Benzene dynamics and biodegradation in alluvial aquifers affected by river fluctuations

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Abstract

The spatial distribution and temporal dynamics of a benzene plume in an alluvial aquifer strongly affected by river fluctuations was studied. Benzene concentrations, aquifer geochemistry datasets, past river morphology and benzene degradation rates estimated *in situ* using stable carbon isotope enrichment were analysed in concert with aquifer heterogeneity and river fluctuations. Geochemistry data demonstrated that benzene biodegradation was on-going under sulphate reducing conditions. Long-term monitoring of hydraulic heads and characterisation of the alluvial aquifer formed the basis of a detailed modelled image of aquifer heterogeneity. Hydraulic conductivity was found to strongly correlate with benzene degradation, indicating that low hydraulic conductivity areas are capable of sustaining benzene anaerobic biodegradation provided the electron acceptor (SO_4^{2-}) does not become rate limiting. Modelling results demonstrated that the groundwater flux direction is reversed on annual basis when the river level rises up to two meters, thereby forcing the infiltration of oxygenated surface water into the aquifer. The mobilisation state of metal trace elements such as Zn, Cd and As present in the aquifer predominantly depended on the strong potential gradient within the plume. However, infiltration of oxygenated water was found to trigger a change from strongly reducing to oxic conditions near the river, causing mobilisation of previously immobile metal species and vice versa. Monitored natural attenuation appears to be an appropriate remediation strategy in this type of dynamic environment provided that aquifer characterisation and targeted monitoring of redox conditions is adequate and electron acceptors remain available until concentrations of toxic compounds reduce to acceptable levels.

Keywords: surface water – groundwater interaction; aquifer heterogeneity; hydrogeochemistry; organic contaminants; metal trace elements; aquifer remediation.

INTRODUCTION

Numerous chemical and metallurgical industries were historically situated close to rivers in order to facilitate the transport of raw materials and supply process water. Improper disposal of solid and toxic waste over decades has resulted in numerous heavily polluted brownfields located in alluvial plains, close to rivers (Schirmer et al. 2006). These sites present major environmental risks, including groundwater deterioration and contaminant dispersion, particularly through groundwater discharge into surface water.

Benzene is a toxic and carcinogenic monoaromatic hydrocarbon petroleum component, which combined with its higher solubility in comparison to other hydrocarbons, makes it a serious threat to environmental health and groundwater quality (Fahy et al. 2006; Rooney-Varga et al. 1999). Although benzene naturally biodegrades under aerobic groundwater conditions (Chiang et al. 1989; Pruden et al. 2003), aquifers affected by petroleum contaminants are generally characterised as strongly reducing environments. During the past two decades benzene biodegradation under anaerobic conditions has been extensively studied, either in laboratory microcosm batches and column tests (Hunt et al. 1997; Kuhn et al. 1988; Anderson et al. 1998) or, more recently, in the field using carbon isotope fractionation techniques (Fischer et al. 2007). Heavy metals are often present in petroleum contaminated aquifers, and have been found to enhance benzene anaerobic biodegradation due to reduction of metal oxides (Villatoro-Monzón et al. 2008). Conversely, extreme redox gradients in organic pollutant plumes have the potential to cause the reverse effect and mobilise previously immobile inorganic species.

Either natural or forced infiltration of polluted surface water into aquifers (bank filtration) is commonly used to adsorb and degrade dissolved contaminants in surface water (Hiscock and Grischek 2002; Doussan et al. 1998). The opposite process, where clean surface water infiltrates

into contaminated aquifers contributing to accelerate or enhancing aquifer contaminant degradation, has only occasionally been studied (Woessner 2000). Vogel and Grbic-Galic (1986) provided evidence for enhanced toluene and benzene biodegradation by incorporating oxygenated water into anaerobic aquifer environments, although their study did not involve any river influence.

Alluvial aquifers are strongly heterogeneous porous media with spatially variable hydraulic properties that lead to preferential flow and solute transport (Anderson et al. 1999; LaBolle and Fogg 2001). Aquifer heterogeneity directly affects groundwater dynamics and geochemistry, patterns of groundwater fluxes, contaminant migration, dispersion and reactivity in the subsurface (Carleton and Montas 2009; Fritz and Arntzen 2007). Scholl (2000) attributed discrepancies between observed and modelled BTEX biodegradation rates to variability in estimates of groundwater flow velocities, with increased discrepancy in areas where heterogeneity was higher. Heeren et al. (2010) found subsurface physical heterogeneity to be responsible for preferential flow paths for contaminants but also for causing spatially non-uniform river – aquifer interaction. Maier et al. (2007) showed the direct influence of aquifer thickness and aquifer heterogeneity on natural attenuation processes in aquifers. Given that the thickness of alluvial aquifers can be reasonably determined provided borehole data is available to the base of the aquifer, aquifer heterogeneity remains the most challenging issue to solve. Such information is paramount for choosing the most appropriate remediation measure, such as monitored natural attenuation (Blum et al. 2009), pump and treat systems (Bear and Sun 1998), or permeable reactive barriers (Hemsi and Shackelford 2006). Aquifer characterisation that focuses on assessment of the presence and extent of low permeability areas, their contaminant

concentration and potential for pollutant degradation is therefore an essential component in the design of effective remediation strategies.

In this paper we analyse the spatial and temporal evolution of a benzene plume and its related aquifer geochemistry in an alluvial aquifer in concert with fluctuations in the adjacent river level. We particularly focus on relating the combined effect of aquifer heterogeneity, spatial variability of hydrogeochemistry, and strong river fluctuations to biodegradation rates quantified in-situ from carbon stable isotope analysis at multiple piezometers. We explore the co-occurrence effect of redox conditions caused by benzene biodegradation and the seepage reversal induced by river fluctuations on the variably mobile and immobile metal trace elements in groundwater. The ramifications of these processes are illustrated using a contaminated alluvial aquifer where principal and secondary benzene sources, together with other organic contaminants and metal trace elements, have mixed over several decades to create a complex contaminated groundwater environment that is highly responsive to river fluctuations.

DESCRIPTION OF THE RESEARCH SITE

The site is located 15 km upstream the city of Liège (Belgium, EU), an important centre for the metallurgical industry in Europe during the last century. The brownfield covers an area of approximately 10 ha, where a coke and gas production factory operated for 62 years from 1922. In 1984 the factory was abandoned and dismantled. The site is located 25 m from the Meuse River (Figure 1), which has an average water level at a baseline of 59.4 m a.s.l. (above sea level) and a water depth of around 8.5 m. Although river level is artificially maintained by a series of dams, the river level continuously fluctuates with typical daily amplitudes of centimetres and typical seasonal amplitudes of up to 2 meters during winter and spring.

Approximately 4 m of backfill deposits (materials from demolition of buildings, ashes, brick fragments, and iron pipes) directly overlie 2 m of silt-sand-clay deposits, and 8 m of alluvial gravels (constituting the alluvial aquifer). The carboniferous shale bedrock at 52 m a.s.l. is considered to be the impervious lower boundary of the alluvial aquifer. The mean piezometric water level in the alluvial aquifer is 60 m a.s.l. and the general groundwater flow direction is towards the Meuse River with a mean hydraulic gradient of 0.3% (Batlle-Aguilar 2008).

Soil and groundwater pollution was discovered at the beginning of the 1990's. Soil samples taken at multiple locations in the brownfield in 1992, 2001 and 2005 identified considerable contamination of the backfill deposits (0 to 4 m) by mono and polyaromatic hydrocarbons (BTEX and PAH). At the time when the soil samples were collected, the Belgian soil legislation defined compound-specific intervention values as a cut-off risk: soils and/or groundwater concentrations above this value led to mandatory further action, like remediation, engineering controls and land-use restrictions or monitoring. Most soil samples contained benzene concentrations that exceeded, by several orders of magnitude, the benzene intervention value in

106 Belgium, fixed at 0.6 mg kg^{-1} (SPAQuE 2007). Toluene, ethylbenzene and xylene concentrations
107 also significantly exceeded their intervention values (fixed at 85, 76 and 20 mg kg^{-1},
108 respectively). The results for PAHs were similar, e.g. naphthalene and fluoranthene overshot
109 their intervention values by several orders of magnitude (fixed at 17 and 30 mg kg^{-1},
110 respectively). The heavy metals Zn, Pb, As and Cd, although less abundant than the organic
111 pollutants, were also found in concentrations close to or slightly above their individual
112 intervention values.
113 Simultaneously, more than 60 piezometers were sampled across the brownfield, revealing very
114 high concentrations of benzene (up to 560,000 μg L^{-1}), toluene (77,000 μg L^{-1}), m-xylene
115 (15,200 μg L^{-1}), naphthalene (63,000 μg L^{-1}) and fluoranthene (2,000 μg L^{-1}), up to three orders
116 of magnitude above respective groundwater intervention values. Heavy metals (e.g. As, Cd, Zn,
117 Pb) were occasionally detected in high concentrations in groundwater samples, although less
118 frequently than the organic contaminants.

MATERIALS AND METHODS

Tracer injection experiments

In order to estimate hydrodispersive properties of the alluvial deposits, such as effective porosity (θ) and longitudinal dispersivity (α_L), forced gradient (induced hydraulic) radial-convergent flow tracer tests were performed, consisting of pumping water from a well while a tracer is added into adjacent wells. The arrival of the tracer is monitored in the pumping well, obtaining a tracer breakthrough curve. In a first step (phase I) different salt (nitrate, lithium and iodide) and fluorescent tracers (naphthionate and uranine) were injected in several piezometers (U5, 7, 6, 1 and 2) located upgradient of the pumped recovery well (P5) (Figure 1). Unexpectedly, none of the tracers were detected at the pumped recovery well. A second injection of a mix of different salt (lithium and iodide) and fluorescent (eosin yellowish, naphthionate, sulforhodamine B and uranine) tracers was performed in an injection piezometer (U15) downgradient from the same pumped recovery well of injection Phase I (P5). This time, all tracers were recovered (in P5) at significant rates and generally after short travel times (Figure S1a-b).

Groundwater flow and solute transport modelling

In this study we make use of the calibration results of a numerical groundwater flow and transport model, developed for the site with MODFLOW-2000 (Harbaugh et al. 2000). The model was previously presented by Batlle-Aguilar *et al*. (2009), and only a brief summary covering its main characteristics is presented here. The model extended to a larger part of the alluvial plain than the contaminated brownfield, in order to avoid influence of self-defined boundaries in the brownfield site. Upstream and downstream Dirichlet boundary conditions were set up, while a no flow boundary condition was set up in the limit between the alluvial plain and

141 the shaly up-hill bedrock (Figure 1). A Fourier boundary condition was applied at the limit
142 between the alluvial plain and the river, so river fluctuations and riverbank effects were
143 considered. The finite difference model domain had variable grid refinement from 5 m × 5 m
144 inside the brownfield to 25 m × 25 m at the edges of the regional modelled area. More than 3,000
145 daily groundwater head measurements at 16 monitoring wells located at different distances from
146 the river and covering the entire site were used during calibration, which was performed using a
147 combined approach of zonation outside the brownfield and pilot-points (de Marsily et al. 1984)
148 distributed across the contaminated area. Calibration was accomplished using PEST (Doherty
149 2008), and modelled groundwater heads showed a correlation coefficient (R^2) of 0.967 with
150 measured ones. Groundwater flow model calibration resulted in a detailed heterogeneous spatial
151 distribution of the hydraulic conductivity of the alluvial aquifer in the brownfield area (Figure 2).
152 The hydraulic conductivity values range from 1×10^{-5} ($\log_{10}$ -5) to 5×10^{-3} ($\log_{10}$ -2.3) m s^{-1}, with a
153 distinctive low permeability zone in the eastern part of the brownfield (blue area) near the Meuse
154 River and several zones of higher hydraulic conductivity (red zones) in the West and North-West
155 of the brownfield. Modelling results clearly highlight noticeable aquifer heterogeneity in the
156 brownfield with the potential to influence contaminant transport, dispersion and degradation
157 rates in the alluvial aquifer.
158 For the purpose of this study a groundwater transport model was built with MT3DMS (Zheng
159 and Wang 1999) using the previously calibrated groundwater flow model. The transport model
160 was calibrated by fitting modelled to measured breakthrough curves obtained from field tracer
161 injections (Figure S1c-d). The dimensions of the groundwater transport model were limited to
162 the brownfield. At the limit between the alluvial plain and the river Fourier boundary conditions
163 were applied, while Dirichlet boundary conditions, directly imported from the calibrated

groundwater flow model, were considered elsewhere. Variable grid refinement from 0.5 m × 0.5 m in the benzene source to 10 m × 10 m at the limits of the model was applied. Calibration of the groundwater solute transport model identified the presence of a mobile (θ_m) and an immobile (θ_{im}) porosity, the later associated with small-scale heterogeneities of the alluvial deposits attributed to (nearly) immobile water. The groundwater flow and transport model was used to evaluate the behaviour of the benzene plume from 2005 to 2007, a period for which detailed time series were available for river and groundwater levels.

Riverbanks: past and present morphology

According to historical maps dating from XIXth – XXth century, the morphology of the Meuse River has been substantially altered. Historically, a river channel crossed the current brownfield site. Between 1908 and 1910 the channel was filled up with materials of unknown origin, and riverbanks were constructed with a conglomerate of concrete and rock to prevent flooding of the alluvial plain. The position of the former river channel on the brownfield was determined by overlapping historical and modern maps of the area (Figure 1). The location of the channel agrees well with the piezometric line contours and the change in the hydraulic gradient at the former channel location.

According to numerical model calibration the hydraulic conductivity of the semipervious concrete-rock riverbank was 6.7×10^{-4} m s^{-1}. This result was in good agreement with the range of hydraulic conductivities found using STWT1 (Barlow et al. 2000), between 1.9×10^{-5} and 1.1×10^{-4} m s^{-1}. The STWT1 analytical model calculates the response of an aquifer to a stress created by river fluctuations using convolution of the river – aquifer system's response.

Groundwater geochemistry and benzene degradation

The major source area of benzene around piezometer D2bis was located by combining information about the historical locations of industrial waste disposal in the brownfield and the monitored benzene contamination. Secondary sources (with benzene concentrations several orders of magnitude lower) were related to the location of a former benzene recovery (around piezometers U24 and U25), and around piezometer 14, where NAPL (non-aqueous phase liquid) were present. Contaminants trapped locally in the unsaturated zone may leak into the aquifer, especially during rain periods when perched aquifers are formed. However, considering the substantially lower contaminant concentrations in the unsaturated zone in comparison to concentrations in groundwater, this mechanism for contribution to groundwater pollution was considered to be of minor importance.

The source area (nearby piezometer D2bis) is characterised by strongly reducing conditions (Eh -300 mV), groundwater concentrations of sulphide (HS^-) above 1 mg L^{-1} and methane (CH_4) above 15 µg L^{-1}. Concentrations of nitrate (NO_3^-) are between 0 and 3 mg L^{-1}, clearly below the background concentrations (> 15 mg L^{-1}) determined upgradient of the contamination area. Closer towards the river, groundwater becomes less reducing to oxic, with positive Eh values (+100 mV) and concentrations of NO_3^- close to background values.

Due to its high toxicity and mobility, benzene was considered to be the most problematic contaminant on the site. Benzene biodegradation under strictly reducing conditions and presumably with SO_4^{2-} as main electron acceptor was quantified *in situ* using compound-specific carbon isotope analysis (Morasch et al. 2007). $\delta^{13}C$ ratios in benzene increased continuously between the source zone (piezometer D2bis) and the piezometers located along the contaminant plume in the strictly reducing part of the aquifer. Based on the ^{13}C enrichment, 80% of the

residual benzene was found to be biodegraded anaerobically with an average half-life of 180 days. The benzene biodegradation rate was quantified to be 2×10^{-3} d^{-1} along the preferential groundwater flow direction towards East/Southeast (Batlle-Aguilar et al. 2009). Towards the river, where moderately reducing to oxic conditions prevail, no further ^{13}C-enrichment in the residual benzene was found. Consequently, the approach could not be used to calculate benzene degradation under less reducing/oxic conditions in our field site (Morasch et al. 2011).

RESULTS AND DISCUSSION

River morphology

The location of the actual in-filled former river channel corresponds to an observable change in the modelled hydraulic conductivity field of the site (Figure 2). The modelled aquifer heterogeneity, obtained independently of the historical geomorphological changes of the Meuse riverbanks, closely reflects these changes and their effect on the aquifer hydraulic conductivity distribution. Furthermore, it is likely that the spatial distribution of saturated hydraulic conductivity, and particularly the former river channel, influenced the tracer experiments. The recovery well P5 and the injection piezometer U15 (phase II) are both located in the relatively high hydraulic conductivity alluvial deposits of the former river channel, while piezometers 1, 2, 6, 7 and U5 used during injection phase I are located within the low hydraulic conductivity zone upgradient of the recovery well. It is hypothesised that the individual tracers injected in phase I remained below their limits of detection in the pumped water in P5 because they travelled slowly through the low hydraulic conductivity area, and consequently, were strongly dispersed and diluted before they reached the recovery well. On the contrary, in phase II the migration of the tracers injected in U15 downgradient of the recovery well was facilitated by the higher hydraulic conductivities in this area.

Aquifer geochemistry and benzene biodegradation

Datasets of benzene concentrations and associated parameters including Eh potential, SO_4^{2-}, and HS^- were examined in concert with the spatial distribution of hydraulic conductivity obtained from the numerical groundwater flow model calibration, and benzene biodegradation estimated from stable carbon isotope analysis (Figure 3 and Table S1).

As benzene left the major source zone, it was dispersed and preferentially travelled south-eastwards following the alluvial deposits with higher hydraulic conductivity (Figure 3a). The biodegradation of benzene and other organic contaminants resulted in strongly reducing conditions around the main and secondary sources of contamination, particularly close to piezometer U25 (Figure 3b). NO_3^-, the preferred electron acceptor for anaerobic microorganisms, was depleted around the major benzene source (close to piezometers C3bis and D2bis) but was present in the vicinity of the river (up to 7.3 mg L^{-1} and 45.5 mg L^{-1} in piezometers U10 and U19, respectively). SO_4^{2-}, however, appears to be abundant everywhere in the aquifer indicating that, unlike NO_3^-, SO_4^{2-} as electron acceptor is not a limiting factor for benzene degradation (Figure 3c). The most elevated concentrations of biogenic HS^- were measured in piezometer D2bis, which is located in the major source zone, an area that appears to be a hotspot for methanogenesis (Figure 3d).

In a flow-through system like an aquifer, enrichment in the heavier carbon isotope relative to the source is indicative of *in situ* biodegradation of the compound not at a single point but between two points connected in space. Moving away from the source zone, residual benzene ($\delta^{13}C$ = -24.5‰; D2bis) became continuously enriched in the heavier carbon isotope ^{13}C as biodegradation occurred during passage through the aquifer. The significant anaerobic degradation of benzene between the source and the low-permeability zone in the eastern part of the brownfield towards the Meuse River are evidenced by isotope ratios of $\delta^{13}C$ = -21.5‰ (e.g. piezometers 7, 8 and 15, Figure 4a). At first glance there seems to be a clear correlation between the rate of anaerobic benzene degradation and hydraulic conductivity zones, as illustrated in the relationship of K to $\delta^{13}C$ (Figure 4a). Since the continuous enrichment of the heavier carbon isotope integrates benzene degradation between the source and a sampling point downgradient, a

general link between the local hydraulic conductivity and microbial activity cannot be drawn that easily. Nevertheless, the very good observed correlation between K and $\delta^{13}C$ suggests that with the large excess of the electron acceptor SO_4^{2-}, microorganisms find favourable conditions for benzene degradation in the lower hydraulic conductivity areas around piezometers 7, 8, 15 and U13 (Figure 4a); in other words, low-permeability areas have a significant impact on benzene remediation. This finding is contrary to the hypothesis presented by Maier et al. (2007), based on modelling results, that natural attenuation is enhanced in areas where groundwater flow paths converges, as these zones are characterised by steep gradients that amplify dispersion of mass fluxes.

Unexpectedly, low HS^- concentrations in piezometers 7, 8, 15 and U13 appear to contradict the relationship between local microbial activity and low permeability areas (Figure 4b). However, less negative Eh potential and lower HS^- content around piezometer 7, 8, 15 and U13 may be a consequence of occasional (but annual) infiltration of oxic surface water into parts of the brownfield (Figure 4c). As a consequence of this process HS^- decreases while Eh increases to positive values.

All the piezometers where $\delta^{13}C$ was estimated fall within the 95% confidence interval of a linear correlation to hydraulic conductivity with a Pearson coefficient as high as 0.832, with the exception of piezometers P5, C3bis, 11 and 12 (Figure 4a). Piezometer P5 is the only sampling location at which ^{13}C enrichment ($\delta^{13}C$ = -23.9‰) is lower than expected for its hydraulic conductivity ($\log_{10}$ K -4.3 m s^{-1}). P5 is located in the area corresponding to the former river channel of intermediate hydraulic conductivity and geochemically distinct from the highest hydraulic conductivity area of the aquifer. Conversely, the cluster of piezometers formed by C3bis, 11 and 12 presents the highest ^{13}C enrichment in benzene at the site ($\delta^{13}C$ = -20.9‰;

282 piezometers 11 and 12). These three wells are located in zones of intermediate to high hydraulic
283 conductivities ($\log_{10}$ K -3.5 m s^{-1}) and show much higher $\delta^{13}C$ ratios than other piezometers
284 located in zones of similar hydraulic conductivities. Piezometer C3bis is located close to the
285 major source zone around D2bis and the high ^{13}C enrichment can be explained by local but very
286 efficient benzene degradation. Around piezometers 11 and 12 mixing of the main benzene plume
287 with secondary plumes of substantially different stable isotope composition can explain these
288 outliers in the hydraulic conductivity - stable isotope correlation. These results emphasize again
289 that low permeability zones can sustain anaerobic biodegradation of benzene when the electron
290 acceptor is not rate limiting. Due to the longer residence time of contaminants in comparison to
291 high hydraulic conductivity areas, niches of efficient anaerobic biodegradation can establish.
292 It is interesting to note that piezometers D3p and D1p, located close to the source area, fall into
293 the 95% confidence interval between $\log_{10}K$ and $\delta^{13}C$ (Figure 4a), yet groundwater analysed
294 from these piezometers have low $\delta^{13}C$ enrichment and low HS^- concentrations (Figure 4b). On
295 the other hand, D3p has positive Eh values, while negative Eh values were found in D1p (Figure
296 4c). These apparently contradictory observations may be attributed to the kinetic biodegradation
297 behaviour of benzene. Nitrate and iron are today nearly depleted across the entire study site,
298 although nitrate was found at background concentrations of up to 190 mg L^{-1} upstream. The site-
299 specific absence of these compounds implies that benzene biodegradation is occurring today
300 using SO_4^{2-} as electron acceptor, and the SO_4^{2-} concentration is far in excess of that required for
301 this purpose. Historical benzene biodegradation using alternative electron acceptors to SO_4^{2-} can
302 explain the low HS^- concentrations together with positive Eh potentials found in some areas,
303 such as around piezometer D3p.

River fluctuations and benzene dynamics

River fluctuations are responsible for the changes in piezometric levels in the alluvial aquifer. Cross-correlation analyses revealed that rainfall had almost no direct influence on water table fluctuations on the site (cross correlation coefficient, r_k = 0.1), while river fluctuations in the vicinity of the site were highly correlated to piezometric level fluctuations on the site (r_k = 0.9). Numerical and analytical results indicate that riverbanks of the Meuse River at the study site are sufficiently permeable to allow strong exchanges between surface water and groundwater. Exchanges between the aquifer and the river are thus expected to vary over the year according to river level fluctuations.

The benzene dataset available reveals unexpected fluctuations in benzene concentrations by several orders of magnitude from one sampling period to another, both in piezometers screened in the upper and deeper part of the gravel aquifer (Figures 5a-b). Most of the piezometers show high benzene concentrations in 1991, 2001 and 2005, when the sampling was performed during the summer period (low river levels). In contrast concentrations are generally lower in 1992 and 2006, when sampling took place during the winter period (high river levels). This concept is in good agreement with findings of Vermeul et al. (2011), who observed that aqueous concentrations in bores and vertical wellbore flows were significantly impacted by river stage fluctuations. Similar processes have also been related to groundwater level rises due to rainfall (Davis et al. 1999).

River fluctuations (Figure 6a) during the period 2005-2007 are shown to be responsible for a highly dynamic river – aquifer system (Figure 6b). During summer and autumn computed Darcy fluxes are positive, corresponding to groundwater discharge into the river. Over this period of the year, the river level is relatively constant at its baseline (59.4 m), with river fluctuations in the

order of centimetres causing changes in Darcy fluxes of $\Delta q = 5\times10^{-7}$ m s^{-1} at the river-aquifer interface. Despite these changes the water flow direction is constantly from the aquifer to the river. However, as a direct response to high water levels in the Meuse River during winter and early spring period, negative Darcy flux values regularly occur, indicating infiltration of river water into the aquifer. Computed benzene concentrations are presented for control points located at 25 and 125 m downgradient of the benzene source towards the river (Figure 6c-d). Every winter-spring the water level of the Meuse River rises by up to 2 metres, which exacerbates the lateral dispersion of the benzene plume around its source area (Figure 6e). Conversely, longitudinal dispersion of the benzene plume towards the river is enhanced by low river water levels, contributing to the formation of a relatively narrow and elongated benzene plume (Figure 6f). Contrasting spatial coverage of the benzene plume at different periods of the year emphasised the forward and backward movements of the benzene plume as a response to river fluctuations. This temporal variability of benzene plume dispersion caused by river fluctuations explains the variation in benzene concentrations from one sampling period to another by several orders of magnitude. Groundwater sampling over several years is thus likely to produce results that indicate unexpected shifts in benzene concentrations if the sampling is not performed during the same season.

Mobilisation of metal trace elements

According to the concept of co-contamination of organic and inorganic compounds, HS^- released by microbial SO_4^{2-} reduction reacts with divalent heavy metal ions like Zn and Cd and immobilises them in the form of metasulphides (Sandrin and Maier 2003), whereas the reduced form of arsenic As(III) is more mobile, particularly compared to its oxidised As(V) form (Dixit and Hering 2003). Accordingly, Zn and Cd have been found at low concentrations in the source

area and within the plume, where strongly reducing conditions prevail, but they have been found downgradient of the plume, close to the river. Conversely, As(III) has been observed within the plume and source area, but never close to the river.

Towards the Meuse River, benzene and other mono- and polyaromatic hydrocarbons are barely observed and the aquifer turns mildly reducing to oxic. It appears that As(III) mobilised close to the source area and along the plume is partly re-oxidised to a less mobile form (As(V)) downstream of the benzene plume close to the river. On the contrary, immobile reduced Zn and Cd in the form of precipitated metasulphides are likely to be mobilised if the aquifer environment changes to mild reducing or oxic. Additionally, Kao and Want (2000) showed that aerobic fringes, commonly present downgradient of dissolved BTEX groundwater plumes, contribute to complement benzene degradation. It is hypothesised that benzene degradation in our site near the river, mainly due to infiltration of oxic surface water, is complemented by these aerobic fringes. These two processes combined appear to be sufficient to enhance the immobilisation of As in its oxic form (As(V)) and mobilisation of oxic species of Zn close to the river. This hypothesis agrees well with available sampling results, showing the presence of Zn relatively close to the river but not As (Figure S2). Arsenic concentrations are significantly different nearby the benzene source area and close to the river, where concentrations below the detection limit were found. Regarding Zn concentrations, the difference between the source area and close to the river is not that notorious due to an upgradient contamination coming from an adjacent scrapyard (see piezometer 251 in Figure S2b). Zn concentrations are however high in piezometers U15, 7 and 8, an area particularly oxic and identified as a preferential infiltration path for river water following the former river channel.

CONCLUSIONS AND REMEDIATION REMARKS

The analysis of benzene concentrations and geochemical datasets in concert with river fluctuations and benzene biodegradation can be used to obtain a sound understanding of temporal and spatial benzene plume dynamics. Cost-effective mid- to long-term datasets of groundwater heads and river water levels form an essential platform for aquifer characterisation and hence, understanding of solute dynamics. Benzene *in situ* biodegradation (based on stable carbon isotopes) and independent data (such as past river morphology), supports understanding of the river-aquifer system and its influence on benzene plume dynamics.

Our results emphasize that low permeability zones can sustain benzene anaerobic biodegradation provided the electron acceptor does not become rate limiting. It is hypothesised that due to longer residence times in low hydraulic conductivity areas, niches of efficient anaerobic biodegradation may establish. Furthermore the anaerobic degradation of benzene affects the mobilisation of some heavy metals but immobilisation of other species, a process that appears to be reversed by the input of fresh, oxygen-rich, surface water during high river level conditions.

Characterisation of contaminated sites is particularly challenging when located close to rivers. Monitoring networks that do not consider the dynamic nature of both the river and the aquifer are likely to result in inappropriate or incomplete pictures of the whole river-aquifer system. We demonstrated that it is essential to perform groundwater sampling when the system is in an equivalent hydraulic state, e.g. each year in the same season, to avoid unexpected variability in contaminant concentrations and thereby misleading results. Furthermore, consideration of the temporal dynamics of such environments and spatial variability of aquifer geochemistry arising from both aquifer heterogeneity and presence of contaminants are essential to the effective implementation of remediation measures.

Permeable reactive barriers can be used effectively to treat contaminated aquifers (McGovern et al. 2002), although their performance depends on aquifer heterogeneity and uncertainty in the reaction mechanism (Eykholt et al. 1999). Effective implementation requires excellent characterisation of the aquifer, particularly groundwater fluxes. Pump and treat systems have been effectively used in hydrocarbon contaminated sites (Rabideau and Miller 1994), although this technique can easily become unaffordable, as large volumes of water are pumped and need to be treated. Furthermore, efficacy of this technique in contaminant removal has been recognised to be limited in some particular situations (Voudrias 2001).

Monitored natural attenuation (MNA) is an efficient cost-effective remediation technique that is applied at many contaminated sites where natural conditions meet the essential environmental requirements for contaminant biodegradation without human intervention (Alvarez and Illman 2006). The technique has low remediation costs, is not intrusive and does not generate large volumes of contaminated land and water. However longer periods of time are needed to achieve the desired environmental target and a sound understanding of the plume dynamics, aquifer geochemistry, heterogeneity and hydrological boundaries of the contaminated site are imperative. If all the conditions are not properly met and transport of contaminant compounds to susceptible downgradient receptors is probable, MNA can be bioestimulated (i.e. by adding electron acceptors) or applied in combination with other techniques (Colombani et al. 2009). Based on the results obtained and the sound knowledge of river-aquifer dynamics and aquifer heterogeneity at the study site, MNA appears to be the most suitable measure to apply. The implementation of this technique would need to be accompanied by a groundwater monitoring program to ensure SO_4^{2-} is not depleted and that redox conditions continue to be favourable for the enhancement of benzene degradation and immobilisation of heavy metals. This is particularly

419 important at the study site, as the input of fresh and oxidised water, combined with the depletion
420 of the main electron acceptor of the benzene degradation process, could lead to a serious
421 environmental issue by mobilizing heavy metals and allowing benzene plume to flow
422 downgradient into the river.
423 Finally, it is worth noting that information on historical industrial activities at the site and
424 nearby, as well as morphological changes such as riverbank construction/modification, certainly
425 helps to explain apparently inconsistent results found during site characterisation and as a
426 consequence, helps to improve the understanding of the river-aquifer system and associated
427 contaminant transport.

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569 **FIGURE CAPTIONS**

570 Figure 1. Position of the former river channel associated with the morphology of the Meuse
571 River before 1908. Piezometric contours correspond to the groundwater survey performed in
572 April 2006. The arrow indicates groundwater flow direction. Only piezometers and wells
573 discussed in the paper are labelled.

574 Figure 2. Spatial distribution of the hydraulic conductivity (in $\log_{10}$ m s^{-1}) resulting from the
575 transient calibration of the groundwater flow model. The former river channel and the tracer
576 injection and recovery wells during tracer injection phases I and II are shown, as well as
577 positions where stable carbon isotope signatures were determined in residual benzene.

578 Figure 3. Measured concentrations of (a) benzene; (b) redox potential; (c) sulphate; and (d)
579 sulphide, during the sampling period of 2006. Arrow indicates groundwater flow direction. Only
580 piezometers and wells discussed in the paper are labelled.

581 Figure 4. Correlation of $\delta^{13}C$ with (a) $\log_{10}K$; (b) HS^-; and (c) Eh. Dashed lines show the 95%
582 confidence limit of its correlation. Only piezometers shown as empty circles are considered in
583 the correlation.

584 Figure 5. Measured concentrations of benzene in groundwater between 1991 and 2006 for all
585 sampled piezometers screened in the (a) upper; and (b) deeper part of the alluvial aquifer. Red
586 and blue vertical bars indicate summer-autumn and winter-spring sampling period, respectively.

587 Figure 6. (a) Monitored fluctuations of water levels in the Meuse River; (b) computed Darcy flux
588 variations at the river-aquifer interface. Modelled benzene concentrations at control points at (c)
589 25 m; and (d) 125 m downgradient of the benzene source. Computed expansion and narrowing
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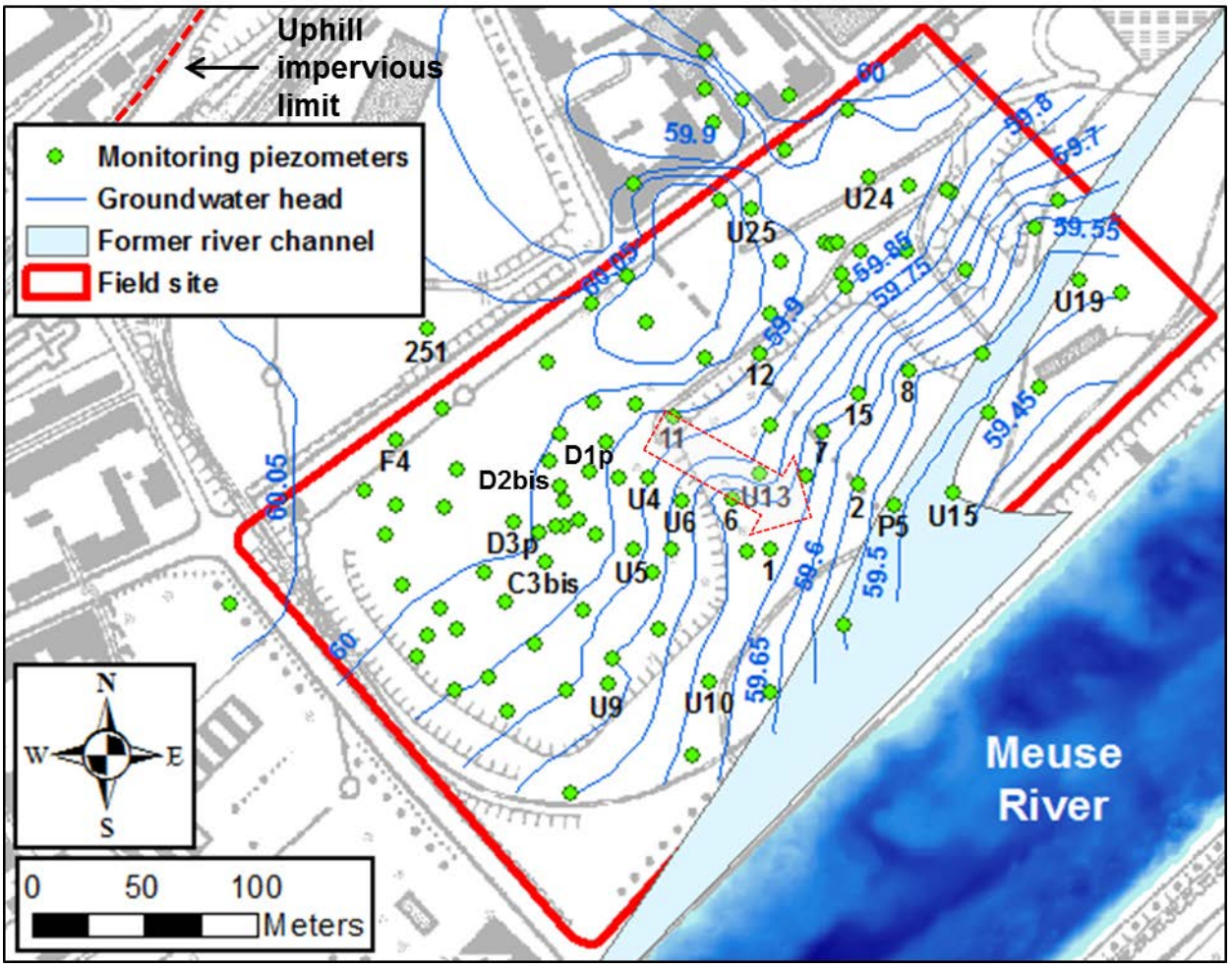

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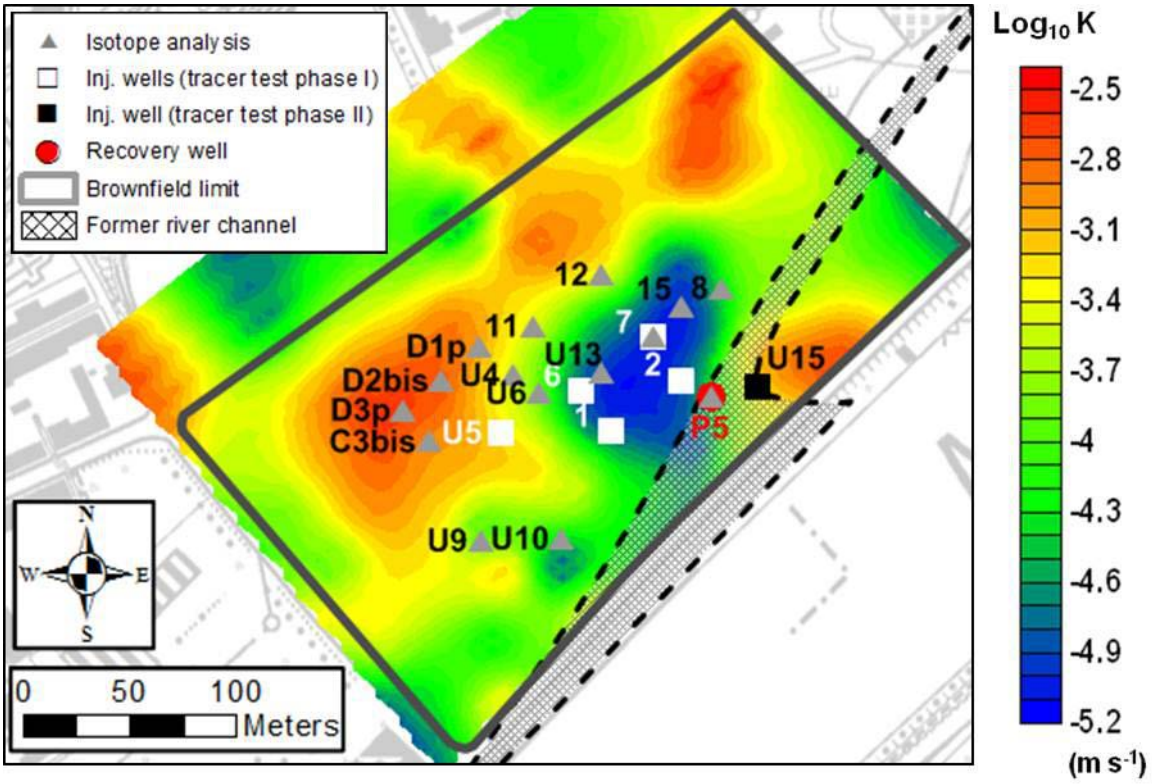

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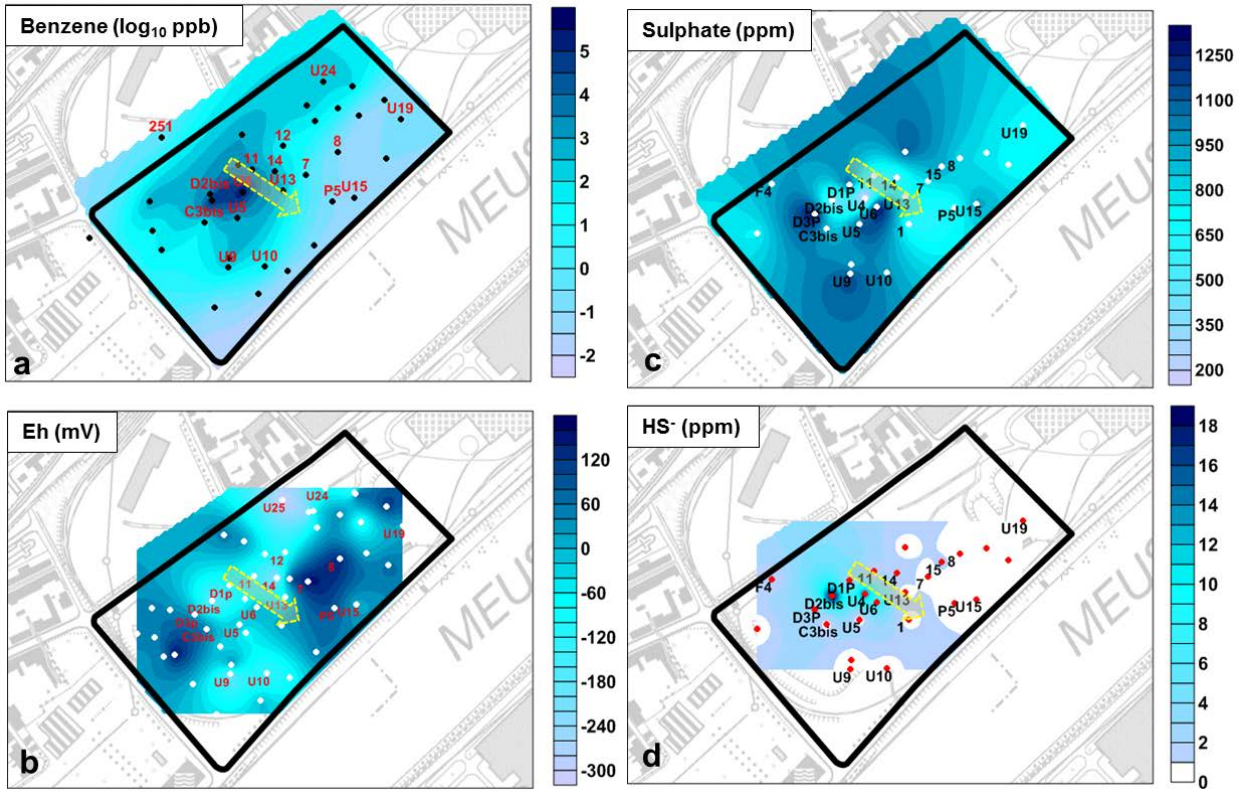

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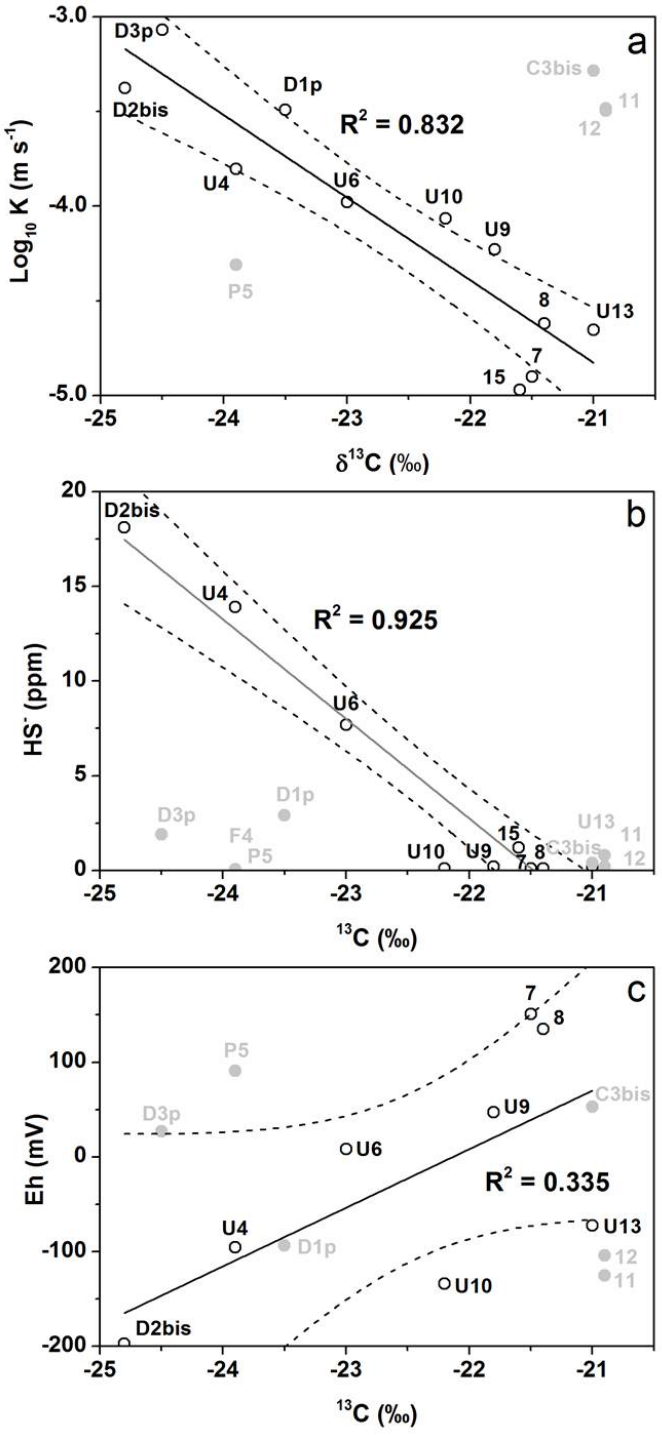

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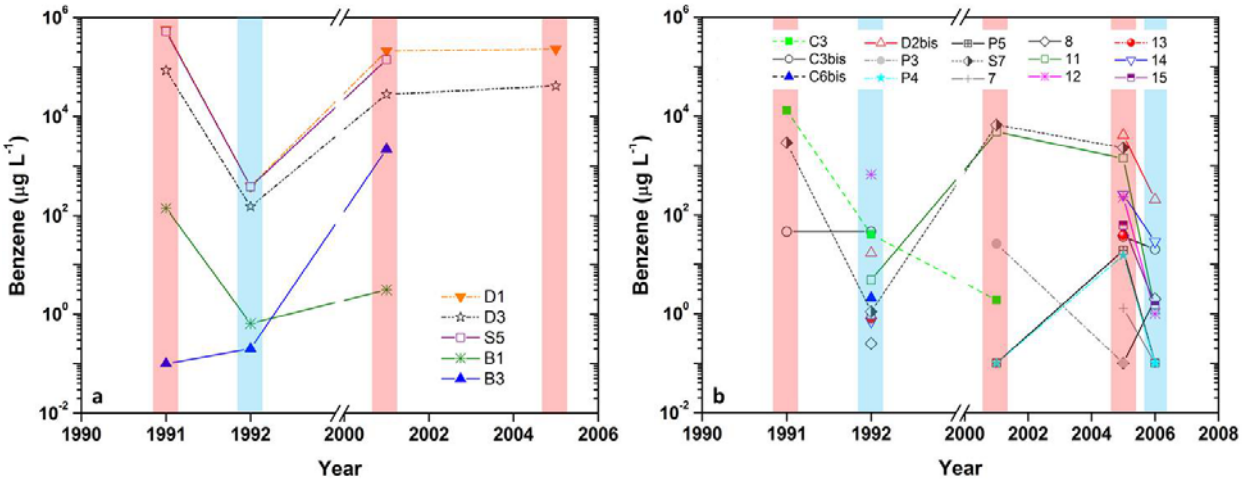

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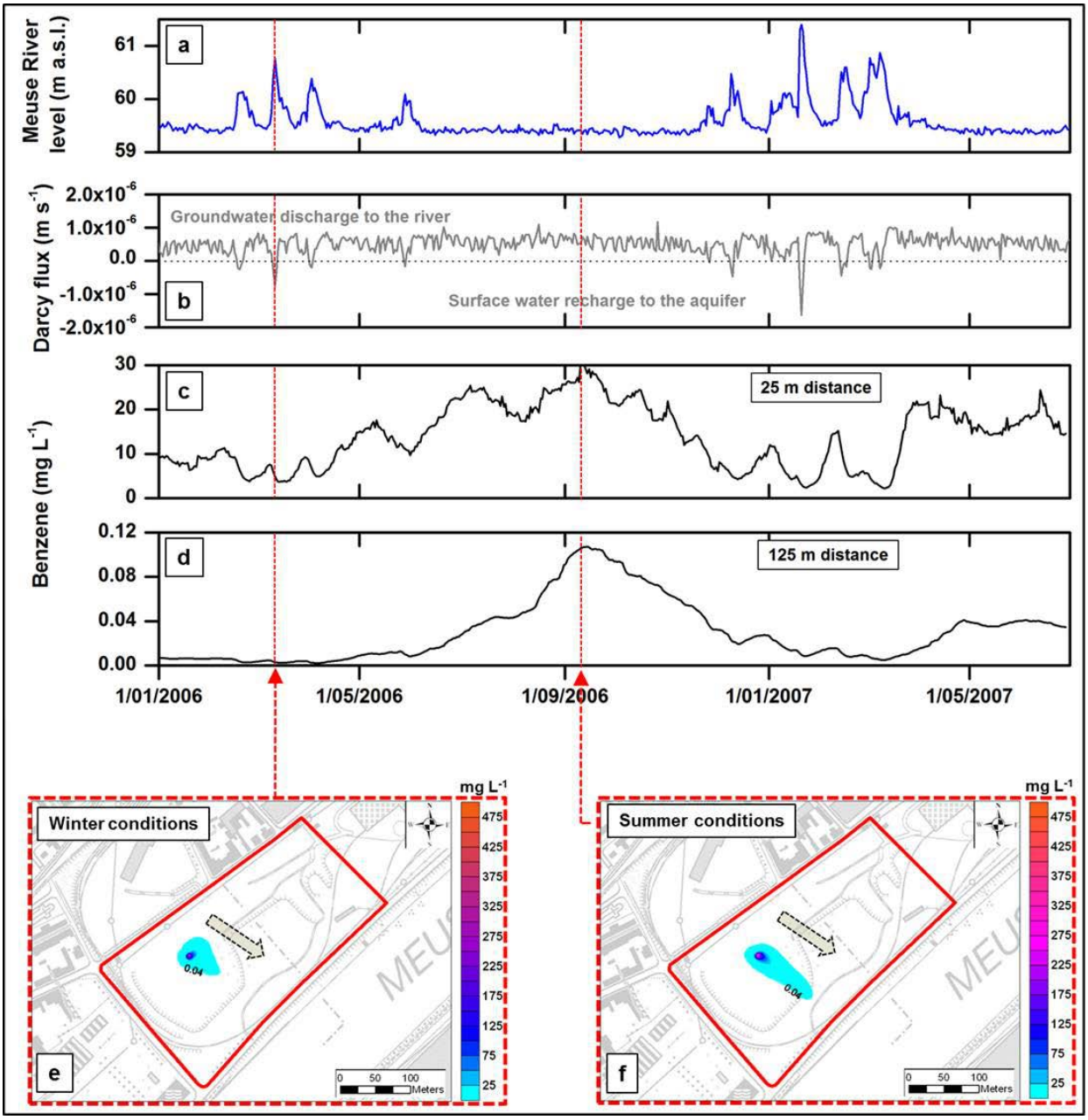

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