Sequential Desorption of Nitroaromatic Compounds (NAC) from Soils

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by

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Abbreviations

General abbreviations

CEC	Cation exchange capacity
L/S ratio	Liquid-to-solid ratio
NAC	Nitroaromatic compounds
TOC	Total organic carbon

List of compounds

HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
NB	Nitrobenzene
TNB	1,3,5-Trinitrobenzene
1,3-DNT	1,3-Dinitrotoluene
2,4-DNT	2,4-Dinitrotoluene
TNT	2,4,6-Trinitrotoluene
2A-4,6DNT	2-Amino-4,6-dinitrotoluene

List of soils

CE-11	Camp Edwards
Crane	Crane Firing Range
FJ	Fort Jackson
IAAP	Iowa Army Ammunition Plant
WS	Weldon Spring

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1 Introduction

Nitroaromatic compounds (NACs) are widely used energetic chemicals. Especially at many military facilities and former ammunition plants the contamination of soil and water with explosives and related NACs has been recognized as a serious environmental problem. Studies, performed on ranges in both the United States and Canada, have shown that there is a large degree of variability in NACs contamination type, concentration, and spatial distribution [11, 12, 15, 16].

2,4,6-trinitrotoluene (TNT) is one of the most frequently occuring nitroaromatic contaminant in soils [10]. It is often accompanied by co-contaminants, such as dinitrotoluenes (2,4-DNT and 2,6-DNT), aminodinitrotoluenes (2A-4,6DNT and 4A-2,6DNT), and 1,3,5-trinitrobenzene (TNB), which result as byproducts of production or metabolites of microbial activity. In addition, Funk et al. [7] and Binks et al. [1] estimated that at least 28 sites in the United States and 200 areas in Germany, respectively, were contaminated with RDX.

Until today, there are no available technologies that can effectively remediate the wide range of type and concentration of NACs found on former ammunition plants, and active training ranges [6]. Alkaline hydrolysis promises to be an effective treatment technology especially for remediation of highly contaminated soils, without any risk of explosive reactions. To obtain basic data for alkaline hydrolysis of NACs as a novel remediation technology for contaminated soils, the chemical kinetics of alkaline hydrolysis of TNT was determined under aqueous homogeneous conditions. The pH values were varied in the range of 10 to 12, and the respective reaction rates were calculated using a pseudo-first-order model. The experimental conditions and results are described in more detail elsewhere [3, 4].

On the basis of these findings, alkaline hydrolysis was applied to two contaminated soils (HTNT 2, and ELBP) from former military sites in Germany to check the applicability of alkaline hydrolysis on inhomogeneous soil systems.

As shown in the second column of Table 1 both soils, HTNT 2 and ELBP, contained TNT, 2,4-DNT and 2,6-DNT as major contaminants. In addition, HTNT 2 contained 2A-4,6DNT, 4A-2,6DNT, and 1,3,5-TNB. In the ELBP soil similar concentrations (58 to 143 mg/kg) were measured for TNT, 2,4-DNT und 2,6-DNT, whereas in the HTNT 2 soil the TNT content was 16.1 g/kg, i.e. the TNT concentration was up to 665-fold higher than the concentration of the other NACs.

Alkaline hydrolysis was performed at pH 11 and pH 12 by addition of $Ca(OH)_2$. The alkaline treatment at pH 12 led to TNT hydrolysis in both soils within a few hours (Figure 1). 2,4-DNT decreased continuously by about 63 %, whereas 2A-4,6DNT and 4A- 2,6DNT decreased by about 75 % in the HTNT 2 soil. At pH 11 TNT also

Table 1: NACs detected in the untreated HTNT2 and ELBP2 soils (C_0), and maximum recovery rates (RR_{max} as sum of solid and liquid phases) measured during alkaline soil treatment. (*cda*: *c*ontinuously *d*ecreasing *a*mounts due to alkaline hydrolysis) [5]

Substance	untreated soil	pH 12		pH 11	
	C_0	RR_{max}		RR_{max}	
	[mg/kg]	[mg]	[%]	[mg]	[%]
HTNT2					
1,3-DNB	8.7	17.0	(195)	26.4	(303)
TNB	24.2	88.6	(366)	238.6	(986)
3,5DN-An	2.8	12.0	(428)	22.6	(808)
2,3-DNT	2.8	5.0	(177)	5.2	(184)
2,4-DNT	289.2	*cda*		*cda*	
2,6-DNT	70.5	77.6	(110)	82.5	(117)
3,4-DNT	4.8	8.8	(183)	10.2	(212)
TNT	16109.8	*cda*		*cda*	
2A-4,6DNT	66.7	*cda*		*cda*	
4A-2,6DNT	80.3	*cda*		*cda*	
ELBP2					
1,3-DNB	0.07	3.6	(5206)	0.2	(277)
TNB	1.10	18.1	(1648)	4.8	(438)
3,5DN-An	0.08	7.0	(8756)	0.9	(1148)
2,3-DNT	0.19	3.0	(1561)	0.3	(134)
2,4-DNT	142.7	*cda*		*cda*	
2,6-DNT	58.0	85.3	(147)	65.5	(113)
3,4-DNT	0.13	2.7	(2045)	0.3	(197)
TNT	115.7	*cda*		141.2	(122)
2A-4,6DNT	0.69	5.3	(767)	1.8	(266)
4A-2,6DNT	0.51	16.3	(3201)	3.1	(617)

dropped to almost zero in HTNT 2. The aminodinitrotoluenes were hydrolysed by about 55 %, and 2,4-DNT decreased by about 30 %.

However, instead of the expected decrease, a temporary or even permanent increase was observed for several NACs during alkaline treatment. Regarding ELBP an almost complete TNT hydrolysis was also achieved at pH 12. As in the case of HTNT 2, the concentration in the solid phase of ELBP continuously decreased. However, the concentration in the aqueous phase temporarily increased at pH 11, even more than expected. As a consequence, up to 122 % of the initial TNT was detected during the first two days (Figure 1). Subsequently, TNT hydrolysis prevailed and TNT almost

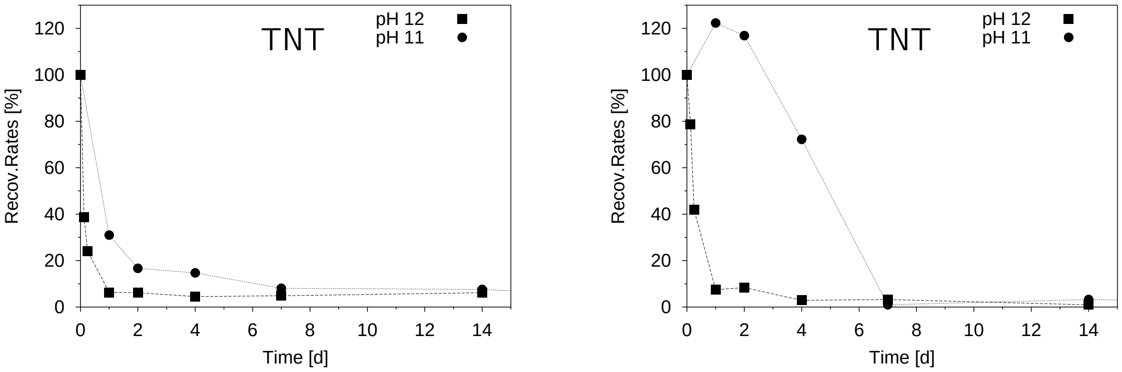

Figure 1: Recovery rates in [%] of TNT in soils HTNT 2 (left) and ELBP (right) during alkaline hydrolysis

completely disappeared.

A similar increase was observed for most of the NACs. The maximum amounts of these substances measured in the reaction vessels during alkaline treatment of HTNT 2 and ELBP are summarized in Table 1. Of the compounds investigated, only those continuously decreased where hydrolysis prevailed during alkaline treatment, namely TNT, 2A-4,6DNT, 4A-2,6DNT, and 2,4-DNT in HTNT 2 soil and TNT (pH 12), and 2,4-DNT in ELBP soil. The amounts of all other compounds temporarily or even persistenly increased during alkaline treatment.

The absolute concentrations of TNB are an extreme example. Figure 2 shows the recovery rates versus time for TNB. An initial concentration of 24.2 mg/kg TNB was measured in the untreated soil. At pH 11 a steady increase in recoveries was noted, first in the solid phase, and later also in the aqueous phase, with maximum amounts reaching 500 % in each case. Within the first four days this led to an increase of up to 986 %, corresponding to 239 mg/kg TNB. This represents a ten-fold higher concentration measured in the treated HTNT 2 soil compared with the initial value of 24 mg/kg TNB measured in the untreated soil. TNB hydrolysis may be only partial at pH 11. Hence, 272 % of TNB was still detected at the end of the alkaline treatment.

The observed increase of the compounds during alkaline hydrolysis is not attributable to inhomogeneities of the HTNT 2 and ELBP soil samples, since the soils were well homogenized prior to the investigations. In addition, the concentration of the NACs in the untreated soils were determined using three independant soil samples. Furthermore, the increase of substances like TNB and their subsequent decrease developed rather continuously and is too pronounced to be explained by analytical errors only. The compounds do certainly not represent by-products of alkaline TNT hydroly-

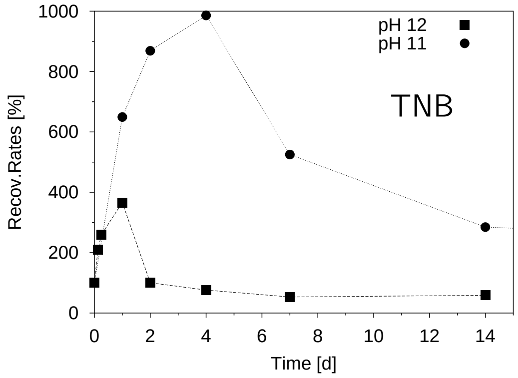

Figure 2: Recovery rates in [%] of TNB in soil HTNT 2 during alkaline hydrolysis

sis [3, 4].

Rather, this sometimes very pronounced increase during alkaline treatment and its pH dependence suggests the existence of desorption processes of the NACs from the soil. Several alternative hypotheses are possible to interpret the observations.

Adsorption is frequently associated with soil organic matter. Hydrophobic distribution of organic compounds into organic matter is commonly assumed to be the major sorption mechanism, especially in soils with a high organic content [13]. The observed increase of the NACs may be due to pH effects. With increasing pH values soil organic matter becomes more soluble and may release NACs. In addition, at high pH values disaggregation of clays and other soil aggregates occur.

Pennington and Patrick [14] found that adsorption isotherms of TNT are most closely correlated with extractable iron, cation exchange capacity, and clay percentage, even in the case of soils with high organic content. Furthermore, Haderlein et al. [8, 9] demonstrated a specific adsorption of NACs to clay minerals which strongly depends on the cation composition in the soil solution. Weissmahr et al. [20] suggest an electron donor acceptor (EDA) complex between oxygens of the siloxane surface of the clays and the NACs.

The results indicate that increasing desorption rates occured with increasing $Ca(OH)_2$ concentrations. Compounds that were not detectable previously now become accessible to the extraction method, leading to the effects measured. As $Ca(OH)_2$ dissociates into Ca^{2+} and OH^--ions, it is not possible to reason which one of the underlying processes dominantly contributes to the observed desorption of the NACs. On the one hand, the findings of Haderlein et al. [8, 9] and Weissmahr et al. [20] indicates that Ca^{2+} may induce the observed desorption of the NACs from clay minerals. On the other hand, the inceased solubility of soil organic matter and disaggregation of clays at pH 11 or 12 may lead to a release of NACs into the soil solution.

At high pH values desorption is superimposed by NACs hydrolysis. Therefore, increasing pH values impedes the measurement of desorption processes of NACs from soils. In contrast, only desorption processes take place at lower pH values. Since the findings presented demonstrate that both the cation present in the soil solution and its concentration may affect the desorption behavior of NACs in contaminated soils, the main objective of the present study is to investiagte the effect of different cations on the desorption behavior of NACs at pH values at which alkaline hydrolysis does not occur.

In addition, the findings suggest that desorption and remobilization of these compounds are possible although the adsorption of nonextractable NACs is frequently considered to be an irreversible process. Sorption of organic compounds on soils appears to be affected by the time over which the compounds have been in contact with the soils [17]. Furthermore, increasing ageing of soils is frequently accompanied by decreasing extractability of the NACs. This may be due to changes of binding properties, sorption processes and diffusion or migration of compounds into soil particles [19]. Therefore, NAC contaminated soils naturally aged over a long period of time are used for the investigations instead of soils artificially contaminated in the laboratory.

2 Material and Methods

2.1 Salt solutions

Solutions of KCl, $MgCl_2$, $CaCl_2$, $FeCl_3$, and $AlCl_3$ with concentrations of 0.1 M/L and 0.5 M/L were prepared in deionized water. Deionized water was produced by filtration through a Millipore "MillQ" system.

2.2 Desorption experiments

Depending on the NACs concentrations of the soils 0.1 g to 10 g of the soil were used for the desorption experiments. The soil sample was transferred into a 200 ml centrifuge vessel and 100 ml of the desorption solution were added. Deionized water and the salt solutions were used as desorption solutions. The centrifuge vessel was then covered with aluminum foil and rotated at 40 rpm using a Glas Col® rotator (Terre Haute, USA). After 24 hours the mixture was centrifuged at 2000 rpm for 10 minutes to separate the solid phase from the liquid phase. Some milliliters of the supernatant were filtered into an HPLC vessel using Acrodisk® Syringe Filters (25 mm diameter, 0.45 µm pore size). The pH of the remaining supernatant was determined. Then the supernatant was discarded.

The centrifuge vessel, still containing the soil was refilled with 100 ml of fresh solution and treated as described. The procedure was repeated until no or only trace amounts of NACs were detected in the desorption solution.

2.3 Saturation experiments

The saturation experiments (chapter 3.7) were peformed with the soil WS-1. 100 ml of deionized water or salt solution was added to a soil sample of 0.1 g. The mixture was rotated and centrifuged as decribed for the desorption experiments. After centrifugation and separation of the solid and the liquid phases, the soil was discarded.

3 ml of the supernatant were filtered into an HPLC vessel for HPLC analysis. Then, the supernatant was poured back into the centrifuge vessel. After adding 0.1 g of fresh WS-1 soil the mixture was treated again as described. In total, the whole procedure was repeated four times.

2.4 Soil analysis

Untreated soils: Explosives contaminants were analyzed for both treated and untreated soils according to USEPA-SW846, Method 8330 [18]. A 5 g soil sample was placed in a 40 ml amber vial and 25 ml of acetonitrile were added. The vial was capped with a Teflon-lined cap and swirled for one minute. The sample was then placed in a cooled ultrasonic bath for 18 hours.

After sonication, the sample was allowed to settle for 30 minutes. 5 ml of the supernatant was placed in a 20 ml vial, and combined with 5 ml of a $CaCl_2$ (5 g/L) solution. The sample was shaken and allowed to settle for 15 minutes.

The supernatant was placed in a disposable syringe and filtered through a 0.45 µL Teflon filter (Acrodisk®). The first 3 mL were discarded. The remainder was used for HPLC analysis.

Treated soils: To determine the residual NAC concentrations in the treated soil samples after performing the desorption experiments, the same procedure was applied as described for the untreated soils except that the whole treated soil samples were used for extraction, i.e. 0.1 g to 10 g of the respective soils.

2.5 HPLC analysis

All analyses were performed with a Dionex high performance liquid chromatograph (HPLC) consisting of a degassing unit (DG-1210), a pump (P580), an ultraviolet detector (UVD340 U) set at 254 nm, an ASI-100 automated sample injector. The injection volume was 10 µL. Separation of analytes were achieved using a Supelco LC-18 reverse phase column (25 cm · 4.6 mm) with a particle diameter of 5 µm. The eluent was a filtered 1:1 mixture of methanol and water. The flow rate was set to 1 mL/min.

A representative HPLC chromatogram of a standard solution is shown in Figure 3. The calibration lines for the relevant NACs are shown in Figure 4.

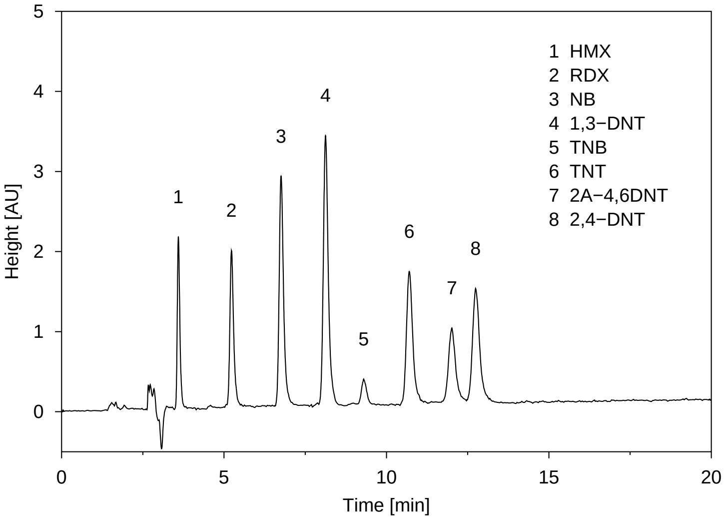

Figure 3: Chromatogram of a standard solution containing 2.0 mg/L NACs, each

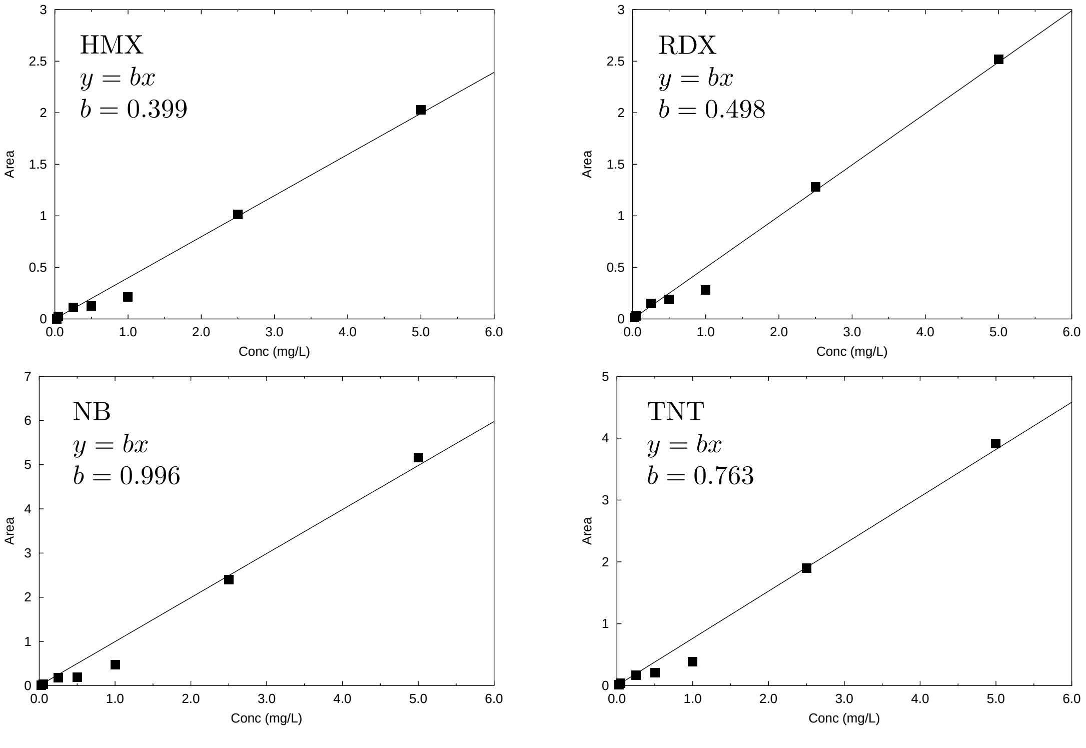

Figure 4: Calibration lines for HMX, RDX, NB, and TNT. The calibrations lines ($y = b \cdot x$) are forced through zero.

3 Results

The soils available for the desorption experiments are listed in Table 2 together with the abbreviations used in this report and a short site description. The soil samples have been collected over time by the Waterways Experimental Station, Vicksburg, MS for various investigations.

Table 2: Soils available for the desorption experiments, the abbreviations used in this report, and a short descritpion of the site

No.	Soil	Abbrev.	Description
1	Camp Edwards	CE-11	Cell 11
2	Crane Firing Range	Crane	An open-detonation disposal facility at the Naval Surface Warfare Center - Crane
3	Fort Jackson	FJ-2	Hand grenade range, Bay 2 , 0-1 ft
4		FJ-4	Hand grenade range, Cell 4
5	Iowa Army Ammunition Plant	IAAP	Former TNT munitions load and pack facility
6	Camp Shelby	Camp Shelby	Clay
	Weldon Spring		Explosive production from 1941 to 1945
7		WS-1	Soil fraction <0.18 mm
8		WS-2	Soil fraction 0.18 - 0.42 mm
9		WS-3	Soil fraction 0.42 - 0.84 mm
10		WS-4	Soil fraction 0.84 - 1.40 mm
11		WS-5	Soil fraction 1.68 - 2.38 mm

3.1 NACs concentrations in the soils

Prior to the desorption experiments, the NACs concentrations of all soils available were determined according to EPA Method 8330 [18]. The NAC concentrations of the untreated soils are summarized in Table 3.

Very different contamination and concentration patterns were detected in the soils investigated. Since no NACs were detected in the soil samples from Camp Shelby, this soil was not taken into further consideration for the desorption experiments. Furthermore, only low concentrations of HMX and RDX were measured in the soil samples from Fort Jackson. To study the desorption behavior of the compounds a definite amount of soil will be treated several times with 100 ml of desorption solution, thus leading to a high dilution of the NACs. As a consequence, an extensive and time consuming extraction procedure may become necessary to measure the NACs in the

Table 3: NACs concentrations measured in the untreated soils, and the soil amount used for extraction.

Soil	Sample No.	Soil Amnt [g]	HMX [mg/kg]	RDX [mg/kg]	NB [mg/kg]	TNT [mg/kg]
CE-11	1	4.92	10.5	52.8	0.2	855.4
CE-11	2	5.19	8.1	66.3	–	631.5
CE-11	3	5.35	7.0	52.3	–	418.5
Crane	1	5.18	148.8	1365.9	–	20.9
Crane	2	5.10	155.7	1403.5	–	9.2
Crane	3	5.40	108.2	1021.3	0.2	5.6
Crane	4	5.00	146.9	1313.0	–	–
FJ-2	1	5.00	0.3	1.6	–	–
FJ-2	2	5.30	–	2.3	–	–
FJ-2	3	5.00	–	2.1	–	–
FJ-4	1	5.04	–	0.5	–	–
FJ-4	2	4.98	0.3	0.3	–	–
FJ-4	3	5.11	–	0.3	–	–
IAAP	1	5.12	102.1	796.5	–	8.1
IAAP	2	5.12	162.5	1058.3	–	11.5
IAAP	3	5.00	93.5	748.3	–	7.7
MMR	1	5.00	26.4	215.3	0.2	239.2
MMR	2	5.00	24.7	134.4	0.2	219.1
MMR	3	5.00	17.8	178.1	0.2	260.5
Camp Shelby		4.96	–	–	–	–
WS-1	1	0.54	–	18.1	220.7	37900.2
WS-1	2	0.51	–	8.1	234.0	39291.4
WS-1	3	4.97	2.8	13.2	167.7	40969.9
WS-2		5.29	1.9	11.6	172.2	37439.4
WS-3		5.03	1.7	4.5	206.5	38004.4
WS-4		5.15	1.4	4.8	219.6	37667.4
WS-5		5.32	1.1	3.4	148.6	21354.5

Table 4: Estimated NAC concentrations [mg/L] in the first desorption solution. NAC concentrations in the soil [mg/kg] and liquid-to-solid ratios of 2:1 to 1000:1 are used for estimation. A complete mass transfer from the solid to the liquid phase is assumed for calculation of the NAC concentrations.

Soil [mg/kg]	NAC concentrations in the desorption solution [mg/L]							
	5:1	10:1	20:1	50:1	100:1	200:1	500:1	1000:1
10	2	1						
100	20	10						
1 000	200	100	50	20	10	5		
10 000	2 000	1 000	500	200	100	50	20	10
50 000		5 000	2 500	1 000	500	250	100	50

desorption solution. For that reason and with respect to the limited time frame, no desorption experiments were performed with the Fort Jackson soil.

Similar considerations hold true for the soil MMR. Although it contains higher amounts of RDX and TNT than the Fort Jackson soils still low concentrations may be expected in the desorption solutions during the course of the experiment. The NAC concentrations in the desorption solutions depend on the NAC concentrations in the soil, the liquid-to-solid ratio, and the equilibrium of desorption and adsorption of the NACs between the soil and the liquid. A rough estimation of the NAC concentrations in the first desorption solution applied is given in Table 4 assuming a complete transfer of the NACs into the liquid phase. If, for example, a soil containing 100 mg/kg of NACs is treated using a liquid-to-solid ratio of 5:1 or 10:1 NAC concentrations of 20 mg/L and 10 mg/L, respectively may be expected in the desorption solution. Since a complete mass transfer is assumed to occur during the first desorption step the calculated concentrations in Table 4 represent the maximum concentrations possible. In practice, lower concentrations are more likely and extensive extraction procedures may become necessary to measure the NACs in the successive desorption solutions. For that reason no desorption experiments were performed with the soil MMR.

Higher NAC concentrations were detected in the remaining soils CE-11, Crane, IAAP, and WS-1 to WS-5. Representative chromatograms of the CE-11, Crane, and IAAP soils are shown in Fig 5. Due to the similarity of the contamination pattern of WS-1 to WS-5 a chromatogram only of WS-1 is selected to represent the Weldon Spring soils.

The two soils Crane and IAAP show similar NAC patterns with RDX and HMX being the dominant contaminants. With a mean value of 1276 mg/kg the Crane soil has a slightly higher RDX concentration than the IAAP soil (868 mg/kg). The major contaminant of the CE-11 soil is TNT with a mean concentration of 635 mg/kg. In contrast to CE-11, Crane, and IAAP all five soil fractions of Weldon Spring contain significant amounts of TNT in the range of 21 to 41 g/kg. In additon, NB is detected in minor amounts of 149 to 234 mg/kg. With respect to the high TNT concentrations of the Weldon Spring soils, complete extraction was checked by lowering the soil amount for the extraction procedure of EPA Method 8330 [18]. For that reason 0.5 g of WS-1 were extracted in addition to the 5 g soil samples of WS-1. As listed in Table 3 no significant differences in TNT concentrations were measured when using 0.5 g instead of 5 g WS-1 soil, indicating complete extraction of NACs when using 5 g soil samples.

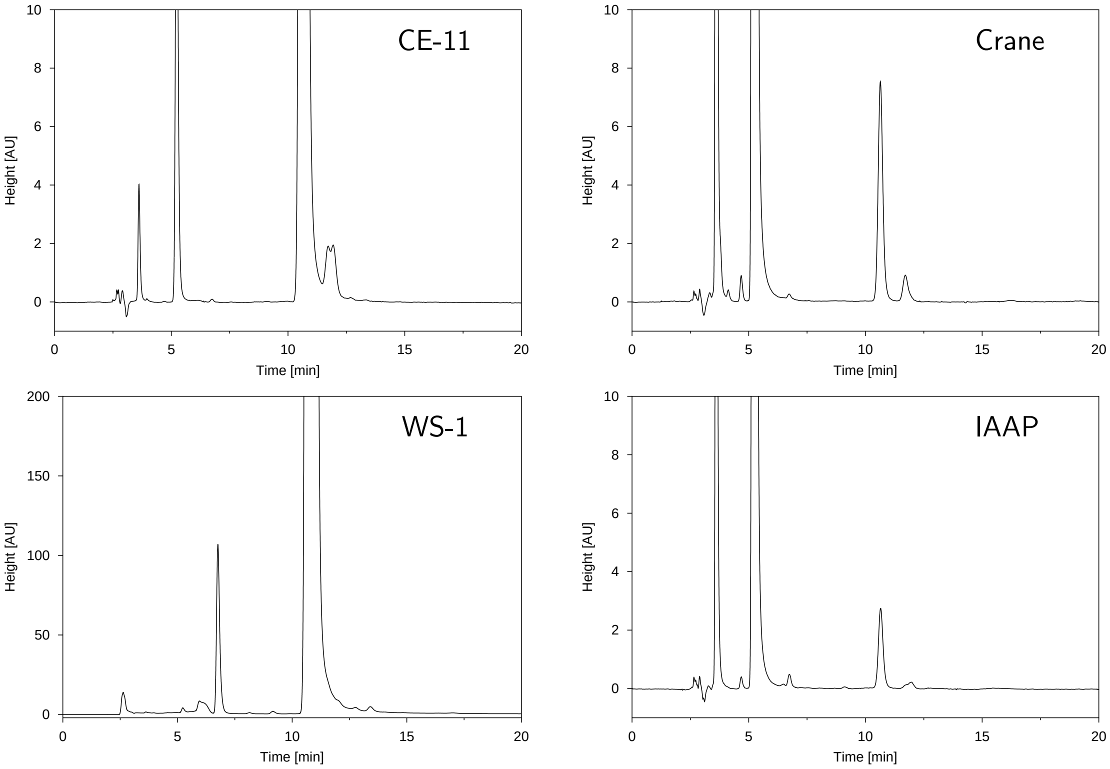

Figure 5: Chromatograms of the extracts of the untreated soils. For the WS-1 soil a chromatogram of a 1:100 dilution is shown, due to the high TNT concentration.

3.2 NACs desorption using 0.1 molar salt solutions

The selected soils were treated using 0.1 molar and/or 0.5 molar salt solutions for the NACs desorption experiments. The respective pH values of the salt solutions are listed in Table 5.

The pH values of the 0.1 and 0.5 molar solutions of the respective salts show pH differences less than 0.6 pH units, except for $CaCl_2$. Only the pH values of two $CaCl_2$ solutions differ by 1.7 pH units. Since all solution show pH values of less than 10, alkaline hydrolysis of NACs cannot take place during treatment of the soils with the salt solutions [3, 4]. This is a prerequisite to measure NACs desorption processes only.

Table 5: Initial pH values of the 0.1 and 0.5 molar salt solutions.

Concentration	KCl	$MgCl_2$	$CaCl_2$	$FeCl_3$	$AlCl_3$
0.1 Mol/L	5.27	9.28	7.40	1.82	3.50
0.5 Mol/L	5.42	8.75	5.66	1.32	2.89

3.2.1 Soil IAAP

The pH values in the desorption solutions of soil IAAP versus time are shown in Figure 6. They were measured in the supernatant of the centrifuged soil-water mixtures, just before exchanging the desorption solutions.

The pH values in the soil-water mixtures depend on the desorption solutions applied. When using deionized water the pH value is raised from pH 7 to 8 and 9, indicating

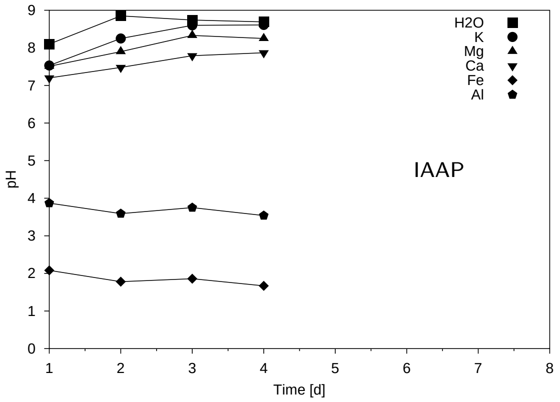

Figure 6: pH values in the desorption solutions of soil IAAP using 0.1 molar salt concentrations.

that the IAAP soil buffers the pH at slightly alkaline values. The same holds true for the KCl, $MgCl_2$, and $CaCl_2$ desorption solutions. In contrast, the soil is not able to buffer the pH when using $FeCl_3$ and $AlCl_3$. The pH values drops to about pH 2 and 4, respectively. For all desorption solutions, the measured pH values are below the pH values, where alkaline hydrolysis of NACs may take place.

Desorption of RDX

RDX concentrations between 748 and 1058 mg/kg were measured in the untreated IAAP soil samples (Table 3). According to Table 4 maximal NAC concentrations of about 200 mg/L, 100 mg/L, and 50 mg/L may be expected in the desorption solutions when applying a liquid-to-solid ratio of 5:1, 10:1, and 20:1, respectively. On the one hand, the liquid-to-solid ratio is selected as low as possible. On the other hand, a ratio of 5:1 is more difficult to handle than a ratio of 10:1. In both cases the solubility of RDX in water (about 42 mg/L at 20 °C [2]) is below the maximum values estimated. Hence, a liquid-to-solid ratio of 10:1 is selected for the desorption experiments of soil IAAP.

In practice, the liquid-to-solid ratio of 10:1 was adjusted by adding 100 ml desorption solution to a 10 g soil sample. After rotating the mixture for 24 hours, the NAC concentrations were measured in the desorption solutions. For the IAAP soil calculated values of the extracted amounts of RDX, HMX, and TNT versus time are shown in the left column of Figure 7. Calculated values referring to one kilogram of soil are preferred over measured NAC concentrations to simplify a comparison of the results of different desorption experiments, e.g. when using different liquid-to-solid ratios.

The NAC amounts desorbed from the soil sample are calculated by multiplying the measured NAC concentrations by the volume of the desorption solution. Since these NAC amounts originate from the 10 g of soil used in the specific experiment the desorbed amounts were calculated by refering these amounts to one kilogram soil according to Equation 1.

$$NAC_{Des} = \frac{Conc_{DesSol}[mg/L] \cdot Vol_{DesSol}[L]}{SoilAmount[kg]} \cdot 1\ kg\ Soil \tag{1}$$

These values are presented at the left hand side of Figure 7. Between 320 and 340 mg of RDX, the dominant contaminant in soil IAAP are desorbed per kilogram soil by the first desorption solution, corresponding to measured RDX concentrations of 30 to 35 mg/L. This is close to the RDX saturation concentration of about 40 mg/L in water. No significant differences are observed for the respective salt solutions and deionized water.

The amounts desorbed during the second day are only slightly lower than the amounts

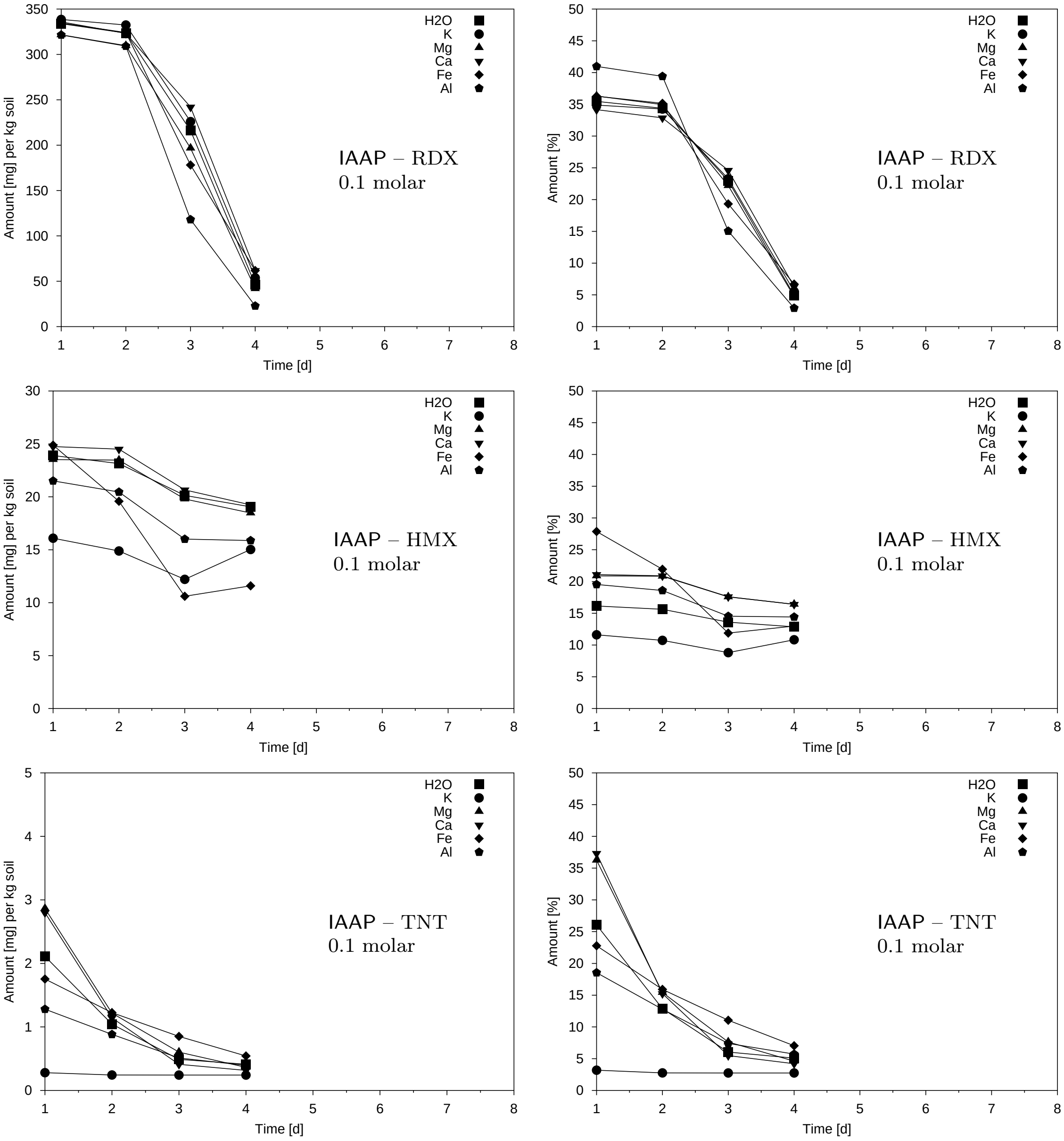

Figure 7: Desorbed amounts of RDX, HMX, and TNT in [mg] per kilogram IAAP soil (left) and desorbed amounts in [%] relativ to the total amount (right) versus time.

of the first day. Subsequently, the concentrations in the desorption solutions and, hence, the desorbed amounts decrease. Compared to the remaining desorption solutions, slightly less RDX is desorbed with the $AlCl_3$ solution during the whole course of the desorption experiment.

Table 6: Sum of the NAC amounts ($\text{Sum}_{Des.Sol}$) desorbed from soil IAAP using the 0.1 molar desorption solutions, the residual NAC amounts measured in the treated soil samples ($\text{Soil}_{Treated}$), and the total sum of NACs (Sum_{Total}). The amounts are calculated per kilogram soil.

Compound	H_2O [mg]	KCl [mg]	$MgCl_2$ [mg]	$CaCl_2$ [mg]	$FeCl_3$ [mg]	$AlCl_3$ [mg]
RDX						
$\text{Sum}_{Des.Sol.}$	919.9	950.7	869.8	962.9	898.5	771.5
$\text{Soil}_{Treated}$	21.5	19.7	16.0	20.4	23.5	13.0
Sum_{Total}	941.4	970.4	885.8	983.3	922.0	784.5
HMX						
$\text{Sum}_{Des.Sol.}$	86.2	58.2	85.2	89.2	66.7	73.7
$\text{Soil}_{Treated}$	61.9	80.5	27.4	28.1	22.6	36.4
Sum_{Total}	148.1	138.7	112.6	117.3	89.3	110.1
TNT						
$\text{Sum}_{Des.Sol.}$	4.0	1.0	5.1	4.7	4.4	3.1
$\text{Soil}_{Treated}$	4.1	7.8	2.8	2.8	3.3	3.8
Sum_{Total}	8.1	8.8	7.9	7.5	7.7	6.9

Soils in general are inhomogeneous and the individual 10 g soil samples used for the respective desorption experiments may slighty vary despite prior homogenization of the IAAP soil. Therefore, the NAC concentrations in the remaining soil samples were also analysed after finishing the desorption experiments to be able to peform a complete mass balance of the NACs. Table 6 shows the sum of the NAC amounts desorbed from soil IAAP for the respective desorption solutions, the residual NAC amounts measured in the treated soil samples, and the total sum of NACs.

A minimum amount of 772 mg/kg ($AlCl_3$) and a maximum amount of 963 mg/kg RDX ($CaCl_2$) are desorbed from soil IAAP during the desorption experiment, while residual RDX concentrations of 13 mg/kg ($AlCl_3$) to 23.5 mg/kg ($FeCl_3$) are measured in the treated soil samples. The low residual concentrations in the treated soil samples of 1.6 % to 2.5 % compared to the total RDX concentration of 785 mg/kg ($AlCl_3$) to 983 mg/kg ($CaCl_2$) indicate that complete desorption of RDX is achieved from the IAAP soil during the course of the desorption experiment. The total RDX amounts correspond to the range of the RDX concentrations measured in the untreated IAAP soil (Table 3).

It might be concluded by the graphs at the left hand side of Figure 7 that $AlCl_3$ posses the lowest desorption efficiency for RDX and soil IAAP. However, the desorbed NAC amounts depend among others on the initial NAC concentrations in the respective soil sample. To eliminate the influence of the total NAC concentrations measured, NAC amounts are calculated relative to the total sum of the respective NACs in the soil sample. These resulting graphs are shown at the right hand side of Figure 7.

With about 40 % $AlCl_3$ now exhibits the highest desorption efficiency during the first two days. This is 5 % higher than the values of the remaining desorption solutions. Hence, 80 % of RDX is desorbed from the soil after two days when using $AlCl_3$ compared to about 70 % of the other desorption solutions. During the third day the graph of $AlCl_3$ drops below the other graphs, since now less RDX remained in the soil sample.

Desorption of HMX

According to Table 3 HMX concentrations of 94 to 163 mg/kg are detected in soil IAAP. Using a liquid-to-solid ratio of 10:1 the HMX concentrations are high enough to be detected in the desorption solutions. The corresponding time courses are presented in the second row of Figure 7.

Using deionized water, and $MgCl_2$, $CaCl_2$, and $FeCl_3$ solutions HMX concentrations of about 2.5 mg/L are measured in the desorption solution of the first day. This is close to the solubility of 2.6 mg/L at 20 °C [2]. With increasing temperature the solubility inceases to about 5 mg/L (22-25 °C). The concentrations of 2.5 mg/L in the desorption solutions indicate, that the desorption process of HMX from soil IAAP is affected by the maximum solubility of HMX in water.

Regarding deionized water, $MgCl_2$, $CaCl_2$ the relatively high amounts of HMX are desorbed during the whole course of the experiment. Only little differences in HMX concentrations are observed comparing the first and last desorption solutions. In contrast, $FeCl_3$ initially also presents high amounts of HMX, but is then followed by a decrease to about 10 mg/kg. Slightly less amounts of HMX are measured for $AlCl_3$. The lowest amounts are desorbed when using KCl.

In contrast to RDX relatively high residual amounts of HMX are measured in the treated soil samples ranging from 22 to 80 mg/kg (Table 6), corresponding to 24 % to 58 % of the total HMX amount of the respective soil samples. With KCl only 42 % of the total HMX amount are desorbed. This is also reflected by the graphs of HMX at the right hand side of Figure 7. The KCl curve is the lowest of all curve and vary between 10 and 12 %. A slight improvement is achieved when using deionized water. Altogether, 58 % of the total HMX amount are desorbed with water. With respect to desorption efficiency comparable results are obtained for $MgCl_2$, $CaCl_2$, and $FeCl_3$. About 75 % of HMX are desorbed when using these salts. However, the graph of $FeCl_3$ decreases more rapidly indicating a faster desorption process compared to $MgCl_2$, and $CaCl_2$.

The relatively high residual HMX concentrations are probably due to the short desorption time of four days in combination with the relatively low solubility of HMX in water. A prolonged desorption treatment would probably lead to lower residual HMX concentrations in the treated soil samples.

Desorption of TNT

Similar total TNT concentrations of 6.9 to 8.8 mg/kg are measured in the soil samples used for the desorption experiments (Table 6) compared to the TNT concentrations measured in the untreated IAAP soil (Table 3).

Significant differences are observed in the desorption behavior of TNT in combination with the several desorption solutions. Best desorption results are obtained for $MgCl_2$, and $CaCl_2$ with inital desorption amounts of 37 %, followed by a rapid decrease to finally 6 %. In contrast, hardly no desorption of TNT is achieved using KCl. Still 7.8 mg/kg of TNT is detected in the treated soil sample, corresponding to 89 % of the initial TNT concentration. Somewhat lower residual amounts are obtained when using $FeCl_3$, $AlCl_3$, and deionized water, i.e. still 43 %, 51 %, and 55 % of the initial TNT are still detected in the treated soil samples.

3.2.2 Soil Crane

Crane was the first soil from which NAC concentrations were available and, hence, was the first soil investiagted. A subset of three desorption solutions were selected in combination with Crane to check the experimental design of the desorption experiments: deionized water, which served as reference, and the two- and three-fold charged ions Ca^{2+} and Fe^{3+}.

The contamination pattern of the Crane soil is similar to the pattern of IAAP soil with RDX being the dominant contaminant. The time courses for RDX, HMX, and TNT are shown in Figure 8, the respective mass balances are summarized in Table 7.

Desorption of RDX

Similar desorption curves are observed for all three desorption solutions. The initial RDX concentrations are about 30 mg/L corresponding to calculated amounts of 293 to 300 mg/kg. Then desorption slightly increases, leading to increased RDX concentrations of 33 to 35 mg/L during the second day. These concentrations are close to the concentrations in the respective desorption solutions of IAAP soil during the first day. During the next two days relatively high RDX concentrations of 29 to 35 mg/l

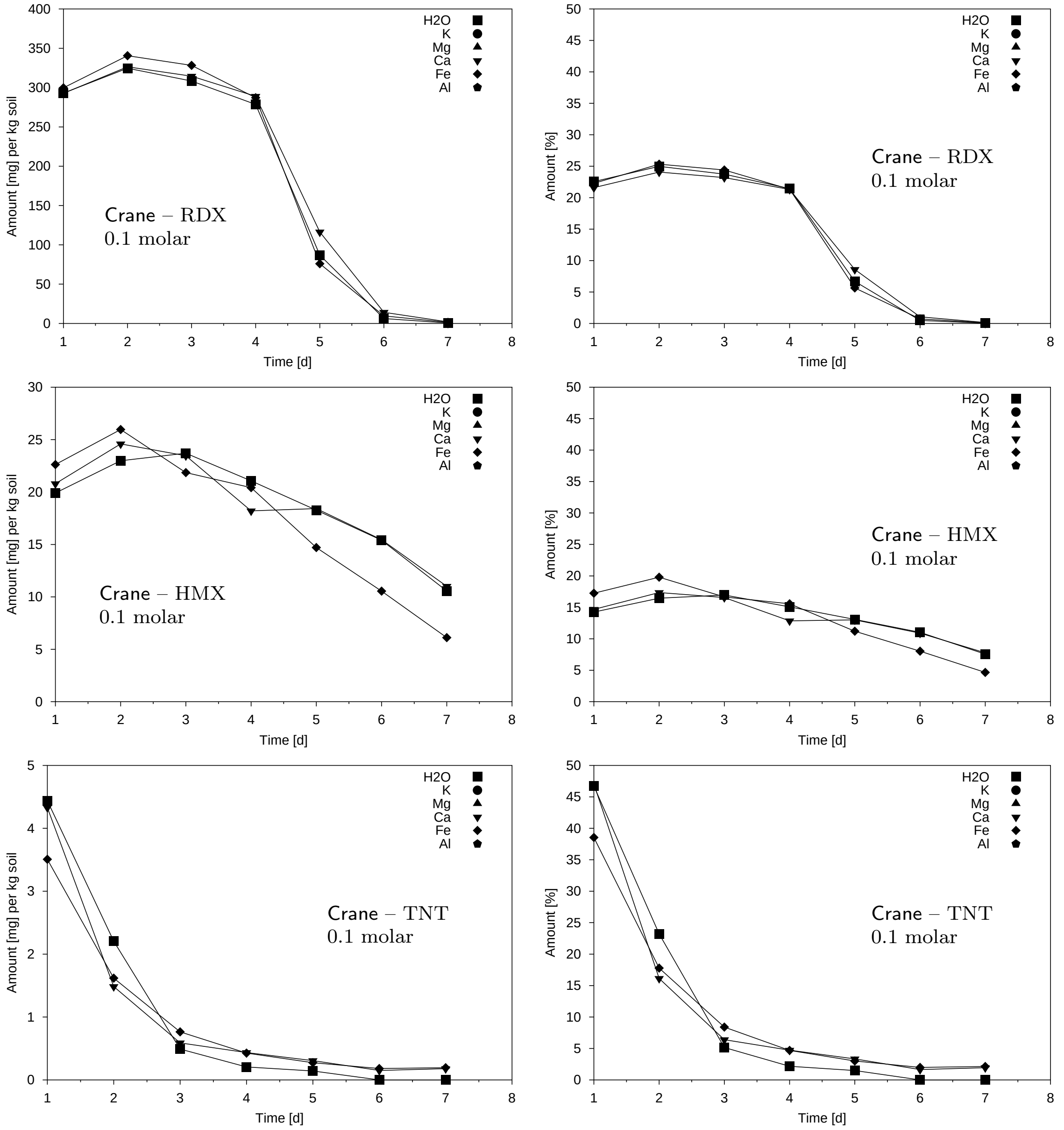

Figure 8: Desorbed amounts of RDX, HMX, and TNT in [mg] per kilogram Crane soil (left) and desorbed amounts in [%] relativ to the total amount (right) versus time.

are reached, followed by a rapid decrease within two days.

Both, the initial increase and the four days lasting high RDX amounts differ from the RDX amounts of the IAAP soil. In IAAP soil the maximum concentrations occur only during the first day followed by an initially slow (day two) then more rapid decrease

Table 7: Sum of the NAC amounts ($\text{Sum}_{Des.Sol}$) desorbed from soil Crane using the 0.1 molar desorption solutions, the residual NAC amounts measured in the treated soil samples ($\text{Soil}_{Treated}$), and the total sum of NACs (Sum_{Total}). The amounts are calculated per kilogram soil.

Compound	H_2O [mg]	KCl [mg]	$MgCl_2$ [mg]	$CaCl_2$ [mg]	$FeCl_3$ [mg]	$AlCl_3$ [mg]
RDX						
$\text{Sum}_{Des.Sol.}$	1298.5	–	–	1355.3	1342.7	–
$\text{Soil}_{Treated}$	0.7	–	–	0.7	0.8	–
Sum_{Total}	1299.2	–	–	1356.0	1343.5	–
HMX						
$\text{Sum}_{Des.Sol.}$	131.8	–	–	131.9	122.2	–
$\text{Soil}_{Treated}$	7.9	–	–	9.8	9.0	–
Sum_{Total}	139.7	–	–	141.7	131.2	–
TNT						
$\text{Sum}_{Des.Sol.}$	7.5	–	–	7.5	6.9	–
$\text{Soil}_{Treated}$	2.0	–	–	1.7	2.2	–
Sum_{Total}	9.5	–	–	9.2	9.1	–

(days three and four) of the HMX in the desorption solutions.

However, when comparing both soils, the different RDX amounts measured in the soil samples used for the Crane and IAAP desorption experiments, must be taken into consideration. Concentrations of 1299 to 1356 mg/kg of RDX are measured in the soil samples used for the Crane desorption experiments (Table 7). This is 370 to 420 mg/kg higher than the concentrations in the IAAP soil samples (Table 6). Regarding deionized water, $CaCl_2$, and $FeCl_3$ the cumulative amounts desorbed from soil IAAP are about 335 to 658 mg/kg, respectively during the first two days. Similar amounts of about 295 to 630 mg/kg are desorbed from soil Crane during this time. After two days there are 260 to 325 mg/kg of RDX remaining in the IAAP soil samples compared to still 680 to 740 mg/kg remaining in the Crane soil samples. Hence, the remaining RDX amounts in the IAAP soil samples is less than the observed maximum amount of about 340 mg/kg desorbed during one desorption step, compared to still two to three times higher RDX amounts in the Crane soil samples. As a consequence, the amount desorbed in the IAAP soil samples must decrease after the second day, while there is still sufficient RDX in the Crane soil samples. Finally, in the treated Crane soils similar low residual RDX concentrations are obtained compared to the treated IAAP soils.

This indicates that desorption of RDX from both soils is closely related to the remaining RDX concentration in the soils in relation to the saturation concentration of RDX in water. However, the RDX increase using the soil Crane during the first two days may point at additional affects influencing the RDX desorption process, e.g. the respective soil properties of Crane.

Desorption of HMX

According to the low HMX solubility in water of 2.6 to 5 mg/L at 20 to 25 °C maximal concentrations of up to 2.6 mg/L are measured in the desorption solutions corresponding to 26 mg/kg desorbed. Similar to RDX the HMX amounts desorbed are highest at the second day. The HMX concentrations still remain high for the next two days, followed by a slow decrease. Finally, about 93 % of the total HMX amount are dissolved from the Crane soil samples due to the seven day lasting desorption procedure.

The results obtained with the Crane soil confirm the results of IAAP that desorption of HMX from soils is predominantly restricted by the solubility of HMX in water. This may also explain the high residual HMX concentrations in the treated IAAP soil samples. Prolonged desorption treatment would probably also lead to lower residual HMX concentrations in the treated IAAP soil samples.

However, slighty better results are obtained when using $FeCl_3$, indicated by somewhat higher initial HMX amounts desorbed during the first days, followed by somewhat lower amounts compared to deionized water and $CaCl_2$. A similar behavior was observed for the IAAP soil in combination with the $FeCl_3$ solution, indicating that a more efficient desorption process may take place in the presence of Fe^{3+}-ions.

Desorption of TNT

In the soil samples used for the dsorptions experiments TNT concentrations of about 9 mg/kg TNT were measured (Table 7). This is within the range of the TNT concentrations of 7 to 9 mg/kg measured in the untreated IAAP soil. No significant differences are observed for the different desorption solutions. However, a faster desorption is achieved for Crane. Between 38 ($FeCl_3$) and 47 % (deionized water and $CaCl_2$) of the total TNT desorbed from Crane during the first day compared to 23 % ($FeCl_3$) to 37 % ($CaCl_2$) for IAAP.

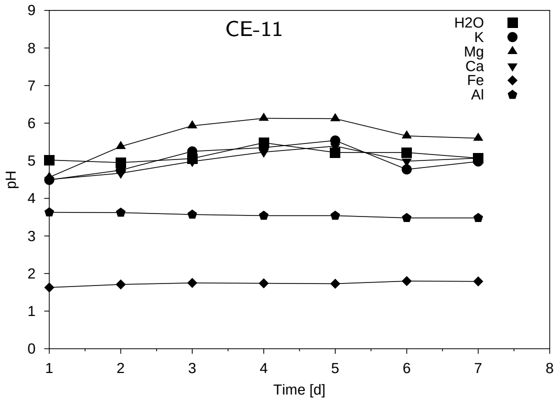

Figure 9: pH values in the desorption solutions of soil CE-11 using 0.1 molar salt concentrations.

3.2.3 Soil CE-11

The dominant contaminant in soil CE-11 is TNT with a mean concentration of 635 mg/kg (Table 3). Since the TNT concentration of TNT is similar to the RDX concentrations in the soils IAAP and Crane the same liquid-to-solid ratio of 10:1 is applied to soil CE-11.

The pH values of the desorption solutions are shown in Figure 9. In combination with deionized water the CE-11 soil buffers the pH at values of 5 to 5.5. Similar pH values are obtained for KCl, and $CaCl_2$. Slightly higher pH values up to 6 are reached when using $MgCl_2$. Similar to the soils IAAP and Crane the $AlCl_3$ and $FeCl_3$ desorption solutions show pH values of 3.8 and 1.8, respectively.

Desorption of TNT

The concentrations of TNT, RDX, and HMX in the desorption solutions versus time are presented in Figure 10. TNT concentrations between 37 and 43 mg/L are measured in the desorption solutions, corresponding to 468 to 567 mg/kg of TNT being desorbed from the CE-11 soil samples during the first day. The total TNT amounts range from 604 to 798 mg/kg (Table 8). Hence, 75 % (KCl) to 86 % (H_2O) of the total TNT amount in the CE-11 soil samples are desorbed during the first day, except for the $FeCl_3$ with 61 %. This somewhat lower relative desorption rate is caused by the high TNT concentration of the soil sample used for the $FeCl_3$ desorption experiment. The concentration is between 100 to 200 mg/kg higher than the concentrations in the other soil samples. For that reason a 14 % to 24 % lower desorption rate is calculated for the $FeCl_3$ desorption solutions.

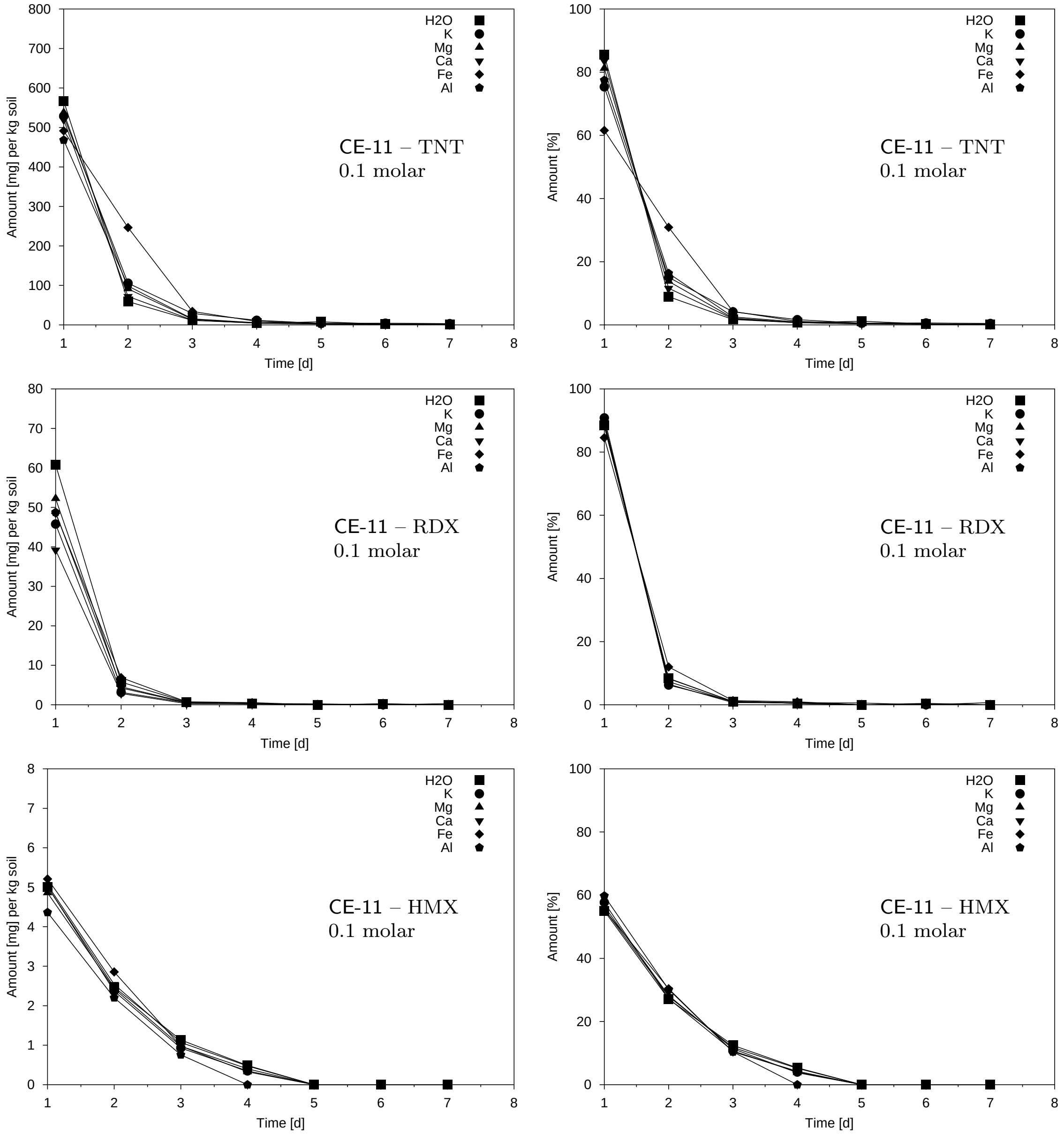

Figure 10: Desorbed amounts of TNT, RDX, and HMX in [mg] per kilogram CE-11 soil (left) and desorbed amounts in [%] relativ to the total amount (right) versus time.

Since most of the TNT is desorbed during the first day, there are relatively low TNT amounts remaining in the soil samples. As a consequence, low TNT concentrations between 5 and 8 % are detected during the second day, corresponding to 12 % to 16 % of the total TNT amounts in the CE-11 soil samples. Only in the $FeCl_3$ desorption

Table 8: Sum of the NAC amounts ($\mathrm{Sum}_{Des.Sol}$) desorbed from soil CE-11 using the 0.1 molar desorption solutions, the residual NAC amounts measured in the treated soil samples ($\mathrm{Soil}_{Treated}$), and the total sum of NACs (Sum_{Total}). The amounts are calculated per kilogram soil.

Compound	H_2O [mg]	KCl [mg]	$MgCl_2$ [mg]	$CaCl_2$ [mg]	$FeCl_3$ [mg]	$AlCl_3$ [mg]
TNT						
$\mathrm{Sum}_{Des.Sol.}$	653.6	686.5	652.9	613.6	788.7	593.4
$\mathrm{Soil}_{Treated}$	9.5	15.0	8.8	8.2	9.5	10.8
Sum_{Total}	663.1	701.5	661.7	621.8	798.2	604.2
RDX						
$\mathrm{Sum}_{Des.Sol.}$	67.8	49.7	57.6	43.2	56.7	54.2
$\mathrm{Soil}_{Treated}$	0.9	0.7	0.7	0.7	0.7	1.1
Sum_{Total}	68.7	50.4	58.3	43.9	57.4	55.3
HMX						
$\mathrm{Sum}_{Des.Sol.}$	9.1	8.7	8.6	9.1	9.4	7.3
$\mathrm{Soil}_{Treated}$	0.0	0.0	0.0	0.0	0.0	0.1
Sum_{Total}	9.1	8.7	8.6	9.1	9.4	7.4

solution a somewhat higher TNT concentration of 19 mg/L, corresponding to 31 %, is measured, which is caused by the higher TNT amount remaining in the treated CE-11 soil sample after one day.

During the following days the concentrations in all desorption solutions and the respective amounts further decrease. Altogether, less than 2 % of the total TNT remain in the treated CE-11 soil samples.

Desorption of RDX

Similar desorption curves are obtained for RDX. After initially high RDX desorption amounts of 85 % to 90 % of the total RDX concentration in the CE-11 soil samples, desorption rapidly decreases and falls below 1.5 % at the third day. Finally, the treated soil samples contain less than 2 % of the initial RDX amount. Although similar relative desorption curves are obtained, different amounts of RDX (40 to 60 mg/L) are measured in the desorption solutions during the first day.

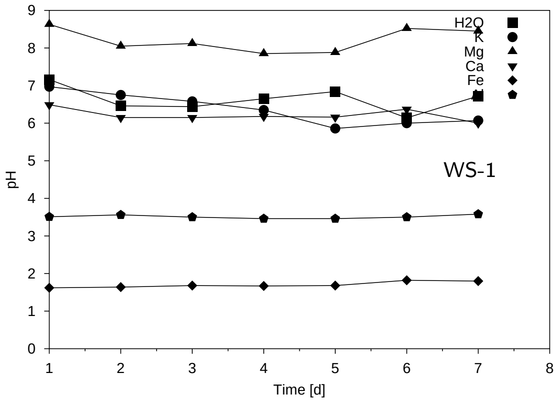

Figure 11: pH values in the desorption solutions of soil WS-1 using 0.1 molar salt concentrations

Desorption of HMX

No significant differences are observed for the different desorption solutions. The untreated CE-11 soil samples contained 7.4 to 9.4 mg/kg HMX (Table 8). Between 4.4 mg/kg ($AlCl_3$) and 5.2 mg/kg ($FeCl_3$) are desorbed during the first day. Subsequently the amounts continuously decrease till, after four to five days no HMX can be detected in the desorption solutions.

3.2.4 Soil WS-1

Soil fractions are used for the WS desorption experiments in contrast to the IAAP, Crane, and CE-11 experiments. WS-1 comprises the particle fraction <0.18 mm. This fraction is highly contaminated with TNT and to minor amounts also with NB (Table 3). Due to the high TNT concentration a liquid-to-solid ratio of 200:1 is selected for the WS desorption experiments. In practice, 100 ml desorption solution are added to a 0.5 g soil sample.

Figure 11 shows the pH values in the WS-1 desorption solutions versus time. In case of deionized water, KCl, and $CaCl_2$ the soil WS-1 buffers the pH values between pH 6 and 7. In combination with $MgCl_2$ the buffering capacity of soil WS-1 is exceeded and the pH increases to pH 8 to 9, whereas the $AlCl_3$, and $FeCl_3$ desorption solutions show pH values of 3.5 and 1.8, respectively.

Desorption of TNT

The WS-1 soil samples used for the desorption experiments contained concentrations of 39.9 g/kg to 41.1 g/kg (Table 9). The small standard deviation of 0.42 g/kg in

Table 9: Sum of the NAC amounts ($\text{Sum}_{Des.Sol}$) desorbed from soil WS-1 using the 0.1 molar desorption solutions, the residual NAC amounts measured in the treated soil samples ($\text{Soil}_{Treated}$), and the total sum of NACs (Sum_{Total}). The amounts are calculated per kilogram soil.

Compound	H_2O [mg]	KCl [mg]	$MgCl_2$ [mg]	$CaCl_2$ [mg]	$FeCl_3$ [mg]	$AlCl_3$ [mg]
TNT						
$\text{Sum}_{Des.Sol.}$	40487.9	40800.7	39784.9	40357.5	40766.4	40961.1
$\text{Soil}_{Treated}$	90.7	138.5	123.7	122.9	101.0	120.4
Sum_{Total}	40578.6	40939.2	39908.6	40480.4	40867.4	41081.5
NB						
$\text{Sum}_{Des.Sol.}$	258.6	268.8	261.2	232.2	160.8	150.1
$\text{Soil}_{Treated}$	8.6	9.0	8.9	9.8	7.7	7.7
Sum_{Total}	267.2	277.8	270.1	242.0	168.5	157.8

relation to the mean value of 40.6 g/kg indicates a well homogenized soil fraction.

The concentrations of TNT, and NB in the desorption solutions versus time are presented in Figure 12. Significant differences are observed in the TNT desorption behavior with respect to the different desorption solutions. Maximum desorption occurs in combination with the $FeCl_3$ desorption solution. Relatively high TNT amounts of 13.8 g/kg and 13.1 g/kg are desorbed during the first two days, followed by a slighty lower amount of 11.1 g/kg. Hence, in total 38.0 g/kg of TNT corresponding to 93.1 % of the initial TNT amount are desorbed from soil WS-1 during the first three days. Then desorption decreases to 2.4 g/kg (5.8 %) due to the low remaining TNT concentration.

In contrast, a significantly slower TNT desorption takes place in the $MgCl_2$ solution. During the first three days the TNT amounts remain relativly constant between 8.8 g/kg and 9.5 g/kg, yielding a total desorption of 27.4 g/kg. Hence, 10.6 g less TNT are desorbed from WS-1 soil within the first three days compared to the $FeCl_3$ solution. This corresponds to 68.6 % of the initial TNT being desorbed in case of the $MgCl_2$ solution compared to 93.1 % in case of the $FeCl_3$ solution.

In contrast to the $FeCl_3$ solution, the desorbed TNT amounts remain relatively high due to the high residual TNT concentration in the soil sample. It takes five days for TNT to desorb almost quantitatively (98.6 %) from soil WS-1 when using the $MgCl_2$ solution.

The other desorption solutions (deionized water, KCl, $CaCl_2$, and $AlCl_3$) yields des-

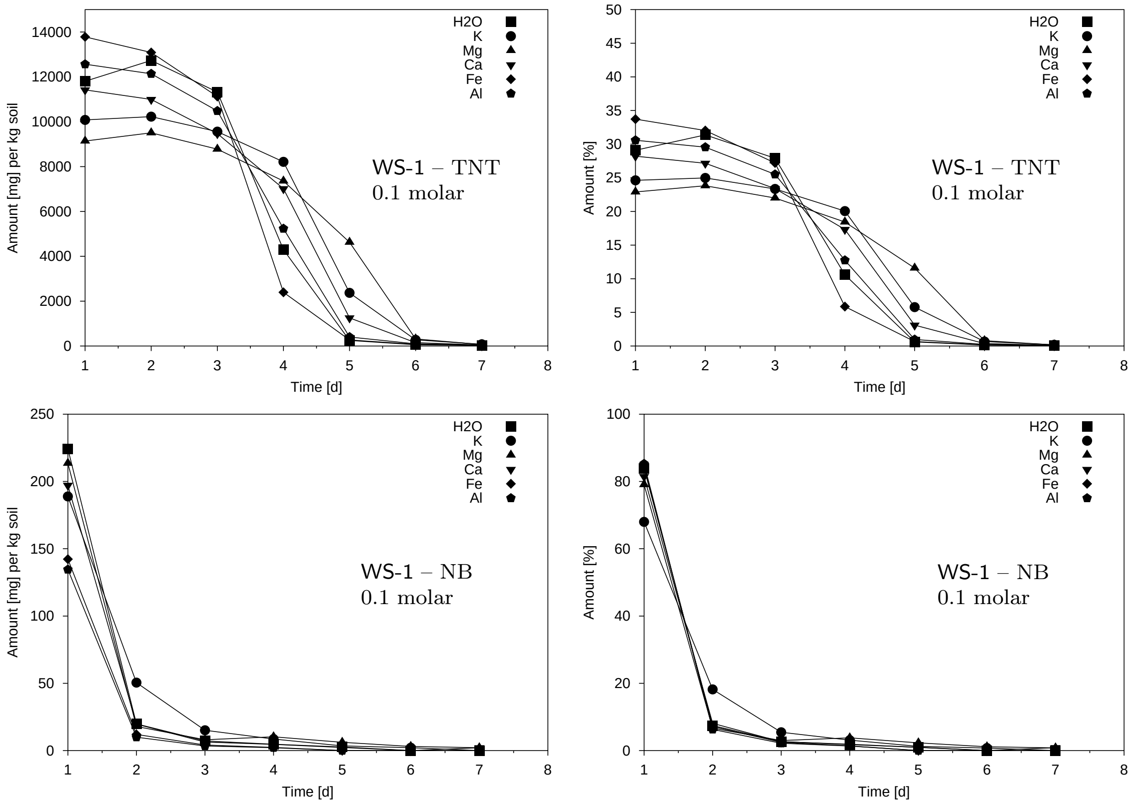

Figure 12: Desorbed amounts of TNT, and NB in [mg] per kilogram WS-1 soil (left) and desorbed amounts in [%] relativ to the total amount (right) versus time.

orption curves laying in-between the desorption curves of $FeCl_3$ with the fastest and $MgCl_2$ with the slowest desorption rate.

Desorption of NB

Compared to TNT, the WS-1 soil contains a relatively low NB concentration. According to Table 3 higher variations of NB (168 - 234 mg/kg) are detected in the untreated WS-1 soil fraction, which is probably due to a more inhomogeneous distribution of NB in the soil matrix.

Except for KCl, the relative desorption curves are similar for the other desorption solutions. About 79 to 85 % of the total NB amount is desorbed during the first day. Subsequently, the NB amounts decrease and fall below 8 %. Only when KCl is applied a lower NB desorption of 68 % is measured during the first day, whereas a higher value of 18 % is achieved during the second day, due to the higher remaining NB concentration in the soil sample after the first day.

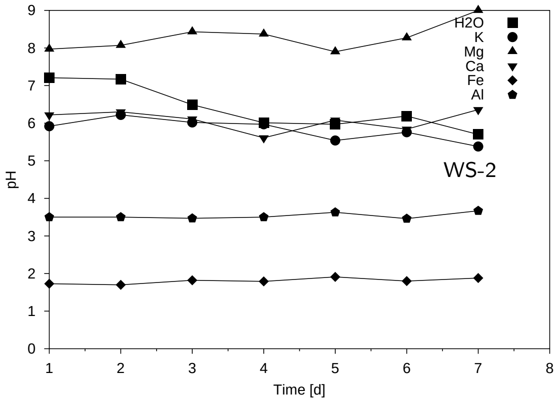

Figure 13: pH values in the desorption solutions of soil WS-2 using 0.1 molar salt concentrations.

Although the relative desorption curves are much alike, the absolut NB amounts are different. The lowest amounts are calculated for the $AlCl_3$, and $FeCl_3$ solutions with 135 and 142 mg/kg, while the highest amounts are obtained for deionized water, and the $MgCl_2$ solution with 224 and 214 mg/kg, respectively. After the second day the NB amounts of the different desorption solutions decreases due to the decreasing NB concentrations in the soil samples. Only KCl show higher values (50.5 mg/kg) compared to the other desorption solutions (9.9 to 19.9 mg/kg). Finally, all solutions desorb between 95 to 97 % of the total NB from the WS-1 soil samples.

3.2.5 Soil WS-2

The soil fraction WS-2 contains particles between 0.18 – 0.42 mm and shows a similar contamination pattern as WS-1 with about 37 g/kg TNT and 172 mg/kg NB (Table 3). Hence, the desorption experiments were performed using the same conditions as with WS-1 i.e. a liquid-to-solid ratio of 200:1.

The pH values of the desorption solutions versus time are shown in Figure 13. Due to the buffering capacity of the soil fraction WS-2, the pH values of the KCl and $CaCl_2$ desorption solutions and deionized water layed between pH 6 and 7. The desorption solutions of $MgCl_2$ show a slighty alkaline pH value of 8 to 9, while the solutions of $AlCl_3$, and $FeCl_3$ are in the acidic range with values of about 3.5 and 1.8. Hence, the buffering properties of the WS-1 and WS-2 soil fraction are alike.

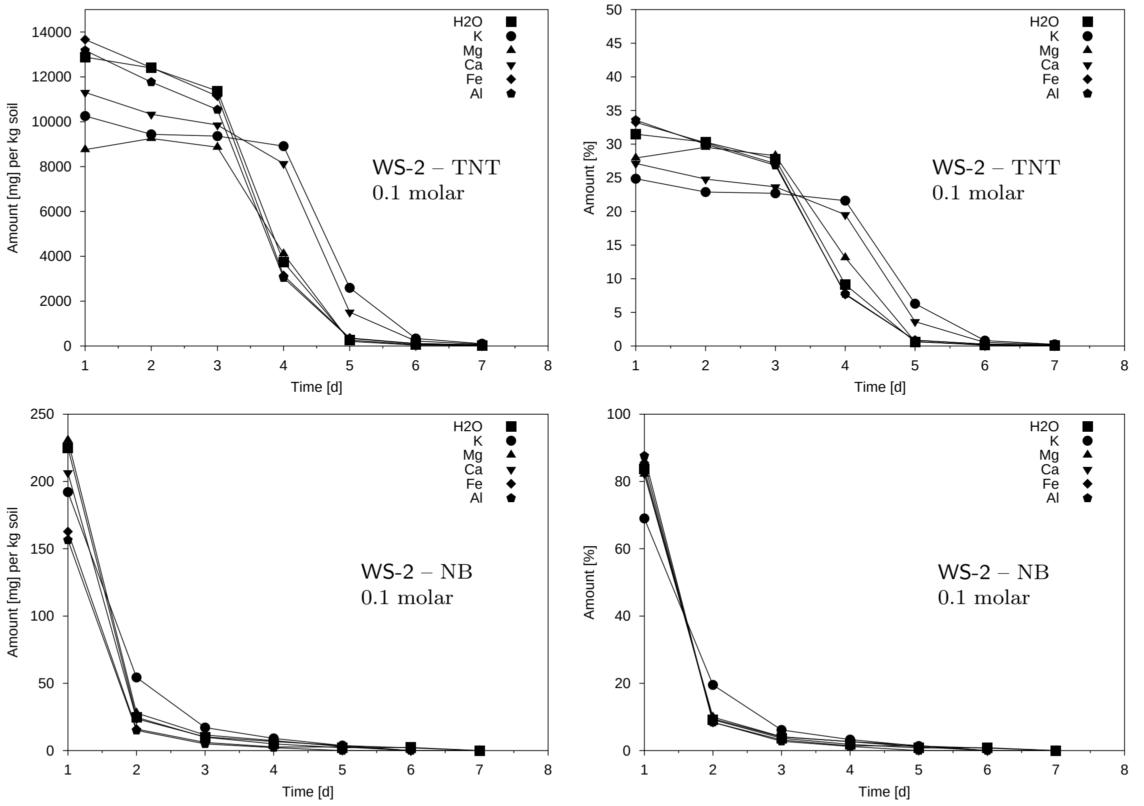

Figure 14: Desorbed amounts of TNT, and NB in [mg] per kilogram WS-2 soil (left) and desorbed amounts in [%] relativ to the total amount (right) versus time.

Desorption of TNT

Compared to soil fraction WS-1 a similar desorption pattern is obtained for the soil fraction WS-2 (Figure 14). The best desorption rates are achieved with the $FeCl_3$ desorption solution. During the first three days 11.1 to 13.7 g/kg corresponding to about 90.5 % of the initial TNT are desorbed from WS-2, followed by a rapid decrease of TNT in the desorption solution. After four days, only 2.5 % of the initial TNT remains in the soil fraction WS-2.

Only slightly minor TNT amounts are observed for the $AlCl_3$ desorption solution and deionized water during the first two days. Altogether, after three days 90.3 % and 89.6 % of the initial TNT amounts are extracted from the WS-2 soil samples.

Similar to the soil fraction WS-1 low TNT desorption amounts of 8.7 to 9.3 g/kg are achieved when using the $MgCl_2$ desorption solution. In contrast to the $MgCl_2$ desorption solution and the WS-1 soil fraction the TNT amount in the $MgCl_2$ desorption

Table 10: Sum of the NAC amounts ($\text{Sum}_{Des.Sol}$) desorbed from soil WS-2 using the 0.1 molar desorption solutions, the residual NAC amounts measured in the treated soil samples ($\text{Soil}_{Treated}$), and the total sum of NACs (Sum_{Total}). The amounts are calculated per kilogram soil.

Compound	H_2O [mg]	KCl [mg]	$MgCl_2$ [mg]	$CaCl_2$ [mg]	$FeCl_3$ [mg]	$AlCl_3$ [mg]
TNT						
$\text{Sum}_{Des.Sol.}$	40755.0	41001.1	31251.7	41435.4	40884.3	39025.4
$\text{Soil}_{Treated}$	159.4	244.2	88.8	224.5	206.5	223.7
Sum_{Total}	40914.4	41245.3	31340.5	41659.9	41090.8	39249.1
NB						
$\text{Sum}_{Des.Sol.}$	269.0	278.4	280.7	250.7	190.2	178.6
$\text{Soil}_{Treated}$	2.9	2.8	2.5	3.3	4.6	2.0
Sum_{Total}	271.9	281.2	283.2	254.0	194.8	180.6

solution of WS-2 then decreases to 3.1 g/kg. This decrease may be caused by the relatively low initial TNT concentration of 31.3 g/kg in the WS-2 soil sample used for the $MgCl_2$ desorption experiment (Table 10). This is about 20 % less TNT compared to concentrations of 39.2 to 41.7 g/kg in the other soil samples. Hence, after three days 4.5 g/kg of TNT remained in the WS-2 soil sample compared to 12.5 g/kg in the WS-1 soil sample.

The results obtained with the soils WS-1 and WS-2 indicate that desorption is affected by both, the TNT concentration present in the soil and the cation present in the desorption solution.

Desorption of NB

The WS-2 soil samples contained 181 to 283 mg/kg NB (Table 10). Similar to WS-1 the lowest total NB concentrations of 181 and 195 mg/kg are detected in the soil samples used in combination with $AlCl_3$, and $FeCl_3$, while the highest concentrations of 281 to 283 mg/kg are detected with KCl, and $MgCl_2$, followed by deionized water. The WS-2 soil sample used for $CaCl_2$ desorption experiment shows a medium TNT concentration of 254 mg/kg similar to the respective WS-1 soil samples.

The desorption curves for all solutions are very similar to the curves obtained for the WS-1 soil fraction. Hence, the statements of chapter 3.2.4 for WS-1 holds true also for NB and the WS-2 soil fraction. As with the WS-1 soil fraction the relative desorption curves are similar to each other except for KCl, which exhibits the slowest relativ

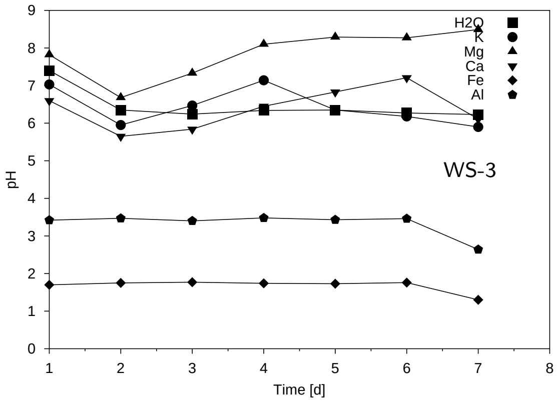

Figure 15: pH values in the desorption solutions of soil WS-3 using 0.1 molar salt concentrations.

desorption. Between 82 and 87 % of the total NB amount is desorbed during the first day, followed by a rapid decrease during the second day.

Despite the similar relative desorption curves for the different solutions, the absolute NB amounts desorbed from WS-2 soil fraction differ from each other. During the first day the lowest NB amounts are obtained for $AlCl_3$ (156 mg/kg), and $FeCl_3$ (163 mg/kg), while the highest values are found for $MgCl_2$ (231 mg/kg), deionized water (225 mg/kg), and $CaCl_2$ (207 mg/kg). Hence, the NB amounts obtained for WS-1 and WS-2 and the respective desorption solutions are more alike than the NB amounts found for the different desorption solutions and the same soil fractions.

3.2.6 Soil WS-3

The soil fraction WS-3 contains particles between 0.42 – 0.84 mm. Like the soil fractions WS-1 and WS-2 the dominant contaminant is TNT with a concentration of 38.0 g/kg and minor amounts of 207 mg/kg NB (Table 3). Hence, the same liquid-to-solid ratio of 200:1 is applied for the WS-3 desorption experiments.

The pH values of the WS-3 desorption solutions are presented in Figure 15. As with WS-1 and WS-2 the $AlCl_3$ and $FeCl_3$ solutions show acidic pH values of about 3.4 and 1.8. The values of deionized water, KCl, and $CaCl_2$ show slighty stronger varying values pH 5.5 and 7.4 than the respective WS-1 and WS-2 solutions, while the $MgCl_2$ solutions are slightly basic except for the second day.

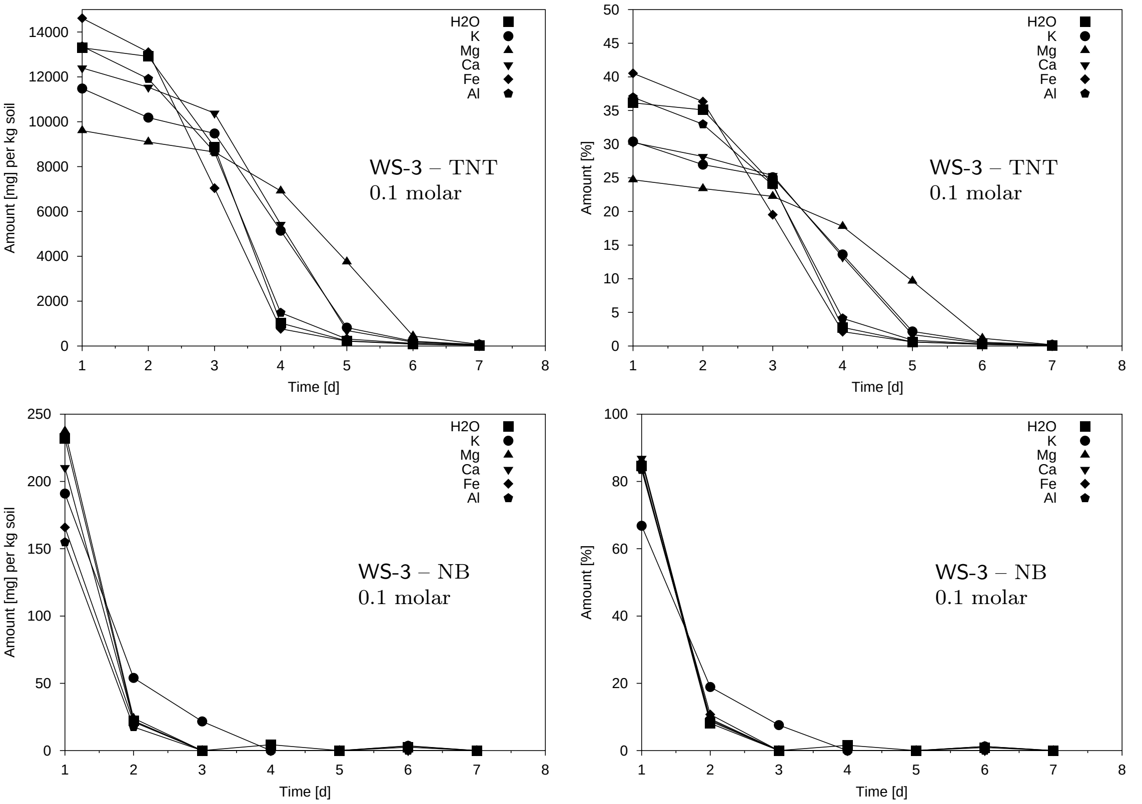

Figure 16: Desorbed amounts of TNT, and NB in [mg] per kilogram WS-3 soil (left) and desorbed amounts in [%] relativ to the total amount (right) versus time.

Desorption of TNT

The time courses of TNT and NB amounts desorbed from the soil fraction WS-3 are presented in Figure 16. The measured TNT and NB concentrations of the respective soil samples are summarized in Table 11.

As with the WS-1 and WS-2 soil fractions, fastest desorption is achieved with the $FeCl_3$ solution, i.e. 96.4 % of the initial TNT are desorbed within three days. Only slightly slower desorption curves are measured for deionized water and $AlCl_3$. Again, $MgCl_2$ shows the slowest desorption curve. Relatively low TNT amounts are desorbed when using the $MgCl_2$ desorption solution compared to $FeCl_3$. As a consequence, it takes five days for $MgCl_2$ to desorb 97 % of the initial TNT, two days longer that with $FeCl_3$. Altogether, similar total TNT concentrations between 36.1 to 40.1 g/kg are measured for the WS-3 soil samples.

Table 11: Sum of the NAC amounts ($\mathrm{Sum}_{Des.Sol}$) desorbed from soil WS-3 using the 0.1 molar desorption solutions, the residual NAC amounts measured in the treated soil samples ($\mathrm{Soil}_{Treated}$), and the total sum of NACs (Sum_{Total}). The amounts are calculated per kilogram soil.

Compound	H_2O [mg]	KCl [mg]	$MgCl_2$ [mg]	$CaCl_2$ [mg]	$FeCl_3$ [mg]	$AlCl_3$ [mg]
TNT						
$\mathrm{Sum}_{Des.Sol.}$	36455.7	37386.1	38541.0	40660.4	35852.7	35864.7
$\mathrm{Soil}_{Treated}$	342.9	388.1	338.5	314.6	205.3	278.4
Sum_{Total}	36798.6	37774.2	38879.5	40975.0	36058.0	36143.1
NB						
$\mathrm{Sum}_{Des.Sol.}$	261.0	270.3	264.9	232.4	187.2	172.4
$\mathrm{Soil}_{Treated}$	13.1	15.5	10.6	9.7	10.9	13.2
Sum_{Total}	274.1	285.8	275.5	242.1	198.1	185.6

Desorption of NB

The NB concentrations measured in the WS-3 soil samples vary between 186 and 286 mg/kg (Table 11) with a mean value of 244 mg/kg and a significantly higher relative standard deviation of 18 % compared to TNT. The lowest total NB concentrations are calculated for the $FeCl_3$ and $AlCl_3$ solutions, while the highest values are obtained for deionized water, and the KCl, and $MgCl_2$ solutions. $CaCl_2$ lies in-between and has a concentration close to the mean value. This is in accordance with the soil fractions WS-1 and WS-2, where a similar concentration pattern is obtained for NB.

It may happen that the soil samples used for the $FeCl_3$ and $AlCl_3$ desorption experiments contains significantly lower NB concentrations than the remaining soil samples. It may also randomly happen that the soil samples used for deionized water, KCl, and $MgCl_2$ solutions always contain significantly higher NB concentrations. However, it seems to be more likely, that the cation of the respective desorption solution significantly affects the NB concentrations measured in the respective soil samples.

The same holds true for the NB desorption curves. The desorption curves of the salt solutions obtained for the WS-3 soil fraction are more alike the respective desorption curves of WS-1 and WS-2 than the desorption curves for the different salt solutions obtained for one soil. For example, between 135 and 156 mg/kg are measured for the $AlCl_3$ solutions and the three soil fractions, while 224 to 232 mg/kg and 213 to 237 mg/kg are measured for deionized water and the $MgCl_2$ solution, respectively.

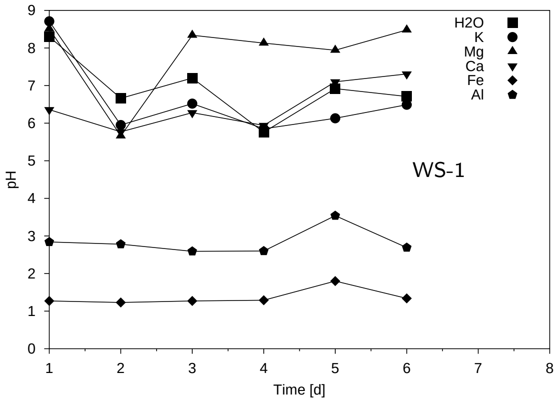

Figure 17: pH values in the desorption solutions of soil WS-1 using 0.5 molar salt concentrations.

Thus, a relative order may be established for all three soil fraction WS-1, WS-2, and WS-3. Increasing NB amounts desorbed from the soils are obtained in the order: $AlCl_3$, $FeCl_3$, KCl, and $CaCl_2$, followed by deionized water and $MgCl_2$ with partly overlapping ranges.

3.3 Soil WS-1 using 0.5 molar salt solutions

The results obtained with the WS-1 to WS-3 soil fractions indicate an influence of the cation on the desorption behavior on both, TNT and NB. For that reason, the influence of more concentrated salt soltutions (0.5 molar) are investigated in combination with the WS-1 soil fraction.

For the desorption experiments with the 0.5 molar solutions the same liquid-to-solid ratio was used as for the desorption experiments with the 0.1 molar solutions, i.e. 100 ml desorption solution were added to 0.5 g WS-1 soil. The pH values of the desorption solutions are shown in Figure 17.

Due to the higher salt concentrations slightly lower pH values are obtained for $AlCl_3$, and $FeCl_3$ compared to the 0.1 molar solutions. Regarding KCl, $MgCl_2$, and $CaCl_2$ the pH values oscillate between pH 5.8 and 8.7 compared to the 0.1 molar solutions. This may be caused by the high salt concentrations, which may affect the glas membrane of the pH electrode system. This is indicated by instable pH values during pH measurements. The pH values drifted by 1 to 1.5 pH units over a time period of 15 minutes. Although the pH values were still drifting the pH mesurements were stopped after that time.

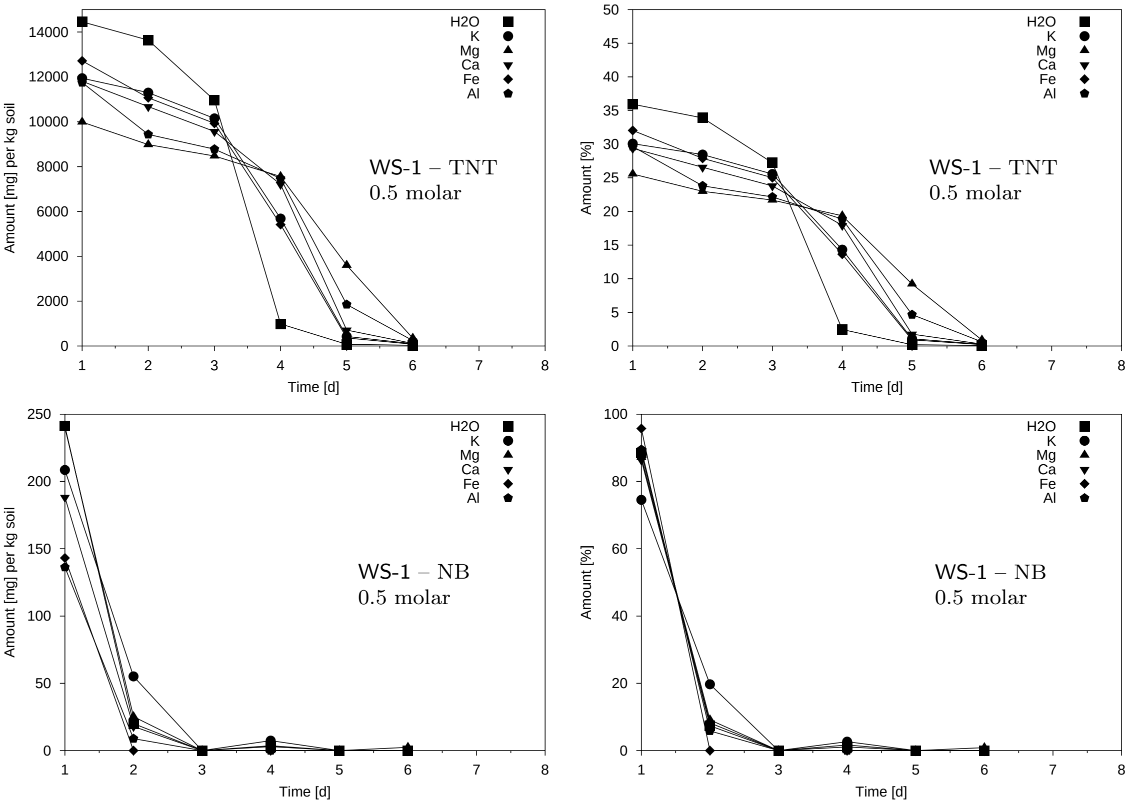

Figure 18: Desorbed amounts of TNT, and NB in [mg] per kilogram WS-1 soil (left) and desorbed amounts in [%] relativ to the total amount (right) versus time.

The pH measurements also yield instable pH values for deionized water, although there cannot be a direct effect of salt ions. However, the measurements of the pH values of the deionized water samples were performed together with the 0.5 molar desorption solutions. Since it takes some time for the glas membrane of the pH electrode to stabilize, the measurements of the deionized water samples may also be affeceted by the 0.5 molar salt solutions.

Desorption of TNT

The desorption curves using the 0.5 molar salt solutions versus time are shown in Figure 18. Some minor differences are obtained compared to the curves obtained with the 0.1 molar salt solutions and WS-1.

For the 0.5 molar solution experiments the highest desorption rate are measured for deionized water during the first three days, followed by a rapid decrease during the fourth day due to the low residual TNT concentration in the soil sample. The desorbed

TNT amounts when using the $FeCl_3$ solution are about 1 to 2 g/kg lower than the amounts of the respective 0.1 molar solutions. During the fourth day about twice the TNT amount of the 0.1 molar solution is detected in the 0.5 molar solution. In total, 83 % of TNT are desorbed with the 0.5 molar $FeCl_3$ solution compared to 93 % obtained with the 0.1 molar solution after three days.

The 0.5 molar KCl solution shows higher desorption efficiency than the 0.1 molar solution. After three days 83.1 % of the inital TNT is desorbed with the 0.5 molar solution compared to 75.1 % obtained with the 0.1 molar solution. However, after four days similar amounts (97.4 % compared to 95.8 %) are desorbed.

As with the 0.1 molar $MgCl_2$ solution, the lowest desorption rate is achieved with the 0.5 molar $MgCl_2$ solution. During the first four days 88.7 % of the TNT is desorbed, and only after the fifth day almost complete desorption of 97.9 % of the initial TNT is achieved.

Comparing the TNT amounts desorbed during the first day, the variations between the respective 0.1 and the 0.5 molar salt solutions are less significant than the variations between the different cations. As with the 0.1 molar solutions high TNT amounts are desorbed when using $FeCl_3$, $AlCl_3$, and $CaCl_2$. The lowest desorption efficiencies are obtained with KCl, and $MgCl_2$.

Only deionized water makes an exception in that it shows the highest desorption efficiency of the 0.5 molar experimental series, while its efficiency in the 0.1 molar series is similar to $CaCl_2$ and $AlCl_2$. This is not attributable to the total TNT concentrations of the two soil samples used for the experiments, since both have nearly identical concentrations of 40.2 g/kg (Tables 9 and 12). It is more likely, that this may be caused by an error in HPLC measurement for the 0.1 molar solution. It is the only value of the first day, that is followed by a significant TNT increase the second day.

Desorption of NB

As summarized in Table 12 the total NB concentrations in the WS-1 soil samples range from 149.5 to 279.8 mg/kg. As with the WS-1 to WS-3 soil fractions and the 0.1 molar desorption solutions high total NB concentrations of 272.4 to 279.8 mg/kg are measured when using deionized water, KCl, and $MgCl_2$. This is about 50 mg/kg more than the mean value of 224.6 mg/kg. On the other hand, total NB concentrations of 150 mg/kg, about 75 mg/kg less than the mean value are measured in combination with $FeCl_3$, and $AlCl_3$, while a total NB concentration of 218 mg/kg was measured for $MgCl_2$, which is close to the mean value.

Relative NB amounts of 86 % (deionized water) to 96 % ($FeCl_3$) of the total NB

Table 12: Sum of the NAC amounts ($\text{Sum}_{Des.Sol}$) desorbed from soil WS-1 using the 0.5 molar desorption solutions, the residual NAC amounts measured in the treated soil samples ($\text{Soil}_{Treated}$), and the total sum of NACs (Sum_{Total}). The amounts are calculated per kilogram soil.

Compound	H_2O [mg]	KCl [mg]	$MgCl_2$ [mg]	$CaCl_2$ [mg]	$FeCl_3$ [mg]	$AlCl_3$ [mg]
TNT						
$\text{Sum}_{Des.Sol.}$	40142.5	39600.4	38942.8	40082.2	39569.9	39525.1
$\text{Soil}_{Treated}$	86.5	97.3	114.7	103.4	112.5	97.5
Sum_{Total}	40229.0	39697.7	39057.5	40186.2	39682.4	39622.6
NB						
$\text{Sum}_{Des.Sol.}$	264.1	271.1	267.6	209.9	143.1	145.2
$\text{Soil}_{Treated}$	8.3	8.7	7.9	8.1	6.4	7.1
Sum_{Total}	272.4	279.8	275.5	218.0	149.5	152.3

are desorbed during the first day, except for the KCl solution, which desorbed 75 %. These are 4 % to 12 % higher NB amounts compared to the 0.1 molar solutions.

Although, all of the relative NB amounts desorbed during the first day are higher than the relative amounts obtained with the 0.1 molar solutions, the absolute NB amount obtained with $CaCl_2$ is lower, and the NB amounts obtained with $FeCl_3$, and $AlCl_3$ are identical to the 0.1 molar solutions.

This indicates that the amounts desorbed are affected by both, the initial NB concentration in the soil sample and the salt concentration in the desorption solution. For example, a 24 mg/kg lower total NB amount is measured in the soil sample, used for the 0.5 molar $CaCl_2$ solution compared to the respective soil sample of the 0.1 molar $CaCl_2$ solution. This explains the lower total NB amount in the desorption solution of the first day. Nevertheless higher relative NB amounts are desorbed due to the higher $CaCl_2$ concentration in the desorption solution. Similar holds true for $FeCl_3$, and $AlCl_3$.

3.4 Soil WS-1 using a L/S ratio of 1000:1

For the soils investigated a liquid-to-solid ratio of 10:1, and 200:1 was applied, depending on the NAC concentrations in the soils. Due to the differences in desorption of TNT and NB when applying the various salt solutions the WS-1 soil fraction was selected to measure the effect of the liquid-to-solid ratio on the desorption behavior

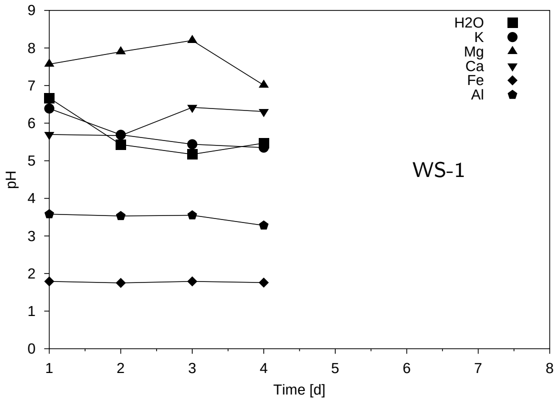

Figure 19: pH values in the desorption solutions of soil WS-1 using 0.1 molar salt concentrations and a liquid-to-solid ratio of 1000:1.

of the NACs.

The WS-1 experiments performed with 0.5 g soil desorption took up to six days. Lowering the liquid-to-solid ratio (such as 100:1 or 50:1) would lead to an increased and, from a practical view too long desorption time. On the other hand, taking too small soil samples would lead to an increased risc of measuring irreproducible results due to inhomogeneities in both, the soil matrix itself and the distribution of NACs in the soil. For that reason, soil samples of 0.1 g are selected in combination with 100 ml of the 0.1 molar desorption solutions, yielding a liquid-to-solid ratio of 1000:1.

The pH values of the desorption solutions versus time are shown in Figure 19. Compared to the experiments with a ratio of 200:1 similar pH values of 1.8 and 3.5 are measured in the $FeCl_3$, and $AlCl_3$ solutions. Slightly lower values are obtained especially with deionized water, but also with the $MgCl_2$, and $CaCl_2$ solutions. Since, only 0.1 g soil is used for the 1000:1 liquid-to-solid ratio experiments, one would expect a reduced effect of the soil samples on the desorption solutions and hence, pH values which are closer to the pH values of the pure desorption solutions (Table 5). Compared to the experiments performed with a liquid-to-solid ratio of 200:1, this holds true only for KCl.

The experiments were performed simultaneously with the 0.5 molar desorption experiments. The pH values of one set of samples were normally measured in the order: deionized water, KCl, $MgCl_2$, $CaCl_2$, $FeCl_3$, and $AlCl_3$. Although the pH electrode was rinsed with deionized water between two measurements, there may still be some effect on the measurements after changing from the 0.5 molar to the 0.1 molar desorption solutions. Hence, especially measurement of the deionized water samples may be affected by the high salt concentration of the foregoing 0.5 molar $AlCl_3$ solution. This

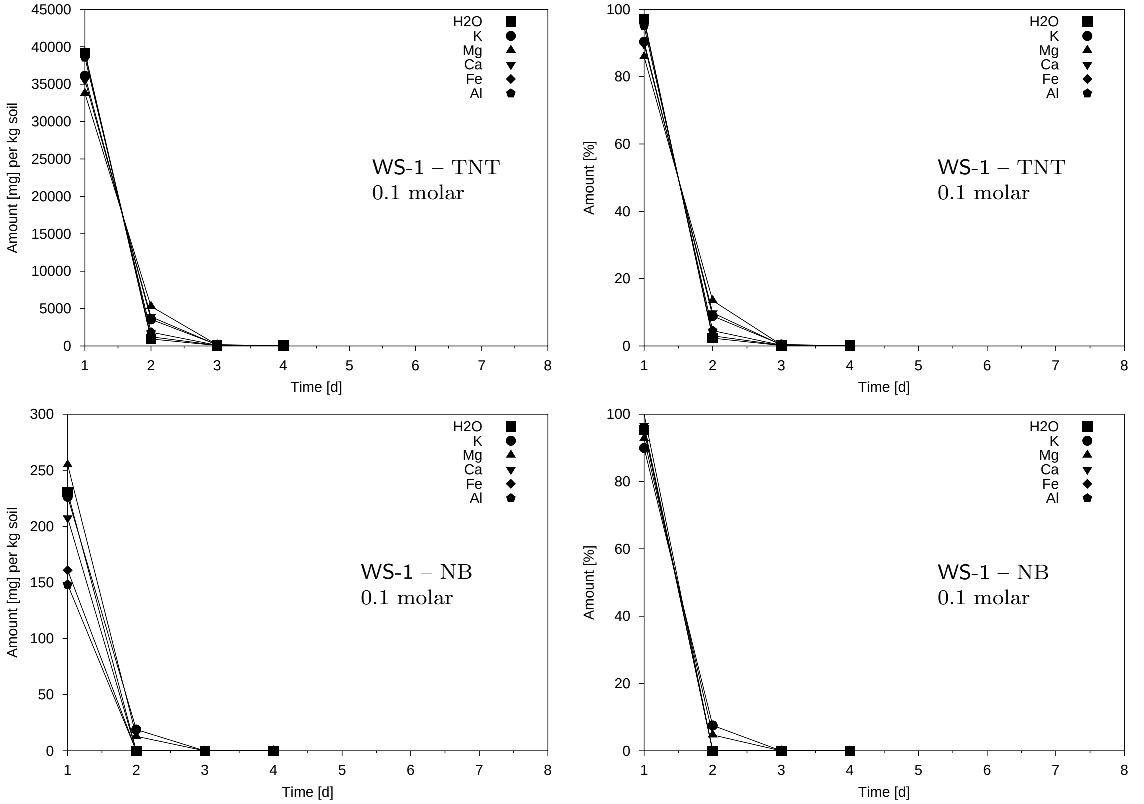

Figure 20: Desorbed amounts of TNT, and NB in [mg] per kilogram WS-1 soil (left) and desorbed amounts in [%] relativ to the total amount (right) versus time (liquid-to-solid ratio of 1000:1)

may explain the occasional drifting pH values, especially of the samples containing deionized water.

Desorption of TNT

A increased liquid-to-solid ratio of 1000:1 has a significant effect on TNT desorption. Almost all TNT desorbed (86 to 97 %) during the first day (Figure 20). This is followed by a rapid decrease of desorption during the second day, which is due to the low TNT amounts remaining in the soil samples.

TNT concentrations of 33 to 40 mg/L are measured in the desorption solutions during the first day compared to 43 to 70 mg/L of the 0.5 g soil experiments. Altogether, higher TNT amounts of 33.8 and 39.3 g/kg are calculated since the TNT originates from smaller soil samples (Figure 20). However, comparing the relative order of TNT desorbed during the first day, similar patterns are obtained for both liquid-to-solid

Table 13: Sum of the NAC amounts ($\text{Sum}_{Des.Sol}$) desorbed from soil WS-1 using the 0.1 molar desorption solutions and a liquid-to-solid ratio of 1000:1, the residual NAC amounts measured in the treated soil samples ($\text{Soil}_{Treated}$), and the total sum of NACs (Sum_{Total}). The amounts are calculated per kilogram soil.

Compound	H_2O [mg]	KCl [mg]	$MgCl_2$ [mg]	$CaCl_2$ [mg]	$FeCl_3$ [mg]	$AlCl_3$ [mg]
TNT						
$\text{Sum}_{Des.Sol.}$	40164.7	39882.0	39256.0	39605.8	40617.5	40550.1
$\text{Soil}_{Treated}$	98.0	80.3	59.1	58.5	63.1	50.6
Sum_{Total}	40262.7	39962.3	39315.1	39664.3	40680.6	40600.7
NB						
$\text{Sum}_{Des.Sol.}$	230.6	245.3	267.9	207.6	160.9	148.1
$\text{Soil}_{Treated}$	11.3	6.4	7.0	7.2	7.4	0.0
Sum_{Total}	241.9	251.7	274.9	214.8	168.3	148.1

ratios, 1000:1 and 200:1. The highest amounts are desorbed when using the $FeCl_3$ and deionized water. Only slighty lower amounts are desorbed by the $AlCl_3$ solution. The lowest TNT amount desorbs when using $MgCl_2$, while KCl and $CaCl_2$ lying in-between. Altogether, a higher liquid-to-solid ratio accelerates the TNT desorption rate.

In total, TNT concentrations between 39.3 to 40.7 g/kg are measured in the soil samples used for the desorption experiments (Table 13). This is comparable to the concentrations measured in the WS-1 soil samples used in combination with the 200:1 ratio (Table 9). With a liquid-to-solid ratio of 1000:1 desorption occured within one to two days compared to five to six days when using a ratio of 200:1.

Desorption of NB

As already observed for TNT, desorption of NB is accelerated by the higher liquid-to-solid ratio of 1000:1. More than 90 % of the total NB measured in the treated soil samples are desorbed during the first day. Desorption is complete after two days (Figure 20).

However, significant differences are obtained with respect to the absolute NB amounts measured in the different soil samples. As summarized in Table 13 between 148 and 275 mg/kg are detected in the soil samples with a mean value of 216.6 mg/kg. As with all the desorption experiments performed with the WS soil fractions, the lowest values are always obtained with the $AlCl_3$, and $FeCl_3$ solutions, whereas the highest

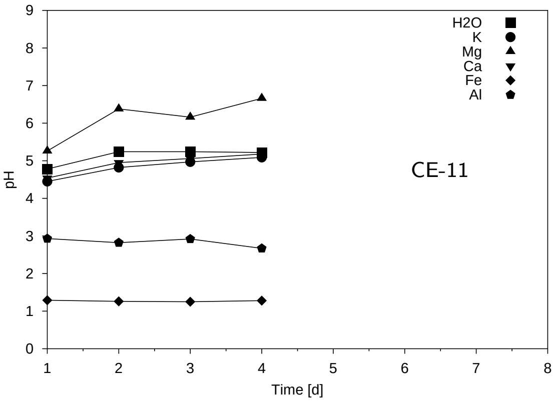

Figure 21: pH values in the desorption solutions of soil CE-11 using 0.5 molar salt concentrations.

concentrations are measured in combination with deionized water, KCl, and $MgCl_2$. The concentrations measured with $CaCl_2$ are always close to the mean values (Tables 9 to 13).

This is also reflected by the NB amounts desorbed during the first day. The lowest NB amount is measured in combination with with $AlCl_3$ (184 mg/kg), while the highest value is achieved together with $MgCl_2$ (255 mg/kg). This makes a difference of 71 mg/kg of NB being additionaly desorbed from the WS-1 soil during the first day when using the $MgCl_2$ solution.

3.5 Soil CE-11 using 0.5 molar solutions and a L/S ratio of 40:1

In combination with CE-11, the effect of a 0.5 molar desorption solutions in combination with an altered liquid-to-solid ratio of 40:1 are measured. For the experiments 100 ml desorption solution was added to 2.5 g soil samples.

Figure 21 shows the pH values of the 0.5 molar desorption solutions in combination with the CE-11 soil versus time. As with the 0.1 molar solutions the pH values of the 0.5 molar KCl, and $CaCl_2$ solutions lay between 4.5 and 5.2. Due to the higher molarity and thus, higher effects on the buffering capacity of CE-11 soil, pH values closer to the pH values of the original 0.5 molar salt solutions are obtained for $MgCl_2$, $FeCl_3$, and $AlCl_3$ as compared to the respective 0.1 molar solutions. Slightly higher pH values of up to pH 6.7 are measured for $MgCl_2$, while slightly lower pH values of 2.9 and 1.3 are achieved with the 0.5 molar $FeCl_3$, and $AlCl_3$ solutions.

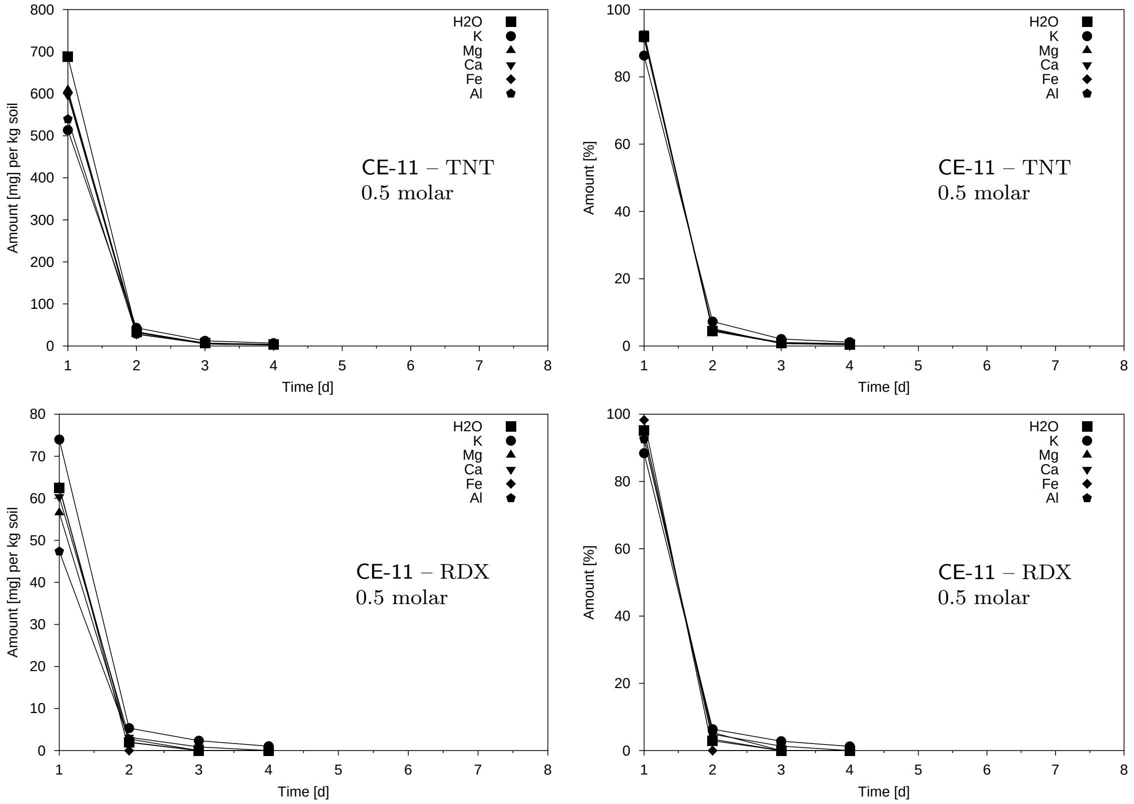

Figure 22: Desorbed amounts of TNT, and RDX in [mg] per kilogram CE-11 soil (left) and desorbed amounts in [%] relativ to the total amount (right) versus time (liquid-to-solid ratio of 40:1)

Desorption of TNT

The time course of the desorbed NAC amounts are shown, in Figure 22. Similar relative TNT desorption rates of about 92 % are obtained for all desorption solutions during the first day, except KCl with a slightly lower value of 86 %. Although, there are similar relative desorption rates, differences in the absolute desorbed TNT amounts of up to 175 mg/kg are measured for the different salt solutions. The highest absolute desorption rate is obtained with deionized water (688 mg/kg), while the lowest is achieved with KCl (513 mg/kg).

The desorption rates rapidly decrease to less than 7 % of the total amount after the first day, due to the low residual TNT concentrations in the soil samples. Therefore, the differences in the TNT amounts desorbed during the first day reflect the total TNT concentration of the CE-11 soil samples, ranging from 590 to 748 mg/kg (Table 14).

Table 14: Sum of the NAC amounts ($\text{Sum}_{Des.Sol}$) desorbed from soil CE-11 using the 0.5 molar desorption solutions and a liquid-to-solid ratio of 40:1, the residual NAC amounts measured in the treated soil samples ($\text{Soil}_{Treated}$), and the total sum of NACs (Sum_{Total}). The amounts are calculated per kilogram soil.

Compound	H_2O [mg]	KCl [mg]	$MgCl_2$ [mg]	$CaCl_2$ [mg]	$FeCl_3$ [mg]	$AlCl_3$ [mg]
TNT						
$\text{Sum}_{Des.Sol.}$	731.9	575.8	649.2	633.2	643.6	577.9
$\text{Soil}_{Treated}$	16.2	18.8	9.4	7.6	12.4	11.9
Sum_{Total}	748.1	594.6	658.6	640.8	656.0	589.8
RDX						
$\text{Sum}_{Des.Sol.}$	64.4	82.7	58.6	64.4	62.8	50.1
$\text{Soil}_{Treated}$	1.3	1.0	1.0	0.7	1.1	1.1
Sum_{Total}	65.7	83.7	59.6	65.1	63.9	51.2

Compared to the CE-11 desorption experiments with a liquid-to-solid ratio of 10:1 (chapter 3.2.3) higher relative TNT amounts are desorbed by deionized water and a 40:1 ratio. In the special case of deionized water desorption cannot be affected by a higher salt concentration. For that reason the higher TNT desorption must be caused by the increased liquid-to-solid ratio. However, the high absolute TNT amount may not only be attributed to the increased 40:1 ratio. The CE-11 soil sample used for the desorption experiment with deionized water contained a TNT amount of 748 mg/kg. This is by about 85 mg/kg higher than the respective CE-11 soil samples used in combination with the 10:1 ratio (Table 8).

On the other hand, the soil sample used for the 0.1 molar $FeCl_3$ desorption experiment and a liquid-to-solid ratio of 10:1 contained the highest TNT amount (798 mg/kg) of all CE-11 soil samples (Tables 8 and 14). Although, a 142 mg/kg higher TNT concentration was measured in this soil sample, 111 mg/kg more TNT desorbed from the soil sample used for the 0.5 molar $FeCl_3$ solution and the 40:1 ratio during the first day.

A similar behavior is observed for the KCl solutions. The TNT concentration of the soil sample used for the 0.5 molar KCl solution together with the 40:1 ratio is lower than the concentration of the soil sample used for the 0.1 molar KCl solution. Nevertheless, similar TNT amounts (513 and 528 mg/kg) are desorbed during the first day. Hence, a higher percantage of the total TNT amount is desorbed with the 0.5 molar KCl solution and the liquid-to-solid ratio of 40:1.

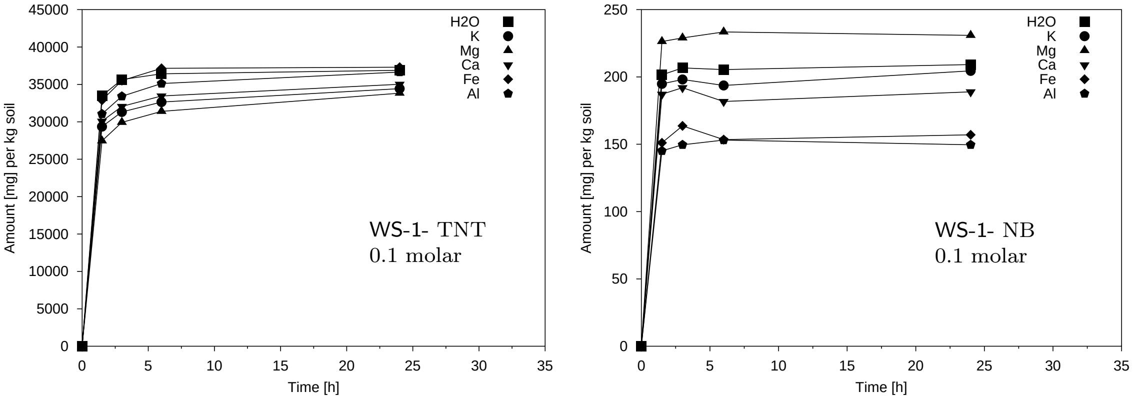

Figure 23: Desorption isotherm for TNT, and NB using a liquid-to-solid ratio of 1000:1.

Desorption of RDX

Similar effects are observed for RDX. Although an already high RDX desorption is obtained with the 0.1 molar solutions, desorption increases in combination with the 0.5 molar salt solutions and a higher liquid-to-solid ratio of 40:1. A desorption of more than 88 %, and in case of $FeCl_3$ even almost quantitative desorption is achieved with the 0.5 molar solutions and the ratio of 40:1 during the first day.

3.6 Desorption isotherms using soil WS-1

A desorption time of 24 hours was selected for the desorption experiments to assure that desorption equilibrium of NACs is achieved within each desorption step. To verify this assumption desorption isotherms were measured using the WS-1 soil fraction, 0.1 molar desorption solutions and a liquid-to-solid ratio of 1000:1. After 1.5, 3.0, 6.0, and 24 hours the mixture was centrifuged. After filtration of 3 ml of the supernatant into HPLC vessels the mixture was again rotated until the next sample has to be drawn. The NAC concentrations in the filtrated samples were measured by HPLC. The resulting desorption curves of TNT and NB are presented in Figure 23.

Desorption of TNT

The concentrations in the solutions increase, since TNT and NB desorbed from the soil samples into the liquid phases. The isotherm curves exhibit a saturation-type curvature approaching a maximum concentration in the desorption solution.

The maximum TNT concentrations are reached within 6 to 24 hours for all desorption solutions. However, different maximal TNT amounts are obtained for the different solutions. TNT amounts of about 37 g/kg are desorbed in combination with deionized water, $FeCl_3$, and $AlCl_3$, while the lowest TNT amount is achieved with $MgCl_2$ (33.8 g/kg). Medium amounts are obtained together with KCl, and $CaCl_2$.

A liquid-to-solid ratio of 1000:1 and 0.1 molar salt concentrations were used. These are the same experimental conditions as were applied for the desorption experiments with a liquid-to-solid ratio of 1000:1 presented in chapter 3.4. Therefore, it is possible to compare the results after 24 hours. In both experimental sets not only similar TNT amounts between 33.8 and 39.1 g/kg are measured but also the same relative order of desorption efficiency is observed for the different salt solutions. In both experimental sets the lowest TNT amounts are obtained with $MgCl_2$, while the highest amounts are obtained with deionized water, $FeCl_3$, $AlCl_3$.

The relative order of desorption efficiency for the different salt solutions holds true also for the WS-1 desorption experiments with a liquid-to-solid ratio of 200:1, although the absolute TNT amounts desorbed are affected by the liquid-to-solid ratio. Again the lowest TNT amounts are obtained with the $MgCl_2$, while deionized water, and the $FeCl_3$, and $AlCl_3$ solutions lead to high TNT amounts. The same holds true for the desorption experiments with the WS-2, and WS-3 soil fractions. In every case, highest amounts are desorbed with deionized water, and the $FeCl_3$ and $AlCl_3$ solutions. KCl and $CaCl_2$ yields medium amounts.

Desorption of NB

Compared to TNT a slighly faster desorption of NB take place. The maximum NB concentrations are reached within 1.5 to 3 hours. This may be caused by the lower NB concentration in the WS-1 soil fraction.

NB amounts of 150 to 231 mg/kg are desorbed within 24 hours. As with TNT the differences in NB desorption seem to be affected by the different salt solutions. The highest amount is obtained with $MgCl_2$, followed by deionized water and KCl. Lowest desorption is achieved in combination with the $AlCl_3$, and $FeCl_3$ solutions.

The same relative order of desorption efficiency is observed for the different salt solutions of the WS-1 desorption experiments with a liquid-to-solid ratio of 1000:1 (chapter 3.4). A similar order is also measured for the WS-1, WS-2, and WS-3 desorption experiments with a liquid-to-solid ratio of 200:1. Deionized water and the $MgCl_2$ solutions always yields the highest desorbed NB amounts with similar values. In contrast, the lowest amounts are desorbed by the $AlCl_3$ solutions, closely followed by the $FeCl_3$ solutions, while the $CaCl_2$ solutions contain NB amounts similar to the calculated mean values of the respective set of desorption experiments.

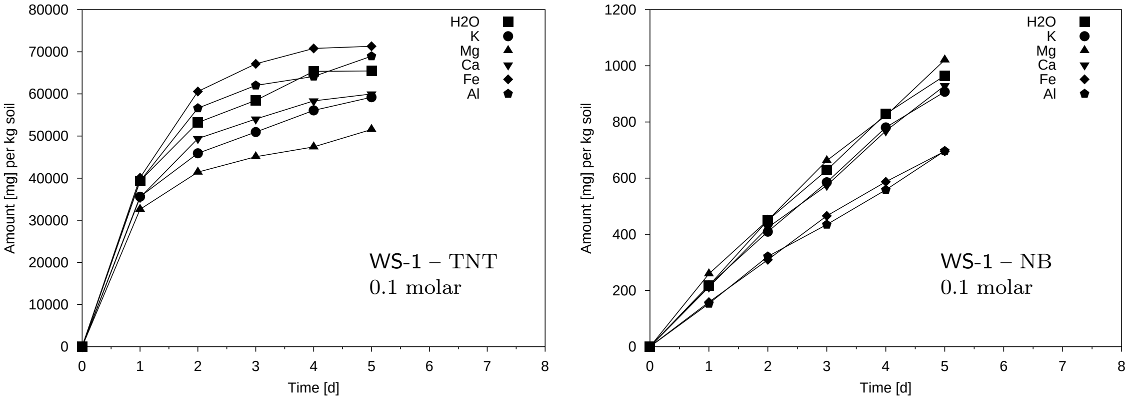

Figure 24: Desorbed TNT and NB amounts versus time. A liquid-to-solid ratio of 1000:1 and 0.1 molar salt solutions are used for the saturation test. The calculated amounts refer to 1 kg soil.

3.7 Saturation test using soil WS-1

For the saturation test 0.1 g of the WS-1 soil fraction is mixed with 100 ml deionized water or salt solution. The mixture is shaken for 24 hours. In contrast to the desorption experiments the soil is discarded after centrifugation instead of the supernatant and a new soil sample is added to the supernatant.

The desorbed TNT and NB amounts versus time are shown in Figure 24. During the first 24 hours the experimental conditions are identical to the desorption experiments described in chapter 3.4, since the same salt concentrations (0.1 molar) and the same liquid-to-solid ratio (1000:1) are applied.

In both desorption experiments almost identical TNT amounts are desorbed by identical salt solutions within the first day. For example, the highest amounts of TNT are desorbed by the $FeCl_3$ solutions (39.3 and 40.1 g/kg), deionized water (39.1 and 39.4 g/kg), and $AlCl_3$ solutions (38.6 and 39.3 g/kg), while the lowest amounts are desorbed by $MgCl_2$ solutions (32.6 and 33.8 g/kg). The different salt solution vary more widely in the desorbed TNT amounts than identical solutions. This order of TNT desorption for the different salt solutions can be observed for all experiments performed with the WS-1, WS-2, and WS-3 soil fractions.

The same considerations hold true also for NB. Similar amounts of NB are obtained with identical salt solutions in relation to the amounts obtained with different salt solutions. However, a different desorption order of NB is observed for the different salt solutions compared to TNT. The highest NB amounts are obtained with $MgCl_2$ (255.0 and 259.3 mg/kg), followed by deionized water (217.5 and 230.6 mg/kg), whereas

$FeCl_3$ (158.6 and 160.9 mg/kg) and $AlCl_3$ (148.1 and 153.3 mg/kg) yields the lowest NB desorption.

There are also differences between TNT and NB considering the whole time period of five days for the saturation experiment. The time course of TNT exhibits a saturation-type curvature, while the time course of NB resembles more a straight line. This is probably due to both, the very different concentrations of TNT and NB in the WS-1 soil fraction and the saturation concentrations of TNT and NB in water. The solubility of NB in water is about 20 times higher than the solubility of TNT in water at 20 °C, whereas the concentration of TNT in the WS-1 soil fraction is about 190-fold higher than the NB concentration.

TNT concentrations between 32 and 43 mg/L are measured in the different desorption solutions after one day. This is about half of the aqueous solubility of 88.5 mg/L [2]. As a consequence, the TNT concentration slowly increases and approaches a maximum concentration of 52 to 72 g/L. The maximum concentrations reached depend on the respective desorption solution. In contrast to TNT, the NB concentrations in the desorption solutions are far below the solubility of NB in water. For that reason, additional NB can dissolve in the desorption solution after exchanging the soil samples. Even after five soil exchanges NB concentrations below 1 mg/L are measured in the desorption solutions and are thus, still far below the solubility of NB in water.

4 Conclusions and discussion

Sorption to and desorption from soils is one of the key processes determining the distribution and fate of NACs in the environment. Sorption of NACs is affected by the NACs itself, soil-related properties, and the constituents of the soil solution.

Important soil-related properties affecting sorption of organic compounds are the soil organic matter and the cation exchange capacity. Since changes in binding properties and sorption processes of NACs may occur over time, naturally aged soils are selected for the desorption experiments. This is advantageous with respect to real sorption status of NACs in soils, which cannot be simulated when using artifically contaminated soils. On the other hand, this decision involves that soils must be used as they are. It is not possible to select specific soil properties (such as a specific texture, cation exchange capacity, soil organic matter) or specific NACs contamination patterns. Table 15 summarizes some soil properties of the soils used for the desorption experiments.

With values of 6 and 7.6 the pH of all soils are close to neutral values. The soils show similar total organic carbon contents (TOC) ranging from 0.89 to 1.55 %, except soil Crane with a higher TOC of 14.1 %. The cation exchange capacity (CEC) of the WS soil fractions are about three times higher compared to the soils CE-11, Crane, and IAAP.

The main objective of this study was to investigate the effect of the cations in the soil solution on the NACs desorption behavior. For this reason, salts differing only in the cation were selected. The anion (Cl^-) remains constant to avoid unpredictable affects which may be caused by different anions. The 0.1 and 0.5 molar salt solutions show varying pH values (Table 5). However, the pH of all salt solutions are below the minimum pH value required for alkaline hydrolsis to occur [3]. This is a prerequisite for the desorption experiments because otherwise desorption would be superimposed by alkaline hydrolysis.

The findings presented in this study indicates that desorption of a specific NAC may

Table 15: Soil properties of the soils used for the desorption experiments.

	Unit	CE-11	Crane	IAAP	WS-1	WS-2	WS-3
pH		6.0	6.0	7.6	6.0	6.0	6.5
CEC	[meq/100 g]	8.1	8.0	10.7	30.7	30.7	30.7
TOC	[%]	0.89	14.1	1.2	1.25	1.55	1.33
Soil fraction	[mm]	-	-	-	<0.18	0.18-0.42	0.42-0.84

Source: Environmental Laboratory, U.S. Army Engineer Research and Development Center, 3909 Halls Ferry Road, Vicksburg, MS 39180-6199

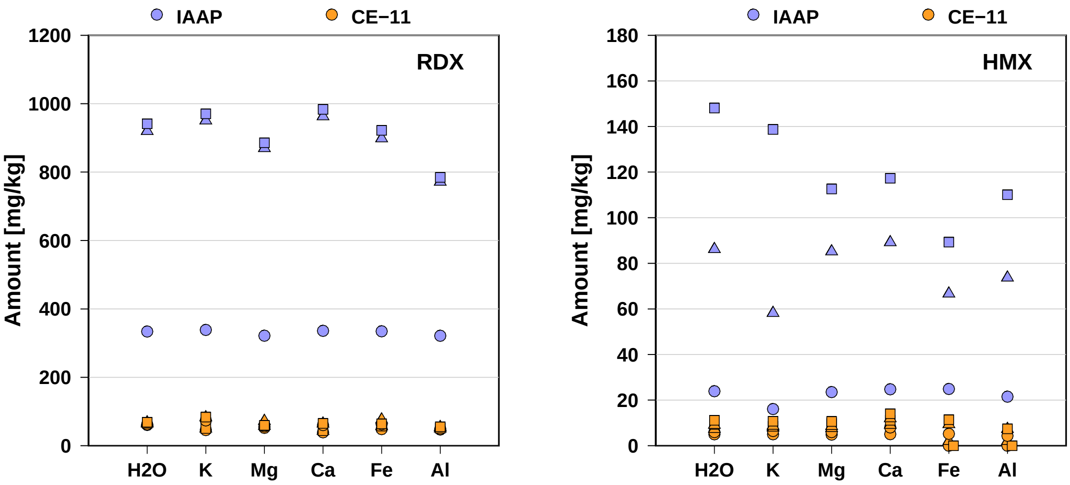

Figure 25: Amounts of RDX (left) and HMX (right) desorbed during the first day (◯), the sum of the amounts of all desorption solutions of the respective salt solutions (△), and the total amounts (☐) calculated for the respective soil sample.

be affected not only by the soil properties but also by the cation present in the soil (respective desorption) solution. This holds true particularly for the nitroaromatic compounds TNT and NB.

Figure 25 summarizes the results obtained for RDX and HMX and the soils IAAP and CE-11. It shows the desorbed amounts measured after the first day, the sum of the amounts found in all desorption solutions of the respective salts and the total amounts calculated for the respective soil samples.

Different amounts of RDX are desorbed of the IAAP and CE-11 soil samples, due to the different concentrations in the untreated soil samples. No significant variation in amounts are observed between the different salt solutions of one soil and the first day. Only little variations are found for the sum of the amounts of the desorption solutions and the total amounts of the soil samples for the different salts. For example, a mean value of 914 mg/kg is found for RDX and the IAAP soil. With a standard deviation of 72 mg/kg a relative standard deviation of 8 % is calculated, which is within the normal range of analytical variations. However, a somewhat lower amount (785 mg/kg) is found for $AlCl_3$. This may be due to either a low RDX amount in the respective soil sample used for the desorption experiment or a lower desorption efficiency of $AlCl_3$ for RDX in soil IAAP. This can only be verified performing additional investigations.

The same holds true for RDX and the soil CE-11. Although higher relative variations in the amounts were measured compared to IAAP soil, there is no regularity in the

RDX desorption behavior of the different salt solutions. For example, the 0.1 molar KCl solution yields a relatively low RDX amount, while the 0.5 molar KCl solution yields a high RDX amount in the desorption solution.

As shown in the right diagram of Figure 25 a more imhomogeneous pattern is obtained for HMX. Probably due to the low solubility of HMX in water, only little amounts of HMX are desorbed during the first day. Tiny differences (22 to 25 mg/kg) are measured for the different salt solutions, except for KCl. Only relatively low amounts are desorbed by the KCl solution although a high HMX amount is measured in the respective soil sample. This is also reflected by the amount found in all KCl desorption solutions.

On the other hand, larger differences in the total HMX amounts are found in the soils samples used for the different salt solutions. Compared to deionized water, a somewhat lower amount is found in combination with the monovalent cation (K^+), again lower amounts are found for the bivalent cations (Mg^{2+}, Ca^{2+}), and again lower amounts are found for the trivalent cation (Fe^{3+}), while Al^{3+} shows a similar low amount as Mg^{2+}. Subsamples of the IAAP soils may be taken accidentally in the way that the samples contained decreasing HMX amounts in the order: K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+}. Nevertheless, it is also possible that the differently charged ions with their different surface charges and different degrees of hydration affect desorption behavior of HMX of the IAAP soil.

Figure 26 shows the desorbed amounts of TNT (top) and NB (bottom) of the desorption experiments performed with the WS soil fractions. The graphs on the left hand side summarizes the TNT and NB amounts desorbed during the first day (◯), the sum of the amounts found in all desorption solutions of the different salts (△), and the total amounts (□) calculated for the respective soil samples. For clarity only the results of the desorption experiments of the WS-1, WS-2, and WS-3 desorption experiments with a liquid-to-solid ratio of 200:1 and 0.1 molar desorption solutions are selected.

As can be seen from the graph on the left hand side of Figure 26, total TNT amounts of about 40.7 g/kg, except for $MgCl_2$, were measured in the WS-1 and WS-2 soil samples used for the desorption experiments. Slighty lower amounts of 37.8 g/kg are measured in the WS-3 soil samples. The sum of the amounts in the desorption solutions of one salt and the total amount calculated for the respective soil sample differ only be the residual TNT amount in the treated soil sample. Since only minor amounts of TNT were found in the soil samples compared to the total TNT amount (Tables 9, 10, and 11), the sum of the amounts in the desorption solutions are close to the calculated amounts in the respective soil samples.

On the other hand, a typical TNT desorption pattern is repeatedly measured for the

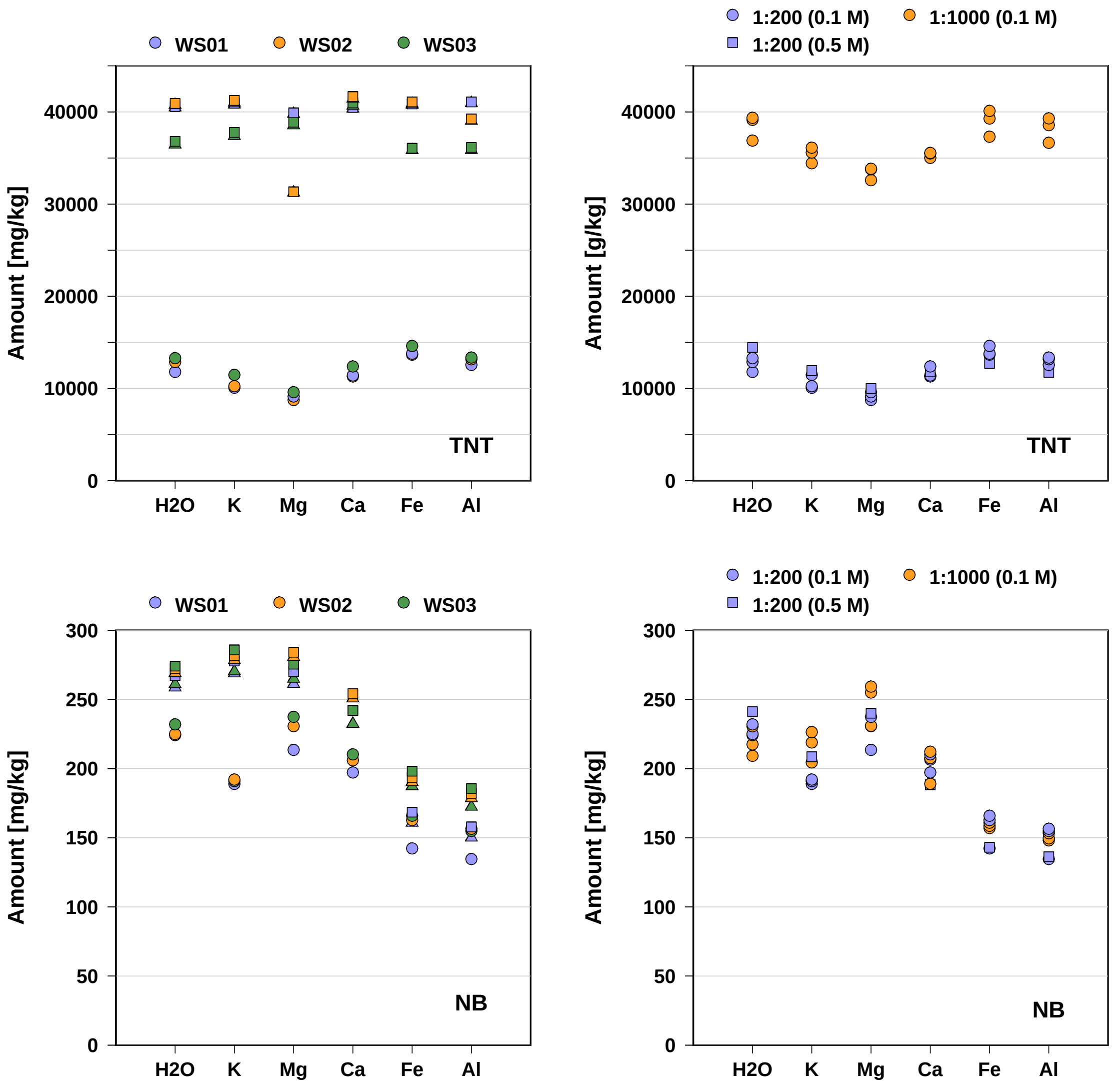

Figure 26: The graphs on the left hand side summarize the amounts of TNT (top) and NB (bottom) desorbed from the WS-1, WS-2, and WS-3 soil fractions in combination with a liquid-to-solid ratio of 200:1 and 0.1 molar desorption solutions. The graphs show the desorbed amounts during the first day (◯), the sum of the amounts of all desorption solutions of the respective salts (△), and the total amounts (□) calculated for the respective soil samples. The graphs on the right hand side summarize the results from all desorption experiments performed with all WS soil fractions. The desorbed amounts of TNT (top) and NB (bottom) are shown only for the first day. (see text for further explanations)

different salt solutions during the first day. For all three soil fractions the salt solutions can be ordered according to the desorbed TNT amounts. The highest amounts are desorbed by the $FeCl_3$ solution, followed by $AlCl_3$, deionized water, $CaCl_2$, and KCl, while $MgCl_2$ contained the lowest amounts. As can be seen from Figure 26 the amounts desorbed of the WS-1, WS-2, and WS-3 soil fractions and a specific salt solution are more likely than the amounts desorbed by the different salt solutions and one soil fraction. For example, with the $FeCl_3$ solution 13.8 to 14.6 g/kg of TNT are desorbed in contrast to the $MgCl_2$ solution with 8.8 to 9.6 g/kg.

The same pattern is obtained independent from the experimental conditions. This can be seen from the graphs on the right hand side of Figure 26. The graphs summarize the results of TNT (top) and NB (bottom) and all desorption experiments performed with the WS soil fractions. For clarity, only the desorbed amounts of the first day are selected. The results of the experiments performed with 0.1 molar solutions are represented by a circle (○), while squares (□) represent the 0.5 molar solutions. Different colors are used for different liquid-to-solid ratios of 200:1, and 1000:1.

The liquid-to-solid ratio significantly affects TNT desorption. Increasing the ratio from 200:1 to 1000:1 leads to an increase in desorption. For the 1000:1 ratio a higher volume of water is used together with a definite amount of soil. An identical amount of TNT, desorbing of the soil sample, leads to a lowered TNT concentration in the desorption solutions compared to the 200:1 ratio. This may cause a change in equilibrium of mass action law and additional TNT desorbs from the soil sample. As a consequence, almost all TNT desorbs from the WS-1 soil samples.

Nevertheless, the same pattern is obtained for the six desorption solutions although different experimental conditions were applied. The TNT amounts desorbed by the different salt solution vary more widely than the amounts of identical solutions. For the different salt solutions the order of TNT desorption can be observed for all experiments performed with the WS-1, WS-2, and WS-3 soil fractions, the different liquid-to-solid ratios, and the 0.1 and 0.5 molar salt solutions.

A similar effect is observed for NB. However, compared to TNT a different desorption order can be established for the different salts. Highest amounts are obtained with $MgCl_2$ and deionized water, followed by KCl and $CaCl_2$, while the lowest amounts are desorbed with $FeCl_3$ and $AlCl_3$. This is just the opposite order especially for $MgCl_3$, $FeCl_3$ and $AlCl_3$.

It is quite unlikely that the soil samples used for example for the $FeCl_3$ and $AlCl_3$ desorption experiments always contained significantly higher TNT and lower NB amounts than the remaining soil samples. It is also quite unlikely that the $MgCl_2$ soil samples always contained higher NB and lower TNT amounts. Rathermore, the repeating TNT and NB patterns strongly indicate that the cation present in the desorption solution affect both

- the absolute amount of NACs measured in the soil sample and
- the NACs desorption behavior of the WS soil samples.

The findings presented in this report indicate that the desorption patterns obtained for the different cations may be attributed to the cation exchange capacity of the WS soil fractions, which is about three fold higher compared to the cation exchange capacity of CE-11, Crane, and IAAP. This is in accordance with the findings of Haderlein et al. [8, 9], who reported that adsorption on natural clay minerals was strongly and consistently affected by the type of exchangeable cations adsorbed to the clay minerals.

In addition, the findings show that desorption also depends on the structure of the compound itself. For example, highest and lowest TNT amounts are obtained with $FeCl_3$ and $MgCl_2$, respectively. The opposite is true for NB, highest and lowest TNT amounts are obtained with $MgCl_2$ and $FeCl_3$, respectively. The difference can only be explained by the compound itself and it's type of substituent, since the corresponding results are obtained from the same set of desorption experiments.

Haderlein et al. [8, 9] reported that adsorption equilibrium was essentially established within a few minutes when using the clay minerals. In contrast to Haderlein et al., it took 2 to 6 hours for NB and TNT and the naturally aged WS-1 soil fraction to achieve desorption equilibrium (chapter 3.6). The slow desorption processes may be attributed to slow diffusion of solutes within pores, or cracks or poorly accessible surfaces of clay minerals due to aggregation or surface coatings.

Furthermore, the saturation experiments described in chaper 3.7 show that the NAC concentration in the respective soil in combination with solubility of the respective NAC in water also affect desorption behavior. The solubility of NB in water is about 20 fold higher than the solubility of TNT at 20 °C, whereas the concentration of TNT in the WS-1 soil fraction is about 190-fold higher than the NB concentration.

The 0.1 g soil samples used for the desorption experiments contained about 4 mg TNT, while 9 mg of TNT are soluble in 100 ml solution. Hence, TNT exhibits a saturation-type curvature, slowly approaching the saturation concentration of TNT in water. On the other hand, the NB concentration is far beyond the maximum solubility during the whole saturation experiment. Therefore, the desorption curve of the relatively low concentrated NB resembles more a straight line and additional NB may be dissolved. A similar desorption–dissolution behavior can be expected in a contaminated soil body. A soil solution trickling through a WS-1 soil body is presumably saturated with TNT after a short distance while NB may still be dissolved.

The saturation test simulates the flow of a definite volume of solution through a larger soil body. The findings indicate that dissolution of NACs in the soil solution depend on the aqueous solubility of the respective NACs and the concentration of the respective NACs in the contaminated soil.

However, as can be seen from Figure 24, NAC desorption is not only affected by soil concentration and solubility but also by the cation present in the desorption solution. During the time course of the saturation experiment the TNT amount in the 100 ml $FeCl_3$ solution sums up to 7.3 mg while an amount of 5.2 mg are obtained with the $MgCl_2$ solution. Referring to one kilogram soil TNT amounts of 71.3 and 51.6 g/kg, respectively, are calculated. Since the soil samples were exchanged several times, higher theoretical TNT amounts than originally being present in one kilogram of the WS-1 soil fraction are possible. Under the experimental conditions applied, the difference between $FeCl_3$ and $MgCl_2$ solutions adds up to 20 g/kg, which is about half the TNT amount in WS-1 soil fraction.

The experiments were performed under static conditions, i.e. the soil samples were exchanged after 24 hours. As shown in Figure 23 desorption equilibrium is achieved within about 6 hours. A faster NAC desorption can presumably be achieved when either shorter equilibration times (e.g. 6 hours) are used for the desorption experiments or even dynamic conditions, such as column experiments are applied.

Altogether, the findings indicate that NAC desorption depend on several factors like:

- structure and chemical properties of the NACs,
- NACs concentration in the contaminated soils,
- soil properties, such as TOC, CEC, and clay minerals,
- the cation(s) present in the soil (respective desorption) solution.

With respect to the large number of possible interactions, a more systematic approach would be desirable, i.e. variation of only one parameter which may affect desorption behavior, such as the clay mineral fraction or cation exchange capacity. However, this is not possible with the restriction to use only soils, aged under natural conditions. On the other hand, usage of naturally aged soils is advantageous, since NAC binding properties may change over time, due to diffusion or migration processes into soil particles. Hence, investigations with soils contaminated in the laboratory may lead to altered sorption processes. One example is the prolonged desorption time of TNT and NB from the WS-1 soil fraction until equilibrium is achieved compared to the findings of Haderlein et al. [8, 9]. Therefore, investigation of naturally aged soils may be more reliable and representative for real field conditions.

Due to the limited number of soils available, only preliminary conclusions can be drawn from the findings presented in this report. Since adsorption and desorption belong to the key processes determining the distribution and fate of NACs in the environment, additional investigations may be performed to elucidate sorption processes and to verify the findings. Work schedule proposed for future studies may include:

- Depending on the soil properties the cation present in the desorption solution may affect TNT and NB desorption. The findings can be verified using soils with a broader range of soil properties (such as TOC, CEC, clay minerals), and / or soils with different NAC contamination patterns.
- The results of RDX and HMX are based on two soils (IAAP and Crane) with relatively low cation exchange capacity of 8 to 11 meq/100 g. Soils with a wider range of soil properties, especially with a higher cation exchange capacity should be used to investigate if there is an influence of cations on the RDX and HMX desorption behavior.
- Explosives contamination can be found in three forms: bound to the soil matrix, as micro-crystals, and as particulates in the soil. It is very likely that cations can affect desorption only on the NACs bonded to soil particles. The fraction of bonded to non-bonded NACs may facilitate interpretation of the results
- Soil specific properties such as soil texture, classification of the soils, content and structure of clay minerals should be determined from the soils used for the desorption experiments. This may help to explain the underlying desorption processes. Depending on the soil properties, soil fractions (such as disaggregated clay fractions, soil organic matter) can be used for additional desorption experiments.
- Dynamic experiments (like column tests) can be performed in addition to static experiments. Column tests simulates more realistic site conditions. The solution trickles through a column filled with the contaminated soil.
- The cation affects desorption behavior of NACs (TNT and NB). This may also cause altered binding properties of NACs on soils. The question raises if altered NACs binding properties in soils may have implications on analytical methods used to measure NAC concentrations in soils.

The results of such studies may affect remediation strategies and techniques of contaminated sites. However, the findings may be used not only for remobilization and remediation strategies but also for fixating strategies to reduce mobility of NACs in soils in order to protect contaminant free groundwater sources and soils.

5 Summary

Nitroaromatic compounds (NACs) are widely used energetic chemicals. Especially at many military facilities and former ammunition plants the contamination of soil and water with explosives and related NACs has been recognized as a serious environmental problem. Until today, there are no available technologies that can effectively remediate the wide range of type, and concentration of NACs.

In former investigations two contaminated soils were pretreated under alkaline conditions using $Ca(OH)_2$ as base, in order to examine alkaline hydrolysis of NACs as a new remediation technology. However, instead of the expected decrease, a temporary or even permanent increase was observed for several NACs. The NACs increase was affected by $Ca(OH)_2$ concentration, suggesting the existence of desorption processes in the soil.

Adsorption is frequently associated with soil organic matter. In addition, adsorption can also be most closely correlated with extractable iron, cation exchange capacity, and clay percentage. Other investigators demonstrated a specific adsorption of NACs to clay minerals which strongly depends on the cation composition in the soil solution.

At high pH values desorption is superimposed by NAC hydrolysis. In contrast, only desorption processes take place at lower pH values. The main objective of the present study is to investiagte the effect of different cations on the desorption behavior of NACs at pH values at which alkaline hydrolysis does not occur. Since increasing ageing of soils is frequently accompanied by decreasing extractability of organic compounds, NACs contaminated soils naturally aged over a long period of time are used for the investigations instead of soils artificially contaminated in the laboratory.

Deionized water and 0.1 and 0.5 molar solutions of KCl, $MgCl_2$, $CaCl_2$, $FeCl_3$, and $AlCl_3$ were used as desorption solutions. The soils CE-11, Crane, IAAP, and WS-1 WS-2, and WS-3 were investigated. The pH of all soils are close to neutral values. The soils show similar total organic carbon contents ranging from 0.89 to 1.55 %, except soil Crane with a higher content of 14.1 %. The cation exchange capacity of the WS soil fractions are about three times higher compared to the soils CE-11, Crane, and IAAP. Dominant contaminants in the Crane and IAAP soils are RDX and HMX, while the CE-11 contains TNT as dominant contaminant. Soil WS is highly contaminated with TNT and also contains NB in lower concentrations.

Different amounts of RDX are desorbed of the IAAP and CE-11 soil samples, due to the different concentrations in the untreated soil samples. No significant variation in the desorbed amounts are observed between the different salt solutions. On the other hand, larger differences in the total HMX amounts are found in the IAAP soils samples used for the different salt solutions. Compared to deionized water, decreasing amounts are found for the monovalent cation (K^+), the bivalent cations (Mg^{2+}, Ca^{2+}), and the trivalent cation (Fe^{3+}) in that order. Al^{3+} shows a similar low amount as Mg^{2+}. Subsamples of the IAAP soils may be taken accidentally in the way that the samples contained decreasing HMX amounts in the order: deionized water, K^{+}, Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+}. Nevertheless, it is also possible that the differently charged ions with their different surface charges affect desorption behavior of HMX of the IAAP soil.

The findings presented in this study indicate that desorption of a specific NAC may be affected not only by the soil properties but also by the cation present in the soil (respective desorption) solution. This holds true particularly for the nitroaromatic compounds TNT and NB.

The liquid-to-solid ratio significantly affects TNT desorption. Increasing the ratio from 200:1 to 1000:1 leads to an increase in desorption. NB desorption is less affected by the liquid-to-solid ratio due to its relatively low concentration in the WS soil fractions.

A typical TNT desorption pattern is repeatedly measured for the WS soil fractions and the different salt solutions during the first day. Independent from the experimental conditions, the TNT amounts desorbed by the different salt solution vary more widely than the amounts of identical solutions. This allows to order the salt solutions according to the desorbed TNT amounts: the highest amounts are desorbed by the $FeCl_3$ solution, followed by $AlCl_3$, deionized water, $CaCl_2$, and KCl, while $MgCl_2$ contained the lowest amounts. This order of TNT desorption can be observed for all experiments performed with the WS-1, WS-2, and WS-3 soil fractions, the different liquid-to-solid ratios (200:1 and 1000:1), and the 0.1 and 0.5 molar salt solutions.

A similar effect is observed for NB. However, compared to TNT a different desoption order can be established for the different salts. Highest amounts are obtained with $MgCl_2$ and deionized water, followed by KCl and $CaCl_2$, while the lowest amounts are desorbed with $FeCl_3$ and $AlCl_3$. This is just the opposite order especially for $MgCl_3$, $FeCl_3$ and $AlCl_3$.

The repeating TNT and NB patterns strongly indicate that the cation present in the desorption solution affect both the absolute amount of NACs measured in the soil sample and the NACs desorption behavior of the WS soil samples. Furthermore, the findings also show that the differences in desorption behavior of TNT and NB also depends on the structure of the compounds itself the type of substituent, since the corresponding results are obtained from the same set of desorption experiments.

Altogether, the findings indicate that NAC desorption depend on the structure and chemical properties of the NACs, concentration of NACs in the contaminated soils, soil properties, and the cation(s) present in the soil (respective desorption) solution.

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