Influence of natural attenuation and river fluctuations on benzene dispersion in an alluvial aquifer subject to strong interactions with surface water

J. BATLLE-AGUILAR[1,2]**, S. BROUYÈRE**[1]**, A. DASSARGUES**[1]**, B. MORASCH**[3,4] **& D. HUNKELER**[3]

1 Department ArGEnCo, Hydrogelogy Unit and Aquapôle, University of Liège, Building B52/3, B-4000 Sart Tilman, Belgium
  serge.brouyere@ulg.ac.be

2 Present address: Ecological Engineering Laboratory, Institute for Environmental Engineering, École Polytechnique Fédérale de Lausanne, Station 2, Building GR, CH-1015, Lausanne, Switzerland

3 Centre for Hydrogeology, University of Neuchâtel, Rue Emile-Argand 11, CH-2009 Neuchâtel, Switzerland

4 Present address: Institute for Geosciences, Center for Applied Geosciences (ZAG), Sigwartstr 10, D-72076 Tübingen, Deutschland

Abstract A numerical groundwater flow and transport model, calibrated under transient conditions, was used to simulate benzene attenuation in an alluvial aquifer discharging into the Meuse River, in Belgium. The mean benzene degradation rate used in the model was quantified in situ along the groundwater flow path using compound-specific carbon isotope analysis (CSIA). The results of the transient solute transport simulations confirmed that benzene concentrations decreased almost five orders of magnitude 70 m downgradient the source, becoming below the detection limit in the zone adjacent to the river and consistent with the absence of benzene in downgradient piezometers located close to the river. Furthermore, benzene concentrations were observed to be inversely correlated to the river water levels, leading to the hypothesis that benzene dispersion is mainly controlled by natural attenuation and river fluctuations.

INTRODUCTION

Resulting from an intense urban and industrial pressure, nowadays exist numerous heavily polluted sites (brownfields) located in alluvial plains, often posing a major environmental threat mainly due to possible dispersion of contaminants into surface water bodies. This is the case of the alluvial plain of the Meuse River in Belgium, where a former gasworks factory was the object of field and laboratory investigations to assess pollutant attenuation and dispersion. Among other organic and inorganic pollutants, benzene was present in groundwater at concentrations as high as 750 mg L^{-1} in the source zone. However, benzene could never be detected near the river which is about 160 m downgradient the main source.

HYDRODYNAMIC CHARACTERIZATION OF THE GROUNDWATER – SURFACE WATER SYSTEM

Measurements of aquifer properties, such as hydraulic conductivity and storativity are often sparse, especially in contaminated sites, and may be influenced with "noise" such

as the influence of water level fluctuations of adjacent rivers and aquifer recharge. The alternative to classical hydraulic experiments performed in controlled conditions is to identify the most influencing factors of groundwater dynamics. Two main potential factors were identified in the studied brownfield as affecting piezometric levels: groundwater recharge related to rainfall events and river fluctuations.

Piezometric levels were continuously monitored in 16 piezometers located in the brownfield, using Level TROLL® pressiometric probes (time resolution: 1h) with automatic data acquisition, for the period 2005-2007. River water levels and rainfall records were obtained in the vicinity of the brownfield for the same period.

Cross-correlation coefficients between river water and piezometric levels ranged between 0.8 and 0.98 for piezometers located close to the river. Although the cross-correlation coefficient decreases as the distance to the Meuse River increase, cross-correlation coefficients remain very significant far from the river (250 m distance), with values ranging between 0.5 and 0.6. Cross-correlation analysis performed between rainfall and piezometric levels highlighted a secondary role of rainfall recharge in piezometric level fluctuations, with maximum cross-correlation coefficients equal to 0.3.

ASSESSMENT OF BENZENE BIODEGRADATION USING STABLE CARBON ISOTOPE ANALYSIS

Degradation of benzene along the groundwater flow path was assessed and quantified using compound-specific carbon isotope analyses (CSIA) of groundwater samples. Carbon isotope fractionation of benzene occurs because molecules consisting of light ^{12}C isotopes are degraded faster than those containing a heavy ^{13}C isotope, the remaining benzene becoming increasingly enriched in ^{13}C, thus used to track the progress of biodegradation (Fischer *et al.*, 2008).

Groundwater samples from 18 piezometers were analyzed for stable carbon isotope ratio in benzene. The carbon isotope ratio is reported relative to the VPDB standard using the δ-notation according to:

$$\delta^{13}C[‰] = \left(\frac{^{13}C_{sample} / ^{12}C_{sample}}{^{13}C_{reference} / ^{12}C_{reference}} - 1 \right) \times 1000, \qquad (1)$$

where a shift in positive direction corresponds to an enrichment in ^{13}C. Subsequently, first order degradation rates were retrieved from isotope data using the following equation (Hunkeler *et al.*, 2002; Blum *et al.*, 2009):

$$\lambda = -\Delta\delta^{13}C / (\varepsilon \times t), \qquad (2)$$

where $\Delta\delta^{13}C$ is the shift in the carbon isotope ratio between the source and a downgradient monitoring point, ε is the isotope enrichment factor and t the travel time. Travel times were estimated based on the average groundwater flow velocity (1.04 × 10^{-5} m s^{-1}), calculated from the average hydraulic gradient, saturated hydraulic conductivity and effective porosity. A mean first-order degradation rate equal to 1.7 ×

10^{-2} d^{-1} was obtained, mainly attributed to strongly sulphate-reducing conditions (Morasch *et al.*, 2007), in the same range of rate constants obtained on fuel contaminated sites and gas plants in the USA (Lewandoski and Mortimer, 2004).

RESULTS ON BENZENE TRANSPORT MODELLING

In order to evaluate the influence of biodegradation and groundwater-surface water dynamics on benzene dispersion and attenuation in the alluvial aquifer, a numerical groundwater flow and transport model was developed, using MODFLOW-2000 (Harbaugh *et al.*, 2000) and MT3DMS (Zheng and Wang, 1999). Full details on groundwater flow and transport model boundary conditions, parameterization and calibration are presented in Batlle-Aguilar (2008) and Batlle-Aguilar *et al.* (2009). The transport model was run under transient conditions considering river fluctuations as the main stress factor. The first order biodegradation rate constant for benzene, estimated applying Eq. (2), was used, and constant benzene concentrations at the source were applied. Resulting modelled benzene concentrations at 50 and 115 m downstream the source area and monitored Meuse River levels are presented in Fig. 1.
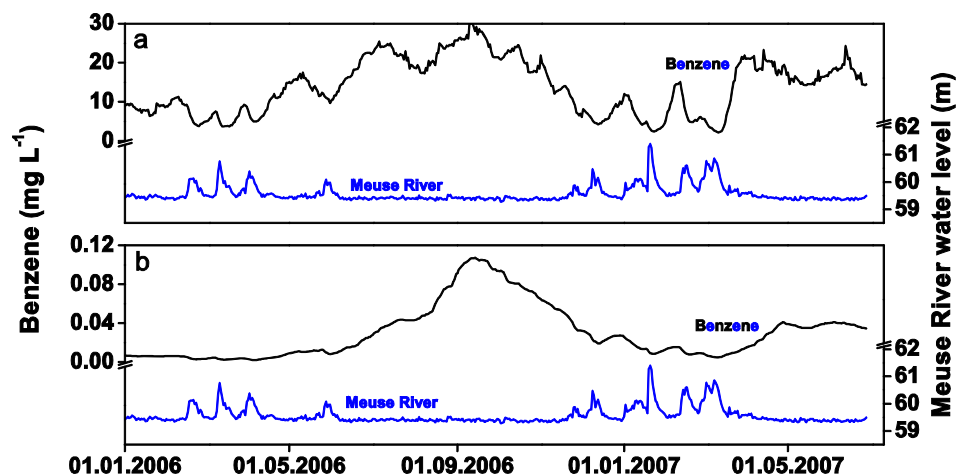

Fig. 1 Modelled transient benzene concentrations at (a) 50 m, and (b) 115 m downstream of the source area.

Benzene concentrations change over time inversely to river fluctuations. When the river is at its baseline (i.e. 59.4 m a.s.l.), benzene concentration is at its maximum, while when the river water level rises up to 61 m (hydraulic gradient inversion; e.g. February 2007), benzene concentration decreases to its minimum. This is due to the fact that the benzene plume moves back as a consequence of the hydraulic gradient inversion between the river and the aquifer. When the river water level returns to its baseline, the benzene plume moves forward; this is translated in an increase of the benzene concentration. During the modelled period, benzene concentrations calculated in the zone adjacent to the river remain under the detection limit (µg L^{-1}), which is in good agreement with sampling results obtained between 2005 and 2006, highlighting the performance of benzene biodegradation to reduce its concentration of five orders of magnitude within 100 m downgradient the source area.

CONCLUSIONS

In the absence of biodegradation and under the assumption of a constant benzene source, the contaminant plume would extend, at high concentrations, close to the Meuse River. However, benzene was never detected in the different sampling points located at shorter distances to the Meuse River. The strong decrease in benzene concentrations over such a short distance (i.e. 100 m) can be attributed to biodegradation under strongly reducing conditions, as confirmed by the enrichment of ^{13}C in benzene with increasing distance from the source.

Under prevailing conditions, the risk of contaminant dispersion to the Meuse River through groundwater discharge seems low. The largest fraction of benzene is predominantly degraded under sulphate-reducing conditions. As long as sulphate remains available, one can expect an efficient attenuation of benzene. However, if geochemical conditions change, for example, due to a continuous entry of surface water as a consequence of a relatively long period of hydraulic gradient inversion, aquifer reducing conditions could shift to less reducing or even oxidizing conditions, diminishing the benzene biodegradation effectiveness or even halting it. For this reason, we claim that monitored natural attenuation remediation technique is a good choice as a remediation tool for such contaminated sites.

REFERENCES

Batlle-Aguilar, J. (2008). Groundwater flow and contaminant transport in an alluvial aquifer: *in-situ* investigation and modelling of a brownfield with strong groundwater-surface water interactions. PhD Thesis. Applied Sciences Factulty, Univesity of Liège (Belgium), pp. 245.

Batlle-Aguilar, J., Brouyère, S., Dassargues, A., Morasch, B., Hunkeler, D., Höhener, P., Diels, L., Vanbroekhoven, K., Seuntjens, P. and Halen, H.. (2009). Benzene dispersion and natural attenuation in an alluvial aquifer with strong interactions with surface water. *J. Hydrol.*, **369**(3-4), 306.317.

Blum, P., Hunkeler, D., Weede, M., Beyer, C., Grathwohl, P. and Morasch, B. (2009). Quantification of biodegradation for o-xylene and naphthalene using first order decay models, Michaelis-Menten kinetics and stable carbon isotopes. *J. Contam. Hydrol.*, **105**(3-4), 118-130.

Fischer, A., Herklotz, I., Herrmann, S., Thullner, M., Weelink, S.A.B, Stams, A.J.M., Scholmann, M., Richnow, H.H. and Vogt, C. (2008). Combined carbon and hydrogen isotope fractionation investigations and elucidating benzene biodegradation pathways. *Environ. Sci. Technol.*, **42**(12), 4356-4363.

Harbaugh, A.W., Banta, E.R., Hill, M.C. and McDonald, M.G. (2000). MODFLOW-2000: the US geological survey modular ground-water model. User guide to modularization concepts and the ground-water flow process. Open-File Report 00-92. US Geological Survey, Restorn, Virginia. 121 pp.

Hunkeler, D., Höhener, P. and Zeyer, J. (2002). Engineered and subsequent intrinsic in situ bioremediation of a diesel fuel contaminated aquifer. *J. Contam. Hydrol.*, **59**(3-4), 231-245.

Lewandowski, G. and Mortimer, G. (2004). Estimation of anaerobic biodegradation rate constants at MGP sites. *Ground Water*, **42**(3), 433-437.

Morasch, B., Höhener, P. and Hunkeler, D. (2007). Evidence for in situ degradation of mono- and polyaromatic hydrocarbon in alluvial sediments based on microcosm experiments with ^{13}C-labelled contaminants. *Environ. Pollut.*, **148**(3), 739-748.

Zheng, C. and Wang, P.P. (1999). MT3DMS: a modular three-dimensional multispecies transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems; documentation and user's guide. Contract Report SERDP-99-1. US Army Engineer Research and Development Center, Vicksburg, MA, USA. 202 pp.