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Characterization of Predominant Reductants in an Anaerobic Leachate-Contaminated Aquifer by Nitroaromatic Probe Compounds

KIRSTEN RÜGGE,*,†
THOMAS B. HOFSTETTER,‡
STEFAN B. HADERLEIN,*,‡
POUL L. BJERG,† SØREN KNUDSEN,†
CLAUDIA ZRAUNIG,‡
HANS MOSBÆK,† AND
THOMAS H. CHRISTENSEN†

Department of Environmental Science and Engineering/ Groundwater Research Centre, Building 115, Technical University of Denmark, DK-2800 Lyngby, Denmark, and Swiss Federal Institute for Environmental Science and Technology (EAWAG) and Swiss Federal Institute of Technology (ETH), CH-8600 Dübendorf, Switzerland

The biogeochemical processes controlling the reductive transformation of contaminants in an anaerobic aquifer were inferred from the relative reactivity patterns of redox-sensitive probe compounds. The fate of five nitroaromatic compounds (NACs) was monitored under different redox conditions in a landfill leachate plume of a sandy aquifer. Results of field experiments (continuous injection and *in situ* microcosms) were compared to the findings of laboratory batch and column experiments (using aquifer matrix and model systems for sulfate- and iron-reducing conditions). NACs were transformed within 2−70 days in the leachate plume as well as in microbially active and in microbially deactivated experiments. Generally, aromatic amines were the predominant reduction products, and these compounds were stable within the time frame and under the conditions of our experiments. Despite the presence of various potential reductants (e.g., H_2S/HS^-, $Fe(II)_{aq}$, reduced organic matter, microorganisms), the patterns of relative reactivity of the probe compounds indicated that ferrous iron associated with iron(III) (hydr)oxide surfaces was the dominant reductant throughout the anaerobic region of the plume. Our results suggest that Fe(II) associated with ferric iron minerals is a highly reactive reductant in anaerobic aquifers, which may also determine the fate of other classes of reducible contaminants such as halogenated solvents, azo compounds, sulfoxides, chromate, or arsenate.

Introduction

Several classes of priority pollutants, e.g., halogenated organics, organic azo and nitro compounds, and sulfoxides, undergo reductive transformation reactions under laboratory conditions as well as in anaerobic aquifers (*1*−*4*). Reductive transformation of such compounds often leads to less harmful products that are more mobile, more bioavailable, and more easily to degrade. In certain cases, however, the products of such reactions may also be more toxic than the parent compounds. Furthermore, reaction rates of a given pollutant with reductants commonly present in anoxic aquifers may vary by many orders of magnitude. For instance, the reduction of substituted nitrobenzenes to the corresponding anilines by dissolved HS^- or Fe(II) is quite slow, but proceeds orders of magnitude faster if electron transfer mediators such as dissolved organic matter or catalytic surfaces such as iron oxides also are present (*5*, *6*). Thus, knowledge of the *in situ* processes that cause reductive transformation of organic pollutants is essential to evaluate the risks of pollution and the need for remediation of contaminated anaerobic aquifers.

In anaerobic groundwater, such as landfill leachate plumes, characterization of the active redox species based on chemical analysis is very difficult if feasible at all. This is related to the fact that several biogeochemical redox processes may take place in parallel (*7*−*9*), giving rise to the presence of a variety of potential reductants.

The major objectives of this work were to identify reactants and processes that control the reductive transformation of contaminants in an anaerobic aquifer. We focused on an evaluation of the relative importance of biotic and abiotic processes and on the type of reductants involved. The reactivity of a series of nitroaromatic probe compounds (NACs) was studied within the anaerobic leachate plume of the Grindsted Landfill, Denmark, and compared to their respective reactivities in model systems.

NACs are very suited probe compounds to characterize the type of active reductants present in anaerobic aquifers since the relative reactivity of a relevant set of NACs is characteristic for the type of reductant involved in the transformation process (*1*, *5*, *6*, *10*). The reactivity of substituted nitrobenzenes may vary by orders of magnitude, depending on the type and position of substituents. A set of five nitroaromatic model compounds exhibiting very different reduction potentials was used in this study. Their patterns of reactivity were studied in the anaerobic leachate plume by means of an injection experiment in the plume area, by *in situ* microcosm experiments installed at five distances along a flow line in the plume, and by laboratory batch experiments containing groundwater and aquifer sediment from the same locations. Laboratory experiments in well-defined homogeneous and heterogeneous model systems were conducted in order to mimic the reactivity of NACs with reductants present under sulfate-reducing and iron-reducing conditions, as found in the plume. The relative reactivities of the NACs in these model systems were compared to the *in situ* reactivity of the compounds in the aquifer, which allowed the identification of the processes and reductants that were active in the leachate plume.

Materials and Methods

Description of the Field Site. The study area was a shallow sandy aquifer downgradient from the Grindsted Landfill, Denmark. Investigations were performed within the anaerobic part of the plume at a distance of 15−60 m from the edge of the landfill site. The landfill is placed on top of the original ground surface and was operated from 1930 to 1977. The waste disposed of consisted of a mixture of municipal waste and industrial waste (*11*). The landfill is located on a glacial outwash plain. The glaciofluvial sediments of the aquifer are composed of medium- and coarse-grained sand and gravel. The average hydraulic gradient is approximately

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* Corresponding authors: (K.R.) telephone: +45 45 25 15 58, e-mail: kr@imt.dtu.dk; (S.B.H.) telephone: +41 1 823 5524, e-mail: haderlein@eawag.ch.

† Technical University of Denmark.

‡ EAWAG and ETH.

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TABLE 1. Characteristics of Groundwater in Grindsted Landfill Leachate Plume in Study Area[a]

species	concentration	species	concentration
Cl^-, mg/L	19−134	NH_4^+, mg/L	22−57
NO_3^{2-}, mg/L	<0.02	CH_4, mg/L	4−25
NO_2^{2-}, mg/L	<0.02	S^{2-}, mg/L	<0.02
SO_4^{2-}, mg/L	0.8−4.1	pH	6.6−6.8
Fe^{2+}, mg/L	99−158	alkalinity, mequiv/L	17−23
Mn^{2+}, mg/L	2.6−4.4	DOM, mg of C/L	47

[a] Water samples have been obtained from the driven wells used for ISM and LB experiments.

1.3‰ and the porosity of the aquifer is 0.30−0.35, giving an average pore flow velocity of 40−50 m/year. The average groundwater temperature is 10 °C (*12*). The aquifer material has a low organic carbon content (f_{oc} = 0.01−0.03%) (*13*).

The redox conditions of the Grindsted Landfill leachate plume have previously been characterized by measurements of soluble redox-sensitive species (*8, 12*), sediment chemistry (*13*), and microbial bioassays (*8*). Generally, the leachate-contaminated groundwater is rich in dissolved organic carbon, 50−120 mg/L (4−10 mM), and has very high concentrations of Fe(II), >75 mg/L (>1.4 mM), within the first 60−80 m of the plume (Table 1). The microbial bioassays indicated a complex redox environment within this area, where many of the observed redox processes occurred simultaneously. However, closest to the landfill, methane production and sulfate reduction prevailed, followed by sulfate and iron reduction.

Experimental Setup. The fate of the five nitroaromatic probe compounds (for names and abbreviations, see Table 2) in the contaminated aquifer was studied under anaerobic conditions using three different experimental setups: The compounds were continuously injected to the leachate-contaminated groundwater over a period of 195 days. *In situ* microcosm experiments (ISMs) were performed along a flow line of the leachate plume at five locations within the aquifer (15, 25, 35, 45, and 55 m downgradient from the landfill). Laboratory batch experiments (LBs) were set up with groundwater and aquifer material sampled at the locations corresponding to the ISMs.

The redox conditions in the LBs, in the ISMs, and in the field injection experiment were monitored during the experiments in terms of the concentrations of dissolved CH_4, S^{2-}, SO_4^{2-}, Fe^{2+}, Mn^{2+}, NO_3^-, and NO_2^- (Table 1). To these systems, the five NACs were added together with 13 other xenobiotic compounds: seven aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene, and naphthalene), four chlorinated solvents (tetrachloroethylene, trichloroethylene, tetrachloromethane, and 1,1,1-trichloroethane), and two pesticides (mecoprop and atrazine). The initial concentrations of the NACs were about 2 μM (246−336 μg/L) while the accompanying compounds had concentrations ranging from 0.7 to 2 μM (150 μg/L). This paper addresses only the NACs. In addition to the systems described above, laboratory experiments were performed in model systems to characterize the reactivity of major reductants present in the plume.

Field Injection Experiment. Six injection wells were installed approximately 15 m downgradient from the landfill border. The initial width of the injected plume was 1.5 m and the depth was 1 m. The injection took place at 4.5−5.5 m below ground surface (approximately 3−4 m below the groundwater table). Downgradient from the injection wells, a dense network of multilevel samplers was installed. The fences of samplers were placed 1−5 m apart, with transversal horizontal spacing of the samplers of 0.5−1.0 m, dependent on the distance from the injection wells. The vertical spacing of the sampling points was 0.25 m.

A stock solution containing the organic compounds and bromide (conservative tracer) in distilled, anaerobic water was injected into the injection wells, where it was mixed with the leachate-contaminated groundwater. The volume of stock solution injected in the natural gradient experiment was only approximately 5% of the natural groundwater flux passing the injection wells, yielding concentrations of the NACs of approximately 2 μM (246−336 μg/L), of the other organic compounds of 0.7−2 μM (150 μg/L), and of bromide approximately 100 mg/L just downgradient from the injection wells.

During the 195 days of continuous injection, samples were taken once a week in discrete sampling points in the central part of the plume. After that period, the sampling frequency was reduced to approximately once a month.

***In Situ* Microcosm Experiments (ISM).** An ISM is a stainless steel column that isolates about 2 L of the aquifer. It is equipped with valves allowing for loading and sampling from the ground surface as described by Nielsen et al. (*14*). The ISMs were installed in the aquifer at five distances from the landfill at 5−5.5 m below the surface. The stock solution of the 18 different xenobiotic compounds and ^3H_2O as a tracer was mixed with anaerobic water in a Tedlar bag. The water was obtained from nearby driven wells and was collected as described by Lyngkilde and Christensen (*15*). The spiked concentrations of the xenobiotic compounds were approximately 1.5−2 μM. About 7 pore vol was pumped through the ISM, and loading took approximately 2−3 h. At 25 and 45 m distance, two ISMs were biologically deactivated by adding formaldehyde (250 mg/L) to the loading water in the Tedlar bag. The ISMs were sampled with a few days interval for the first two weeks and later on with increasing intervals for a period of up to 250 days.

Laboratory Batch Experiments (LBs). Anaerobic sediment cores were sampled as described in Heron et al. (*13*). Anaerobic groundwater was obtained from the driven wells placed near the corresponding ISMs. The laboratory batch experiments were conducted in 2.3-L glass bottles equipped with a glass valve used for sampling. All experiments were performed as duplicates with compound concentrations corresponding to the concentrations used in the injection experiment and the ISM. The bottles were prepared in an anaerobic glovebox and contained approximately 1.3 kg of wet sediment and approximately 1 L of groundwater from the various sampling sites in the aquifer plume (1.3 L in total). To avoid interference of H_2 from the atmosphere of the glovebox, the bottles were purged and stored under slight overpressure of an atmosphere containing 80% N_2 and 20% CO_2. By opening the valve, a water sample was siphoned out of the bottle. The bottles were incubated in the dark at groundwater temperature (10 °C). During the incubation, the bottles were kept submerged in water, which was kept anoxic by addition of a large excess of SO_3^{2-} and by purging with N_2. The bottles were gently shaken once a week. The LB were sampled with a few days interval for the first two weeks and later on at larger intervals for a period of 120 days.

Two sets of control experiments were performed with sediment and groundwater sampled at 25 and 45 m distance from the landfill. They were biologically deactivated by adding NaN_3 (2 g/L). Additionally, an experiment with groundwater only was conducted in duplicates using groundwater from a driven well at 15 m distance. These experiments were also conducted in 2.3-L bottles and handled as the other LBs.

Iron-Reducing Batch Model System. Batch experiments in homogeneous solution as well as in suspensions were set up in an anaerobic glovebox. All experiments where performed in 58-mL serum flasks that were equipped with Teflon-coated stirring bars and sealed with Viton rubber stoppers and aluminum crimp caps. The suspensions

TABLE 2. Names, Abbreviations, One-Electron Reduction Potentals ($E_h^{1'}$), Pseudo-First-Order Rate Constants (k_{obs}) and Binary Competition Coeffients (Q_c) for Reduction of NACs in Various Systems

		sulfate-reducing model system		iron-reducing model systems		Grindsted Landfill site	
compound	abbrev	$E_h^{1'}$ [a] (mV)	landfill-derived reduced DOM; calcd k_{DOM} normalized to NB (−)	Fe(II)$_{aq}$/goethite; batch $k_{Fe(II)/Fe(III)}$ normalized to NB (−)	affinity for reactive Fe(II) sites; column Q_c reference NAC = NB (−)	groundwater only; batch $k_{groundwater}$[b] normalized to NB (−)	groundwater and sediment; batch $k_{aquifer}$ normalized to NB (−)
1,2-dinitrobenzene	1,2-DNB	−287[c]	2240	24	17	170	≈28[d]
1,3-dinitrobenzene	1,3-DNB	−345[c]	234	3.7	8.5	65	6.7
nitrobenzene	*NB*	*−485*[c]	*1.00*	*1.0*	*1.0*	*1.0*	*1.0*
4-methylnitrobenzene	4-CH_3-NB	−500[c]	0.56	0.38	1.4	nd[e]	0.73
2-methylnitrobenzene	2-CH_3-NB	−590[c]	0.02	0.72	2.8	nd[e]	0.72
3-aminonitrobenzene	3-NH_2-NB	−500[f]	0.55	0.72	0.71	nd	nd
2-aminonitrobenzene	2-NH_2-NB	≪−560[f]	≪0.05	0.41	0.23	nd	nd
absolute values of nitrobenzene rate constants in various systems (h^{-1})			0.003[g]	0.65		0.00019	0.0036
corresponding half-lives (h)	$t_{1/2}$		220	1.1		3616	194

[a] According to the half-reaction: $ArNO_2 + e^- = Ar\text{-}NO_2^{\bullet-}$. [b] The values of $k_{groundwater}$ given were determined in the experiments showing the highest reactivity, since in some of the experiments the compounds did not react at all within the experimental period. [c] Ref 31. [d] Average value, roughly estimated on the basis of only two data points in each batch. [e] Not determined due to very low reactivity. nd, not determined. [f] This study; determined according to ref 10. [g] Calculated as follows: k_{DOM} (h^{-1}) = k_x [h^{-1} L (mg of C^{-1})] C_{DOM} (mg L^{-1}); k_x is the second-order rate constant for the reduction of a given NAC by DOM; C_{DOM} is the concentration of nonvolatile dissolved organic carbon present in the studied part of the Grindsted aquifer (47 mg of C L^{-1}). The k_{NB} value used here [6.7×10^{-5} h^{-1} L (mg of C^{-1})] was calculated from $k_{3-Cl-NB}$, the carbon-normalized rate constant reported for 3-chloronitrobenzene reduction by DOM originating from Kölliken Landfill leachate [$k_{3-Cl-NB} = 1.2 \times 10^{-3}$ h^{-1} L (mg of C^{-1}) at pH = 7.0 and H_2S_{tot} = 5.0 mM (*5*)]. Relative reactivities for the reduction of NACs by DOM are independent of pH and the type of DOM present and thus were taken from the literature (*5*). k_x values for dinitrobenzenes, methylnitrobenzenes, and aminonitrobenzenes were estimated using a LFER of the type $k_x = 1.0E_h^{1'}/0.059\text{ V} + \text{const}$, according to ref 5.

contained 11.2 m^2/L goethite (α-FeOOH) and 25 mM 3-(*N*-morpholino)propanesulfonic acid (MOPS) buffer to keep the pH constant at 7.22. The ionic strength ($I = 20$ mM) was adjusted with NaCl. Assays were kept in a water bath (25 °C) in the dark and were stirred at 600 rpm for 24 h before Fe(II) was added (1.5 mM) with a gas-tight glass syringe from a stock solution of $FeCl_2$ (85 mM), which was also prepared in the glovebox. Goethite suspensions spiked with ferrous iron were equilibrated for 48 h before adding NACs, which guaranteed a very reproducible reactivity of Fe(II) in all experiments (*16*). To start an experiment, 50 μL of oxygen-free methanolic NAC stock solution was added with a gas-tight glass syringe in order to establish 50 μM initial concentration of NACs. Control assays were prepared similarly, except for adding goethite or Fe(II), respectively. At given time intervals, 500-μL samples were withdrawn from the solution. To stop NAC reduction, 300 μL of each sample was filtered (0.2 μm) into an autosampler vial and stabilized with 9 μL of $HClO_4$. Pseudo-first-order reaction rate constants were calculated from linear regression analysis.

Iron-Reducing Aquifer Columns. Experiments in aquifer columns operated under iron-reducing conditions were set up and operated as described in Heijman et al. (*17*). Columns were wet-packed with sandy material from the banks of a small stream (Chriesbach, Dübendorf, CH) that contained 5.7 mg of Fe_{tot}/g and 0.88 mg of C/g (C, determined as total organic carbon), but negligible amounts of other electron donors. The influent contained 100 μM acetate and 2 μM of each NAC when mixtures of NACs were studied. Acetate was added in order to stimulate the activity of dissimilatory iron-reducing bacteria within the columns. Experiments were run either as single compound assays (10 μM initial concentration) or as competition experiments with mixtures of two or five different NACs. Binary competition coefficients of NACs, Q_c, were calculated using the measured zero-order rate constants, k_{obs} (NAC), in a binary mixture of the two respective NACs according to

$$Q_c = \frac{k_{obs}(\text{NAC})}{k_{obs}(\text{reference NAC})} \tag{1}$$

with

$$k_{obs}(\text{NAC}) = \frac{([\text{NAC}]_{in} - [\text{NAC}]_{eff})}{\tau} \tag{2}$$

where $[\text{NAC}]_{in/eff}$ are the stationary concentrations of NACs in the influent and effluent, respectively, and τ represents the residence time of the compound in the column. Our results and those of Heijman et al. (*17*) indicate that competition coefficients, Q_c, were fairly independent of both the initial concentration of the NACs and the initial concentration of acetate (data not shown).

Analytical Methods. Groundwater samples were analyzed for Cl^-, NH_4^+, NO_3^-, NO_2^-, SO_4^{2-}, Fe^{2+}, Mn^{2+}, pH, and NVOC either immediately or as preserved samples by techniques standard to the laboratory (*15*). S^{2-} was analyzed immediately by a sulfide-sensitive electrode (Radiometer F1212S) (*12*). ^3H_2O was quantified by liquid scintillation counting as described by Nielsen et al. (*18*), and Br^- by ion chromatography with a Dionex system.

NAC Analysis in Groundwater Samples. All samples containing nitroaromatic compounds were frozen to −80 °C in the field/laboratory immediately after sampling and kept at this temperature until analyzed in the laboratory. Here, the aqueous samples were filtered on Sartorius 0.45-μm filters and analyzed on a binary gradient HPLC equipped with a diode array UV detector. Two injections under different conditions on a reversed-phase HPLC system allowed us to quantify all NACs and most of their reduction products in the very complex matrix of leachate-contaminated groundwater.

Method 1 quantified NB, 1,2-DNB, 1,3-DNB, 2-CH_3-NB, 4-CH_3-NB, and aniline on two C-8 columns operated in series (Chrompack Chromspher C-8 100 × 3.3 mm). The gradient program (eluents A and B) started with 73% of A for 8 min followed by 10 min of linear gradient to 35% of A. This eluent composition was kept for 3 min to clean the system followed by 4 min of linear gradient back to 73% A and equilibrated at 73% for another 18 min. Method 2 quantified NB, 1,2-DNB, 1,3-DNB, 2-NH_2-NB, 3-NH_2-NB, aniline, 2-CH_3-aniline, and 4-CH_3-aniline on two C-18 columns operated in series (Chrompack Chromspher C-18 100 × 3.3 mm). The conditions were isocratic for 28 min with 100% C. After each injection, the system was rinsed by a linear gradient starting with 0% B to 75% B over 6 min, 3 min isocratic, followed by a linear gradient back to 100% C over 4 min. To equilibrate the system, the mobile phase was kept 100% C for another 17 min. The flow rates were 0.6 mL/min in both methods.

The composition of the eluents were as follows: Mobile phase A: Milli Q water/acetic acid (glacial)/diethylamine in the ratio 1000/2/2.3 v/v. Mobile phase B: ethanol/acetonitrile/mobile phase A in the ratio 45/45/10 v/v. Mobile phase C: 82% A and 18% 50/50 methanol/acetonitrile. All eluents were adjusted to $\text{pH} = 6.5 \pm 0.05$ by addition of acetic acid (glacial) and diethylamine.

In both methods, chromatograms were recorded simultaneously at 230 and 270 nm. Compound identification was performed at four levels: 1, comparison of retention times with reference compounds; 2, standard addition; 3, comparison of the signal radiograms at 230 and 270 nm; 4, by comparison of entire UV spectra obtained between 230 and 270 nm using a diode array detector. Quantification was based on external standards.

NAC Analysis in Model Systems. Aqueous samples were analyzed by HPLC equipped with a diode array UV detector. Samples containing mixtures of five NACs were injected on a reversed-phase Supelcosil C-18 column (250 × 4.6 mm, 5 μm spheres, 20 mm Supelcoguard C-18 guard columns; Supelco, CH). The eluent consisted of a mixture of 2-propanol/acetonitrile/H_2O buffered with 5 mM phosphate at $\text{pH} = 7.0$. Samples from single-compound experiments as well as from binary competition experiments were run on either C-18 or C-8 columns (125 × 4 mm, 5 μm spheres; Merck, D) with various MeOH/H_2O mixtures, buffered with 5 mM phosphate at $\text{pH} = 7.0$. The flow rate was 1.0 mL/min for all measurements; UV−VIS detection was performed at several wavelengths according to maximum wavelength of absorption of the compounds analyzed.

Results and Discussion

Reactivity of Nitroaromatic Probe Compounds with Potential Reductants. Table 2 contains data on the relative rate constants of reduction, i.e., the patterns of reactivities of the probe compounds with reductants present under sulfate-reducing and iron-reducing conditions similar to the conditions found in the plume. In the model systems, NACs exhibited a large variety of relative reduction rate constants. Although dissolved H_2S is a quite poor reductant for many NACs (*10, 19*), it is efficiently able to reduce dissolved organic matter (DOM), which again can meditate NAC reduction (*5*). DOM was present in considerable concentrations in the Grindsted aquifer (Table 1). The reduction rates of NACs by reduced DOM in the Grindsted aquifer can be estimated from the literature, since DOMs from different origins exhibit quite similar (carbon-normalized) reactivities (*5*). The calculated pseudo-first-order rate constants for the reduction of the various model NACs by DOM in the aquifer, k_{DOM}, span 5 orders of magnitude (for details, see footnote in Table

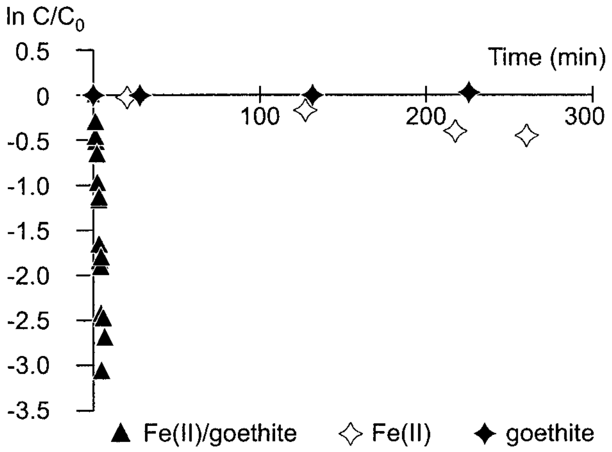

FIGURE 1. Reduction kinetics of 1,2-DNB in iron-reducing batch model systems containing: (▲) 11.2 m^2/L goethite and 1.5 mM Fe(II), $k_{obs} = 2.4$ h^{-1}; (◇) 1.5 mM Fe(II), $k_{obs} = 0.12$ h^{-1}; (♦) 11.2 m^2/L goethite, no decrease in concentration observed.

2). This corresponds to half-lives in the order of 0.1−1 h for dinitrobenzenes and 220 h and more for NB and methylnitrobenzenes. Reduction rate constants by reduced DOM strongly depend on the one-electron reduction potentials ($E_h^{1'}$) of the NACs. A slope of unity was found in linear free energy relationships (LFERs) of log k_{obs} versus $E_h^{1'}$/0.059 V. This indicates that transfer of the first electron from DOM to NACs is the rate-determining step in the overall reduction of NACs in these systems (*1, 10*). Since e$^-$ transfer from reduced DOM to NACs occurs by an outer sphere mechanism (*10*), NACs present in mixtures are reduced independently, i.e., without any competition effects by DOM. Thus, if DOM was the predominant reductant in the leachate plume, the NAC mixture is expected to be reduced without competition effects, and dinitrobenzenes are expected to react 2−3 orders of magnitude faster than the mono-NACs.

In iron-reducing model systems containing dissolved Fe(II), reduction rates of most of the selected NACs were negligible at the pH of the groundwater. Only 1,2-DNB was reduced at measurable rates by dissolved Fe(II). However, Fe(II) sorbed to iron(III) (hydr)oxide minerals such as goethite is a very efficient reductant for NACs (*6, 19*). The reduction rate constant of 1,2-DNB increased by almost 2 orders of magnitude in the presence of Fe(II) adsorbed to goethite as compared to systems containing only dissolved ferrous iron (Figure 1). The reduction of NACs by ferrous iron adsorbed to Fe(III) surfaces followed first-order kinetics with respect to NAC concentrations. Half-lives of the NACs investigated in heterogeneous Fe(II)/Fe(III) systems ranged from about 3 min to 2.8 h (Table 2). Thus, in such systems the relative reduction rate constants, $k_{Fe(II)/(III)}$, varied only by about 2 orders of magnitude among the nitroaromatic probe compounds. In contrast to the reaction with reduced DOM, considerable competition effects occur among NACs present in mixtures when surface-associated Fe(II) is the reductant (*6, 19*), (see Q_c values in Table 2). High Q_c values indicate that a given NAC is a strong competitor for reactive Fe(II) sites as compared to a reference NAC. In mixtures, such compounds are reduced preferentially (see below). The fact that competition for reactive Fe(II) sites is observed in mixtures of NACs is one indication that the formation of precursor complexes with Fe(II) plays a role in the rate-determining step(s) of the overall reaction of NACs in such systems. Other indications include a slope of much less than unity in log k_{obs} versus $E_h^{1'}$/0.059V LFERs and the rate-promoting effects of certain substituents when present in ortho position to the nitro group (*6, 19*).

If surface-bound Fe(II) was the predominant reductant in the anaerobic part of the aquifer, the various NACs present in the injected mixture should be reduced sequentially according to their respective Q_c values. Furthermore, the reduction rate constants of the probe compounds are expected to vary by about 2 orders of magnitude. Thus, under conditions prevailing in the anaerobic region of the leachate plume, reduced DOM or Fe(II) associated with Fe(III) surfaces might be the most effective reductants for NACs. The results presented in Table 2 demonstrate that the predominant reductants may be inferred by the differences in the reactivity pattern, i.e., from the competition behavior and from the range of relative reactivities of the probe compounds used.

Field Injection Experiment. The elevated concentrations of dissolved CH$_4$, Fe(II), Mn(II) and NH$_4^+$ (Table 1) demonstrate that the leachate-contaminated groundwater in the study area is anaerobic. Note that the concentration of dissolved Fe(II) was particularly high (>1 mM). The redox conditions in the aquifer were not affected by the injection experiment as indicated by measurements of redox-sensitive species with time (data not shown).

The first fence of multilevel samplers was installed 1 m downgradient from the injection wells corresponding to a residence time of 7−14 days according to the bromide breakthrough data (see Figure 2b). In all samples taken from this first sampling location within the aquifer, the concentrations of the NACs were below the detection limits of our methods, indicating a very rapid transformation with half-lives of less than 7 days. Aniline, 2-CH$_3$-aniline, and 4-CH$_3$-aniline were detected as transformation products of the mono-nitro compounds, and fairly good mass balances were obtained (Figure 2a−c). 2-NH$_2$-NB and 4-NH$_2$-NB were detected as transformation products of the two dinitrobenzenes injected but were present only in trace concentrations. Note that phenylenediamines, the expected reduction products of aminonitrobenzenes, could not be quantified by our HPLC methods in the complex leachate matrix. Samples taken further downgradient in the reduced part of the plume showed no further transformation of the anilines (data not shown). Due to the very rapid transformation of NACs, their reactivity pattern could not be inferred from the field injection experiment and was studied in more detail by the following experimental systems.

***In Situ* Microcosm Experiments (ISMs).** Loading the stock solution of xenobiotics to the ISMs took 2−3 h, and within this period, some transformation of the nitroaromatic compounds, particularly of the dinitrobenzenes occurred. The initial concentrations of the NACs measured in the ISM therefore are below the spiked concentrations of about 1.5−2 μM (Figure 2d−f). Typical results are shown in Figure 2 (d−f) for an ISM at 25 m distance from the landfill. Fast reduction rates and a similar sequence of NAC transformation were observed in all ISM throughout the plume. After 50−70 days, all NACs were transformed below the detection limit. In general, the NACs showed a fast initial concentration drop followed by a period with slower rates of disappearance. This initial drop can be ascribed to a combination of a fast initial reduction and maybe rate-limited sorption. Since NACs were reduced even in biologically deactivated systems (see below), we cannot obtain independent information on the extent and kinetics of sorption processes of NACs in our systems. However, distribution constants of the NACs for the Grindsted aquifer matrix are expected to be in the range as found for toluene [0.03−0.1 L/kg (*20*)], which is only slightly more hydrophobic than the NACs used. In addition to hydrophobic partitioning into organic matter, certain NACs may sorb specifically to clay minerals (*21*). However, among the NACs used, only 1,3-DNB exhibits a significant affinity for clays (*22, 23*). This may indicate that the most important

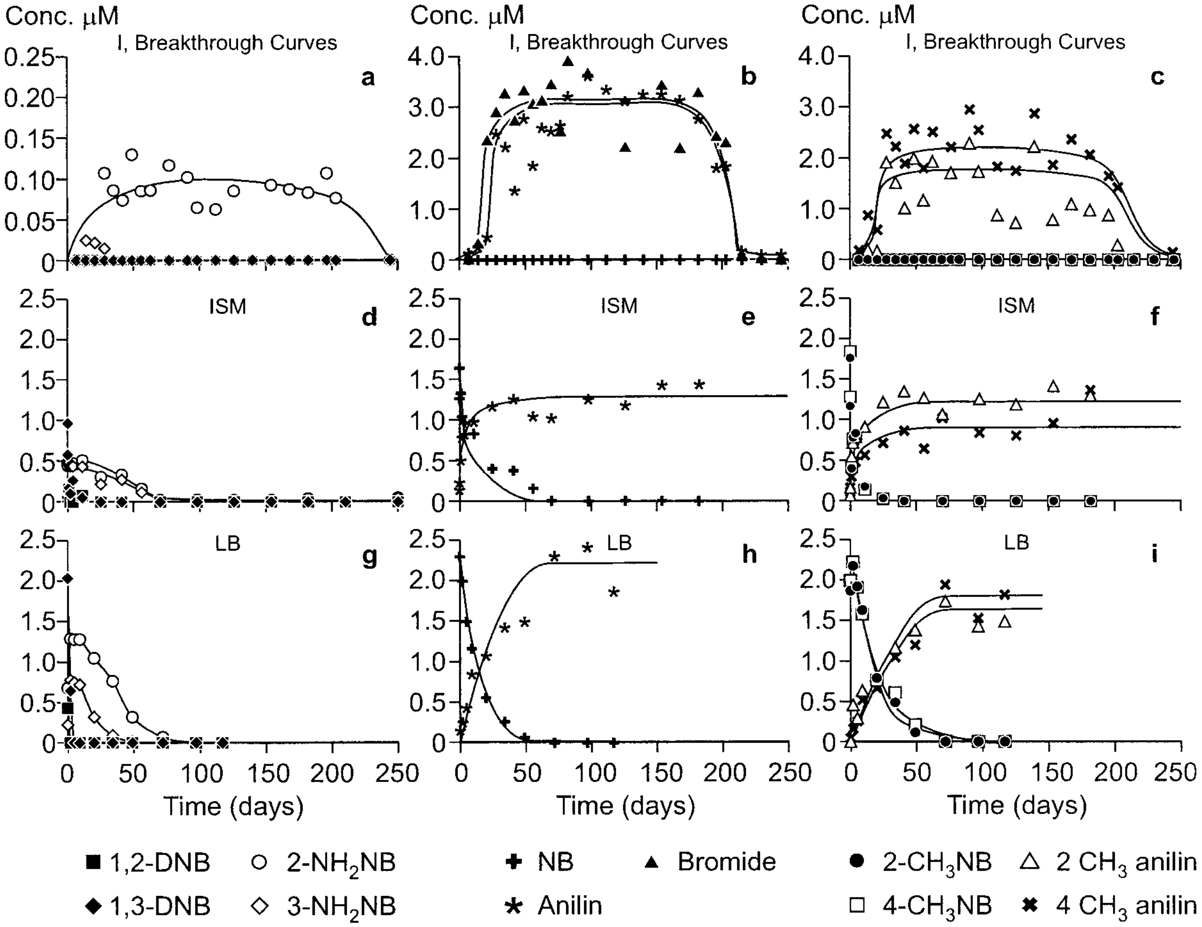

FIGURE 2. Typical results of transformation of NACs in the experiments at the Grindsted Landfill site (Denmark). (a–c) Injection experiment, (d–f) *in situ* microcosm experiments, and (g–i) laboratory batch experiments.

contribution to the initial drop may be ascribed to a fast reduction.

At all sample locations in the plume, 1,2-DNB showed the fastest reduction rate followed by 1,3-DNB. NB, 2-CH$_3$-NB, and 4-CH$_3$-NB showed significantly slower reduction rates, but only minor differences between the locations. The corresponding anilines were formed, and fairly good mass balances were obtained considering the respective anilines as the only degradation products of the NACs. Within the experimental period (up to 250 days), the anilines remained stable. However, 3-NH$_2$-NB and 2-NH$_2$-NB exhibiting another NO$_2$ moiety were further reduced within 100 days. In the biologically deactivated ISM, rates and sequence of NAC reduction were similar to the active experiments. However, the biphasic disappearance of NACs did not allow us to come up with meaningful rate constants for NAC transformation in the ISM.

All active ISM indicated methane production with time, while the biologically deactivated ISM did not show any methane production. Low concentrations of sulfate and sulfide were observed in all ISM, but no significant changes with time occurred. Fe(II) and Mn(II) were present, but did not show any clear changes in concentrations, except at a distance of 55 m from the landfill. Here, concentrations of both Fe(II) and Mn(II) increased significantly until day 68, followed by a decrease until the end of the observation period. This may indicate more active iron reduction in this area, although high concentrations of dissolved Fe(II) were present at all distances (Table 1).

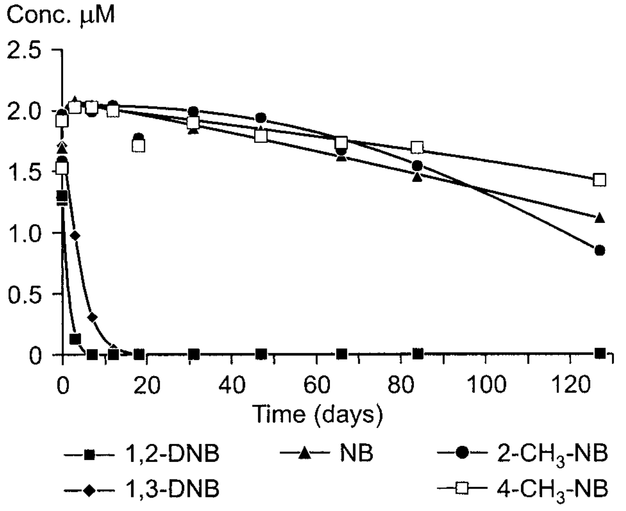

FIGURE 3. Reactivity of the five nitroaromatic probe compounds in a laboratory batch experiment with leachate-contaminated groundwater only from the Grindsted Landfill site (Denmark).

The reduction of NACs in the Tedlar bag prior to loading of the ISMs suggests that NAC reduction might occur to a certain extent in homogeneous solution of the leachate-contaminated aquifer. In order to further investigate this hypothesis and to evaluate to what extent the presence of solid aquifer material is necessary to support NAC reduction, batch experiments with leachate-contaminated groundwater only were conducted (Figure 3). Fast reduction of dinitrobenzenes occurred in the experiments with reaction rate constants comparable to those obtained in the presence of sediment matrix. Reduction rate constants of NB, 2-CH$_3$-NB, and 4-CH$_3$-NB were several orders of magnitude slower

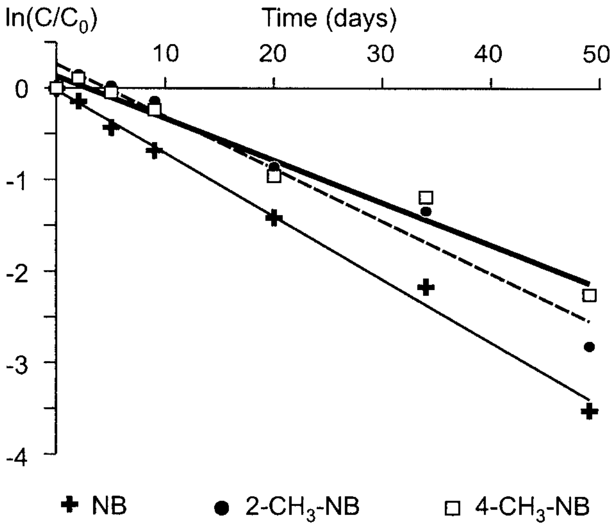

FIGURE 4. Plot of ln (*C*/*C*$_0$) versus time for laboratory batch experiments, Grindsted Landfill site (Denmark) (—): NB, (---) 2-CH$_3$-NB, and (—) 4-CH$_3$-NB. Linear regression yielded k_{obs} values of 0.07, 0.06, and 0.05 d^{-1}, respectively.

in the groundwater. Within the course of the experiment (120 days), the latter compounds were reduced to about half of their initial concentration at most.

As discussed above, Fe(II)$_{aq}$ and reduced DOM were the predominant reductants in the groundwater only experiments. If DOM was the predominant reductant, the relative reactivity of dinitrobenzenes is expected to be 2−3 orders of magnitude higher compared to nitrobenzene, which is consistent with our findings in the groundwater only experiments (Figure 3). At the pH of the groundwater, dissolved Fe(II) is only capable of reducing 1,2-DNB at measurable rates (Figure 1). First-order rate constants for this reaction were about 0.12 h^{-1}, corresponding to a half-life of 6 h at pH = 7.2 and Fe(II)$_{aq}$ = 1.5 mM. These results suggest that, in a homogeneous aqueous solution, reduced DOM in the Grindsted aquifer may contribute significantly only to the reduction of dinitrobenzenes. Fe(II)$_{aq}$ may be considered as an additional reductant of minor importance for 1,2-DNB. The reduction of NB, 2-CH$_3$-NB, and 4- CH$_3$-NB, however, proceeds at significant rates only in the presence of a solid matrix. The fast reduction of the latter compounds in the field injection and ISM experiments is therefore probably caused by a surface-mediated process(es).

Laboratory Batch Experiments (LBs). Batch experiments were carried out with sediment and groundwater sampled at the same locations where the *in situ* microcosms were installed and parallel to the injection experiment. The concentrations of soluble redox-sensitive species indicated fairly constant and strictly anaerobic redox conditions throughout the experiment. Note that complete reduction of all NACs to the corresponding anilines requires only about 80 μM electrons (6 e$^-$ per NO$_2$ group), which is not sufficient to cause measurable changes of the high Fe(II) concentrations within the aquifer even if Fe(II) was the only reductant of NACs. Figure 2g−i shows typical results obtained for a batch experiment representing the conditions at 15 m distance from the landfill. Very similar results were obtained with samples collected along the flow line at other locations within the plume (data not shown). All five probe compounds were reduced at fast rates (see examples in Figure 4). Again, 1,2-DNB exhibited the highest reduction rate constants (k_{aquifer}, Table 2) followed by 1,3-DNB, NB, 2-CH$_3$-NB, and 4-CH$_3$-NB. For 1,2-DNB the reduction took place within a few hours, and the reduction rate can roughly be estimated to 74−37 d^{-1} ($t_{1/2}$ = 0.01−0.02 days). First-order transformation rates ranged from 0.85 to 0.41 d^{-1} ($t_{1/2}$ = 1−2 days) for 1,3-DNB, 0.11−0.07 d^{-1} ($t_{1/2}$ = 6−10 days) for NB, 0.08−0.05 d^{-1} ($t_{1/2}$ = 8−14 days) for 2-CH$_3$-NB, and 0.09−0.04 d^{-1} ($t_{1/2}$ = 7−16 days) for 4-CH$_3$-NB.

The relative rate constants of NAC reduction in these aquifer batch systems varied about 2 orders of magnitude. This is very similar to what can be expected if Fe(II) sorbed at Fe(III) surfaces was the reductant (Table 2). The competition of NACs for reactive Fe(II) sites (Q_c values) as determined in model systems was very similar to the relative rate constants of NAC reduction observed in the presence of the aquifer matrix as well as in heterogeneous Fe(II)/Fe(III) model systems except for NB, which had a somewhat lower Q_c value than the 2- and 4-CH$_3$-NB. Biologically deactivated samples showed very similar results with respect to NAC transformation as compared to active batches. Transformation of NACs occurred without any noticeable lag period and in the same order as described above. However, slightly slower transformation rate constants were observed for NB, 2-CH$_3$-NB, and 4-CH$_3$-NB (data not shown).

Evaluation of Aquifer Experiments. In all experimental systems containing solid aquifer matrix, NACs were completely reduced within a period of 2−70 days. Generally, dinitrobenzenes, i.e., compounds exhibiting the highest $E_h^{1'}$ (Table 2), were reduced at very high rates and without any noticeable lag phase. Furthermore, these compounds were always reduced first within the mixture of the NACs studied. These results and the very similar pattern of NAC reduction in active and deactivated LB experiments suggest that the process of NAC reduction is dominated by abiotic reactions rather than by biotransformation.

In the presence of aqueous Fe(II) and either Grindsted aquifer sediment or goethite, the reduction rates of NACs were strongly enhanced as compared to a homogeneous solution and were significant even for NACs with relatively low reduction potential ($E_h^{1'}$). The sequence and relative rate constants of NAC reduction in the ISM and LB were similar to those measured in goethite/Fe(II) systems. This can be taken as strong evidence that in the anaerobic region of the Grindsted Landfill leachate plume ferrous iron adsorbed to iron(III) (hydr)oxides is the dominating abiotic reductant and significantly contributed to the fast overall rates of reduction of the NACs in the plume. Note that the reactivity of Fe(II) adsorbed to goethite reported here is very typical for Fe(II) sorbed to Fe(III) containing minerals in general, as was demonstrated for nitrobenzenes (*6*) and polyhalogenated aliphatics (*16*). Furthermore, experiments conducted at 1.5 mM concentrations of both, Ca^{2+} and Fe^{2+}, demonstrated that high concentrations of divalent cations present in addition to Fe(II), as found in the leachate-contaminated groundwater, did not significantly interfere with the reduction properties of adsorbed Fe(II) (data not shown). This suggest that the reactivity of Fe(II) sorbed at goethite surfaces by ion exchange is negligible as compared to Fe(II) bound by other mechanisms or that ion exchange is not important at our experimental conditions. Thus, processes very similar to those illustrated by the Fe(II)/goethite system are expected to proceed in anaerobic aquifers in the presence of aqueous ferrous iron and iron(III) (hydr)oxides.

Generally, the reduction of NACs proceeded much faster in the field injection experiment than in the LB and ISM experiments. This may be explained by the difference between a flow system and the static LB and ISM systems. In contrast to the static systems, the compounds in the injection experiment are exposed to fresh aquifer matrix as they migrate from the injection wells toward the first sampling points at 1 m distance.

Factors Controlling the (Re)Generation of Reactive Fe(II) Sites. Strong additional evidence for the pivotal role of surface associated Fe(II) in the reduction of NACs in

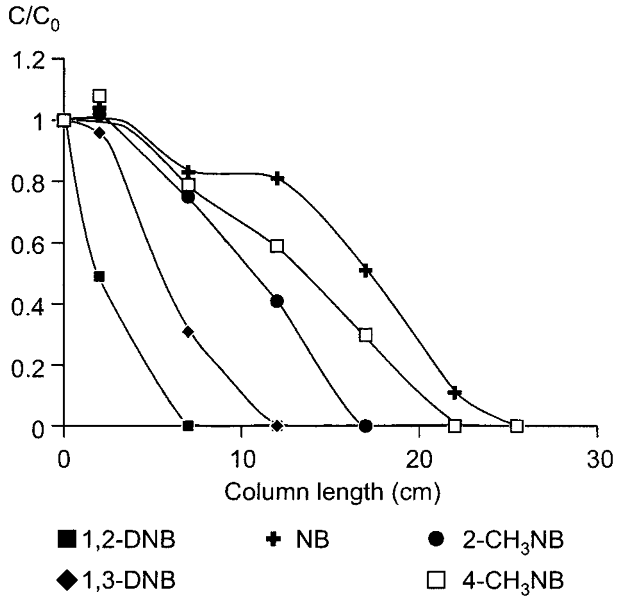

FIGURE 5. Relative concentrations of the five NACs in an aquifer column operated under iron-reducing conditions. Initial concentration of each NAC in the mixture was 2 μM at pH = 7.1 and 100 μM acetate.

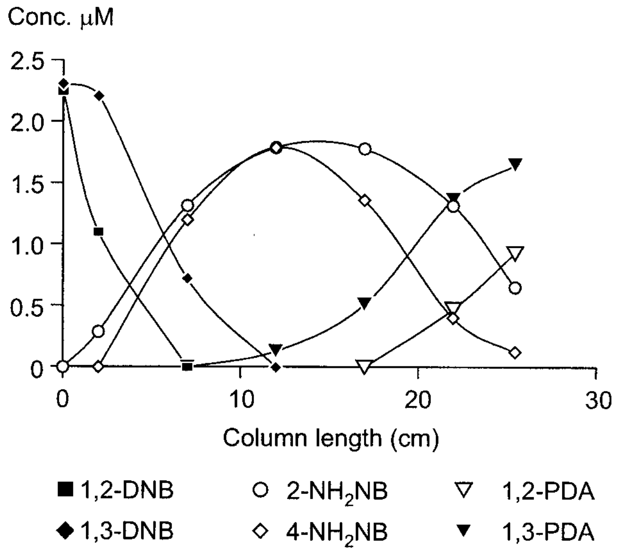

FIGURE 6. Concentration gradients of dinitrobenzenes and their reduction products in an aquifer column operated under iron-reducing conditions. Initial concentration of each NAC in the mixture was 2 μM at pH = 7.1 and 100 μM acetate.

anaerobic natural aquifers was obtained from column experiments operated under iron-reducing conditions. Heijman et al. (*17*) showed that under such conditions NACs were reduced by surface-bound Fe(II) species by a purely abiotic reaction. However, the rate of NAC reduction was determined by the activity of iron-reducing bacteria, which were necessary to produce and regenerate such Fe(II) sites. Figure 5 shows concentration profiles of a mixture of the five nitroaromatic probe compounds in such a column. The sequence of NAC reduction in such iron-reducing columns agreed well with the relative affinities of the NACs for Fe(II) sites as reflected by their binary competition coefficients, Q_c (Table 2). Since the (re)generation and, thus, the number of reactive Fe(II) sites available were limited in the column systems, the reduction of NACs exhibiting relatively low Q_c values [i.e., low affinity for reactive Fe(II) sites] was inhibited as long as strong competitors for Fe(II) sites such as dinitrobenzenes were present. Note that due to the constant activity of iron-reducing bacteria providing reactive Fe(II) sites, the total rate of nitro reduction in these systems was constant, irrespective of the concentration or the number of different NACs present (data not shown). With the exception of NB, the sequence of NAC reduction in the columns agreed with the results obtained in the ISM as well as the batch systems containing Grindsted aquifer sediment and/or Fe(II) sorbed to goethite. These results confirm our interpretation that sediment-associated Fe(II) species dominate the reduction of NACs in iron-reducing aquifers such as the Grindsted Landfill plume. Furthermore, the results demonstrated that microbial processes affected the reduction of NACs only in so far, as the activity of iron-reducing bacteria contributed to the (re)generation of reactive Fe(II) sites.

Nielsen et al. (*24*) studied the transformation of various xenobiotic organic compounds including nitrobenzene in an anaerobic plume downgradient from another landfill (Vejen, Denmark). They used laboratory batch systems and *in situ* microcosms similar to the systems used in this study. In contrast to the Grindsted Landfill plume, the concentrations of aqueous ferrous iron varied considerably throughout the Vejen Landfill plume. At strongly reducing conditions, they found reduction rate constants of NB similar to those obtained in the Grindsted Landfill plume. However, further out in the plume, unlike to the Grindsted aquifer, they observed significantly slower reduction rate constants in biologically inhibited experiments. Their conclusion was that biological processes or chemical processes coupled to biological activity were important in the transformation of NB under iron reducing conditions, while chemical processes seemed to be responsible for the transformation in the more reduced part of the plume. This is in good accordance with our observations and interpretation of the interplay of microbial iron reduction and abiotic transformation of NACs by Fe(II) at the surface of Fe(III) minerals. The fact that there was no significant variation of NAC reactivity throughout the studied part of the Grindsted Landfill plume is consistent with the high concentrations of aqueous Fe(II) present in this part of the aquifer, providing an abundant reservoir of Fe(II) bulk reductants. Under such conditions, the (re)generation of reactive Fe(II) species at the minerals is not, or to a much lesser extent, controlled by the activity of iron-reducing bacteria since regeneration of Fe(II) sites can also proceed by adsorption of aqueous ferrous iron to the mineral surfaces (*6*, *16*).

Thus in anaerobic, iron-rich aquifers, Fe(II) associated with Fe(III)-containing mineral phases may generally be considered as highly reactive species for reducible organic contaminants. As has been demonstrated by Pecher et al. (*16*), such reductants are also capable of reducing certain halogenated aliphatic compounds, e.g., hexachloroethane or tetrachloromethane. Indeed, a rapid reduction of tetrachloromethane paralleling the reduction of NACs was found in both the Vejen and the Grindsted aquifers (*24*, *25*).

Products of NAC Reduction. Aromatic amines (anilines) are expected to be the final products of NAC reduction (*26*). The experiments in laboratory model systems showed that all NACs, including dinitrobenzenes, were reduced almost stochiometrically to the respective anilines. A sequential and fairly quantitative reduction of dinitrobenzenes to nitroanilines and subsequently to phenylenediamines occurred in laboratory aquifer columns under iron-reducing conditions, even though some unidentified peaks in the HPLC chromatograms indicated that some transient intermediates were formed (Figure 6). In the field experiments as well as in the laboratory batch experiments with Grindsted aquifer sediments, mono-NACs were almost quantitatively reduced to the corresponding anilines. 2-NH$_2$-NB and 4-NH$_2$-NB, respectively, were found as transient reduction products of dinitrobenzenes (Figure 2g–i). Phenylenediamines, however, could not be detected in the leachate-contaminated groundwater due to significant matrix effects.

The results suggest that aromatic (poly)amines can be expected as major products of abiotic NAC reduction in anaerobic aquifers. Despite the fact that transformation of anilines by microorganisms (*27–29*) and chemical reactions (*30*) has been reported, the various anilines formed from NAC reduction were very stable within the time frame (i.e., up to 250 days) and under the conditions of our experiments. Due to this apparent stability, an evaluation of the conditions that are necessary to further transform aromatic (poly)amines to less toxic compounds is of great interest.

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