Retardation of various nitroaromatic compounds in highly permeable aquifers

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Abstract

Groundwater in the discharge area of former ammunition production facilities often reveals severe contamination by production residues and waste products. Thus, these can cause health hazard to human beings in case untreated water is consumed.

The investigation of the WASAG explosives plant in Haltern, Germany, revealed lack of scientific knowledge about retardation of nitroaromatic compounds. In this case study we have to deal with a more than 1.65 km elongated contamination plume consisting of various nitroaromatic compounds such as trinitrotoluene, dinitrotoluenes, dinitrobenzens, dinitronaphthenes and various degradation compounds coming from a former production area used for military production during times of war. There, from 1918 until 1922 waste waters from dismantling ammunition were sunk into a deep-reaching extended aquifer of high permeability. Therefore, a laboratory investigation program with column tests was initiated. First results reveal that retention and release processes as well as degradation mechanisms play a considerable role determining the velocity of transportation of contaminants. There is a strong correlation of the retardation coefficients of the nitroaromates with the content of silt, clay and organic substances in the soil. Even very small contents of these substances cause a significant increase of retardation factors. Also, the retardation factors of different nitroaromatic compounds vary in a wide range.

1 Introduction

Cleaning of groundwater, withdrawn from nitroaromatic contamination plumes in highly permeable aquifers e.g. by pump and treat, is extremely cost-intensive as a result of large quantities of water, necessarily to be recharged and very low admissible concentrations. That often means the impossibility of an instant remediation but leads us to considering natural attenuation.

As can be easily shown with the example of the WASAG site, significant degradation of nitroaromatic compounds does take emphasis for place. This can be proved by the presence of degradation products such as 2-Amino-4,6-dinitrotoluene, 4-Amino-2,6-dinitrotoluene and Trinitrobenzene in any single sample and 2-Nitro-6-aminotoluene and 4-Nitro-6-aminotoluene if analyzed.

Thus, application of natural attenuation is a matter of risk assessment. Therefore, the spatial future spreading of the contamination plume must be predicted on the basis of an examination of the past spreading, which has taken place in a period of 84 years.

Mass flow of the ideal tracer by way of groundwater discharge in this specific aquifer is wholly determined by convective-dispersive flow and very well known, unlike the spreading of nitroaromates which cannot yet be described adequately. Therefore, we established an investigation program into the three-dimensional spreading behaviour of nitroaromates in the subsoil, beginning with the laboratory part. This will be followed by application of the results on cases in field dimension. Previous works comprised a 2-dimensional hydraulic finite element model on the basis of SEEP/W Software. This will be the basis for future transport modelling.

2 Results of site investigations

Results of a ten year investigation program of the WASAG site into hydrogeology, risk assessment and remediation planning are summarized in Entenmann & Rappert [1] and Entenmann [2]. These investigations revealed that the production of civil explosives, starting in 1897 and continuing up to now, did not cause any contamination of the aquifer.

On the contrary, the military production which took place from 1914 to 1918 and from 1939 to 1945 caused severe soil contamination: As shown in figure 1 the topsoil is contaminated in a large area of almost 55,000 m² by various nitroaromatic compounds such as trinitrotoluene, dinitrotoluenes, dinitrobenzens, dinitronaphthenes and various degradation compounds. But the extent of contamination is locally very different. The topsoil contamination has been detected with scatter investigations comprising more than 900 chemical analyses. However 56% of the summarized contents of nitroaromatic compounds (Σ NA) were below 1 ppm, while only 8% exceeded 100 ppm, see table 1.

Three “hot spots” could be detected. They can be deduced from the following former activities, see figure 1:

(1) Burning of waste explosives.
(2) Operation of the test plant.
(3) Operation of the trinitrotoluene melting plant and filling station.

These activities led to overall high concentrations in these areas up to several thousands of ppm of nitroaromatic compounds in the topsoil.

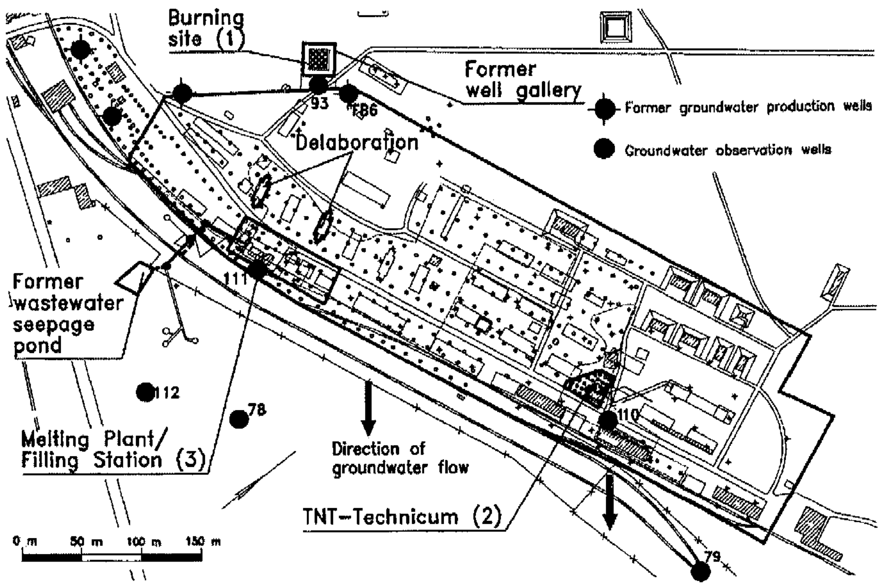

Figure 1: Former WASAG military site for the laboration and delaboration of World War I / II ammunition.

Table 1: Statistical analysis of the analyses of topsoil samples obtained within the areas of severe soil contamination.

cont1)	n2)	$n_0$3)	n_x4)				
			b.d.l. to 5	5 to 10	10 to 100	> 100	mean value
			[ppm]				
TNT	788	210	490	21	35	32	335
DNT	670	206	423	15	18	8	300
DNAPHT	477	62	356	16	21	22	74.5
DNB	497	280	199	4	8	6	17.4
TNB	497	436	57	4	0	0	0.09

1) cont: contaminant
2) n: total number of chemical analyses
3) n_0: number of chemical analyses below detection limit (b.d.l.)
4) n_x: number of chemical analyses related to the concentration range

The emission potential of the contaminated soil was investigated by percolation tests and by a thorough evaluation of the spatial contamination scatter. These results were previously published [2] and revealed that only the “hot spots” had the potential of producing a significant and detectable groundwater contamination. This was proved by groundwater observation, which revealed three minor contamination plumes in the aquifer.

But the major contamination plume in the groundwater, reaching a length of more than 1.65 km, cannot be derived from soil contamination. This could not only be shown with the help of percolation tests but also by mass flow balancing on a basis of discharge rates and contents of nitroaromates in the groundwater [1]. This contamination has its origin in delaboration of ammunition, coming back from the battle-fields, which is documented to have started in 1918 and to have finished in 1922. Waste water from the cleaning of delaborated shells was sunk in a waste water pond, see figure 1.

Table 2: Spreading of nitroaromatic compounds in the groundwater since they have been sunk from 1918 to 1922.

cont1)	**1999**	**1999**	**2002**	**1999**	**1991**	**1994**	**1999**	**1999**	**1991**	**1994**	**1999**
TNT	0.03	399	680	247	37	180	300	44	4.6	8.0	3.8
2,3-DNT	b.d.l.	1.8	6.3	0.2	-	0.36	0.3	0.2	0.3	0.49	0.9
2,4-DNT	b.d.l.	55	110	5.4	9.5	12	9.1	11	6.6	21	28
2,6-DNT	b.d.l.	5.3	53	0.6	0.8	1.6	3.2	1.8	0.4	2	4.9
3,4-DNT	b.d.l.	2.7	10	0.3	0.2	0.06	0.3	0.27	0.5	1	2.4
1,2-DNB	b.d.l.	61	-	5.8	1	0.38	1.7	21	79	150	212
1,3-DNB	0.06	77	260	0.7	1.8	3.8	3.1	27	33	270	1,048
1,4-DNB	b.d.l.	b.d.l.	-	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.1	0.9	3.9	15
TNB	b.d.l.	1.5	-	2.5	1.5	120	48	b.d.l.	-	0.28	4.3
NB	b.d.l.	b.d.l.	0.42	b.d.l.	0.3	b.d.l.	b.d.l.	b.d.l.	-	-	b.d.l.
1,5-DNAPHT	b.d.l.	6.5	7.82	1.6	b.d.l.	b.d.l.	2.5	0.38	-	21	1.1
1,8-DNAPHT	b.d.l.	54		1.7	-	4	1.6	3.7	-	13	21.3
2-A-4,6-DNT	0.1	45	84	15	0.9	2.3	3.5	3.8	0.5	1.3	0.7
4-A-2,6-DNT	0.18	55	82	19	1.2	3	4.4	4.5	-	1.9	0.9
RDX	-	-	-	-	b.d.l.	b.d.l.	-	-	0,24	-	-
picric acid	-	-	-	-	b.d.l.	b.d.l.	-	-	0,28	-	-
s3) [m]	**80**	**400**		**700**	**970**			**1,075**	**1,400**		
t4) [a]	**2.7**	**13.5**		**23**	**32.3**			**36.3**	**47**		

1) cont: contaminant

2) b.d.l.: below detection limit

3) s: spreading-distance from the seepage-pond to the monitoring well

4) t: spreading-time of the ideal tracer

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In the groundwater downstream, the resulting concentration scatter, is therefore very heterogeneous. This can be seen from the example given in table 2 which shows the time-dependant development of spreading along the axis of the contamination plume. This table also shows that the contamination plume has separated from its source.

As a result of the different initial distribution of the contaminants in the waste water, depending on the different types of ammunition, in every monitoring well, the distribution of contaminants varies time-dependent. This can be seen by the example of table 3.

Table 3: Time-dependant variation of the distribution of contaminants indicated with the example of well N° 110, placed in the groundwater downstream.

[μg/l]	**09.04.1997**	**18.09.1997**	**03.11.1998**	**22.10.1999**	**12.06.2002**
2,3-DNT	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
2,4-DNT	1.8	26	b.d.l.	0.2	1.9
2,6-DNT	0.8	15	b.d.l.	0.4	1.6
3,4-DNT	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Σ	2.6	41	-	0.6	3,5
2,4,6-TNT	179	3,059	1,272	260	2,100
1,2-DNB	b.d.l.	b.d.l.	b.d.l.	b.d.l.	-
1,3-DNB	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.4
1,4-DNB	b.d.l.	b.d.l.	b.d.l.	b.d.l.	-
1,3,5-TNB	13	23	20	4.3	-
Nitrobenzene	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
2-Nitro-6-aminotoluene	-	-	-	-	-
4-Nitro-6-aminotoluene	-	-	-	-	-
2-Amino-4,6-DNT	7.1	160	176	98	240
4-Amino-2,6-DNT	12	215	249	105	210
1,3-DNAPHT	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
1,5-DNAPHT	b.d.l.	b.d.l.	b.d.l.	0.5	b.d.l.
1,8-DNAPHT	b.d.l.	b.d.l.	b.d.l.	0.7	b.d.l.
Σ total	213.7	3,498	1,717	469.1	2,554.9

3 Results of the hydraulic model

On the basis of a thorough determination of the hydraulic parameters of the aquifer, under estimation of many additional values from publications, a hydraulic model was established by using SEEP/W finite element software.

This was possible, as the coefficient of permeability as well as the hydraulic gradients are very well known and the random conditions can be chosen quite appropriately.

Figure 2 shows one of 7 established groundwater isograph plans which were used to calibrate the model. The hydraulic gradients vary in a small range and reveal mean values of $i = 6.7\text{x}10^{-3}$. The aquifer parameters are the coefficient of permeability, amounting to $k = 1.5\text{x}10^{-4}$ m/s and the effective porosity amounting to $n_{eff} = 0{,}25\%$. The aquifer's depth was assumed 100 m.

From the model result field velocities of $v_a = 1\text{x}10^{-6}$ m/s = 0,0864 m/d = 31,5 m/a, and specific discharge rates of $Q = 2.5\text{x}10^{-5}$ m^3/s = 800 m^3/a in the axis of the contamination plume. This discharge rate is related to one meter discharge width.

4 Transport model

In order to establish a future transport model, dispersion coefficients and retardation coefficients must be known. Dispersion coefficients of the described aquifer are very well known by previous investigations [3] and must not be derived. So, our aim was to determine retardation coefficients of the above mentioned substances which are not known at all.

Previous estimations of spreading velocity and freight rates, derived from field observations concerning the WASAG plume, revealed the following preliminary clues: Considering an 84-year spreading time of contaminants, the centre of the contamination plume could have reached a total distance from its source of 2,520 m. The actual maximum of contamination has a distance of approximately 1,200 m from the source. This means an average retardation factor of $R_D = 2.10$.

The contamination plume has separated from its source. The distance is about 275 m. Thus, maximum retardation is about 9.1.

The front of the contamination plume has reached a distance of approximately 1,650 m from the source. Considering dispersion, the minimum retardation in the aquifer is more than 1.5 but less than 2.1.

The different retardation must be derived from the different properties of the aquifer in sedimentary structures of slightly different composure as there is no strict spectrum of the array of different chemical compounds within the plume. This means, that the overall retardation is an integrated value of many different retardation factors related to the single sedimentary structure, that builds up the aquifer.

There is a differentiation of chemical compounds in the plume, but it can not be described yet, as its structure is overlain by the discontinuity of the former source. This can only be overcome with the help of laboratory tests.

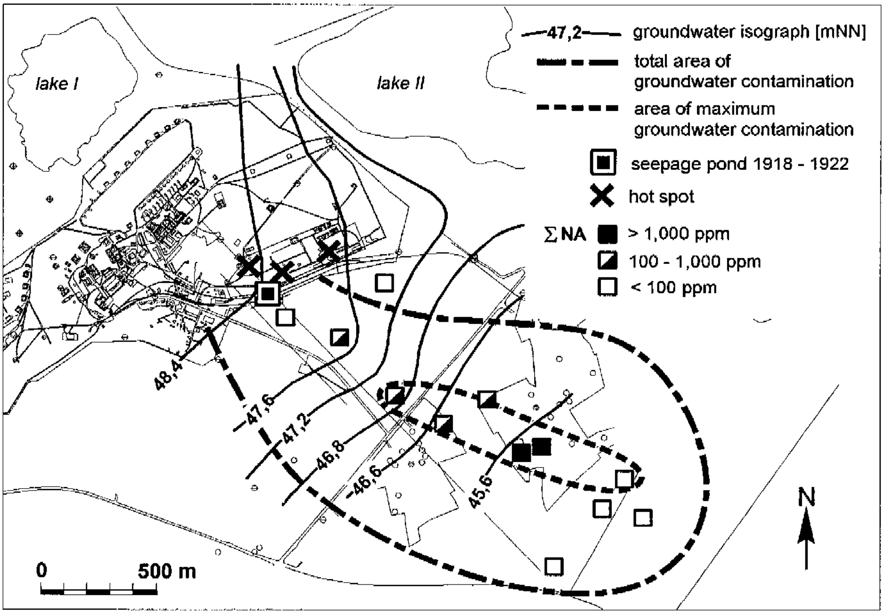

Figure 2: Actual extension of the contamination plume regarding to the groundwater isograph plan.

A future transport model will depend on the following premises: The specific hydrogeological and hydrochemical situation, resembling a large-scale field experiment, is very suitable for modelling the transport of nitroaromates in the groundwater:

- The starting time-span of the contamination and the precise location are known.
- The spreading rate of the plume can exactly be derived from the present extension of the plume, see figure 2.
- There are more than 300 chemical analyses of groundwater samples from monitoring wells in the time-span from 1991 to 2002. Each analysis comprises at least 23 parameters.

There are some aspects in favour of future mass flow modelling:

- The aquifer is very deep-reaching and covers an area of more than 770 km^2 [4]. The aquifer reaches depths of 100 m to 300 m.
- The aquifer is comparably very homogeneous.
- The content of fines and organic material in the aquifer is very low.
- The hydraulic parameters are very well known.
- Diffusive processes can totally be neglected.

But there are also some aspects that will probably cause problems:

- The rate of infiltrated nitroaromates was not constant but depending on the washing and infiltration process.
- The composition of the different compounds in the wash-water was not always the same but depended on the type of ammunition delaborated. For example French ammunition often contained a significant proportion of dinitronaphtenes.

5 Results of preliminary laboratory investigations

In order to receive retardation factors under defined random conditions, column tests were carried out. These were carried out with inverse flow. Breakthrough-curves were recorded in order to find out the time-dependant behaviour. Figure 3 shows the test array. Breakthrough-curves of the almost ideal tracer Cl^- were compared with the breakthrough-curves of every single analyzed nitroaromatic compound. The test-fluid was gained from a well amid the contamination plume. Its chemical composition is given as follows: 2,076 μg/l TNT; 67 μg/l 1,3,5-Trinitrobenzene; 159 μg/l 2-Amino-4,6-dinitrotoluene; 207 μg/l 4-Amino-2,6-dinitrotoluene; 16 μg/l 1,5-Dinitronaphthene and 30 μg/l 1,8-Dinitronaphthene. This is a total content of 2,555 μg/l of nitroaromatic compounds.

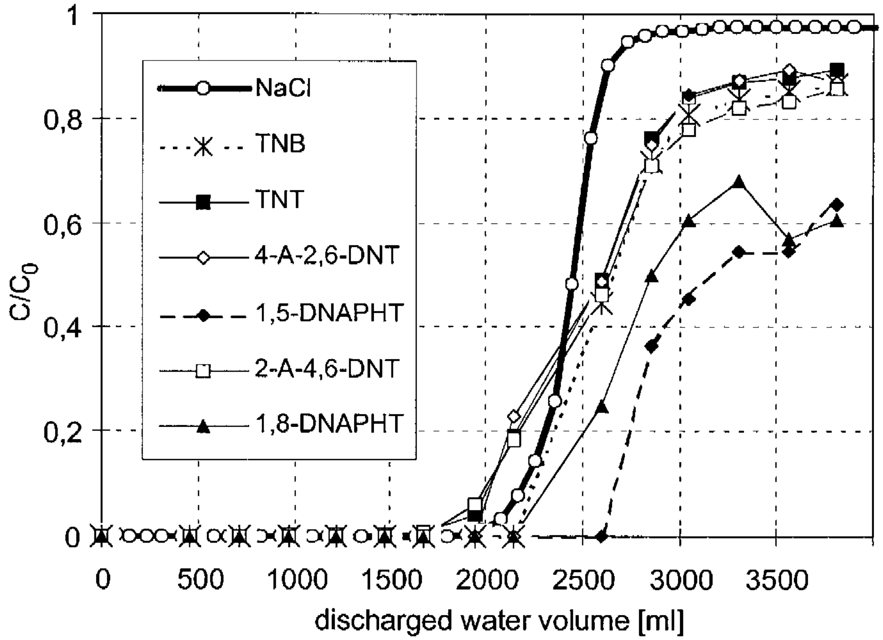

Figure 3: Breakthrough-curve of the ideal tracer Cl^- compared with the breakthrough-curves of every single nitroaromatic compound derived from column test A.

The Cretacious sands of the aquifer are comparably very homogeneous. Undisturbed core samples from the closer downstream of the WASAG site were available. These represent the back part of the contamination plume which contains only little fine grain such as silt and organic material. In the front part of the plume, more thin layers with increasing content of silt are present in the aquifer. So, we chose the widest possible spectrum of different grain size distribution of the sand in the core samples. The soil-mechanical and mineralogical parameters of these samples are given in table 4.

The column tests were carried out with hydraulic gradients ranging from 1.26 to 1.27. This is about 500 times the value of the natural groundwater flow in the aquifer. The factors of retardation received, are given in table 5.

The results show clearly that the assumption from the field evidence is correct: There is a strong dependence of the retardation factor on the content of silt and the organic content.

Core D, comprising 0.3% organic matter, reveals a significantly higher factor of retardation than the cores A and C comprising 0.1% organic matter. The silt content is medium for cores C (0.1%) and A (0.6%), while core D has maximum silt content of 1.5% and represents the uppermost content in sand samples within the area of the WASAG site, see table 4.

The retardation factors of the very refined quartz sands of the facies of Cretacious “Halterner Sands” are therefore dependent on smallest contents of fines and organic matter. Only small variations in these contents lead to significant variation in the retardation behaviour.

Samples of very small content of fines and organic matter (cores A and C) reveal retardation factors close to 1. The values for the different substances are not very much differentiated. Slightly elevated values, as with core-sample D, reveal retardation factors between 1.5 and 10 and also much more differentiation in content regarding the different substances, see table 5.

Table 4: Soil-mechanical and mineralogical parameters of the cores investigated.

core	**A**	**B**		**C**	**D**
depth [m]	44 – 45	4 - 5		20 - 21	3.5 - 4
description*	mS, fs, cs’	fS, ms		mS, fs, cs’	fS, ms
		4 m	5 m		
0.125 [%]	15.41	72.83	78.78	28.66	62.91
0.063 [%]	1.07	2.82	4.57	1.02	1.95
< 0.063 [%]	0.43	3.03	0.86	0.33	1.52
organic content [%]	0.13	0.78		0.06	0.26

* cS: coarse sand - mS: middle sand - fS: fine sand

Table 5: Factors of retardation R_D from column tests.

core	**A**	**C**	**D**
i	1.26	1.27	1.26
R_D TNT	1.13	1.14	1.47
TNB	1.14	1.17	1.54
4-A-2,6-DNT	1.13	1.18	2.72
2-A-4,6-DNT	1.14	1.13	3.36
1,5-DNAPHT	1.37	-	-
1,8-DNAPHT	1.24	1.13	9.88
1,2-DNB	-	1.12	-
1,3-DNB	-	1.12	-
1,4-DNB	-	1.14	-
2,4-DNT	-	1.15	-

6 Further investigations

Considering the results quoted above, it will be necessary not only to know the breakthrough curves in a single distance from the injection level but also in different levels between. These tests are being carried out just now. Their results will be published later.

Acknowledgement

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