

Trace metal stabilisation in a shooting range soil: Mobility and phytotoxicity

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Abstract

Due to impact and abrasion of projectiles firing berms of shooting ranges frequently exhibit increased levels of bullet-borne contaminants. Stabilisation of backstop soils may be a promising pre- and post-use treatment to minimise leaching and bioavailability. This study focused on mobility and phytotoxicity of antimony, copper, and lead in stabilised berm material compared to an untreated control. Ferric (goethite, deferrisation sludge) and phosphatic amendments (diammonium phosphate, calcium dihydrogen phosphate) were used. Batch and column experiments demonstrated effective stabilisation of the contaminants by ferric amendments. Sequential extractions showed an increase of contaminant fractions associated with iron (hydr)oxides. Stabilisation was accompanied by a detoxification of seepage water compared to the control soil as shown by Duckweed growth inhibition. Contrasting the ferric additives, phosphatic amendments effectively stabilised lead but mobilised copper and antimony possibly due to a competitive displacement process. Thereby, benefits of lead stabilisation were completely overridden; this was underlined by increased phytotoxicity relative to the untreated soil. Overall, understanding stabilised soil as a multicomponent system is a prerequisite for the choice of appropriate amendments. This requires the synopsis of results from complementary test methods and a screening for a wide range of substances. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Contamination of shooting range soils by the impact of bullets has been of increasing concern, recently. Depending on firing activities, considerable amounts of inorganic contaminants accumulate in shooting range soils and backstop materials. Due to the alloys used for bullets and jacket housings lead, antimony, arsenic, bismuth, silver, copper, and nickel may be present [1,2]. The annual amount of lead discharged by ammunition at civil and military shooting ranges varies from a few hundred to several thousand tons in Europe [1–4]. Annual antimony input into Swiss rifle shooting ranges is estimated to be between 10 and 25 tons [1]. As a result of bullet abrasion following impact of the projectile and weathering [5], heavily contaminated soils have been found at shooting ranges. This may imply a significant risk of groundwater pollution at these sites and poses a challenge to innovative soil treatment technologies. The primary pathway of lead mobilisation in shooting range soils appears to be dissolution and oxida-

tion of metallic lead to form lead carbonates, hydrocarbonates and/or sulphates. Solubility products of $\log K_{sp} = -12.80$ (cerussite: $PbCO_3$) and -7.79 (anglesite: $PbSO_4$), respectively, have been reported [6,7]. Iron (hydr)oxides have been identified as important sorbents for antimony in soils. In addition, secondary mineral phases like $Ca(Sb(OH)_6)_2$ or $Pb(Sb(OH)_6)_2$ with solubility products ($\log K_{sp}$) of -12.55 and -11.02 , respectively, may control antimony mobility [1]. However, in spite of their low solubility secondary minerals and sorbents may be susceptible to changes of the soil environment, such as pH decreases, dissolved organic matter increases, etc.

Stabilisation to enhance retention within the soil could be a promising pre- and post-use risk abatement strategy for bullet-derived contaminants in firing berms. Stabilisation of inorganic contaminants in soils is based on the modification of pollutant characteristics (e.g. speciation, valence) and soil properties (sorption capacity, buffering potential, etc.) by means of additives [8]. These amendments induce or enhance physico-chemical and/or microbial processes, which render pollutants less mobile and less bioavailable. Due to specific interactions with the constituents of the solid phase, cationic and anionic contaminants require different additives.

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Cation exchange capacity may be increased by addition of synthetic or natural clay minerals and iron oxides [9–11]. An alternative approach involves the addition of soluble salts, which provide anions to react with cationic contaminants forming leaching resistant minerals. A typical example is the addition of phosphate using commercially available phosphate fertilisers to stabilise heavy metals by precipitation of minerals with low solubility like chloropyromorphite [12] and thereby minimise both plant uptake and leaching [13].

Anion sorption capacity in soils of the temperate zone is primarily controlled by iron(III)- and aluminium(III)-(hydr)oxides like ferrihydrite, goethite, gibbsite, etc. Oxyanions like arsenate, chromate, molybdate, etc. as well as cations like cadmium, copper, lead, and zinc are sorbed specifically by these media [14–17]. The resulting inner sphere complexes are resistant to competing anions/cations at typical levels in soil solutions. In addition, sorption may be accompanied by redox processes [18] leading to less toxic contaminant species.

Following the reduction of mobility also bioavailability can be expected to be reduced in stabilised soils. Beneficial effects to plant growth [19] as well as minimised contaminant concentrations in the plant tissue [20] have been reported.

Due to the manifold interactions imposed by the addition of soil amendments, an array of tests is needed to evaluate the advantages and possible drawbacks of stabilisation strategies. This study focuses on the stabilisation of bullet-borne metals in the backstop soil of a shooting range using ferric and phosphatic amendments. Comparative batch experiments, column leaching tests, sequential extractions, and plant growth inhibition assays were performed to assess the suitability of additives and to provide a deeper understanding of (i) the processes involved in contaminant stabilisation, (ii) the impact on soil hydraulic properties, and (iii) possible antagonistic effects of soil/additive interaction.

2. Materials and methods

2.1. Soil and additives

The backstop material with a fine sandy texture originated from a German Army shooting range. It was provided from a soil cleansing plant in Southern Germany (AzBiburg, Biburg, Germany). Prior to use, the soil was air-dried at 293 K, manually mixed, and sieved to a grain size of 2 mm. The oversized grain was discarded. Total (aqua regia-extractable [21]) and mobile (water-extractable [22]) contaminant con-

centrations are given in Table 1 together with selected soil properties.

The additives were drinking water deferrisation sludge (DFS), goethite, diammonium phosphate {DAP: $(\text{NH}_4)_2\text{HPO}_4$ }, and calcium phosphate monobasic {CPM: $\text{Ca}(\text{H}_2\text{PO}_4)_2$ }. The DFS was sampled at the waterworks of Donauwörth, Bavaria, Germany. Groundwater of this region is treated in oxygenated trickle bed reactors to remove excess concentrations of ferrous iron by precipitation as hydrous ferric oxide. To recover the precipitate, reactors are intermittently backflushed. This yields a hydrous ferric oxide slurry with a dry matter content of approximately 50 g/kg. From this slurry, 10 L were sampled in a polyethylene container and transferred to the laboratory. After phase separation by sedimentation the supernatant was discarded. The sediment was air dried for 3 weeks at 293 K and ground in an agate mortar. Goethite was obtained as a synthetic pigment (Bayferrox[®] 920 Z) from Lanxess GmbH, Leverkusen, Germany. Both, DAP and CPM, are commercially available phosphate sources. To minimise secondary contaminations analytical grade qualities were used (Merck, Darmstadt, Germany, and Sigma-Aldrich, Buchs, Switzerland, respectively) instead of technical formulations.

Purity of the additives was confirmed by single batch extractions with a deionised water to amendment ratio of 10 (w/w) according to DIN 38414 S4 guideline [22]. After end-over-end shaking at 298 K for 1 day the DAP had completely dissolved, whereas the CPM, goethite and DFS phases were separated from the supernatant by sedimentation/centrifugation (13000 g, 600 s). Followed by membrane filtration using 0.45 μm cellulose nitrate filters (Sartorius AG, Göttingen, Germany) the aqueous phases were acidified with 1 mL nitric acid (65%, w/w) per 100 mL sample volume and stored at 277 K until analysis.

2.2. Batch experiments

To give insight into water-soluble contaminant levels, to study basic geochemical effects of amendment addition, and to investigate the required treatment levels, single batch tests were conducted as described in Section 2.1. Goethite and DFS were used at a dosage of 20, 50, and 80 g/kg soil. Due to their solubility, DAP and CPM were expected to have a strong impact on geochemical conditions. Therefore, lower amounts corresponding to 5, 10, and 20 g/kg soil were tested. The soil amendments were added to aliquots of the soil and thoroughly mixed with a spatula. Batch experiments were done with 50 g of treated/untreated soil and 500 mL of deionised water.

Table 1
Contaminant levels and physico-chemical properties of the shooting range soil

Element	Unit	Contaminant level		Soil properties		
		Total	Water-extractable			
Copper	mg/kg	817	8.6	pH ($\text{H}_2\text{O}/\text{CaCl}_2$)	–	8.0/7.0
Lead	mg/kg	16760	74.2	Electric conductivity (EC)	mS/m	10
Antimony	mg/kg	437	17.4	Acid neutralising capacity ($\text{ANC}_{\text{pH}4}$)	mmol/kg	68

2.3. Column experiments

Column experiments were performed as parallel leaching tests under unsaturated flow conditions using a commercial computer-controlled soil column system (IPM-ISC-01, EMC GmbH, Erfurt, Germany). The main focus of the experiments was a process-oriented comparison of mobilisation and stabilisation processes in amended and unamended soils.

Based on the results of batch tests amendments with 50 g/kg DFS and a mixture of 20 g/kg DAP and 10 g/kg CPM were compared to an untreated soil column. Soil treatment corresponded to the procedure of the batch experiments. The amended/control soils were poured into cylindrical PMMA tubes using a short-stem funnel and manually compacted with a plunger. Table 2 shows experimental conditions and physical properties.

Feed and effluent solutions were delivered with a peristaltic pump. Tygon tubes were used to attach the pump to the sprinkling unit equipped with 28 hypodermic needles (inner diameter 0.25 mm) and to a flow through cell at the column outlet, respectively (cf. Fig. 1). To assure homogeneous irrigation, the void volume of the sprinkling unit and the needles were filled with degassed water prior to installation.

Fig. 2 illustrates the experimental sequence. Before starting the irrigation the fixed beds were saturated from bottom to top using degassed tap water to produce defined initial conditions and improve availability of the additives to the contaminants. To study kinetics of stabilisation, intermittent periods of irrigation and flow interruption were performed.

Overall, a cumulative irrigation volume of 22 L corresponding to an infiltration of 3459 mm was applied to each soil column. This is equivalent to a real-time period of approximately 5 years assuming 700 mm annual precipitation [23]. Possible changes in soil hydraulic properties induced by the treatment were characterised at the end of the experiments by monitoring the breakthrough of an inert tracer step-injection (bromide added as 0.01 M potassium bromide). Solutions of the convection–dispersion equation (linear equilibrium model) were fitted to the breakthrough curves with the numerical code CXTFIT [24], using the retardation factor and the dispersion coefficient as variables.

Effluent concentrations were plotted against the number of pore volumes exchanged (PV, a dimensionless time). For each of

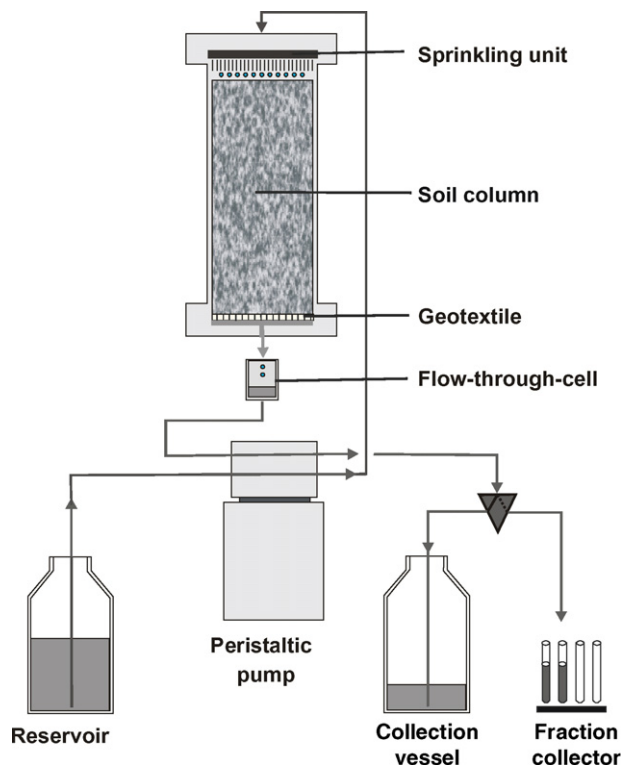


Fig. 1. Scheme of the soil column system.

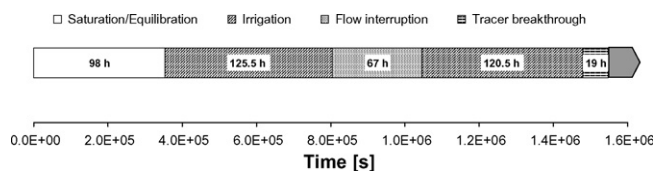


Fig. 2. Sequence of experimental steps.

the effluent fractions PV was calculated as the ratio of cumulative volume leached and resident water volume of the corresponding column. Thus, differences in PV among soil columns reflect the differences in water contents. The higher water holding capacity of DFS treated soil compared to the control is consistent with the introduction of clay-sized iron oxides [10].

Table 2
Column properties and experimental conditions

Parameter	Unit	Control	DFS-treatment	DAP/CPM-treatment
Dry mass of soil	g	2505	2393	2439
Amendment level	g/kg soil	–	50	20 + 10
Height of packed bed	m	0.260	0.261	0.260
Cross-sectional area	$\times 10^{-3} \text{ m}^2$	6.36	6.36	6.36
Bulk density	$\times 10^3 \text{ kg/m}^3$	1.51	1.44	1.48
Resident water volume ^a	$\times 10^{-6} \text{ m}^3$	482.5	580.3	397.2
Volumetric flow rate	$\times 10^{-9} \text{ m}^3/\text{s}$	25	25	25
Darcy velocity	$\times 10^{-6} \text{ m/s}$	4	4	4
Pore water velocity	$\times 10^{-6} \text{ m/s}$	15	11.6	15
Pore water residence time	s	18966	22812	15612

^a Determined after experiment.

Table 3
Extractants used for binding form analysis after [25]

Fraction	Extractant
Mobile	1 M NH ₄ NO ₃
Exchangeable	1 M NH ₄ OAc
Mn-oxides	0.1 M NH ₂ OH-HCl + 1 M NH ₄ OAc
Organic matter	0.025 M NH ₄ EDTA
Fe-oxides (I) ^a	0.2 M NH ₄ -oxalate
Fe-oxides (II) ^b	0.1 M ascorbic acid + 0.2 M NH ₄ -oxalate
Residual ^c	14.9 M HNO ₃ + 9.5 M HCl

^a Amorphous fraction.

^b Crystalline fraction.

^c According to DIN 38414 S7 [21].

2.4. Binding form analysis

To identify major contaminant pools, after column experiments sequential extractions were carried out with the control and the treated soils according to Zeien [25]. This involved the stepwise digestion by reagents of increasing reactivity (cf. Table 3) to release contaminants from operationally defined solid phase constituents. The consecutive leaching was carried out with sample residuals from previous steps. Duplicate extractions were performed employing 2 g of soil. For quality control, blanks were run with each extractant and a certified reference material (RTH 907, Dutch soil, LGC Promochem, Teddington, UK) was included with the final extraction step.

2.5. Duckweed (*Lemna minor*) growth rate inhibition test

To evaluate the impact of soil treatment on biota, Duckweed (*Lemna minor*) growth inhibition tests [26] were conducted. In contrast to chemical analysis, bioassays provide integral information on interactions between the test organism and its environment. Duckweed is a monocotyledonous, free-floating higher aquatic plant whose foliar (frond) area and chlorophyll content show high sensitivity towards aqueous toxicants [27,28].

Briefly, the test evaluates the dose-response curve of a test medium by the dilution levels at which a certain growth rate inhibition relative to a control is observed (effect concentration). The lower the concentration for a selected degree of growth rate inhibition, the higher the toxic effect of the medium on the test organism is.

As a test medium effluent samples of the column experiments (cumulative leachate of the first six pore volumes exchanged) were used. The optimum effective range of the samples was determined in a previous screening. Dilution series of the test medium were then prepared as follows: test sample volumes between 0.4 and 25 mL were added to 10 mL of a modified Steinberg nutrient solution and made up to 100 mL with deionised water. For each test medium five different dilution levels with three replicates each were done together with six replications of a control. Solutions were transferred into glass beakers and three Duckweed colonies with four fronds each were added. Test assemblies were kept under static conditions at controlled illumination (400–700 nm at 2000 lx, approximately) for seven

days. The evolution of lemna populations (frond number and area) in the test solutions was evaluated by digital image analysis (Lemnatec, Würselen, Germany).

According to ISO guideline [26], the effect concentrations for 10–60% growth rate inhibition were calculated with the Lemnatec BioStat statistics program using probit analysis.

2.6. Sample preparation and analytical methods

Contaminant concentrations in the solid phase were determined by digestion (boiling time 2 h) of a 3 g aliquot of dry soil using nitric acid/hydrochloric acid at a ratio of 1:3 following the DIN DEV S7 guideline [21]. A block system (Gerhardt SMA 2000, Königswinter, Germany) connected to a recirculating cooler and a scrubber unit were employed. Quality control comprised digestion of blanks and the above-named reference material. Effluent samples from the column experiments were treated in the same manner as the batch extracts including membrane filtration and stabilisation. No additional digestion was performed prior to analysis.

Metals and metalloids in aqueous samples and aqua regia digests were analysed by ICP-MS (ELAN 6000, Perkin-Elmer Sciex, Ontario, Canada). Specific surface area of ferric amendments and soil samples was measured by nitrogen adsorption (BET method [29]) using an ASAP 2000 station (Micromeritics, Mönchengladbach, Germany). Phosphate was determined in non-acidified aliquots of the aqueous samples by anion chromatography using a 733 Metrohm IC Separation Centre (Herisau, Switzerland). Using a carbonate/hydrogen carbonate eluent, phosphate retention time was 10.6 min and free of interference with other anions. Dissolved organic carbon determination in leachates was done by high temperature catalytic oxidation followed by infrared spectrometry of the evolved carbon dioxide. To analyse the acid neutralising capacity down to pH 4 (ANC₄) a continuously stirred suspension (soil–water ratio 1:10) was titrated with 0.1 mol/L hydrochloric acid using a 686 Metrohm Titroprocessor. The pH of soils (water/calcium chloride extracts) and eluates was determined by a combination electrode. Electrical conductivity (EC) was measured with a graphite conductivity cell. Bromide in the effluent of the tracer breakthrough experiment was monitored using an ion selective electrode. To assure a constant background an ionic strength adjustor (0.3 mL 5 M NH₄NO₃) was added to each sample [30].

3. Results and discussion

3.1. Batch experiments

Treating the soil with iron (hydr)oxides caused a pronounced reduction of copper, lead, and antimony release compared to the control soil (see Fig. 3). On average, concentrations were reduced by 95%, 97% and 77%, respectively.

Stabilisation may be the result of specific sorption (ligand exchange) mechanisms. The higher efficacy of DFS compared to goethite agrees with its higher specific surface area (DFS: 262.9 m²/g, goethite: 23.5 m²/g) and lower crystallinity. This is supported by the fact that increased goethite amendment

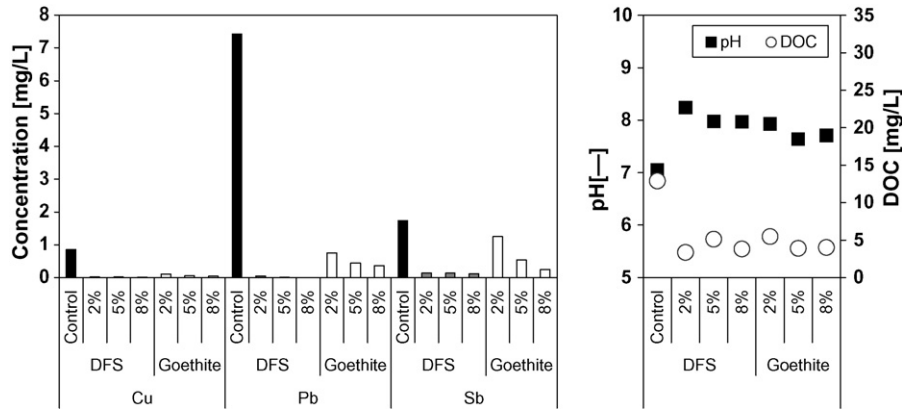


Fig. 3. Contaminant (left) and DOC concentrations/pH-values (right) in batch extracts of control and iron (hydr)oxide-amended soil. DFS: deferrisation sludge.

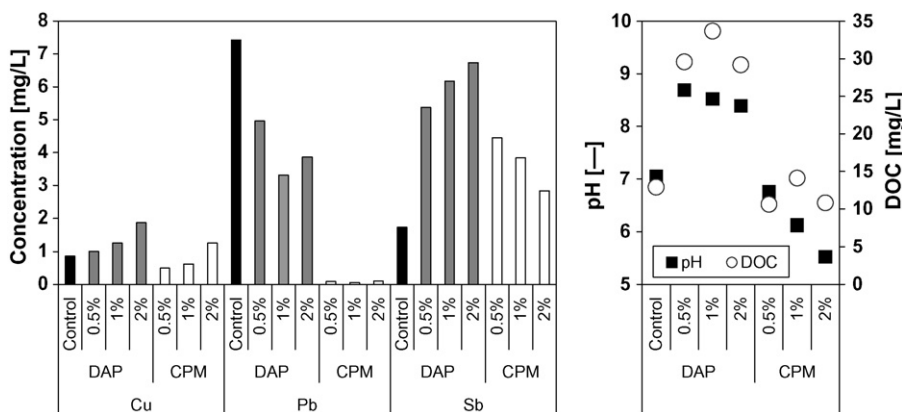


Fig. 4. Contaminant (left) and DOC concentrations/pH-values (right) in batch extracts of control and phosphate-amended soil. DAP: diammonium phosphate; CPM: calcium phosphate monobasic.

levels yielded lower aqueous contaminant concentrations. An indirect stabilisation mechanism related to dissolved organic carbon (DOC) may be operative, too. In DFS and goethite batches DOC concentrations were reduced relative to the control. This is consistent with ligand exchange reactions of carboxylic and phenolic functional groups of DOC for OH^- of the iron (hydr)oxide surface [31]. As DOC is known to complex cationic trace metals and enhance their mobility [11], lowered DOC concentrations may indirectly contribute to the stabilisation of contaminants by DFS and goethite.

The effects of phosphatic amendments on bullet-borne metals are shown in Fig. 4. Average lead concentrations were reduced by 45% (DAP) and 99% (CPM).

Lead stabilisation may have been due to the formation of sparingly soluble lead phosphate mineral phases such as $\text{Pb}_3(\text{PO}_4)_2$ or $\text{Pb}_4\text{O}(\text{PO}_4)_2$ following dissolution of the phosphate source [32]. As further important lead sequestering minerals of very low solubility lead hydroxypyromorphite ($\log K_{\text{sp}} = -76.8$) and lead chloropyromorphite ($\log K_{\text{sp}} = -84.4$) have been identified in phosphate amended soils [12,13]. The lower stabilisation by DAP compared to CPM is consistent with (i) the limited availability of phosphate in this compound (see below: Eqs. (1)–(3)) and the (ii) concomitant increase of DOC concentrations in the DAP treatment (cf. Fig. 4, right). Release of DOC may also be responsible for constant or even increased copper concentra-

tions relative to the control soil due to formation of DOC-copper complexes [33].

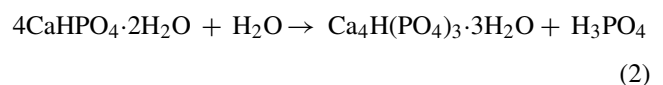
A pronounced mobilisation of antimony was observed in the phosphate amended samples compared to the control. This agrees with a competitive displacement of antimonate by phosphate at the surfaces of pedogenic iron (hydr)oxides similar to the behaviour of arsenic [34]. Extractions with oxalate and dithionite/citrate/bicarbonate indicated the presence of pedogenic iron (hydr)oxides equivalent to 10 g Fe/(kg soil) providing a relevant sorbent pool. The different levels of antimony release are in accordance with Johnson et al. [1], who observed a strong increase in aqueous antimony concentrations at pH-values above eight.

The pH-values of the DAP- and CPM-amended samples differ due to individual dissolution reactions. A fast and a slow reaction characterises the two-stage dissolution of CPM-phosphate [35]:

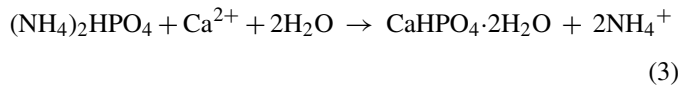
Fast reaction:



Slow reaction:



In turn, DAP in the presence of Ca^{2+} forms sparingly soluble calcium hydrogen phosphate (Eq. (3)), which further reacts according to Eq. (2)



Thus, the release of phosphoric acid by CPM is considerably higher resulting in lower pH-values due to the limited acid neutralising capacity of the soil. The pH dependence of antimony release may thus explain the different antimony concentrations observed in the DAP and CPM treatments.

To evaluate the additive-specific stabilisation efficiency, observed aqueous phase concentrations may be compared to standard leaching limits. Given the fact that the material was provided by a soil cleansing plant, the copper and lead values defined for different disposal routes of mineral wastes in Germany were considered [36]; no direct comparison was possible for antimony, since no leaching limits for this particular element are given. Disregard the dosage both ferric amendments yielded aqueous phase concentrations for copper and lead that may allow a reutilisation of the backstop material at least under favourable hydrogeological conditions. Conversely, both phosphatic amendments failed to meet the copper leaching limits for material reutilisation. This holds for lead in the DAP treatment, whereas lead leachate concentrations in the CPM-amended batches were below the limits that apply to a reutilisation when additional technical safety measures are provided.

3.2. Column experiments

Following 98 h of equilibration under saturated conditions the columns were drained and irrigation was started. The columns were leached with degassed tap water under free drainage conditions. The second irrigation period following 67 h of flow interruption was characterised by a continuity of effluent concentrations. The non-existence of residence time effects indicates that equilibrium effluent concentrations were observed. To highlight the dynamics of leaching, the following elution curves are presented for the first irrigation period.

3.2.1. Hydrochemical parameters

For all columns, effluent pH-values were similar and ranged from 6.4 to 8.4 without a clear temporal trend (compare Fig. 5); the electric conductivity (EC) showed high initial values and decreased exponentially to a constant level of about 40 mS/m by exchange of five pore volumes.

This characteristic points the release of charged mobile constituents into the aqueous phase during column equilibration. Lowest initial EC values were observed in the DFS treated soil owing to the increased sorption capacity relative to the control system. Highest values of up to 8.5 S/m were observed in the phosphate amended soil column due to the solubility of the DAP/CPM additive. This was confirmed by high initial phosphate concentrations of more than 60 g/L and DOC levels of up to 1.6 g/L (Fig. 6).

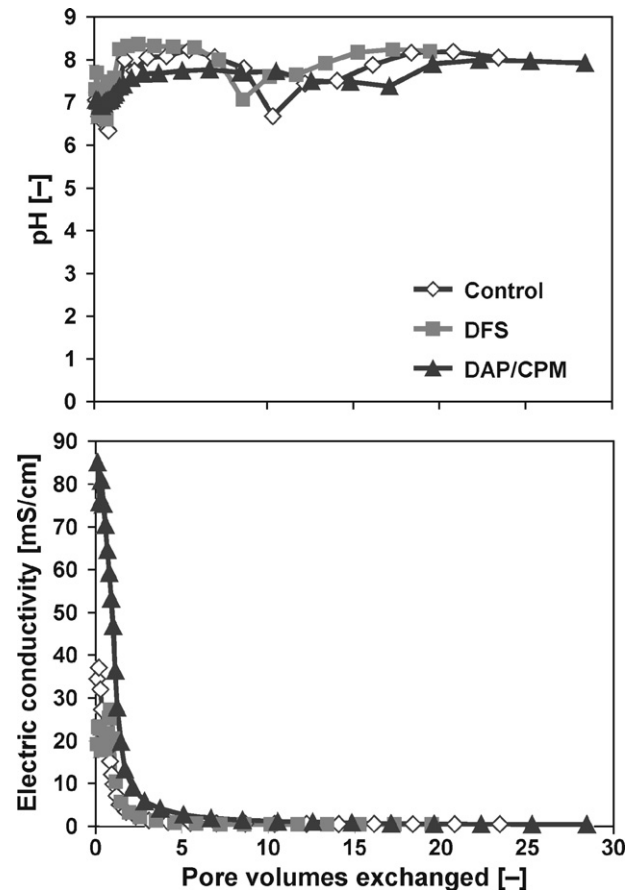


Fig. 5. pH-values and electric conductivity in the effluent of the control and treated soil columns. DFS: deferrisation sludge; DAP: diammonium phosphate; CPM: calcium phosphate monobasic.

Altogether, the cumulative phosphate load equals 82% of the mass added as DAP/CPM. Synchronous release of DOC from the DAP/CPM-amended soil corroborates findings of the batch experiments. The results also agree with observations by Kaiser and Zech [37], who found that DOC release was enhanced in the presence of competing oxyanions (e.g. SO_4^{2-} , PO_4^{3-}). Unlike the phosphate-amended system and reflecting the electrical conductivity, effluent DOC concentrations of the DFS-amended soil were similar to the control.

3.2.2. Trace metals

As in the batch experiments, the DFS-treated soil columns showed markedly reduced contaminant concentrations compared to the control (cf. Fig. 7) confirming enhanced sorption. Inner sphere complexation by iron (hydr)oxides has been reported for lead and antimony [1,16], whereas copper sorption seems to be partially due to ion exchange [38]. In this study the large specific surface area of DFS (262.9 m^2/g) together with the predominance of ferrihydrite {oxalate-soluble iron (hydr)oxides [39]} over the crystalline (DCB-extractable) fraction [40] favours sorption. Particularly, the permeability of ferrihydrite allows the diffusive access of contaminant ions to binding sites located on inner surfaces [41].

Elution characteristics in the DAP/CPM-treated soil indicated compound-specific stabilisation/mobilisation effects.

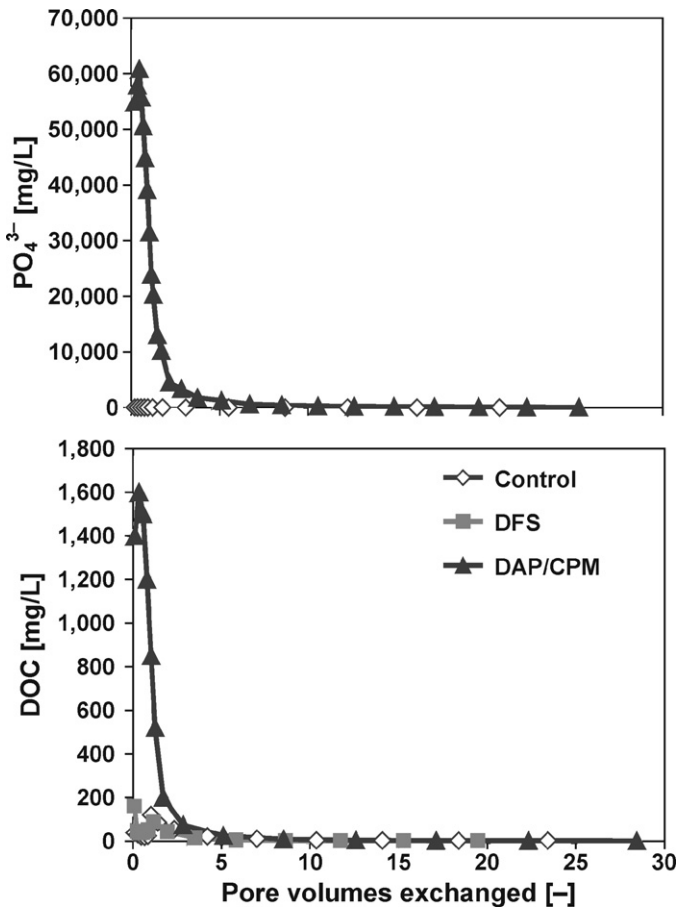


Fig. 6. Phosphate and dissolved organic carbon (DOC) concentrations in the effluent of the control and treated soil columns. DFS: deferrisation sludge; DAP: diammonium phosphate; CPM: calcium phosphate monobasic.

Lead leaching was below the control and characterised by a sharp initial peak of up to $970 \mu\text{g/L}$. By exchange of 18 pore volumes, effluent concentrations dropped below the detection limit of $10 \mu\text{g/L}$. In contrast, the control soil reached a maximum of $3000 \mu\text{g/L}$ and equilibrated at a constant base level of approximately $800 \mu\text{g/L}$. Thus, also under flow conditions the phosphatic additive effectively stabilised lead in the backstop sand. According to Lang and Kaupenjohann [42] DOC is a limiting factor for lead pyromorphite formation in soils. Increasing the DOC concentration lowers the particle size due to hampered crystal growth, which may cause leaching of colloidal lead. Therefore, the high DOC levels observed during leaching of the phosphate-amended soil conflict with low lead concentrations indicating an alternative stabilisation mechanism.

Contrasting the findings for lead in the DAP/CPM-amended soil, effluent copper (Fig. 7, upper panel, right axis) and antimony concentrations were clearly above the control. Regarding copper and antimony behaviour in multicomponent systems individual release mechanisms can be hypothesised. Copper is known to bind stronger to organic matter than any other divalent metal [11]. Consistently, the mobilisation of organic matter as highlighted by the elevated DOC concentrations favours the leaching of mobile copper-DOC complexes. The suggested

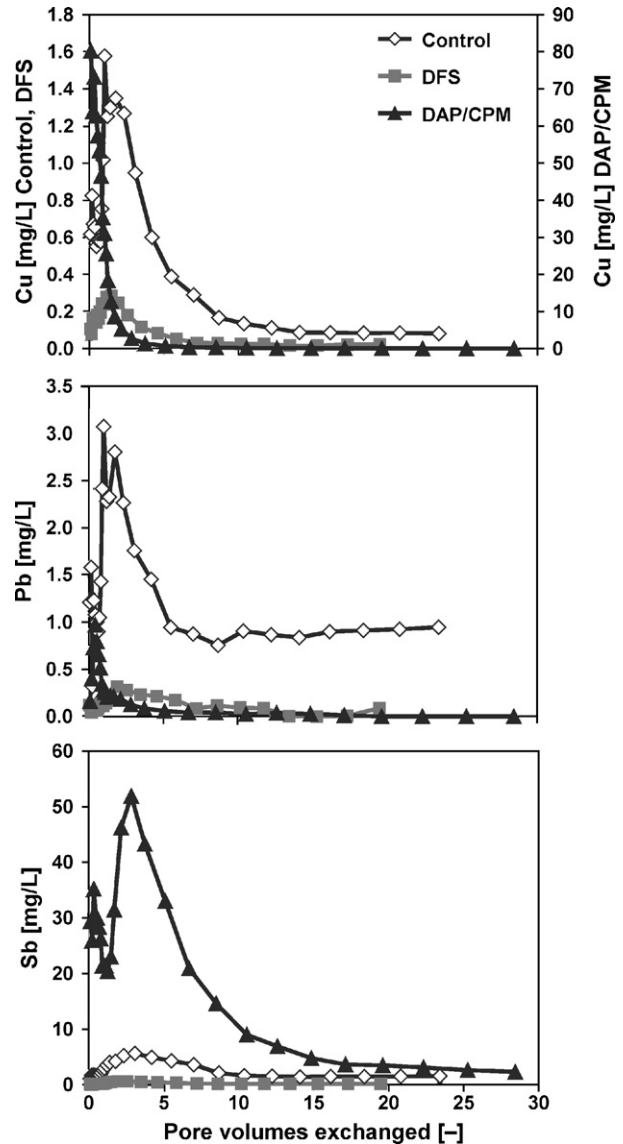


Fig. 7. Copper, lead, and antimony concentrations in the effluent of the control and treated soil columns. DFS: deferrisation sludge; DAP: diammonium phosphate; CPM: calcium phosphate monobasic.

mechanism is supported by the similar shape of the copper and DOC elution curves. Antimony in soil environments predominantly exists in the oxidation states III and V. The corresponding species in soil water are $\text{Sb}(\text{OH})_3$ and $\text{Sb}(\text{OH})_6^-$, both known to undergo inner sphere complexation with iron (hydr)oxides [1]. Thus, a direct competition for sorption sites can be expected in the presence of high phosphate concentrations which may explain antimony mobilisation in the DAP/CPM-amended column. Inspection of the leaching curves shows pronounced differences between phosphate and antimony. While the prior peaked immediately after irrigation started, maximum concentrations of the latter were observed after exchange of five pore volumes. This stronger retardation of antimony suggests that most of the phosphate is readily leached from the soil while the rest competitively displaces antimony from its binding sites.

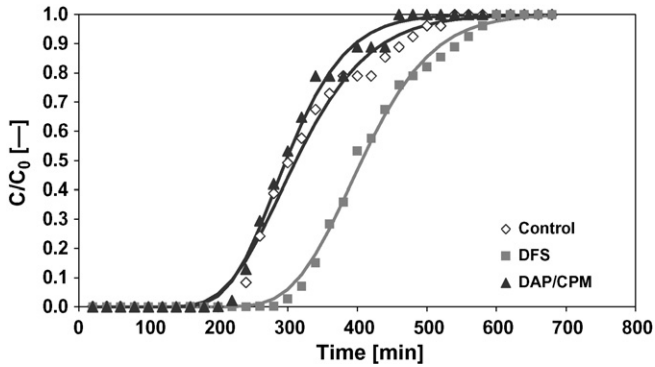


Fig. 8. Measured (symbols) and fitted (lines) tracer breakthrough in the effluent of the control and treated soil columns. DFS: deferrisation sludge; DAP: diammonium phosphate; CPM: calcium phosphate monobasic.

3.2.3. Tracer breakthrough curves

The tracer breakthrough curves, recorded at the end of column leaching experiments (cf. Fig. 8) are sigmoidal and largely symmetric. Shape similarity between soil columns indicates that amendment additions did not affect the dispersion properties of the porous media. This is confirmed by the parameters of the one-dimensional convection-dispersion equation [24] fitted to the measured data.

Longitudinal dispersivities were estimated as 9.2×10^{-3} m (control), 5.0×10^{-3} m (DFS), and 6.6×10^{-3} m (DAP/CPM). The corresponding Péclet numbers (related to column length) of 28, 52, and 39 indicate a convective-dispersive flow-regime with dominance of convection [43]. Tracer breakthrough in the DFS treated soil was clearly delayed (approximately 6000 s) in comparison to the control and the DAP/CPM-amended soils. This relates to the higher water content due to an increase of the clay-sized grain fraction by the addition of iron (hydr)oxides. This observation was supported by the specific surface area of the soils with $2.8 \text{ m}^2/\text{g}$ for the control and $9.8 \text{ m}^2/\text{g}$ for the DFS treatment.

3.2.4. Mass balance

Contaminant stabilisation can be adequately compared by the ratio of cumulative mass eluted (effluent load) from the amended and unamended systems. Thereby, addition of DFS yielded a degree of copper, lead, and antimony stabilisation of 77%, 90%, and 89%, respectively (see Table 4, both irrigation periods considered). Adverse side effects were not observed. DAP/CPM effectively stabilised lead (97% reduction compared to the control) but distinctly enhanced the mobility of copper (87% increase) and especially antimony (261% increase).

Table 4
Contaminant load released from control and treated soil columns (both irrigation periods)

	Effluent load (mg)			Mobilisation (+) or stabilisation (-) (%)	
	Control	DFS	DAP/CPM	DFS	DAP/CPM
Copper	3.9	0.9	30.7	-77	+87
Lead	21.2	2.1	0.6	-90	-97
Antimony	41.6	4.4	150.3	-89	+261

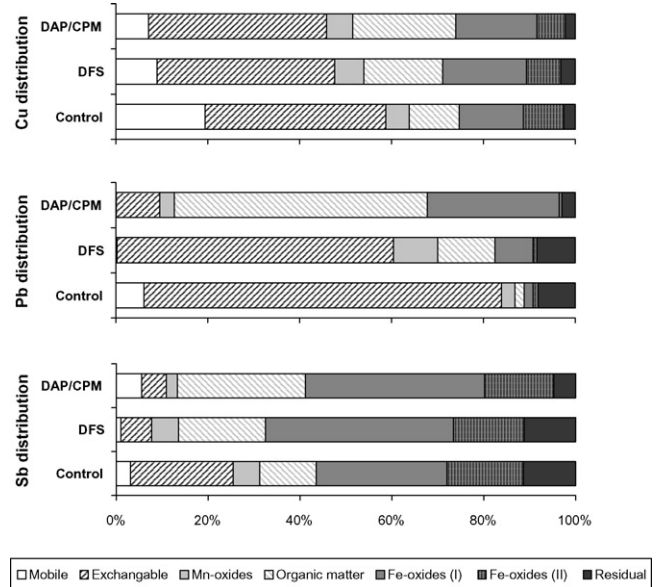


Fig. 9. Contaminant binding forms in the control and amended soils after the column experiment, extractants compare Table 3. DFS: deferrisation sludge; DAP: diammonium phosphate; CPM: calcium phosphate monobasic.

3.3. Binding form analysis

Results of the binding form analyses are shown in Fig. 9. In the DFS treated soil all investigated contaminants decreased in the mobile and exchangeable fractions in favour of the manganese oxides as well as the organic and the amorphous iron oxides fractions.

The latter is consistent with the increase of oxalate-extractable iron (hydr)oxides by 13.2 g/kg and the concomitantly enhanced sorption capacity. The shift towards the organic and manganese oxides fractions is explicable regarding the distribution of iron itself.

Table 5 indicates that the iron content distinctly increased within the organic fraction and to a minor degree within manganese oxides following DFS treatment. This limited selectivity of the extractants confirms previous findings [44]. Thus, the contribution of organic and manganese oxide fractions to the distribution of the contaminants in the DFS treated soil is most likely an artefact of the extraction scheme. Despite these shortcomings, binding form analyses demonstrate that contaminant stabilisation in the DFS-amended soil happened due to a shift towards less mobile and potentially less bioavailable contaminant pools.

In the phosphate-amended soil, lead was shifted from the mobile/exchangeable fractions to organic matter/amorphous iron oxides pools. The formation of lead phosphate minerals could not be proved since these are not targeted by the extractants employed. For copper and antimony an increase in the organic/amorphous iron fractions is suggested by the results. This conflicts to some extent with the observed leaching behaviour. Mass balances showed that 1.8% and 16.4% of the initial copper and antimony contents were leached from the DAP/CPM treated column compared to 0.2% (copper) and 4.0% (antimony) in the control column. Therefore, it can be hypoth-

Table 5
Binding forms [25] of iron in the control and DFS treated soils (after experiments)

	Iron concentration (mg/kg)						
	Mobile	Exchangable	Manganese oxides	Organic matter	Ferric oxides (I) ^a	Ferric oxides (II) ^b	Residual
Control	30	15	75	217	2807	4147	5125
5% DFS	95	147	417	3740	15975	4320	5241

^a Amorphous fraction.

^b Crystalline fraction.

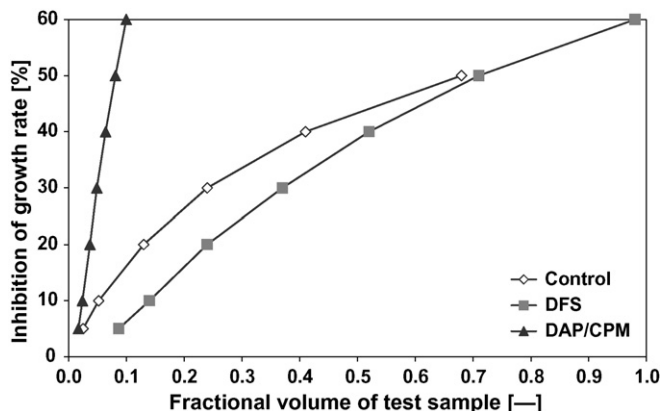


Fig. 10. Effect concentrations from 5% to 60% Duckweed (*Lemna minor*) growth rate inhibition of control and treated soil effluents. DFS: deferrisation sludge; DAP: diammonium phosphate; CPM: calcium phosphate monobasic.

esised that co-transport and competitive sorption may not only cause the mobilisation of contaminants but also affect their redistribution among different constituents of the solid phase.

3.4. Phytotoxicity testing

Duckweed growth rate as calculated from the frond area showed a pronounced inhibition by the DAP/CPM treatment in comparison to the effluent of the control soil (see Fig. 10). Against that, Duckweed growth was slightly enhanced by amending the soil with DFS. Therefore, the results of the growth inhibition test agree with the findings of batch and column experiments.

Although phosphate concentrations were clearly increased in the DFS/CPM soil, phytotoxicity by enhanced copper and antimony mobility was not overridden by the improved nutrient supply. This makes the Duckweed growth inhibition test a suitable tool for additional investigations with respect to biocompatibility of stabilisation techniques.

4. Conclusions

Both, batch and column experiments showed effective stabilisation of target contaminants by the use of DFS as a soil amendment. The mechanism is most probably specific sorption favoured by the high surface area and the amorphous structure of the DFS.

Treatments with phosphate effectively stabilised lead. This is assumed to happen by formation sparingly soluble mineral

phases. However, adverse side effects were evident from the enhanced mobility of copper and antimony. Release of antimony is attributed to competitive sorption between the antimonate and phosphate. Copper is supposed to have become mobilised by the release of DOC. In spite of methodological shortcomings regarding specificity, binding form analysis corroborates the formation of less mobile contaminant species in case of successful stabilisation.

The Duckweed growth rate inhibition tests confirm the data obtained by chemical analysis. Owing to a reduction of contaminant mobility, effluents of the DFS treated soil were less toxic. In contrast, side effects of the DAP/CPM treatment increased phytotoxicity compared to the control in spite of successful lead stabilisation.

Understanding multicomponent behaviour of contaminants in stabilised soils requires test arrays and a screening for a wide range of compounds. Crucial factors for the success of a particular stabilisation scheme are, e.g. the impact on pH-values and the release of DOC as well as competitive reactions between the constituents of the system. Thus, to identify suitable additives not only the response of target substances has to be followed but also possible changes imposed on major soil constituents need to be considered. In view of the suggested stabilisation mechanisms future work should also consider the durability of surface complexes and precipitates under changing soil conditions, e.g. acidification, to evaluate long-term stability.

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