Beneficial effects of dynamic groundwater flow and redox conditions on Natural Attenuation of mono-, poly-, and NSO-heterocyclic hydrocarbons

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ABSTRACT

Natural Attenuation (NA) processes have been demonstrated to reduce pollutant loads at different contaminated groundwater sites world-wide and are increasingly considered in contaminated site management concepts. However, data are mainly available for steady state groundwater flow and stable redox conditions as well as pollutants listed in standard regulatory schemes. In this study, the influence of transient groundwater flow and redox conditions on NA was examined at a former gas works site near the river Rhine in Germany. The investigated 78 pollutants included 40 mono- and polyaromatic hydrocarbons (MAHs, PAHs) and 38 NSO-heterocyclic aromatic hydrocarbons (NSO-HET). In the highly polluted areas, the MAHs benzene, indene and indane, the PAHs naphthalene, acenaphthene, 1- and 2-methylnaphthalene and the NSO-HET 2-methylquinoline, carbazole, benzothiophene, dibenzofuran and benzofuran were predominant. Pollutant concentrations decreased with increasing distance from the sources of contamination. At the plume fringes, the MAHs benzene and indane, the PAH acenaphthene, the NSO-HET carbazole, 5-methylbenzothiophene, 2- and 3-methylbenzofuran and 2-methyl-dibenzofuran were predominant, indicating low retention and slow intrinsic biodegradation of these compounds. The influence of surface water on groundwater level, pollutant concentrations, and redox conditions in the monitoring wells was observed with a permanently installed groundwater sensor. The temporary availability of oxygen was observed at the plume fringes, resulting in aerobic and ferric iron reducing biodegradation processes. Field and laboratory data were used to set-up a groundwater flow and reactive transport model used for quantification of the field mass transfer rates. In conclusion, the study demonstrates that NA is effective under transient flow and redox conditions. A conceptual model and reactive transport simulation can facilitate the interpretation of pronounced fluctuations of pollutant concentration in monitoring wells. Based on the analysis of 78 pollutants, indane, indene and several NSO-HET like carbazole, benzothiophene and 2-methyl-dibenzofuran are recommended for monitoring at tar oil polluted sites, besides EPA-PAHs and BTEX.

1. Introduction

Tar oil processing plants, gasworks sites and abandoned deposit sites containing gasworks residues have caused a large number of long-lasting soil and groundwater contamination issues. Natural attenuation (NA) is defined as a wide range of processes happening without human intervention such as evaporation, dilution, biodegradation and adsorption. Similarly, monitored natural attenuation means the extensive monitoring of the natural processes in soil and groundwater (Brown et al., 2017; U. S. EPA, 1999). Monitored Natural Attenuation (MNA) concepts became a reliable and economic method to manage a wide range of contaminated sites in Germany and other parts of the world (Declercq et al., 2012; Rügner et al., 2006). The crucial process of MNA-concepts is microbial degradation as it leads to an effective reduction of pollutant loads at contaminated sites (Schulze and Tiehm, 2004). During bioremediation processes, organic pollutants serve as carbon sources whereas oxygen, nitrate, ferric iron, sulfate and carbonates are used as electron acceptors. The energy yield differs strongly depending on the available electron acceptor. The most powerful electron acceptors are oxygen and nitrate followed by ferric iron (Borch et al., 2010; McMahon et al., 2011; 

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must continuously follow or re-establish in other strata. Those or shrinking and degradation needs to be proved (Blum et al., 2011; Scholl et al., 2006) observed that besides biodegradation seasonal groundwater recharge was the most important factor controlling the distribution of hydrocarbon contaminants within a sandy aquifer. Fritz and Arntzen (2007) demonstrated a relationship between hydraulic gradient changes due to river fluctuations and uranium fluxes discharging to the river. Meckenstock et al. (2015) described that biodegradation activity was controlled by the availability of specific electron acceptors, rather than by thermodynamics. Under transient conditions a better distribution of electron acceptors in an aquifer is feasible.

Different effects of transient groundwater conditions on NA are possible: In most cases, the surface water will contain higher concentrations of dissolved electron acceptors such as nitrate, sulfate or oxygen than the corresponding contaminated aquifer. Recharge of those electron acceptors to the aquifer could thus have a positive effect on NA. Scholl et al. (2006) described the effect of seasonal changes of sulfate concentrations in a shallow alluvial aquifer, the water of the Canadian River near the site is seen as one of the main natural sources of sulfate in the groundwater. This kind of recharge is not only related to the influence of surface waters. van Stempvoort et al. (2007) described a seasonal infiltration of snowmelt water, recharging the groundwater table and replenishing the contaminated zone with sulfate. Decreasing sulfate concentrations in the contaminant plume accompanied with an enrichment of sulfur isotope 34S indicated that sulfate reduction was a dominant terminal electron-accepting process in the natural attenuation of the hydrocarbon plume in the ground water. Wei et al. (2018) demonstrated that the implementation of monitoring approaches with isotopic and molecular-biological procedures can improve the understanding of sulfate reductions processes in petroleum hydrocarbon contaminated groundwater as additional line of evidence. Recharge of dissolved electron acceptors, whether due to an infiltration of surface water or groundwater formation can improve natural attenuation processes.

Additionally, the respiration product ferrous iron could be oxidized into ferric iron, also an efficient electron acceptor. For example, Cozzarelli et al. (2011) summarized results of 10-year study of an leachate-affected aquifer and demonstrated with chemical and isotopic data from different monitoring strategies that measurable rates of Fe reduction are consistent with the advance of the leachate plume into sediments in which relatively labile Fe(III) oxides were incompletely reduced as well as the regeneration of Fe(III) phases near the water table. They confirmed groundwater / surface water interactions and temporal variations in hydrologic flow need to be considered. In the other hand, anaerobic bacteria do not have oxygen as their ability to survive in the presence of oxygen (Pu et al., 2015; Emlay, 2013). A predominantly anaerobic microbial population could therefore suffer from frequently changing redox conditions and microbial degradation processes could be diminished due to infiltration of oxygen-rich surface water into an aquifer. Meckenstock et al. (2015) pointed out that if the prevailing geochemical conditions for microorganisms shift, degraders must continuously follow or re-establish in other strata. Those geochemical shifts could lead to kinetic limitation of biodegradation.

These aspects also play an important role when it comes to Enhanced Natural Attenuation (ENA) e. g. when oxygen is injected in an anaerobic aquifer as an electron acceptor. Not only the primary contaminant degradation but also competing mineral precipitation must be considered. However, increasing degradation rate constants were observed with the availability of oxygen (Herold et al., 2011).

In general, for remediation of tar oil contaminated sites standard risk assessment protocols require the analysis of only a small subset of pollutants namely the 16 EPA-polyaromatic hydrocarbons (PAHs) and 6 monoaromatic hydrocarbons (BTEX). Tar oil contains thousands of organic (PAHs, volatile aromatic compounds, phenols) and inorganic substances (inorganic compounds of sulfur and nitrogen, metals), partly with high toxic potential and persistence to biodegradation (Logeswaran et al., 2018). In recent years, the importance of increased analytical efforts to identify and monitor additional key compounds was demonstrated (Andersson and Achten, 2015a, 2015b), e.g. in case of NSO-heterocyclic aromatic hydrocarbons (NSO-HET) for MNA conditions (Blum et al., 2011). The contamination of groundwater in such cases is dominated by the water-soluble fraction of the coal tar. Due to their toxicity and higher polarity, heterocyclic compounds, containing nitrogen, sulfur or oxygen, are increasingly included in monitoring programmes in addition to BTEX and PAHs (Blum et al., 2011). In the German federal soil protection ordinance, the critical value for EPA-PAHs and “other relevant PAHs such as quinoline” is defined with 0.2 µg/L. The occurrence and distribution of NSO-HET at tar oil contaminated sites has been investigated and presented in different studies (Blum et al., 2011; Tiehm et al., 2008). Blum et al. (2011) pointed out, that the comparison of three tar-oil contaminated sites in Germany showed longer plume lengths for NSO-HET than for PAHs. Ecotoxicity, mutagenicity, dioxin like and estrogenic activity of at least some NSO-HET or their metabolites as well as the monoaromatic hydrocarbons indane and indene are already known and characterized (Brinkmann et al., 2019a; Brinkmann et al., 2019b; Brinkmann et al., 2014a; Brinkmann et al., 2014b; Eisentraeger et al., 2008; Peddinghaus et al., 2012). However, NSO-HET are not yet included in standard risk protocols. Beside NSO-HET, methylated naphthalenes and the monoaromatic carbocycles indane and indene are often reported at tar oil contaminated sites (Mundt and Hollender, 2005; Schulze and Tiehm, 2004), but also not included in standard risk protocols. Toxicity tests on marine plankton organisms showed toxic effects towards different naphthalenes. Methylated naphthalenes were more toxic than naphthalene. The toxicity was not dependent on the number of methyl groups, but rather on their position on the naphthalene molecule (Falk-Petersen et al., 1982).

This study focused on the characterisation of microbial degradation processes under transient groundwater flow and variable redox conditions at a tar oil contaminated site, located in the upper Rhine valley, south-west Germany. The combination of field investigations, laboratory studies and numerical modelling of groundwater flow and contaminant transport was applied to assess the influence of groundwater/surface water interactions on NA processes. Furthermore, for the first time the degradation potential of nearly 80 tar oil pollutants was investigated to identify key constituents important for monitoring at tar oil contaminated sites.

2. Materials and methods
2.1. Site description and sampling

The gasworks site considered in this study was operated from 1867 to 1937. It is located in the upper Rhine valley, south-west Germany. The production wastes of the gasworks were reused in a nearby impregnation site for railroad ties and served as levelling material in urban development. Source of contamination is the gasworks area itself and two secondary sources, an impregnation site where tar-oil products were used and a former pond, filled with gasworks residues. Soil and
groundwater are contaminated with typical tar oil pollutants, i.e., MAHs, PAHs, NSO-HET as well as phenols. In the years 2010 / 2011 removal of hot spots by excavating polluted material from the former gasworks site took place. In total 28 groundwater monitoring wells were set up, covering the entire source and plume areas of the site, and thus allowing for comprehensive monitoring. The three source areas of contamination are located to the west (between 150 m and 250 m) of the receiving surface water, the river Rhine (Fig. 1) flowing past the site at the east. In the west, the site is partly surrounded by a cut-off meander of the river Rhine and another small surface water called Queich. The shallow aquifer consists of sand and gravel layers representing a highly conductive aquifer typical for the upper Rhine valley. The average depth to groundwater is 4.5 m. The thickness of the polluted aquifer ranges from 9 to 15 m with silt and clay layers of low permeability underneath, separating the shallow aquifer from the deeper one. The average value for hydraulic conductivity for the area is about $2 \times 10^{-3}$ m/s.

Groundwater sampling at the field site was performed with a Grundfoss MP1 pump according to general guidelines (ISO, 2009). Samples for chemical analysis were regularly taken over a period of three years between October 2010 and April 2013. All samples were stored at 4°C in the dark for up to 24 h prior to analysis.

2.2. Chemical analysis of tar oil pollutants

Samples for MAH-, PAH-, and NSO-HET-analysis were prepared using liquid – liquid extraction: 45 mL of the groundwater sample were spiked with 10 μL internal standard (toluene-d$_8$ and naphthalene-d8) and 5 mL MTBE, and extracted for 20 min. After phase separation, the extract was dried using sodium sulfate and subsequently analysed by gas chromatography (Agilent technologies GC 6890N). The GC was equipped with an auto sampler (Agilent technologies) and a mass selective detector (Agilent Technologies MS 5973 Network) operated in SIM (Single Ion Monitoring) mode. Separation of the substances took place by a ZB-5 Inferno column (60 m × 0.25 mm × 0.25 μm) by Phenomenex. Limits of detection are listed in table 2 of the supplementary data. The relative deviation of standard procedure ($S_{NR}$) amounted to ±10%, regression coefficients ranged from 0.985 to 0.997.

All used chemicals were of p.a. chemical purity. All substances were purchased from abcr (Karlsruhe, Germany), Sigma (Deisenhofen, Germany), Alfa Aesar (Karlsruhe, Germany), Ehrenstorfer (Augsburg, Germany) or Merck (Darmstadt, Germany).

2.3. Detection of ferrous iron and sulfate reducing bacteria

Ferrous iron and sulfate reducing bacteria were examined by the most-probable-number (MPN) method as described by Steiber et al. (1994) and Tiehm and Schmidt (2007). Ferric iron reducing bacteria were detected by the formation of the respiration product ferrous iron that forms a red complex after bipyrindin addition. Sulfate reducers were detected by iron sulfide precipitation after sulfide formation. Incubation and detection methods for ferric iron and sulfate reducing bacteria are described by Schulze and Tiehm (2004) and Stieber et al. (1994).

2.4. Hydrochemical parameters and multiparameter sensor

During groundwater sampling oxygen was analysed on-site by electrode measurements in a flow-through chamber (limit of detection: 0.1 mg/L). Nitrate (limit of detection: 1.0 mg/L), nitrite (limit of detection: 0.5 mg/L) and sulfate (limit of detection: 1.0 mg/L) were analysed by ion chromatography (Metrohm) as described by Zhao et al. (2010). Rapid test kits (Macherey & Nagel) were used for sulfide, ferric and ferrous iron quantification (limit of detection: 0.01 mg/L).

Automated monitoring of groundwater level and redox conditions was achieved by installing a multiparameter water quality sensor YSI 600XLM-V2-S (EcoTech Umweltmesssysteme GmbH, Bonn) in observation well GWM 17 which is situated approximately 100 m to the west of the river Rhine (Fig. 1). Oxygen concentration (mg/L), redox potential (mV), pH and conductivity ($μS/cm$) of the groundwater as well as the water level in the well were monitored every six hours and recorded continuously over a period of two years.

2.5. Pollutant biodegradation in microcosms

For the microcosm studies in the laboratory, autoclaved 2 L glass bottles were flushed with nitrogen before sampling. Groundwater samples were filled directly into the bottles used for incubation. A stock solution was prepared by mixing MAHs, PAHs and NSO-HET and dissolving them in each other. This resulted in widely differing concentrations of the substances (e.g. indane 80 and toluene 650 μg/L). As Acenaphthene was found in high enough concentrations of 30 μg/L in the groundwater samples this compound was not added to the stock solution. The experimental design included three active processes and one sterile control to distinguish abiotic processes. Anaerobic experiments were conducted in a nitrogen flushed anaerobic chamber. During the anaerobic phase of the experiments, the microcosms were stored in vessels containing anaerogenic bags (AnaeroGen from Oxoid, Germany) to diminish traces of oxygen and an oxygen indicator (Anaerobic indicator from Oxoid, Germany). The AnaeroGen bag rapidly absorbs the atmospheric oxygen present in the storage vessels and simultaneously evolves carbon dioxide. Samples were taken with glass syringes through a Teflon-coated septum. Fe(II) in form of iron hydroxides (FeOOH) was supplied as described in Schulze et al., (2004). Fe-reducing conditions
were maintained for 310 d. After that period, oxygen was added in order to simulate aerobic field conditions. Aerobic conditions were induced by repetitive dosage of air. The microcosms were incubated at 20 °C ± 2 °C for 445 d. The sterile control was inhibited by poisoning with sodium azide.

2.6. Groundwater modelling

In order to consider hydraulic effects at the gasworks site in combination with the experimental findings on degradation processes, a transient groundwater flow and contaminant transport model was developed. The USGS-tool MODFLOW 2005 (McDonald and Harbaugh, 1988) and the transport model MT3DMS (Zheng and Wang, 1999) were applied to simulate groundwater heads and pollutant concentrations. The PMWIN environment model (Chiang, 2016) was used for pre- and post-processing of parameters and results.

The model simulations were run from October 2010 to April 2013. The pollutants considered in the transport model were acenaphthene, naphthalene, benzene, benzo(a)pyrene, dibenzofuran, carbazole, and 2-methylindole, covering typical substance classes found at the site.

The aim of the model application was to reproduce the interaction of hydraulic and hydrochemical processes and to quantify the effect of this interaction on contaminant release and degradation.

The model area stretched over 9 km in south-north direction and 8 km in west-east direction and was thus much larger than the actual gasworks site. Embedding the site into a larger flow model domain was necessary to minimize spurious boundary effects on model results.

In the vertical direction, the model covered the shallow aquifer with the underlying low permeable silt and clay layers acting as an impermeable lower boundary. The aquifer was resolved by an unconfined single model layer. In the vicinity of the gasworks site the aquifer has a saturated thickness of about 10 m to 11 m.

The model domain was resolved with a grid of 10 m by 10 m size around the gasworks site.

The course of the river Rhine, which was close to the gasworks site, formed the eastern boundary of the model area. It was implemented in form of a leakage boundary (3rd type boundary). The smaller watercourses visible in Fig. 1 were treated as 3rd type or leakage boundaries also. The southern, northern, and western boundaries of the model domain were at a distance of 4.5 km to 6.5 km from the gasworks site (not shown in Fig. 1). The western boundary was treated as a fixed head boundary (1st type boundary), the southern and northern boundary as no flux boundaries (2nd type boundaries).

In the transport model, contaminants enter the aquifer via a number of grid cells with a prescribed mass load (mass per time). The contaminant release cells were located manually by a reverse procedure such that the concentrations at the sampling points at the gas works site could be reproduced.

The degradation of contaminants was simulated using a first order degradation model with species dependent rate constants (see Table 5 in the supplement). In order to reproduce contaminant spreading in the model it was not only necessary to consider degradation processes, but also to differentiate between two degradation areas. One is the gasworks site itself and most parts of its downstream area. Here reducing redox conditions prevailed and anaerobic processes presumably governed degradation (i.e. by ferric iron reducing bacteria). In this area lower degradation rates were specified. The other degradation area was the vicinity of the riverbank, where dissolved oxygen was provided by periodic flood events (cf. chapter 3.1.4) and where aerobic degradation processes might develop. The degradation rates specified for the aerobic areas are much higher than those given for the anaerobic areas. This was done to take into account that aerobic degradation is very efficient for the contaminants considered in the model.

3. Results and discussion

3.1. Field studies

3.1.1. Groundwater flow direction

Groundwater levels were recorded at the monitoring wells GWM 1, GWM 10, and GWM 13. The evaluation of the head-time series by hydrologic triangulation for 2.5 years (3636 data points per well) showed a dominant groundwater flow eastward towards the river Rhine for 54% of the overall flow situations during the monitoring period. During flood events of the river, the groundwater flow direction was reversed westward in 11% of the flow situations. Also, any other direction of groundwater flow can occur at the site. The frequency of groundwater flow directions is listed in Table 1 of the supplement information.

3.1.2. Field studies on pollutant patterns

Groundwater samples for chemical analysis were taken at different time points (cf. Section 2.1). Fig. 2 shows the distribution of pollutant concentrations of MAHs, PAHs and NSO-HET during the sampling campaign in May 2012 when the predominant groundwater flow direction was to the west. The data were chosen because the sampling was during high water of the Rhine and demonstrates the influence of the surface water to the groundwater aquifer. A different method of displaying the data is shown in Figs. 1 and 2 of the supplement.

In general, pollutant concentrations were found to be highest in the groundwater of the source areas (GWM 7, GWM 9 and GWM 16). The concentrations in the main eastern directed plume decreased in direction towards the river Rhine.

Fig. 2A shows the predominance of indene and indane in nearly all investigated groundwater wells. In the source areas of contamination, a significant proportion of the total pollutant concentration (25% (GWM 7), more than 75% (GWM 16), nearly 98% (GMW 9)) would not have been quantified by analysing only the standard risk parameters (BTEX). Peripheral ground water wells confirmed these results (GWM 25 and GW 26). The results illustrate that important information on e.g. the length of a plume and the contamination levels of source areas might not be obtained by focusing analysis on the group of BTEX contaminants. These observations are confirmed in previous studies (e.g., Podgorski et al., 2021; Zamfirescu and Grathwohl, 2001). Zamfirescu and Grathwohl (2001) illustrate that concentrations of Alkyl-PAHs, heterocycles and of some presumed metabolites contribute to the overall concentration in the plume of the investigated gas works site.

In the case of the analysed PAHs, pollutant profiles were shifting as the contaminant decreased from the contamination source to the plume (Fig. 2B). Acenaphthene was predominant in most of the groundwater wells (0.1–360 μg/L). Other studies confirm the persistence ofacenaphthene, which is often the only substance within the group of the 16 analysed EPA-PAHs that is still detectable in the contamination plume (Tiehm and Schmidt, 2007; Zamfirescu and Grathwohl, 2001). Naphthalene occurs in high concentrations near the source area of the gasworks site (180 μg/L) as well as in the secondary source wells, i. e. GWM 9 (660 μg/L) and GWM 16 (83 μg/L). The decrease of concentration of this very mobile compound in groundwater of the plume indicate microbiological activity near the source area, limiting groundwater transport of naphthalene. This observation is confirmed by previous studies (Schulze and Tiehm, 2004). In addition to the standard risk parameters (16 EPA-PAHs) 1- and 2-methylnaphthalene were analysed. For 1- and 2-methylnaphthalene an efficient biodegradation under anaerobic conditions is described, the detection of these compounds can be seen as an indicator for contamination sources (Schulze and Tiehm, 2004). In contrast, 1-methylnaphthalene shows higher persistence and was therefore detectable in the plume (between 6.1 μg/L and 25 μg/L). Our results confirm this effect and are consistent with previous studies (Mundt and Hollender, 2005; Tiehm and Schmidt, 2007). In conclusion, the analysis of methylated naphthalenes provides additional information on microbiological degradation processes at...
In addition to the MAHs and PAHs, NSO-HET were also considered in our study (Fig. 2C and D). In total, 38 NSO-heterocycles were examined: 17 N-heterocycles (N-HET), 13 S-heterocycles (S-HET) and 8 heterocycles containing oxygen (O-HET). Comparing the percentage shares of different pollutant groups, O-HET seemed to be relevant in the source area as well as in the plume, N-HET seemed to be relevant especially in the source area and nearby the source area. S-HET accounted for the smallest proportion of the total NSO-HET concentration. Concentrations of many of the analysed N-HET were below the limit of detection (see Table 2 in supplement), including mono-methylated quinolines and isoquinoline. Carbazole was the pollutant found in the highest concentrations, near the sources as well as in many plume-measuring wells, for example in GWM 25 and GWM 26. There were only single findings of quinoline and 2-methylquinoline in the source area. Previous studies confirm the relevance of carbazole (Mundt and Hollender, 2005). Further substances of the group of N-HET were 2,4- and 2,6-dimethylquinoline, acridine and phenanthidine. Evidence of those substances was mainly limited to the source areas.

Benzothiophene accounted for the largest proportion of S-HET in the

Fig. 2. Concentration and pollutant profiles of monoaromatic hydrocarbons (MAHs) (A), polyaromatic hydrocarbons (PAHs) (B), N-heterocyclic compounds (N-HET) (C) and S- and O-heterocyclic compounds (D) in the groundwater samples.
source area, concentrations decreased in the plume. Thiophene was detected solely in or near the source area. Dibenzothiophene, the methylated benzo thiophenes and dibenzothiophenes accounted for the total S-HET pollution in the further groundwater downstream wells. Considering O-HET, only in the source area benzofuran and dibenzofuran accounted for a significant proportion of total O-HET concentration. The wells in the direction of the river were primarily dominated by concentrations of 2- and 3-methylbenzofuran, 2-methyldibenzofuran as well as 2,3-dimethylbenzofuran (Fig. 2D). Similar to the findings of S-HET, the methylated O-HET became more relevant from the source area to the different plume wells. These observations are consistent with previous studies (Tiehm et al., 2008; Tiehm and Schmidt, 2007) and confirmed the importance of the analysis besides the routine parameters such as 16 EPA-PAHs. The heteroatoms within the ring structure induce a higher water solubility for NSO-HET in comparison with their PAH-analogues and NSO-HET are often more persistent towards biodegradation than other coal tar constituents. Therefore, NSO-HET form longer plumes in groundwater than PAHs at some sites. The evaluation of 10 field studies, where the plume lengths of NSO-HET, BTEX and PAHs are reported, indicated higher field-derived half-lives for 2- and 3-methylbenzofuran, 2,3-dimethylbenzofuran, carbazole and benzothiophene as well as for the usually measured pollutants acenaphthene and benzene.

Fig. 3. Oxidation reduction potential (ORP) (A), oxygen concentration (B), ferrous iron (iron (II)) concentration (C), and sulfate concentration (D) in groundwater samples from the sampling campaign May 2012.
Focussing on only the 16 EPA-PAHs and BTEX could lead to an understimation of pollutant concentrations, extent of contamination and the potential risk of exposure (Andersson and Achten, 2015b). Furthermore, the plume length of MAHs, PAHs and NSO-HET at this site was comparatively short (150–200 m). Observed plume lengths at other tar-oil contaminated sites are usually found to be longer than 250 m (Tiehm and Schulze, 2003; Anneser et al., 2008; Blum et al., 2011; Safinowski et al., 2006).

### 3.1.3. Groundwater redox conditions and field studies on patterns of redox-sensitive parameters

The evaluation of redox conditions in groundwater pollution plumes is necessary in order to understand pollutants’ behavior in the plume. But rigorous interpretation of individual oxidation reduction potential (ORP) values are not recommendable because of slow electrode kinetics on the one hand and the common lack of internal equilibrium of redox processes in pollution plumes on the other side (Christensen et al., 2000). To consider predominant groundwater redox conditions at the site samples for hydrochemical parameter analysis were taken. Despite a temporary entry of oxygen the predominant conditions were anaerobic. ORP values are not recommendable because of slow electrode kinetics.

**Fig. 3** shows ORP (Fig. 3A), the oxygen concentration (Fig. 3B), the ferrous iron concentration (Fig. 3C) and the sulfate concentration (Fig. 3D) during the same sampling campaign in May 2012 described in Section 3.1.2 with a westward directed groundwater flow. Redox conditions of the aquifer are mainly anaerobic, resulting in ORP between ~130 mV and ~240 mV (Eh) (Fig. 3A, supplement Table 2). The oxygen concentration was found to be below <0.1 mg/L in most cases, which confirms the anaerobic conditions at this contaminated site. In the groundwater of very few wells oxygen concentrations were determined between 0.1 and 0.5 mg/L, indicating the dynamic conditions (Fig. 3B, supplement Table 2) and an occasional input of oxygen at the site. This occasional input of oxygen close to the riverbank could be demonstrated using a permanently installed multiparameter water quality sensor in one of the groundwater wells (see Section 3.1.4).

The product of Fe(III) reduction, ferrous iron, was detected throughout the whole plume in concentrations from 0.5 to 9.5 mg/L. (Fig. 3C, supplement Table 2). High ferrous iron concentrations are measured at the source areas of contamination, indicating ferric iron reduction. The electron acceptor sulfate was detected in concentrations from 25 to 200 mg/L (Fig. 3D, supplement Table 2). The high sulfate concentrations in the source areas (GWM 7, 153 mg/L, GWM 9, 56.4 mg/L) may be the result of construction waste disposal from the former gas plant buildings. It is feasible that sulfate reduction took place in those areas, but the process was not identifiable on basis of decreasing sulfate concentrations. One explanation could be that the sulfate reduction was inhibited or slowed down by high pollutant concentrations and contaminant matrix regarding to toxic effects in the source areas as described in previous studies (Lerner et al., 2000; Thornton et al., 2001). Nevertheless, the quantification of iron sulfides is difficult because of the precipitation processes of iron sulfides. But sulfate concentration decreased eastward towards the river Rhine, which indicated ferric iron reduction was inhibited or slowed down by high pollutant concentrations, extent of contamination and the potential risk of exposure (Andersson and Achten, 2015b). Furthermore, the plume length of MAHs, PAHs and NSO-HET at this site was comparatively short (150–200 m). Observed plume lengths at other tar-oil contaminated sites are usually found to be longer than 250 m (Tiehm and Schulze, 2003; Anneser et al., 2008; Blum et al., 2011; Safinowski et al., 2006).

### 3.1.4. Dynamics of pollutant concentration and oxygen availability / electron acceptor availability

Pollutant concentrations in the monitoring wells varied throughout the major sampling campaigns. A categorisation in expanding, stable or shrinking plume is not possible by a standard pollutant-monitoring program at sites which are affected by frequent changes in flow conditions. For example, striking differences in concentrations over time were shown for groundwater well GWM 15 located 150 m west of river Rhine that was selected for weekly monitoring (over six months in 2011). This well was located between a contamination source (GWM 16) located 200 m west of the river and the river Rhine. Over a period of six months concentrations of BTEX, indane and indene, EPA-PAHs, 1-methylanthalen, 2-methylanthalen, 1,4-dimethylanthalen as well as 38 NSO-HET were correlated with the surface water level. **Fig. 4** shows the relationship between overall pollutant concentrations of MAHs, PAHs and NSO-HET and surface water level.

During periods of lower surface water levels (Aprial and May), the concentrations of MAHs, PAHs and NSO-HET increased significantly. As surface water levels began to rise (June to July), pollutant concentrations decreased and at the end of the measuring campaign with decreasing surface water levels the pollutant concentrations increased again. The results show clearly that the water level of the surface water influenced pollutant concentrations in the groundwater.

Additionally, the permanently installed multiparameter groundwater sensor in GWM 17 showed an occasional input of oxygen into the groundwater (from Sept. 2011 till August 2012) (**Fig. 5**). A temporary increase of oxygen concentration during flood times was observed and was correlated with ORP measurements. These results were recorded frequently and were reproducible during the two years of sensor operation. The evidence of dissolved oxygen in the groundwater was of high importance as the biodegradability of at least some tar oil pollutants strongly depended on the availability of this electron acceptor. The oxygen concentration in the groundwater was not directly correlated with the surface water level. During December and January high surface water levels resulted in oxygen concentrations of more than 2 mg/L. In June similar surface water levels were measured but oxygen concentrations were much lower (~<0.5 mg/L). Data on Rhine water quality showed a significant lower oxygen concentration in June (7.6–8.0 mg/L) than in January (11.9–12.5 mg/L). The potential of oxygen input was therefore higher in January. In Addition, metabolic processes in soil and groundwater are less active at low temperatures probably resulting in higher oxygen concentrations in the groundwater. As mentioned before methane, ferrous iron and sulfate compete for soluble electron acceptors (van Breukelen and Griffioen, 2004). Methane concentrations in GWM 17 differ from the winter campaign in November 2011 (750 μg/L) to the summer campaign in May 2012 (1200 μg/L) indicating another explanation for lower oxygen concentrations in May and June (Table 2 in the supplement).

### 3.2. Microcosms studies

Microcosm studies were conducted to simulate the dynamics of changing redox conditions under controlled conditions in the laboratory to better understand the varying NA processes at the site. Oxygen...
tolerance of ferric iron and sulfate reducing bacteria were examined. Therefore, for the first 310 days anaerobic conditions were induced, then the conditions were changed into aerobic conditions. Whereas the addition of oxygen seemed to lead to an increase of the number of ferric iron reducing bacteria, no more sulfate reducing bacteria were detected after experimental day 310. Table 3 in the supplement lists oxygen and ferric iron concentrations as well as cell counts of ferrous iron and sulfate reducing bacteria during the experiment. The results show a toxic effect of oxygen on the sulfate reducing species considered in this test. The effect indicates that bacteria with a broad physiological tolerance are in advantage at sites with transient groundwater flow conditions.

DeAngelis et al. (2010) describe significant higher cell counts of active bacteria in tests with fluctuating redox conditions compared to tests with static redox potential. Under transient redox conditions and especially with additional oxygen input, bacteria must be able to tolerate oxygen at least for a certain amount of time and defend cells from oxygen radicals. The ability to synthesise special enzymes like superperoxidase is directly related to the oxygen tolerance of bacteria (Fu et al., 2015; Imlay, 2013).

The findings of our study demonstrated oxygen tolerance of some anaerobic bacteria e.g., ferric iron reducing bacteria suggesting a higher oxygen tolerance of ferric iron than of sulfate reducing bacteria at the site.

According to Lovley (1991) alternative electron acceptors for Fe(III)-reducers include oxygen and nitrate. The capability to use ferric iron as an electron acceptor is thus potentially more widespread than the capability of sulfate reduction. This might be due to the higher energy yields for bacteria using ferric iron as an electron acceptor (Christensen et al., 2000; Lueders, 2017). However, oxygen tolerance and even growth of sulfate reducing bacteria under aerobic conditions is also described in literature (Lin et al., 2004).

In order to evaluate pollutant biodegradation under transient conditions relevant for the study site, pollutant concentrations were measured during incubation time (Fig. 6A). Results are shown for selected compounds representing predominant pollutants in the source areas and at the plume fringes, respectively. For the first 310 days, the microcosms were operated under anaerobic, ferric iron reducing conditions. Directly after sampling at day 310, aerobic conditions were implemented by dosage of air.

As discussed in Sections 3.1.3 and 3.1.4 it is likely that sulfate reduction takes place at the site. However, we observed mainly on ferric iron reducing processes in our microcosm studies. In the microcosms sulfate concentrations were monitored and differed between 66 and 68 mg/L. No significant decrease of sulfate could be detected during the experimental time whereas the concentration of dissolved iron in-creases. In addition, the cell counts of sulfate reducing bacteria did not increase but those of Fe(III) reducing bacteria (Fig. 3, supplement). All three active microcosms showed similar results. Regarding MAHs, indane and toluene degradation was observed during ferric iron reducing conditions. After the dosage of oxygen and the generation of
aerobic condition, benzene and indene were also degraded. In contrast to benzene and toluene, the bicyclic MAHs indane and indene are not measured routinely although their occurrence at tar oil contaminated sites is evident (Mundt et al., 2003; Richnow et al., 2003). Literature reports on the microbial degradation of those two constituents are rare. The fast and complete degradation of indane under ferric iron reducing conditions in our study suggested its potential of anaerobic biodegradation. Concentrations of indene however remained stable until the implementation of aerobic conditions. Kim et al. (2011) describe the aerobic degradation of indane. The bacterium was able to grow with indane as sole carbon and energy source but not with indene. However, our study was able to show the aerobic degradation of indene.

In the case of anaerobic benzene degradation differing results are described in the literature e. g. Jahn et al. (2005), Foght (2008) and Lueders (2017) describe the biodegradation of benzene and toluene under anaerobic conditions. The persistence of benzene however is described as well; and in addition, various substrate interactions can inhibit the degradation of benzene (Foght, 2008; Johnson et al., 2003). Obviously, no appropriate microorganisms for anaerobic benzene degradation were present in the microcosms of our current study, but substrate interactions potentially disturbing the aerobic degradation were also not observed. With oxygen as electron acceptor, all MAHs were degraded during the experiment. Regarding the PAHs, naphthalene was also degraded under ferric iron reducing conditions. The concentration of acenaphthene remained more or less stable until the first dosage of air at day 310. The microbial degradation of naphthalene proceeds under various conditions and is well described e. g. by Meckenstock et al. (2000). The relative enrichment of acenaphthene in relation to naphthalene indicates NA processes at contaminated sites (Schulze and Tiehm, 2004; Tiehm and Schulze, 2003).

Furthermore, Fig. 6B shows the degradation of prominent NSO-HET of the site during the microcosm studies. Microbial degradation of some of the N- and O-HET started under Fe(III) reducing conditions and was completed with the availability of oxygen as electron acceptor. Concerning the S-HET, no degradation occurred during Fe(II) reducing conditions. After the dosage of air, a rapid degradation of carbazole, benzothiophene, 2,3-dimethylbenzofuran and dibenzofuran took place as well. The anaerobic degradation of indole and quinoline is well described in the literature and summarized in Fetzner (1998). None of the S-HET was degraded during the ferric iron reducing part of the biodegradation test. S-HET are often more toxic than their O-HET, N-HET or PAH-Analogue (Eisenträger et al., 2008). Therefore, the...
elimination of these substances is of special interest and the results of our study suggest that the pollutants are degraded as soon as oxygen as an electron acceptor is available at a contaminated site. Although benzothiophene was not degraded under ferric iron reducing conditions in the laboratory experiments, investigations in the field and model results suggested anaerobic benzothiophene degradation (see Section 3.3.3).

Regarding biodegradation of benzo furan, co-metabolic processes are also discussed in literature (Dyreborg et al., 1997; Safinowski et al., 2006). However, in our study degradation started rapidly and was complete. Studies by Dyreborg et al. (1997) provided evidence of aerobic dibenzofuran degradation. Apparently, dibenzofuran can be used as primary substrate (Monna et al., 1993) and can also be degraded co-metabolically (Becher et al., 2000). Microcosm studies represent an essential component of the multiple lines of evidence approach to assess NA processes at contaminated sites particularly for constituents that have not been previously studied. For commonly monitored constituents there is an increasing reliance on diagnostic tools like. Compound-specific stable isotope analysis (CSIA) or multielement CSIA (ME-CSIA) allowing for the differentiation of degradation pathways and distinguishing from biodegradation and abiotic transformation (Kuntze et al., 2020). In this study, microcosms demonstrated anaerobic biodegradation with Fe(III) for many compounds. The demonstration of the effect of hydraulic dynamics by dosage with air after incubation under anaerobic conditions clearly showed the positive effect on microbial degradation by providing oxygen as electron acceptor. In comparison, in the field studies, the temporary increase of oxygen concentration at the groundwater well (see Fig. 5) might accelerate or support microbial degradation of constituents of tar-oil.

However, since the number of sampling points for microcosms is limited, not all processes occurring in the field might be shown in the lab. Therefore, additional evidence for pollutant degradation was obtained by reactive transport modelling.

3.3. Groundwater modelling

3.3.1. Transient flow simulations

The water level in the river Rhine varied by about 4 m during the two and a half years considered in the model. The typical duration of low and high-water conditions was several weeks.

The water level of the river was resolved on a weekly basis resulting in 135 model periods. The flow model was calibrated against the groundwater levels recorded for a period of 2 years and 2 months in the monitoring wells GWM 1, GWM 10 and GWM 13 located at the former gasworks site (see Fig. 1). The critical model parameter adapted during flow calibration was the storage coefficient of the aquifer where confined conditions prevailed.

The general trends in water levels are well reproduced in the model (shown for GMW 10 in Fig. 5 in the supplement). However, the extreme values were underestimated. An explanation for this could be that the only driving forces for water level fluctuations in the model were the water level changes in the river Rhine. In reality, seasonal changes of regional groundwater recharge would also influence water levels.

The calibrated transient flow model formed the basis for the subsequent transport simulations.

3.3.2. Range of influence of the river water

As discussed, infiltration of aerobic river water into the otherwise anaerobic aquifer provides an important source of oxidation capacity in the aquifer which in turn provides the possibility of subsurface contaminant, sulfide and ferrous iron (Fe(II)) oxidation. In addition to oxygen, other electron acceptors such as nitrate and sulfate are dissolved in the river water. The nitrate concentration in the water of River Rhine in 2011 ranged from 4.7 mg/L to 9.3 mg/L, the sulfate concentrations from 19.5 mg/L to 33 mg/L. Fig. 4 in the supplement shows the sulfate concentration in GWM 15 related with the water level of the river. Sulfate concentrations were low (5–10 mg/L) at low water levels and increased (>30 mg/L) with the rising water level.

As the supply of dissolved oxidants by the river was supposed to be essential for the assessment of in-situ degradation processes, the numerical model was first applied to quantify the amount of river water rich in oxygen and other electron acceptors entering the aquifer during flood events. This was accomplished by treating ‘river water’ as a virtual model species and then simulating transport of the species ‘river water’ from the river into the adjacent aquifer in the transient groundwater model.

The model results were compared to the observed oxygen concentrations data collected by the multiparameter probe installed in monitoring well GWM 17 near the riverbank (see Section 3.1.4). Fig. 7 shows the comparison between measured oxygen concentrations and the simulated fraction of river water at the well. For comparison, water level in the river Rhine (gauge Philippsburg, located about 5 km downstream of the gasworks site) is shown.

The simulations showed four distinct periods with increasing amounts of river water in the aquifer caused by flood events. It can also be seen that not every single flood event in the river resulted in an increase in simulated river water content in the aquifer. Rather the simulated river water content was not only controlled by the water level in the river itself but was also depending e.g. on the preceding water level history in the aquifer.

The oxygen recording in the sampling well started in September 2011. The simulated increase in river water fraction beginning in December 2011 coincided with an increase in oxygen concentrations in the aquifer. Increased oxygen contents could also be seen for the following two simulated flood events, although the calculated river water fraction was not directly proportional to the observed oxygen contents. Moreover, enhanced oxygen contents showed up only at the beginning of the simulated penetration of river water into the aquifer. The oxygen content increased during the flood period. This effect might be caused by naturally occurring oxygen-consuming processes in the aquifer.

Despite these deviations, the semi-quantitative comparison was sufficient to show that the model was able to reproduce the periodical penetration of river water into the aquifer and therefore to outline the range of influence of river water. This range in turn was used to delineate a zone of possible aerobic degradation processes in the model.

3.3.3. Simulation of contaminant transport

The goal of the transport simulations was to predict the observed concentration levels of the seven model species in the 28 sampling locations at the gasworks site or its vicinity. The transport model calibration was an iterative process where the model parameters (mainly contaminant release rates and degradation rates) were adjusted to reproduce the important trends in concentration behavior. Due to the unknown detailed distribution of either hydrogeological and hydro-chemical parameters and the limited temporal resolution of transient groundwater flow an exact reproduction of the observed values was not feasible.

Seven distinct areas with contaminant loading were located in the model at the gasworks site (see Table 4 and Fig. 7 in the supplement). Some of these areas were substantiated by independent site investigations, while others were evidenced from model calibration only. The total contaminant release rate in the model amounted to about 170 g/d (sum over the seven model species).

Further contaminant sources (e.g. by groundwater recharge or by boundary fluxes) were not considered in the model. Initial concentrations were set to zero for all contaminants.

With the calibrated release rates and without considering any degradation processes, the contaminant concentrations at the more distal sampling points were clearly overestimated by the model. Reducing the release rates would help to improve simulation results in the downstream areas of the gasworks site, however it would also lead to too low simulated contaminant concentrations at the sampling points.
close to the contamination sources. It can be excluded that the overestimation at the distal sampling points was caused by a completely incorrect simulation of groundwater flow, as the mean flow conditions were confirmed by water level samplings and were clearly defined by the vicinity of the river Rhine, which acted as major groundwater recipient.

The only way to accomplish both elevated concentrations close to the sources and lower concentrations in the downstream area was to assume contaminant degradation processes in the model. This assumption was supported by the field studies and the experimental findings on contaminant degradation described in Sections 3.1 and 3.2. The effect of aerobic degradation processes on contaminant transport was shown for acenaphthene at a sampling point close to the river Rhine (GWM 17), where partly aerobic periods presumably lead to highly efficient contaminant degradation (Fig. 6 in the supplement). It is shown that degradation must have a major effect on acenaphthene fate at this sampling point for neglecting degradation in the model scenario leads to enhanced acenaphthene levels not observed in reality.

No anaerobic degradation was assumed for acenaphthene, carbazole, and 2,3-dimethylbenzofuran in the model. These findings from model calibration are in agreement with the experimental findings presented in Section 3.2, where the three compounds mentioned above showed no degradation under Fe(III) reducing conditions. For benzene model calibrations suggested a relatively rapid degradation also in the reducing parts of the aquifer, while the experimental studies showed no benzene degradation under Fe(III) reducing conditions. Model results also hint on a certain degradation of benzothiophene and dibenzofuran in the anaerobic part of the aquifer, while microcosm studies showed no degradation under Fe(III) reducing conditions. The reasons for these deviations are not clear. Naphthalene was degraded under anaerobic conditions in the model as well as in the microcosm studies.

In contrast to the situation in the anaerobic parts of the aquifer, all seven contaminants were degraded in the model in the partially aerobic region close the riverbank, where periodical flood events provided dissolved oxygen to the aquifer. The rapid degradation process under aerobic conditions was implemented in the transport model by assuming enhanced degradation rates for all contaminants in the partially aerobic part aquifer as delineated by the special simulations presented in Section 3.3.2.

This model assumption was confirmed by the experimental studies, where these species showed a rapid degradation as soon as oxygen was supplied to the system.

In Fig. 8, the effect of the aerobic area is exemplified for acenaphthene distribution for a typical low water situation in the river.

The assumption of an enhanced degradation process in the model for the aquifer close to the river was supported by the experimental findings for aerobic acenaphthene degradation and moreover by the low acenaphthene concentrations in the groundwater of wells GWM 17, GWM 25, and GWM 26. Additionally, the model was run for a hypothetical scenario where aerobic degradation near the river was not active. In this scenario, acenaphthene should reach the riverbank and the acenaphthene values in GWM 17, GWM 25 and GWM 26 should be enhanced, which was not observed during the field studies.

4. Conclusions and perspectives

The study demonstrated the characterisation of microbial degradation processes of tar oil contaminants under transient groundwater flow and redox conditions at a tar oil contaminated site, located in the upper Rhine valley, south-west Germany. A multiple evidence concept was thus considered, including field studies, microcosm studies in the laboratory and groundwater modelling. The following aspects were demonstrated:

- Microbial degradation was observed as key process of NA processes at the contaminated site.
- Based on the analysis of 78 pollutants, indane, indene and several NSO-HET like carbazole, benzothiophene and 2-methyl dibenzofuran are recommended for consideration in NA monitoring concepts at tar oil polluted sites, in addition to EPA-PAHs and BTEX analysis.
- By using sensor technique, the frequent infiltration of oxygen into the aquifer could be proven, which seems to have a stimulating effect on intrinsic biodegradation and therefore a recycling of the electron acceptor Fe(III).
- Frequent monitoring of pollutants proved an impact of the surface water on pollutant concentrations.
- Field and laboratory data were used to set-up a groundwater flow and reactive transport model for quantification of the field mass transfer rates.

In conclusion, the study demonstrates that NA processes are very effective for tar oil pollutants under transient groundwater conditions. The site conditions result in a strikingly short pollutant plume. With the application of groundwater modelling, the processes identified during field and laboratory studies were brought into accordance with the transient groundwater flow conditions at the site. The model helped to delineate the range of influence of aerobic river water and to quantify contaminant release and degradation processes. The model results suggest that NA leads to a complete contaminant removal during a relatively short groundwater passage mainly triggered by the periodical influx of oxygen rich river water during flood events. Thus, the model accords with the field data of the site.

To our knowledge, our study shows the effects of transient groundwater conditions on NA of 78 mono-, poly-, and NSO-heterocyclic compounds for the first time. The combination of field studies (including sensor techniques), microcosms in the lab and reactive transport simulation can facilitate the interpretation of pronounced fluctuations of pollutant concentrations and seems a suitable concept to manage the contaminated site. The study demonstrate that NA can reliably contribute to pollutant elimination at contaminated sites with dynamic groundwater conditions in Germany and other parts of the world.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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