Natural attenuation of naphthalene and benzene at a former gasworks site

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Abstract Naphthalene and benzene are ubiquitously found at former gasworks sites. In order to demonstrate that monitored natural attenuation (MNA) is an alternative strategy for remediation of groundwater at the investigated site, biodegradation was characterized by: (1) reduction of contaminants; (2) correlation of contaminants concentration changes with geochemical parameters; (3) enumeration of anaerobic microorganisms and correlation with geochemical data; (4) laboratory assays with site-specific enrichment cultures and naphthalene as the sole carbon source and electron donor; (5) modeling plume extension of naphthalene along the centerline and (6) carbon stable isotope (CSIA) analysis. The study demonstrated that naphthalene attenuation mainly depends on high sorption on aquifer material. In contrast, benzene is predominantly attenuated by biodegradation.

Keywords Biodegradation; carbon stable isotope analysis; first-order transport model; monitored natural attenuation

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Introduction

In the last century, fuel for lighting, heating and cooking was manufactured from coal and petroleum at manufacturing facilities. The gas manufacturing and purifying resulted in a variety of resistant chemical compounds in groundwater, soil, sediment, sludge and surface water, among which dominate: polycyclic aromatic hydrocarbons (PAH), volatile aromatics (BTEX: benzene, toluene, ethylbenzene, and xylene), phenolics, inorganic nitrogen including cyanide compounds, inorganic sulfur and trace metals (U.S. EPA, 2004). Biodegradation, as a key determinant in natural attenuation (NA) processes was attempted to be characterized by different techniques. The objective of the presented study is to assess NA in the contaminated aquifer and to evaluate whether monitored natural attenuation (MNA) is a sufficient remediation strategy for the former gasworks site.

Methods

Field site

The investigated former gasworks site is located in Southern Germany. Gas was manufactured during the first half of the last century (1910–1966). The geology of the site is fairly homogeneous. The main aquifer, which contains Quaternary loamy gravels is shallow and has a thickness of around 2.0 to 3.5 m. The basis of the aquifer consists of Jurassic mudstones. The top of the Quaternary sediments is made of alluvial clay (confined aquifer) and in some parts of the site of silt (semi-confined aquifer). The prevailing groundwater flow direction is north–west. The estimated effective porosity is approximately 10 %. The average hydraulic conductivity is 2.3×10^{-5} m/s. The hydraulic gradient is approximately 0.02 resulting in an average seepage velocity of around 0.4 m/day.

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In September 2005, a naphthalene and benzene contamination was found in the groundwater wells P35, P2, P1, 28 and P34 (Figure 1).

Sampling procedures

Groundwater sampling was performed with a submersible pump (MP1, Grundfos) using Teflon tubing. Sampling in well P2 was performed using a hand-pump with PVC tubing. In well P28 with a diameter of only two-inches, no pumping was possible; therefore, groundwater samples were taken by a stainless steel container. In-situ parameters such as pH, electrical conductivity, dissolved oxygen concentration, redox potential and temperature were monitored. Samples for naphthalene analyses were collected in 1 litre brown glass bottles and acidified with 1 M hydrochloric acid (pH = 2) to prevent further biological activity. Bottles were closed without headspace by glassy lids. Samples for benzene and for the major anions and cations were filled into 100 ml brown glass bottles without headspace. Samples for stable carbon isotope analyses were collected into 240 ml brown glass bottles (Qorpak, Switzerland) and stabilized with 1 M hydrochloric acid (pH = 2). For most probable number (MPN) studies groundwater samples were taken by a hand-pump using sterile PVC tubing. Prior to sampling, one well volume was pumped out. Samples were taken into 50 ml sterile glass bottles. All bottles were stored at constant temperature of 4 °C until analysis or until incubation.

Analytical methods

Benzene was quantified directly from water (10 ml sample) by Purge and Trap GC/MS. The Gerstel multi purpose sampler (MPS32) device, operated with helium as a carrier (gas flux 1.3 ml/min) was connected to a GC Agilent 6890 with the mass selective detector (MSD) 5973. For separation of the target compounds, a Varian CP select 624 column (interior diameter: 0.32 mm; length: 30 m) was used. Naphthalene was extracted from water samples using cyclohexane as a solvent (2 ml of solvent containing 50 µl of internal standard for 1.0 l water) and analyzed using a GC-MS system (Agilent 6890) with a mass selective detector (MSD) 5973. The GC column used for separation of the target compound was a Varian VF-35 ms (interior diameter: 0.25 mm; length: 30 m). Analysis of major cations and anions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, Br^-, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}) was performed by ion chromatography (Dionex DX − 120). Sulfide

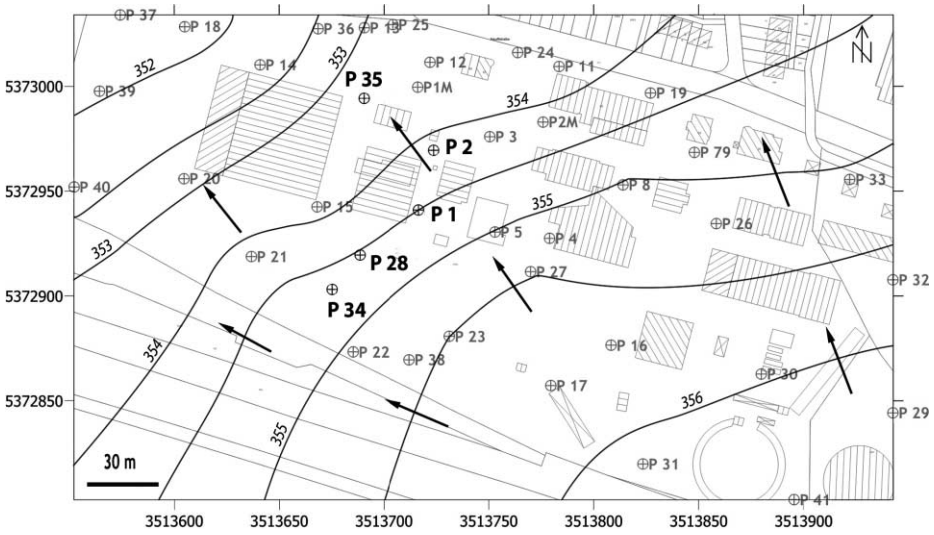

Figure 1 Groundwater isolines at the former gasworks site with arrows showing groundwater flow direction

concentrations from groundwater were quantified by the sulfide assay (Cline and Broenkow, 1969), Fe^{2+} concentrations by the ferrozine assay (Stookey, 1970).

Most probable number technique. The most probable number technique (MPN) was used to enumerate viable Fe(III)-, sulfate- and nitrate-reducing bacteria in groundwater samples from five wells with naphthalene contaminations (P1, P2, P28, P34 and P35; Figure 1). MPN analyses were performed in anoxic, bicarbonate-buffered medium. The medium contained (per litre of distilled water) 0.3 g NH_4Cl, 0.025 g $MgSO_4$ $7H_2O$, 0.4 g $MgCl_2{\cdot}6H_2O$, 0.6 g KH_2PO_4 and 0.1 g $CaCl_2{\cdot}2H_2O$. After autoclaving and cooling under N_2/CO_2 (90/10, vol/vol) atmosphere, 30 mM $NaHCO_3$, seven vitamin solution (1 ml), mixture of eight trace elements (1 ml) and a selenite-tungstate solution (1 ml) (Widdel and Bak, 1992) were added. The pH was adjusted to 7.0. Anoxic medium was supplemented with a mixture of formate (10 mM), acetate (5 mM), propionate (2 mM) and butyrate (2 mM) as substrates. Since MPN analyses were intended to estimate numbers of Fe(III)-, sulfate- and nitrate-reducing bacteria, the medium was supplemented with suitable electron acceptors: ferrihydrite (5 mM), sulfate (2 mM) and nitrate (2 mM). MPN tubes were incubated at 20 °C in the dark for 12 weeks. After 12 weeks of incubation, the pattern of positive and negative tubes was documented, and a standardized MPN table was consulted to determine the most probable number of organisms (causing the positive results) per unit volume of the original sample (De Man, 1975). The estimation of density is based on an application of the theory of probability (Cochran, 1950).

Monitoring microbial growth of anaerobic bacteria. Microbial activity in the tubes inoculated for the MPN studies was checked throughout the period of twelve weeks. Bacterial activity in tubes with sulfate or nitrate as electron acceptors was visually observed (by turbidity increase). In addition, bacterial growth was determined by measuring the optical density with a spectrophotometer (SPECOL 1300, Analytik Jena AG, Jena, Germany) at a wavelength of 578 nm. Sulfate reduction was monitored by sulfide production (sulfide assay, Cline, 1969). Ferrihydrite reduction was monitored by Fe^{2+} production (ferrozine assay, Stookey, 1970). Nitrate reduction and nitrite production were checked using nitrate and nitrite indicator stripes (Merckoquant® Merck KGaA, Darmstadt, Germany). After four weeks of monitoring, tubes that showed the most prominent nitrate-, sulfate-, or ferrihydrite reduction in the highest dilution step were selected for further enrichment under the same condition as for the MPN analyses. After four weeks these enrichment cultures were used for the growth experiments with naphthalene as the sole carbon source and electron donor.

Growth experiment with naphthalene as the sole carbon source and electron donor. Enrichment cultures of Fe(III)-, sulfate-and nitrate-reducing bacteria which exhibited the highest microbial activity were chosen for incubation with naphthalene as the sole carbon source and electron donor in the presence of the solid adsorber resin Amberlite XAD-7 as described in Meckenstock *et al*. (2000). After an equilibration period of five days electron acceptors - sulfate (2 mM), nitrate (2 mM) and ferrihydrite (5 mM) were added via syringes followed by addition of 10% inoculum. All serum bottles were stored in the dark at 20 °C and bacterial growth was checked in one week intervals. Substrate utilization was monitored as sulfide production (sulfide assay), Fe^{2+} production (ferrozine assay), nitrate consumption (via nitrate stripes) and as substrate (naphthalene) depletion. Sampling for naphthalene concentration measurements was performed by taking 1 ml of the medium with a syringe through the Viton stoppers and

adding 1 ml cyclohexane. These samples were shaken for 1 hour at 240 rpm and the measurements were performed directly from the cyclohexane phase.

Stable carbon isotope analyses. Compound-specific stable carbon isotope analyses were carried out by a gas chromatograph (Thermo Finnigan, Milan, Italy) coupled to an isotope ratio mass spectrometer (DeltaPLUS XP, Thermo Finnigan MAT, Bremen, Germany) via a combustion interface (GC Combustion III, Thermo Finnigan MAT, Bremen, Germany) maintained at 940 °C (GC/C/IRMS). The gas chromatograph was equipped with a programmable temperature vaporizer (PTV) injector (Optic 3, ATAS GL International B.V., Veldhoven, Netherlands). The analytical separation was carried out with an Rtx-VMS capillary column (60 m × 0.32 mm, 1.8 μm film thickness; Restek Corp., Bellefonte, PA) with helium 5.0 (Air Liquide, Düsseldorf, Germany) as carrier gas with a constant flow of 1.5 ml/min. For the isotope analyses, target compounds were extracted using the solid phase microextraction technique (SPME). Solid phase microextraction was performed by the direct immersion of an 85 μm Carboxen/polydimethylsiloxane (PDMS) fiber (Supelco, Bellefonte, USA) into an aqueous solution.

Bioscreen. The analytical transport model Bioscreen was used for the simulation of the NA processes such as in-situ biodegradation (U.S. EPA, 1996). The Bioscreen software is based on the three-dimensional analytical transport model of Domenico (1987). It accounts for the effects of advective transport, three-dimensional dispersion, adsorption and first-order decay. Initial conditions were:

1. $c(x, y, z, 0) = 0$ (Initial concentration $= 0$ for $x, y > 0$, where "x" represents the distance downgradient of the source, "y" represents the distance from the centreline of the source and "z" represents the distance from the surface to the measurement point and it is assumed to be equal to zero, since in the Bioscreen software the solute concentrations are always assumed to be at top of water table).
2. $c(0,Y,Z,0) = C_o$. (Source concentration for each vertical plane source $= C_0$ at time 0, where Y and Z are width and depth of the source).

The key assumptions in the model were:

- The aquifer and flow field are homogeneous and isotropic.
- The groundwater velocity is fast enough that molecular diffusion in the dispersion terms can be ignored.
- Adsorption is a reversible process represented by a linear isotherm.

Boundary condition assumes an infinite, fully penetrating source of constant concentration, perpendicular to the groundwater flow.

An average scenario is considered in the current study. The average scenario was assumed to be the case when the average values for hydraulic conductivity ($k = 2.3 \times 10^{-5}$ m/s), average fraction of organic carbon ($f_{oc} = 0.042$), and an average of reported first-order decay rates for naphthalene (Howard *et al.*, 1991), $\lambda = 1.8\ a^{-1}$ were considered. Measured naphthalene concentrations in July 2006 in wells P2, P1 and P28 were input concentrations. It was assumed that the maximum plume length was reached when the naphthalene concentration was below 0.0001 mg/L.

Simulation time was 56 years equal to the time period of gas manufacturing.

Results and discussion

In the central part of the former gasworks site investigated in this study (wells P1, P2, P28, P34 and P35; Figure 1), elevated concentrations of naphthalene and benzene were found (Table 1). The highest concentrations of both naphthalene and benzene were found

Table 1 Naphthalene and benzene concentrations measured in two sampling campaigns

Well	Naphthalene (mg/L)		Benzene (mg/L)	
	Sep. 05	Jul 06	Sep. 05	Jul 05
P35	0.00047	0.00004	0.024	0.019
P2	9.4	2	3.2	3.1
P1	0.38	0.13	0.1	0.1
P28	0.01	0.014	0.052	0.038
P34	0.00011	0.00023	0.045	0.17

in well P2 where also a coal tar phase was observed. The area in close vicinity of this well was therefore considered to be the contaminant source.

Dissolved oxygen concentrations in wells P1, P2, P28, P34 and P35 range from 0.3 to 3.0 mg/L (Table 2). The high oxygen concentrations in wells P2 (2.0 mg/L) and P28 (3.0 mg/L) are most probably measurement artifacts due to the sub-optimal sampling procedure possible at these wells (see methods). Low oxygen concentrations (<1 mg/L) in wells P1 and P35 in combination with the negative redox potentials ranging from -54 to -183 mV in samples from the same wells indicate anoxic conditions.

Naphthalene and benzene concentrations measured in July 2006 are compared to concentrations measured about 1 year earlier, i.e. in September 2005 (Table 1).

The naphthalene concentrations measured in July 2006 (wells P2, P1 and P35) are mostly lower compared to the concentrations in the same wells measured in September 2005 (Table 1). Only slight changes were detected for the benzene concentrations in 2006 compared to the previous campaign in September 2005, except for well P34 where the benzene concentrations were slightly higher in 2006 (Table 1). The highest benzene and naphthalene concentrations were measured in both years in well P2, indicating that the coal tar (a possible naphthalene source) is related to the former benzene distiller facilities (a possible benzene source). We also observed that the benzene concentrations decrease along the groundwater flow line from the source zone (P2) to the next downgradient well (P35) potentially indicating the presence of natural attenuation processes.

Concentrations of possible electron acceptors and dissolved reduced species potentially stemming from the anaerobic degradation of contaminants were measured in July 2006 and are shown together with the data obtained 10 months earlier (September 2005) in Table 2.

Increased sulfide concentrations in wells P28, P2 and P1 (Table 2) indicate the activity of sulfate-reducing microorganisms. Likewise the increased ferrous iron concentration in the downgradient well P35 suggests iron-reducing microbial activity. The decrease of nitrate concentrations in wells P2 and P1 from 2005 to 2006 probably indicates the activity of nitrate-reducing bacteria. A detailed delineation of redox zones was impossible due to the lack of more monitoring wells in the centerline and close to well P2.

Table 2 Concentrations of possible electron acceptors and dissolved reduced species potentially stemming from the anaerobic degradation of contaminants

Well	O_2		NO_3^-		NO_2^-		Fe^{2+}		SO_4^{2-}		S^{2-}	
	Sep. 05	Jul 06	Sep. 05	Jul 06	Sep. 05	Jul 06	Sep. 05	Jul 06	Sep. 05	Jul 06	Sep. 05	Jul 06
P35	0.2	0.3	<0.5	0.47	0.01	1.4	6.6	3.78	81.6	98	<0.01	<0.0004
P2	0.2	2	9.02	<0.5	0.6	1.8	1.2	0.54	254	174	0.18	0.28
P1	0.4	0.5	50.6	10	0.53	2.6	0.81	0.19	411	363	0.12	0.05
P28	0.7	3	<0.5	0.94	0.06	1.8	0.26	2.04	61.9	88	3.2	0.44
P34	0.2	2.8	151	29	0.3	1.5	0.39	0.92	218	141	<0.01	0.04

Sulfide concentrations that are high in the source well P2 increased from 0.18 mg/L (measured in September 2005) to 0.28 mg/L (measured in July 2006). In combination with the decreasing naphthalene concentrations measured in these wells (Table 1), this could indicate naphthalene degradation coupled to sulfate reduction. Degradation of naphthalene by sulfate-reducing bacteria was described by Galushko *et al.* (1999) and Meckenstock *et al.* (2000) and therefore there is a high probability that a similar process is occurring at the site investigated in this study.

In order to quantify the numbers of Fe(III)-, sulfate- and nitrate-reducing microorganisms, most probable number studies were performed. After twelve weeks of incubation all tubes with observed microbial activity were marked positive and a standardized MPN table was consulted to determine the most probable number of organisms per volume of the original sample (De Man, 1975). Table 3 summarizes the results obtained for the field site studied.

In most of the wells the estimated number of nitrate-reducing bacteria is in about the same range as the number of sulfate-reducers. Exceptions are wells P34 (where nitrate-reducers dominate) and P35 (where sulfate-reducers dominate). In comparison to nitrate- and sulfate-reducing bacteria, the numbers of Fe(III)-reducing bacteria are 2–4 orders of magnitude lower in all samples from the investigated site. Similar low numbers of Fe(III)-reducers for a comparable field site were reported previously (e.g. Struchtemeyer *et al.*, 2005).

Comparing the geochemical parameters (Table 2) and MPN counts of microorganisms (Table 3), one can see that the highest number of sulfate-reducing bacteria in the samples from wells P1, P28 and P2 correspond with the highest sulfide concentrations measured in the same wells potentially indicating pollutant degradation coupled to sulfate reduction, which could have caused the measured sulfide concentrations. High numbers of nitrate-reducing bacteria in the wells P1, P2 and P28 (Table 3) correlate with the highest nitrite concentrations measured in those wells (Table 2) indicating a potential for nitrate reduction, which could have caused the measured nitrite concentrations. The geochemical parameters and microbial counts also fit nicely in well P35 where nitrate-reducers are the least abundant and where we measured the lowest nitrite concentration (Tables 2 and 3). The estimated numbers of Fe(III)-reducers were low (in comparison with other microorganisms) in all samples. The number of Fe(III)-reducers was highest in well P28 where also one of the highest Fe^{2+} concentrations was measured (Tables 2 and 3). The comparisons of MPN counts with geochemical parameters (products of microbial respiration: sulfide, Fe(II) and nitrite) showed a good correlation for all three metabolisms analyzed, i.e. microbial respiration of sulfate, Fe(III) and nitrate.

In order to determine whether the MPN-counted sulfate-, nitrate-, and iron(III)-reducing microorganisms are able to degrade the organic pollutants at the investigated site, degradation experiments with naphthalene as the sole carbon source and electron donor were performed. Fresh anoxic medium was inoculated in parallel setups with freshly enriched cultures from either the iron(III)-, sulfate- and nitrate-reducing MPN counts. Naphthalene was added together with the absorber Amberlite XAD-7 as described in Meckenstock *et al.* (2000). The XAD-7 resin was used to keep the naphthalene concentrations low.

Table 3 Estimated numbers of anaerobic bacteria per milliliter of groundwater sample

Well	Nitrate-reducers	Silfate-reducers	Fe(III)-reducers
P1	1.1×10^7	$>2.4 \times 10^7$	1.5×10^3
P2	4.6×10^6	2.4×10^6	2.4×10^2
P28	4.6×10^6	4.6×10^6	2.4×10^4
P34	1.5×10^6	4.3×10^5	7.3×10^2
P35	9.3×10^4	2.4×10^6	2.4×10^2

Naphthalene utilization was monitored in the following six weeks by measuring the naphthalene concentrations, sulfide and Fe(II) production and by examining nitrate concentrations. At the end of the sixth week, naphthalene concentrations did not show any significant differences to the initial naphthalene concentrations and the ferrous iron, sulfide and nitrite concentrations were below detection limits. This showed that, at least within the time period investigated, the added ferrihydrite, sulfate and nitrate could not be used by the enriched bacteria to oxidize a significant amount of naphthalene.

In order to determine whether the decreasing concentrations of the contaminants at the field site were caused by microbial degradation or by an abiogenic process such as sorption, $\delta^{13}C$ values were measured in the residual naphthalene and benzene. Measurements were carried out in triplicates and the mean values are presented in Table 4.

Since the naphthalene concentrations in samples P28, P34 and P35 were significantly lower, only the mean carbon isotope ratios of naphthalene for wells P2 and P1 could be measured.

The carbon isotope ratio for naphthalene of the sample P1 is slightly less negative that the one of the sample P2. However, both values are within the error of the measurement (0.5 ‰). Because of the low naphthalene concentrations in the other wells, carbon stable isotope analyses did not give a qualitative or quantitative parameter of naphthalene biodegradation at the site due to a lack of carbon isotope data in wells downstream from the source (e.g. P35).

Compound specific carbon stable isotope measurements of benzene from the five chosen wells are given in Table 4. An isotope shift (−3.19 ‰) was observed in the residual benzene fraction along the groundwater flow path (between wells P2 and P35) showing that benzene underwent isotope fractionation of carbon isotopes. Isotope fractionation is accompanied by benzene concentration decrease (from 3.1 mg/L in well P2 to 0.019 mg/L in well P35, Table 1) and dissolved ferrous iron concentration increase (from 0.54 mg/L in well P2 to 3.78 mg/L in well P35, Table 2). From the literature it is known that benzene can be oxidized under anoxic iron-reducing conditions in the field (e.g. Lovely *et al.*, 1996; Nales *et al.*, 1998) but a pure culture has not been described yet. Previous facts and literature data indicate a high possibility that benzene is biodegraded by Fe(III)-reducing bacteria at our field site. Carbon isotope ratios in wells P1 and P2 are very close suggesting that benzene contamination in wells P1 and P2 derives from the same source. Since $\delta^{13}C$ values in samples P1 and P2 are significantly lighter from the ones measured in wells P28 and P34, two wells that are not downstream of P1 and P2 (Figure 1 and Table 4), we suggest that two multiple-point benzene contamination sources might exist: one causing benzene contamination in wells P1 and P2 and the second causing contamination in wells P28 and P34.

In order to study the transport behavior of naphthalene three different types of analytical transport models were considered in the present study, (1) sorption and no biodegradation, (2) sorption and biodegradation using the first-order decay model and (3)

Table 4 $^{13}C/^{12}C$ ratios expressed as $\delta^{13}C$ signature in residual naphthalene and benzene

Well	Naphthalene $\delta^{13}C$			Benzene $\delta^{13}C$		
	Conc. (mg/L)	mean (‰)	SD (–)	Conc. (mg/L)	mean (‰)	SD (–)
P35	0.00004	n.d.		0.019	−22.29	0.03
P2	2.00	−24.48	0.23	3.10	−25.48	0.07
P1	0.13	−23.90	0.04	0.10	−25.66	0.04
P28	0.014	n.d.		0.04	−24.73	0.03
P34	0.00023	n.d.		0.17	−24.34	0.08

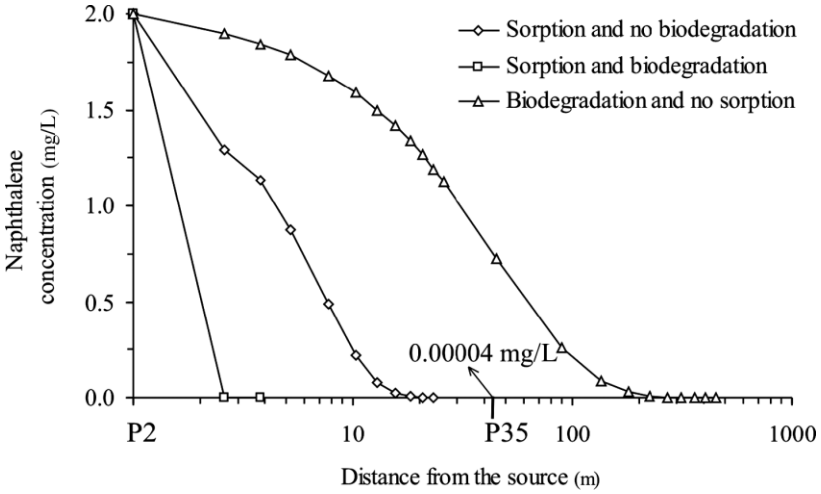

Figure 2 Plume extension and naphthalene concentration along the centreline for sorption and no biodegradation, sorption and biodegradation, and biodegradation and no sorption, considering average scenario

biodegradation and no sorption. The results for naphthalene along the centreline of the plume are shown in Figure 2. Naphthalene concentrations reached a value of 0.0001 mg/L, (set to be the concentration when the naphthalene plume diminishes) after approximately 5 meters from the source for sorption and biodegradation. In the case when only sorption was considered, the naphthalene plume diminished at approximately 25 m downgradient from the source. In case when only biodegradation but no sorption was assumed, the naphthalene plume reaches almost 450 m (Figure 2). Comparison of the simulated concentrations with measured naphthalene concentration in the next downgradient well (P35) from the source zone showed that only two models could be valid: (1) sorption and no biodegradation and (2) sorption and biodegradation. Discrimination between those two models was not possible due to the lack of monitoring wells downgradient and in close vicinity from the source zone. Since the concentration in the next downgradient well, situated 41.5 m from the source zone was 0.00004 mg/L, (lower than Bioscreen predicts as the minimum concentration in naphthalene plume), the third model, for which only biodegradation and no sorption were assumed, appeared to be not valid.

Conclusions

Geochemical parameters observed in the central part of the former gasworks site close to the contaminant source zone and decreasing contaminant concentrations indicate active biodegradation at the site. Increased concentrations of dissolved ferrous iron observed in groundwater downgradient from the source zone (P35) indicated potential for microbial degradation of contaminants by Fe(III)-reducing bacteria. Likewise, increased sulfide and nitrite concentrations in wells P28, P2 and P1, together with high estimated numbers of sulfate- and nitrate-reducing bacteria (10^6–10^7 ml^{-1} in groundwater samples) indicate potential biodegradation by sulfate- and nitrate-reducing bacteria. Nevertheless, the laboratory experiments with Fe(III)-, sulfate-, and nitrate-reducing enrichment cultures from groundwater samples from the site did not show significant naphthalene degradation within six weeks of incubation.

The results of the analytical transport model Bioscreen also demonstrate the natural attenuation of naphthalene at the site. According to the simulations, the naphthalene plume does not extend more than approximately 25 m from the source if no biodegradation

is considered, which is mainly due to the high sorption of naphthalene. If biodegradation is considered, the maximum plume length would be only around 5 m. The analytical transport model when only biodegradation but not sorption is assumed results in around 450 m plume length, which was not measured in the field (e.g. in the well P35); hence the last model is not valid.

Naphthalene degradation could not be verified by carbon stable isotope analyses (CSIA) due to low naphthalene concentrations downgradient from the source. However, carbon isotope measurements of benzene from the central part of the investigated site showed a significant isotopic shift between the sample from the source zone (P2) and the one from the next downgradient well (P35). This showed that microbial degradation of benzene is occurring in the groundwater at the site.

From the current study we conclude that an extension of the groundwater monitoring well network is necessary and in particular downgradient of the contaminant source. In addition, we recommend the monitoring of naphthalene and benzene concentrations 3 to 4 times per year to rule out any artifacts due to seasonal changes. Otherwise it will not be possible to implement Monitoring Natural Attenuation (MNA) for the site.

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