasing out, leading to over-interpreation of pyrogenitcity if the main source was petrogenic, or visa versa, in cold and/or remote areas.

(MethylPHE&ANT)/PHE and (MethylFLT&PYR)/PYR ((MePHE&ANT)/PHE and (MeFLT&PYR)/PYR)
MePHE&ANT)/PHE and (MeFLT&PYR)/PYR ratios pointed to pyrogenic origin of PAHs (Table 1, column l&2) in soil and compost (Table 1), which is in line with the above findings. The development of conversion factors is probably not feasible since this ratio uses sums of methylated isomers with varying individual chemico-physical properties. (MeFLT&PYR)/PYR ratios were found to be stable during composting, whereas (MePHE&ANT)/PHE varied[12], rendering source apportionment with the latter problematic.

1,7- DimethylPHE/(1,7-DimethylPHE&2,6-DimethylPHE) (1,7-/(1,7&2,6)-DimePHE)
1,7-/(1,7&2,6)DimePHE ratios in soil and compost were never below 0.45, which would be characteristic for vehicle emissions (Table 1, column 5&7). One out of 23 soil and five out of 69 compost samples had 1,7-/(1,7&2.6)DimePHE ratios above 0.7 pointing to wood combustion. Only one (compost) sample's FLT/(FLT&PYR) and IPY/(IPY&BPE) ratios were after conversion not above 0.5, which confirmed wood combustion. 1,7-/(1,7&2.6)DimePHE ratio seemed to be stable during composting[12].

Retene/(Retene&Chrysene) (RET/(RET&CHR))
RET/(RET&CHR) ratios in soil were lower (median: 0.04, Table 1) than in compost (median: 0.19). This might be explained by small amounts of wood ash present in compost as indicated by FLT/(FLT&PYR) ratios. However, ratios in soil and compost were clearly below 0.5, identifying fuel combustion as the major PAH source. This contradicts with findings for IPY/(IPY&BPE) and FLT/(FLT&PYR). However, RET can also have petrogenic sources[14]. Together with varying ratios during composting[12], source apportionment is hampered.

Perylene/Σ16 PAH (PER/16PAH)
PER/16PAH ratios suggested only limited diagenic origin of PAH in soil and compost (Table 1, ratios >0.02). However, there is the possibility that PER is formed during organic matter degradation[15] and that it may also have

anthropogenic sources[14]. Combined with the in- and de-creasing concentrations during composting[12], source apportionment applying this marker is problematic.

Benzo(a)pyrene/ Benzo(g,h,i)perylene (BaP/BPE)

There was a significant difference of the BaP/BPE ratios in matrices from traffic and non-traffic origin (Table 1, column 3&4). However, almost 50% of the ratios from traffic sources were lower than 0.6, generally identifying non-traffic PAHs. This limit may need to be reconsidered. Before and even more after conversion BaP/BPE ratios in soil and compost pointed to traffic as the main PAH source, which is an important but not the only source in Switzerland and contradicts with findings for 1,7-/(1,7&2,6)DimePHE. Additionally, this ratio was found to vary during composting[12], and is therefore considered as not suitable for source apportionment in our data.

Coronene/Σ16 PAH (COR/16PAH)

Median COR/16PAHs ratio in soil was 0.02, whereas in Swiss compost it was slightly higher (Table 1, median: 0.03). A possible explanation may be higher contribution of vehicle exhaust in compost compared to soil. Increases of COR/16PAH ratios during composting were observed[12], due to decreasing levels of light PAHs, which calls for a correction factor.

4-H Cyclopenta(def)PHE/ Σ16 PAH (cPHE/16PAH) and Cyclopenta(cd)PYR/ Σ 16PAHs (cPYR/16PAH)

CPHE/16PAHs ratios in Swiss soil were in the same range as in compost (Table 1, column 5&7). During composting a decrease of the ratio was observed[12]. Further research at the source level as well as describing environmental processes is needed to verify if this marker is a suitable pyrogenic tracer. CPYR/16PAH in soil were slightly higher than in compost (Table 1, column 5&7), suggesting that wood and/or traffic combustion contributed more to the PAH concentrations in soil than in compost. This contradicts with findings for COR/16PAH and RET/(RET&CHR). However, the decreasing cPYR/16PAH ratios during composting[12] may account for the difference. However, this still not proves this ratio to be suitable for soil and further research is needed at sources.

Synopsis

Even though for most ratios there was a significant difference between i) petrogenic and pyrogenic ii) fuel and grass/coal/wood combustion and iii) traffic and non-traffic sources, some discrimination levels seemed not to be determined well. Conversion factors accounting for environmental fractionation and possible degradation between sources and recipient matrices seemed to be useful for refined interpretation of the data. However, further research is needed to optimise these factors and to account for other processes.

Acknowledgment

Thanks to the Swiss Federal Office for the Environment and the Federal Office of Energy for the financial support

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Table 1: Characteristic ratios and molecular markers in the emission literature, in soil[5] and compost (own data)

	petrogenic[a]	**pyrogenic[a]**	**petrogenic lit[b]**	**pyrogenic lit[b]**	**Swiss soil[c]**	**soil con[c,d]**	**Swiss compost[e]**	**compost con[f]**
ANT/(ANT&PHE)	<0.1 [g]	>0.1 [g]	0.04* (0;0.69;53)	0.16* (0;1;139)	0.06 (0.03;0.14)	0.03 (0.02;0.08)	0.10 (0.05;0.19)	<; 0.05 (0.03;0.10)
BaA/(BaA&CHR)	<0.2 [g]	>0.35 [g]	0.34* (0;1;48)	0.44* (0;1;139)	0.36 (0.28;0.45)	0.55 (0.46;0.64)	0.42 (0.27;0.5)	=; 0.55 (0.39;0.63)
FLT/(FLT&PYR)	<0.4 [g]	>0.4 [g]	0.24* (0;0.87;52)	0.53*(0.02;1;139)	0.56 (0.54; 0.63)	0.45 (0.43;0.53)	0.60 (0.45;0.75)	=; 0.47 (0.31;0.64)
IPY/(IPY&BPE)	<0.2 [g]	>0.2 [g]	0.22* (0;1;44)	0.48* (0;1;130)	0.51 (0.45;0.54)	0.58 (0.52;0.68)	0.50 (0.44;0.61)	=; 0.58 (0.46;0.63)
ComPAHs/16PAH	0.3 [g]	0.7 [g]	0.07* (0;0.97;53)	0.45* (0;0.98;66)	0.84 (0.57;0.90)	na [h]	0.87 (0.43;0.96)	<; na [h]
(MePHE&ANT)/PHE	5 [g]	0.5 [g]	na	na	0.42 (0.25;0.66)	na [h]	0.47 (0.22;3.07)	>/<; na [h]
(MeFLT&PYR)/PYR	4 [g]	0.3 [g]	na	na	0.43 (0.35;0.53)	na [h]	0.37 (0.23;0.75)	=; na [h]
1,7-/(1,7&2.6)DimePHE	0.45-0.7 [g,i]	<0.45 or 0.7-0.9 [g]	na	na	0.62 (0.60;0.80)	na [h]	0.63 (0.50;0.76)	=; na [h]
	fuel combustion	**biomass combustion[k]**	**fuel combustion lit[a]**	**coal/wood combustion lit[a]**				
FLT/(FLT&PYR)	0.4-0.5 [g]	>0.5 [g]	0.49* (0.14;0.87;46)	0.56* (0.02;1;90)	0.56 (0.54;0.63)	0.45 (0.43;0.53)	0.6 (0.43;0.75)	=; 0.47 (0.31;0.64)
IPY/(IPY&BPE)	0.2-0.5 [g]	>0.5 [g]	0.44 (0; 0.89; 41)	0.5 (0;1;86)	0.51 (0.45;0.54)	0.58 (0.52;0.68)	0.5 (0.44;0.61)	=; 0.582 (0.46;0.63)
RET/(RET&CHR)	0.15-0.5 [l]	0.83 [k]/0.96 [l,m]	na	na	0.04 (0.01;0.44)	na [h]	0.19 (0.03;0.54)	>/=; na [h]
1,7-/(1,7&2.6)DimePHE	<0.45 [n]	0.7-0.9 [m]	na	na	0.62 (0.60;0.80)	na [h]		=; na [h]
	diagenetic	**pyrogenic**						
PER/16PAH	>0.05 [o]	<0.05 [o]	na	na	0.02 (0;0.48)[p]	na [h]	0.02 (0, 0.06)	>/<; na [h]
	non-traffic	**traffic**	**non-traffic lit[a]**	**traffic lit[a]**				
BaP/BPE	<0.6 [g]	>0.6 [g]	1.07* (0;7.7;89)	0.6* (0;7;35)	0.84 (0.57;0.09)	3.74 (1.58;5.94)	0.90 (0.53;1.4)	>/<; 1.50 (0.89;2.34)
1,7-/(1,7&2.6)DimePHE	>0.45 [g]	<0.45 [g]	na	na		na [h]		=; na [h]
Markers								
COR/16PAHs	vehicle exhaust [g]				0.02 (0.01;0.07)	na [h]	0.03 (0.003;0.12)	</=; na [h]
cPHE/16PAH	pyrogenic marker[q]				0.009 (0;0.037)[p]	na [h]	0.01 (0;0.02)	>; na [h]
cPYR/16PAH	wood or traffic marker [r]				0.010 (0;0.092)[p]	na [h]	0.003 (0;0.017)	>; na [h]

a) prevalent discrimination levels, b) literature data, median (min, max, n), c) median (min, max) n=23, d) applying conversion factor for soil suggested by[11], e) median (min, max) n=69, Dibenzo(a,h)anthracene was not determined, instead of Σ16PAHs it is referred to Σ15PAHs f) quantitative alteration during composting[12], < increase, =stable and >decrease during composting, respectively; ratios applying conversion factor for air particles suggested by [11], g) characteristic ratios according to Ref [5] and references therein, h) conversion factor not available, i) also mixed combustion sources, k) grass/coal/wood combustion, l)[16], m) softwood combustion, n) vehicle emission, o)[8], p) own unpublished data (n=87), q) [9], r) [2], Abbreviations: Anthracene (ANT), Phenanthrene (PHE), Benzo(a)anthracene (BaA); Chrysene (CHR); Fluoranthene (FLU), Pyrene (PYR), Indeno(1,2,3,c,d)pyrene (IPY), Benzo(g,h,i)perylene (BPE), Com PAHs (sum of FLT, PYR, BaA, CHR, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene (BaP), IPY, BPE), methylated (Me), dimethylated (dime), Retene (RET), Perylene (PER), Coronene (COR), 4-H CyclopentaPHE (cPHE), Cyclopenta(cd)PYR (cPYR), *significant difference on a 95% level applying the Mann-Whitney-U-Test [10]

9 Short Paper 2

Organic pollutants in source-separated compost

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Organohalogen compounds, accepted.

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ORGANIC POLLUTANTS IN SOURCE- SEPARATED COMPOST

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Introduction

Composting (i.e. aerobic degradation) of crude organic kitchen and green waste represents an important and well established part of waste management in Europe. Digestion (i.e. anaerobic degradation with or without subsequent aerobic process) has been promoted in recent years due to increasing efforts to combine recycling of organic materials with energy production. About $9.3\text{x}10^6$ tonnes of compost and digestate are produced per year in the 25 European Union member states [1] and most of it is applied to agricultural soil. These recycling fertilizers can have positive effects on physical, chemical and biological soil parameters. However, little is known about organic pollutants in source-separated compost and digestate (i.e. not containing sewage sludge, municipal solid waste etc.), as has been shown in a recent compilation [2]. Information on digestate is completely lacking. This is problematic from a risk assessment point of view. Our study inventories the content of a wide range of today's most concerning organic pollutants in compost and digestate from Switzerland: PAHs (Σ16 polycyclic aromatic hydrocarbons as defined by the US EPA), polychlorinated biphenyls (PCBs, including three chiral PCBs), dioxin-like PCBs (DL-PCBs), polybrominated diphenyl ethers (PBDE), hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA), per- and polyfluorinated alkyl substances (PFAS), pesticides, phthalates, nonylphenol and chlorinated paraffins (CP). Most of theses compounds were analysed for the first time in compost.

Materials and Methods

Over 80 samples of composts and digestates derived from source separated green and kitchen waste were collected from 39 commercial composting and digestion plants in Switzerland. Sample selection accounted for factors that were hypothesised to be key determinants for organic pollutant content in these recycling fertilizers [2]: different input materials (green waste with and without organic kitchen waste; small amounts of organic waste materials of industrial origin included in some products were of minor importance), different origin of input material (urban versus rural), different season of input material collection (spring/summer, autumn, winter), and different maturity of compost and digestate. For sampling procedure, sample preparation and analytical methods see Brändli et al. 2006 [3], Bucheli et al. 2006 [4] and Brändli et al in preparation [5]. PAHs and PCBs were analysed in all 80 samples, whereas the remaining organic compounds and pesticides were only determined in a subset of samples (n = 3-18). A linear model was applied to the entire dataset to determine significant factors influencing PAH and PCB concentrations in compost and digestate, whereas for the small dataset the Mann-Whitney-U-Test was used. Some special cases (e.g. compost with manure in the input material) had to be excluded for evaluation.

Results and Discussion

PAHs

Median PAH concentration (Σ15 PAHs, Dibenzo(a,h)anthracene could not be determined due to analytical difficulties) was at 3010 μg/kg dry weight (dw) with a minimum at 600 μg/kg dw and a maximum at 12470 μg/kg dw (Figure 1, n=69). These values were higher than the median from the literature (1870 μg/kg dw [2]).

Median PAH concentrations in Swiss soils were lower by a factor 6 to 40 (arable soils: Σ 16 PAHs 66 µg/kg dw, permanent and pasture grassland: 142 µg/kg dw, urban soils: 451 µg/kg dw [6]). Additionally, the trend of concentration in soil was estimated, assuming a starting level in soil of 225 µg/kg dw [6], an aerial deposition of 1.6 g/ha/a [7] and a compost application rate of 10 t dw/ha/a as only inputs of PAHs to soil. As a simplified, conservative approach, once in soil, the compounds were assumed to be non-degradable and immobilized. The estimated time span to exceed the Swiss guide value for PAHs in soil (Ordinance relating to Impacts on the Soil, 1 mg/kg dw) would be less than 50 years. At this PAH level, the Swiss law calls for actions to prevent further increase of the PAH levels in soil, possibly prohibiting compost application.

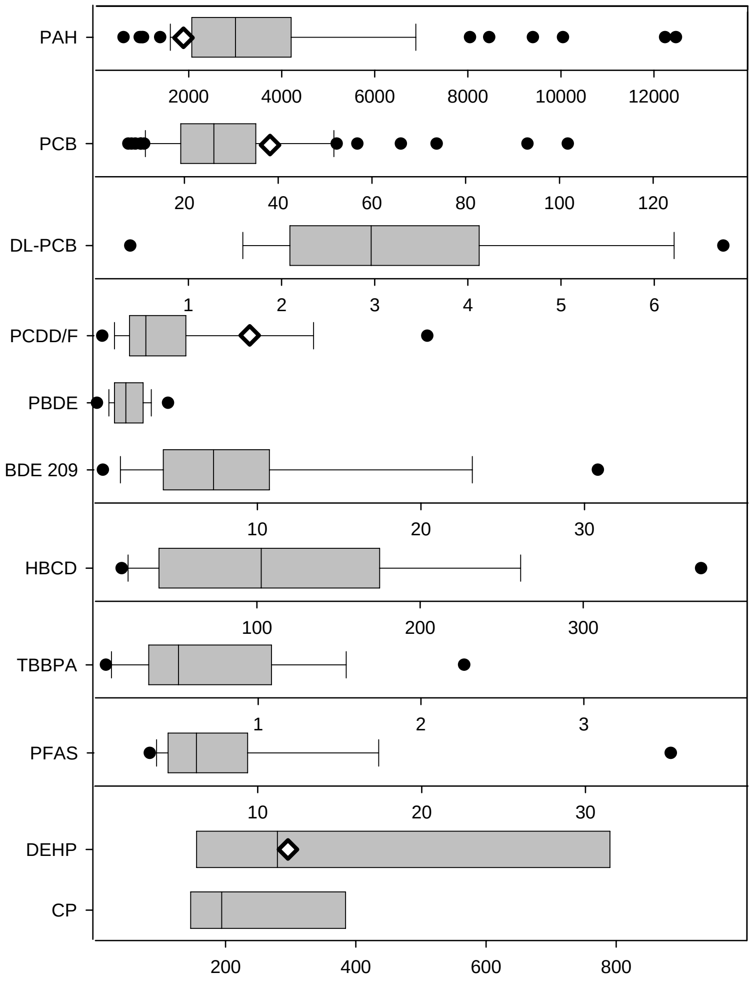

Figure 1: Concentrations of organic pollutants in compost and digestate (line: median; box: 25th and 75th percentile; lines with whiskers 10th and 90th percentile, dots: outliers, diamond: median literature value [2]; where missing: not available), PAH (Σ of 16 PAHs defined by the US EPA, except Dibenzo(a,h)anthracene in µg/kg dry weight (dw), n=69), PCB (Σ of PCB 28, 52, 101, 118, 138, 153, 180, in µg/kg dw, n=69), PCDD/Fs (Σ17PCDD/Fs in ng I-TEQ/kg dw, n=18), DL-PCBs (Σ of PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, #189 in ng WHO-TEQ/kg dw, n=18), PBDE (Σ of BDE28, 47, 99, 100, 153, 154, 183, in µg/kg dw, n=18), BDE 209 (n=18), HBCD (n=18) and TPPBA (n=18) in µg/kg dw, PFAS (Σ of 21 compounds in µg/kg dw, n=18), DEHP in µg/kg dw (n=6), CP (Σ of short and medium chain chlorinated paraffins in µg/kg dw, n=3)

PCBs and dioxin-like PCBs (dl-PCBs)

Median PCB concentration (ΣPCB 28, 52, 101, 118, 138, 153, 180) in Swiss compost and digestate was 26.3 µg/kg dw ranging from 8.1 µg/kg dw to 102 µg/kg dw (Figure 1, n=69). These concentrations were lower than in the literature (38 µg/kg dw for 6 indicator PCBs [2]), possibly reflecting the general decreasing PCB levels in the environment [8]. Median concentration of the DL-PCBs (ΣPCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) accounted for 3.0 ng WHO-TEQ/kg dw (n=18), ranging from 0.4 to 6.8 WHO-TEQ/kg dw. Urban samples had significantly higher PCB concentrations than rural composts. The other factors did not influence PCB concentration significantly. Concentration of DL-PCBs (in WHO-TEQ) was about equal to the PCDD/F concentration (in I-TEQ, see below), and therefore it would be useful to include DL-PCBs if PCCD/Fs in compost are assessed. Enantiomeric fractions of chiral PCBs (95, 132, 149) varied little and were very close to 0.5 in compost, indicating no significant enantioselective degradation during composting.

PCDD/Fs

Median PCDD/F concentration (Σ17 PCDD/F) in composts and digestates was 3.2 ng I-TEQ/kg dw ranging from 0.5 to 21.0 ng I-TEQ/kg dw (Figure 1, n=18). The median literature value was slightly higher (9.3 ng I-TEQ/kg dw [2]). The conservative time span until the Swiss guide value for PCDD/F in soil (5 ng I-TEQ/kg dw, Ordinance relating to Impacts on the Soil) would be exceeded was estimated 112 years, assuming a starting level of 2.4 ng I-TEQ/ kg dw [9] in soil, aerial deposition (deposition rate 22 mg/ha/a [10]) and regular compost application as only input sources, and no removal of PCDD/F due to degradation or other processes. However, the surface specific load (i.e. the load per hectare; g I-TEQ/ha/a) of aerial deposition was estimated to be only a factor two lower than input via compost application.

Brominated flame retardants

The median concentration of the sum of PBDE (ΣBDE 28, 47, 99, 100, 153, 154, 183) in composts and digestates was 2.0 µg/kg dw (0.2 - 4.5 µg/kg dw), BDE 209 accounted for 7.3 µg/kg dw (0.6 - 30.8 µg/kg dw, Figure 1, n=18). Median concentrations of pentaBDE and octaBDE calculated according to Morf et al. 2005[11] were at 1.9 µg/kg dw, and 0.2 µg/kg dw, respectively. Values in Swedish soils [12] were more than a factor ten lower than in compost. Median HBCD and TPPBA concentrations in compost were 100.6 and 0.51 µg/kg dw, respectively (Figure 1, n=18).

PFAS

The median for the sum of PFAS (Σ fluorotelomer sulfonate, four fluorotelomer carboxylates, four perfluorinated sulfonates, seven perfluorocarboxylates, three fluorooctane sulfonamides and two fluorooctane sulfonamidoethanols) was 6.3 µg/kg dw (Firgure 1, n=18). Values ranged from 3.4 to 35.2 µg/kg dw, which is between concentrations found in sludge and sediments. Relative contribution of 6:2 fluorotelomer sulfonate, perfluorobutane sulfonate, perfluorocarboxylic acids and perfluorooctane sulfonamide to the total sum of PFAS was similar in all samples. This may be an indication for the uniform distribution of these compounds irrespective of their emission from different industries, applications and diffuse sources.

Pesticides

Of the more than 270 pesticides and some of their metabolites (86 fungicides, 86 herbicides, 92 insecticides, 5 acaricide) analysed, 30 fungicides, 14 herbicides, eight insecticides, and one acaricide were detected in compost and digestate. Median concentration of the sum of all fungicides was 42.4 µg/kg dw (n=18), whereas for herbicides and insecticides the concentration was lower (4.1 and 1.1 µg/kg dw, n=18, respectively). Highest median concentrations were found for imazalil (9.0 µg/kg dw, detected in 14 out of 18) and thiabendazole (5.3 µg/kg dw, detected in 13 out of 18), two typical post-harvest fungicides applied on citrus fruit.

Phthalates, nonylphenol and CP

The median DEHP concentration in compost and digestate was 280 µg/kg dw (n=6), corresponding well with literature values (300 µg/kg dw[2] and being well below the of 50mg/kg dw of the Danish Statutory Order on application of waste products for agricultural purposes [13]. Even though detected at considerable concentrations in German apples and tomatoes [14], nonylphenol was not detected in compost. Possible reasons are relatively good degradability and high detection limit (1mg/kg dw). Concentration of CPs (short and medium chain CP) were between 86 and 285 µg/kg dw (n=3), which is comparable with Swiss soil data (personal communication, S.Iozza, University of Basel).

Synopsis

Nearly all of the today's most concerning organic pollutants could be quantified in compost and digestate at concentrations at or above levels found in background soil, the main recipient of these recycling fertilisers. On the one hand, total input of organic pollutants to the agricultural surface by compost application seemed to be limited relative to other sources in Switzerland. On the other hand surface specific loads (based on a standard fertilisation of 70kg P_2O_5, in g/ha/a) of organic pollutants to soil can account for equally or more important inputs, compared to aerial deposition, manure and sewage sludge application. This seemingly negative characteristic of compost and digestate needs to be counterbalanced with their apparent and well-documented beneficial aspects, such as soil improvement and the sustainable management of natural resources.

Acknowledgment

Thanks to the Swiss Federal Office for the Environment and the Swiss Federal Office of Energy for the financial support and the EU Perforce project for supporting PFAS analyses.

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10 Synopsis and Recommendations

This thesis presents a comprehensive overview on organic pollutants in source-separated compost. For the first time, digestate and presswater were included in such a study and several classes of contaminants have not been analysed in these matrixes before. Most of the compounds were detected at concentrations above their levels found in background soils, which is the main recipient of these recycling fertilizers.

PCB concentrations in Swiss compost and digestate were lower compared to values measured previously. These compounds probably originate mainly from aerial deposition on input material. PCB levels seemed to be stable during composting. Even though the regular treatment of soil with compost caused higher PCB inputs than other input pathways such as aerial deposition or manure application, absolute numbers were estimated to be low. It would need more than 1400 years to reach Swiss PCB trigger values for plant production in soil by a regular fertilising compost application including inevitable but negligible inputs via aerial deposition. Based on these findings and considering the general decreasing levels of PCBs in the environment, it is suggested that no further measures are needed to reduce PCB levels in Swiss compost and digestate.

In one fourth of the samples, PAH concentrations were above the Swiss guide value for compost (ORRChem). Levels in Swiss compost and digestate were also higher than literature values. The main PAH source in compost seemed to be pyrogenic but a more precise identification of the sources using characteristic ratios, molecular markers and a linear unmixing model proofed to be difficult. Levels of low molecular weight PAH were reduced during composting whereas high molecular weight compounds remained stable. PAH inputs to soil by compost application can be considerable, even if the compost applied to agricultural soil would be spread on the entire agricultural surface in Switzerland. On the basis of a simple and conservative approach, it was estimated that in as little as 50 years the guide value for soil could be reached solely by regular fertilising compost application. Further research and measures are needed to reduce PAH levels in compost and digestate. Several approaches are possible: i) identification of particularly contaminated input material and excluding them from recycling, ii) a broad monitoring study to single out parameter that influence PAH concentrations in compost and digestate, and/or iii) including PAH analysis in the compulsory analytical programme already established for heavy metals combined with a scientific based evaluation for tracking the source. The third measure would give responsibilities to the producers and might be particularly efficient since it would combine the practical and scientific knowledge.

Total input of pollutants assigned second priority (PCDD/F, BFR, PFAS) to agricultural surface seemed to be limited due to low concentrations and the amount of compost and digestate applied. However, where compost is actually employed for fertilising or soil improving purposes, inputs via compost of some organic compounds (e.g. PCDD/F, HBCD) can be equally or more important than other input pathways such as aerial deposition or manure application. This seemingly negative characteristic of compost and digestate needs to be counterbalanced with their apparent and well-documented beneficial aspects, such as soil improvement and the sustainable management of natural resources. Research is needed to describe the fate in soil of organic pollutants introduced via compost and to assess to what extent they are bioavailable and consequently harmful. These and the above outlined research questions are particularly important in the light of sustainable resource management and taking into account the increasing compost production in Switzerland.

11 Acknowledgement

11.1 Formal Acknowledgement

Joseph Tarradellas, Thomas Bucheli, Thomas Kupper, Henrik Kylin and Christian Ludwig to be my supervisors and examiners

Swiss federal office for the environment (FOEN) and the Swiss federal office of Energy (SFOE) for financial support

Markus Zennegg, Peter Schmid (Swiss Federal Institute for Materials Science and Technology, EMPA, Dübendorf, Switzerland), Patrick Edder, Didier Ortelli (Service de Protection de la Consommation, Geneva, Switzerland), Saverio Iozza, Michael Oehme (University of Basel, Switzerland), Urs Berger, Sandra Huber (Norwegian Institute for Air Research, NILU, Tromsø, Norway), Josef Müller (Fraunhofer Institute for Molecular Biology and Applied Ecology, IME, Schmallenberg, Germany) and Christian Schaffner (Swiss Federal Institute of Aquatic Science and Technology, Eawag, Dübendorf, Switzerland) for the analysis of organic pollutants in compost

Hans-Jörg Bachmann, Diane Bürge, Jean Paul, Corinne, Hörger, Urs Nyfeller and Doris Rohner (Agroscope FAL Reckenholz) for the analysis of heavy metals and nutrients in compost

Franziska Blum, Martina Kobližková and Reto Koller for the support in the PAH and PCB analysis

Ernst Brack, Roland Gschwend, Nils Honetschläger, Salvatore Guccione Thierry Suard, Petra Köppe and Anna Kaufmann (FAL Agroscope Reckenholz) for their help in sampling and sample preparation

Reinhard Furrer, Schools Colorado School of Mines, Golden, US and Werner Stahel, Swiss Federal Institute of Technology Zürich, Switzerland for their statistical support

Konrad Schleiss for sampling

Franz X. Stadelmann, Hans-Ruedi Bosshard, Jochen Mayer, Felippe De Alencastro and Dominique Grandjean for their scientific advice

Personnel of composting and digestion plants:
Willi Kohler and Urs Galli, composting plant Oensingen, Christoph Hess, Stefan Dändliker and Jörg Junker, digestion plant Oetwil am See, Nedzadin Asani composting plant Fehraltorf

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Other persons involved:
Vallotton (Eawag), Karl Roth (Agroscope FAL Reckenholz), Cécile Plagellat, Walter Giger (Eawag), Jacques Fuchs (FiBL), Felix Schuppisser (Institut Bachema, Schlieren, Switzerland), René Leisner (Kogas AG, Winterthur, Switzerland)

And the journals Journal of Environmental Quality, Journal of Environmental Analytical Chemistry and Journal of Chromatography A for copy right permission

The CECOTOX/GECOS team from EPFL and the Analytic group from FAL for the good atmosphere.

And of course thanks to my family and friend for listening to my enthusiastic talks about organic pollutants in Swiss compost and to my complaints when things weren’t working the way I planned them.

11.2 Colloquial Acknowledgement

There were so many people involved in this thesis, I really don't know where to start with this acknowledgment (yes, Thomas, everybody worked for me)

Let's start with the supervisors and financers:

Joseph Tarradellas, thank you for accepting me as your last PhD student

Thomas Bucheli, thank you for having always an open door, for answering my questions, for listening to my reflection and for all the analytical and scientific support (and of course of opening the world of wine to me)

Thomas Kupper, thank you for managing this project, for helping me with sampling and sample preparation, and for reading again and again my manuscripts

Henrik Kylin and Christian Ludwig to be my examiners

Swiss federal office for the environment (FOEN) and the Swiss federal office of Energy (SFOE) for financial support

My colleagues from my lab:

Franziska Blum: for helping me with the analysis of PAHs and PCBs in compost. You are the master of efficient and very precise lab work and of reminding me to have breaks

Martina Kobližková and Reto Koller for your support in the PAH and PCB analysis. Great that you came to FAL and Switzerland

Felix Wettstein, for answering my chemical questions and providing me with 'Lindor Kugeln' in hard times

And of course all the rest of the 'Organische Spurenanalytik Group': Marianne Erbs, Niccolo Hartmann (special thanks for asking me again and again about the internal standard quantification method) and Anna Sobek

People from FAL Reckenholz:

Hans-Jörg Bachmann, for reading my manuscripts, for the fruitful discussions on statistical evaluations and on heavy metals in compost and for providing a great infrastructure (analytically and personally) for my PhD.

Franz X. Stadelmann, for all his scientific support

Ernst Brack, Roland Gschwend, Nils Honetschläger and Salvatore Guccione for their help with sampling, sample preparation and turning the Thermo composter

Diane Bürge, Jean Paul, Corinne Hörger, Urs Nyfeller and Doris Rohner for the analysis of heavy metals and nutrients in compost

Hans-Ruedi Bosshard for organising the nutrient analysis, his advises on how to cut down wet, inhomogeneous compost

Jochen Mayer, for his support in managing the project and his advices for analysis of the challenging matrix compost.

Thierry Suard, Petra Köppe and Anna Kaufmann for helping me with sampling and sample preparation

Karl Roth and the rest of the workshop team for helping me with whatever technical construction problem I faced

And the whole analytical group for the good atmosphere

People at EPFL:

Felippe De Alencastro and Dominique Grandjean for their analytical advises, their help with the translation of the abstract to French and for the organisation of the yearly 'weekend de ski' à St. Luc

Cécile Plagellat for her encouragement in the beginning of my (and in the end of her) thesis

And the rest of the CECOTOX/GECOS team for many funny, relaxing and encouraging discussions during coffee breaks and lunch

People from other Institutes:

Reinhard Furrer, Schools Colorado School of Mines, Golden, US, for modelling the PAH and PCB contents in compost (even over night) and for his infinite patience for explaining an environmental scientist statistics

Prof. Werner Stahel, Swiss Federal Institute of Technology Zürich, Switzerland, for trying to fit PAH concentrations in compost with PAH emission patterns

Konrad Schleiss for sampling 83 compost, digestate and presswater samples

Markus Zennegg, Peter Schmid from Swiss Federal Institute for Materials Science and Technology (EMPA), Dübendorf, Switzerland, for the dioxin, furan, brominated flame retardant and dioxin-like PCB analysis, the support with the GPC clean up as well as for the encouraging and fruitful discussions

Patrick Edder, Didier Ortelli (Service de Protection de la Consommation, Geneva, Switzerland), Saverio Iozza, Michael Oehme (University of Basel, Switzerland), Urs Berger, Sandra Huber (Norwegian Institute for Air Research, NILU, Tromsø, Norway), Josef Müller (Fraunhofer Institute for Molecular Biology and Applied Ecology, IME, Schmallenberg, Germany) and Christian Schaffner (Swiss Federal Institute of Aquatic Science and Technology, Eawag, Dübendorf, Switzerland) for the analysis of organic pollutants in compost

Walter Giger (Eawag) for his disposition to accept possible diploma students

Jacques Fuchs (Research Institute of Organic Agriculture, FiBL) for conduction the partner project 'Effects of Composts and Digestate on the Environment, Soil Fertility and Plant Health'

Felix Schuppisser, Institut Bachema, Schlieren, Switzerland for providing datasets on PAH analysis in asphalt

Nathalie Vallotton (Eawag) for her help with the translations to French

Operators of composting and digestion plants

The following persons are kindly acknowledged for supporting the studies on degradation:

Willi Kohler and Urs Galli, composting plant Oensingen, Christoph Hess, Stefan Dändliker and Jörg Junker, digestion plant Oetwil am See, Nedzadin Asani composting plant Fehraltorf.

All operators of the composting and digestion plants that participated in the monitoring study.

René Leisner from the Kogas AG, Winterthur, Switzerland, for the useful discussion on the digestion process

People form the Steering committee:

Kaarina Schenk (Swiss Federal Office for the Environment (FOEN)), Rolf Kettler (FOEN), Marc Chardonnens (FOEN), Bruno Guggisberg (Swiss Federal Office of Energy), Rolf Wagner (Amt für Abfall, Wasser, Energie und Luft des Kanton Zürichs, AWEL), Albrecht Siegenthaler (Swiss Federal Office for Agriculture, FOAG), Andreas Röthlisberger (Verband Kompost-und Vergärwerke Schweiz, VKS), Lucius Tamm (Research Institute of Organic Agriculture, FiBL, Frick, Switzerland)

Journals:

The journals Journal of Environmental Quality, Journal of Environmental Analytical Chemistry and Journal of Chromatography A for copy right permission

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12 Curriculum Vitae

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July 03 - July 06: PhD, École Polytechnique Fédérale de Lausanne (EPFL), Laboratory of Environmental Chemistry and Ecotoxicology (CECOTOX), Faculty of Architecture, Civil and Environmental Engineering, Lausanne, Switzerland

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Sep 97 – Sep 02: study of Environmental Science at the Swiss Federal Institute of Technology Zürich, Switzerland

Oct 99 - March 00: Erasmus Exchange studies at the University of Lancaster, UK

Sep 96 – Sep 97: study of secondary school teacher at the University of Zürich, Switzerland

Sep 95 – Sep 96: seminar for pedagogic, Zürich, Switzerland

Feb 95- Sep 95: working experience in Ecuador and the US

Sep 90- Feb 95: high school, Seminar Küsnacht, Typus Lehramt

April 81- Sep 90: Primary and secondary school in Erlenbach, Switzerland