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Environmental Science: Nano – Supplementary Information

Revealing the long-term behaviour of nZVI and BC in metal(loid) contaminated soil: focus on Fe transformations

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1. Materials and methods

1.1. Activation procedure for the studied amendments

Before application to soil, the activation of NANOFER STAR was performed as recommended by the manufacturer. NANOFER STAR is an air-stable nZVI product in which the Fe⁰ core is covered by Fe oxides. The aim of activation is to remove the protective Fe oxide layer coating the nanoparticles, which has been reported to make nZVI more efficient for contaminant immobilisation ¹. A suspension of nZVI in demineralised water (ratio 1:4 wt.%) was prepared and thoroughly mixed using a vortex device. The suspension was preserved in a closed reactor at ambient temperature for 48 h and then mixed again and immediately applied to the soil, followed by manual homogenisation of the soil with the activated suspension. The same activation procedure was performed for the pure BC and nZVI-BC composite to maintain consistent conditions.

1.2. Recalculation of concentrations of elements in pore water

The concentrations in the pore water (mg L⁻¹) were recalculated to mg kg⁻¹ using Eq. 1:

 $C = C_{pw} * V/m (1)$

where C is the concentration in mg kg⁻¹ of soil, C_{pw} is the concentration in mg L⁻¹ of pore water, V is the total volume of water in the pot in L, and m is the total dry mass of the solid in the pot (soil + sorbent) in kg.

1.3. Experimental conditions of the full-frame SEM/EDS session

Extensive scanning of the samples after 15 months of incubation and selective mapping were conducted and further treated using AZtec software. Feature analysis was used for large sample mapping. Particle classification was fitted to the BSE figure, and then feature analysis was performed with a constant 50000 counts by EDS at a 25 keV accelerating voltage. The average analysis time was 48 hours per sample. Selected particles of interest were analysed in detail.

1.4. Input details for the geochemical modelling

Analytical data from i) the soil water extractions and ii) the pore water were treated appropriately to prepare an input for the PHREEQC geochemical code (version 3 for Windows)². The necessary parameters that were included in the modelling were pH, Eh (recalculated to pe according to the Nernst equation), concentrations of major and trace elements including both cations and anions to ensure that the ion balance was determined. The content of inorganic carbon was recalculated to the concentration of HCO₃⁻ ions and used in the model input. In addition, dissolved organic carbon (DOC) was included in the calculations in the form of humates and fulvates³ using thermodynamic data from the T&H.dat database. In particular, the DOC was calculated as humate (30%) and fulvate (70%) according to Borůvka and Vácha (2006)⁴, who studied the fractionation of DOC in the soil used in our study.

References

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2. Results and Discussion



Figure S1: Backscattered electron images (BSE) of control soil. The respective EDS spectra (numbered points) can be found in Fig. S6. A) Mn oxides with 4 wt. % Zn and 35 wt. % Pb on the surface of soil particles. B) Fe oxides with up to 10 wt. %, C) up to 5.7 wt. % and D) 7.8 wt. % Zn. E) Soil Fe oxides with no contaminants and Fe oxides with up to 1.6 wt. % Zn and 3.2 wt. % Pb. F) Soil particle covered by Fe-Mn oxides with 4.1 wt. % Zn and 13.2 wt. % Pb.



Figure S2: Sphalerite (ZnS) captured in control soil sample by SEM.



Figure S3: Images of BC-treated soil in BSE mode. The corresponding EDS spectra are indicated by number(s) (Fig. S7). Images G and H are taken from the mixed soil, images E, F and I are from the soil-BC interface. E) Mn oxide (7 wt.% Zn and 16 wt.% Pb) and Fe oxide (7 wt.% Zn). F) Mn oxides with up to 17. 8 wt. % Pb. G) Fe oxides (6.3 wt.% Zn) and Mn-Fe oxides (6.2 wt.% Zn and 15 wt.% Pb). H) Fe-Mn oxides with up to 1.2 wt. % of As. I) Soil particles containing Fe oxides on top of or adjacent to BC particle (up to 3 wt.% Zn and 7.7 wt.% Pb).



Figure S4: SEM images of the nZVI treatment with numbered EDS spectra (Fig. S8). Image F is taken from the sorbent layer, image B from the mixed soil and images H and I are taken from the soil-nZVI interface. F) nZVI particles without contaminants. G) Fe-Mn oxides (2.8 wt.% Zn, 30.5 wt.% Pb and 2.8 wt.% As. H) Fe oxides (1.8 wt.% Zn, 2.9 wt.% Pb and 0.6 wt.% As). I) traces of Zn and Pb (< 1 wt.%) bound to Fe oxides.



Figure S5: SEM images from the nZVI-BC treatment with numbered EDS spectra (Fig. S9). Image F is from the sorbent layer and images H and I are from the soil-nZVI-BC interface. F) nZVI on a BC particle (no contaminants). G) Fe oxides with 19.7 wt.% Zn, 1.8 wt.% Pb and 0.6 wt.% As. H) Fe oxides on the surface of a BC particle (up to 2.6 and 7.3 wt.% Zn and Pb, respectively). I) Traces (<1 wt.%) of Zn and Pb bound on Fe oxide on the surface of BC.



Figure S6: Spectra from the EDS analysis of selected points in control soil samples.



Figure S7: Spectra from the EDS analysis of selected points in BC-treated soil samples.



Figure S7: Spectra from the EDS analysis of selected points in BC-treated soil samples (continuation).



Figure S8: Spectra from the EDS analysis of selected points in nZVI-treated soil samples.



Figure S8: Spectra from the EDS analysis of selected points in nZVI-treated soil samples (continuation).



Figure S9: Spectra from the EDS analysis of selected points in nZVI-BC-treated soil samples.



Figure S9: Spectra from the EDS analysis of selected points in nZVI-BC-treated soil samples (continuation).



Figure S10: Fe distribution on the BC particle of Fig. 4D.

During the analysis of the 15-month incubated samples, the EDS chemical composition of the particles was used to determine the different classes presented in Table S1. According to these classes, ternary diagrams were prepared to examine the relationships between the studied contaminants and metal(loid) scavengers (i.e., Fe/Mn/Al oxides).

Element	Minimum value (wt.%)	Maximum value (wt.%)	Class
Pb	10	100	
Mn	0	10	
Si	0	6	— 1
Zn	0	100	
Fe	20	100	
Si	0	6	2
As	0	100	
Fe	0	100	3
Fe	20	100	
Pb	0	100	— 4
Cd	0	100	5
Sb	0	100	6
Pb	0	100	
Zn	0	100	
Fe	15	100	— 7
	No classification		

Table S1: Description of the established classes used during SEM/EDS analysis to check the combined affinity of risk elements to Fe and Mn mineral phases.



Figure S11: Ternary plots presenting combinations of A) Zn and Fe/ Mn oxides B) Pb and Fe/ Mn oxides and C) As and Fe/Al oxides in the control soil samples.

Figure S12: Ternary plots presenting combinations of A) Zn and Fe/ Mn oxides and B) Pb and Fe/ Mn oxides in the BC-treated soil samples.

Figure S13: Ternary plots presenting combinations of A) Zn and Fe/ Mn oxides and B) Pb and Fe/ Mn oxides in the nZVI-treated soil samples.



oxides in the nZVI-BC-treated soil samples.



Figure S15A: Diffractograms derived from the XRD analysis of the sorbent layer of nZVI after different incubation time



Figure S15B: Diffractograms derived from the XRD analysis of the sorbent layer of nZVI-BC after different incubation time.

Figure S16: Proportional Fe solid speciation based on Fe K-edge XANES spectra for the sorbent layers of A) nZVI and B) nZVI-BC from the different incubation time steps.

Table S2: Values used for the calculation of proportions of the most abundant phases according to XANES. The Fe⁰ oxidation rate of Fig. 7C is calculated from the sum of the Fe (oxyhydr)oxides of each sample.

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sample	R factor	nZVI weight	Lepidocrocite weight	Ferrihydrite weight	Magnetite weight	
nZVI 1 month	0.00034	0.50	0.28	0.17	0.06	
nZVI 3 months	0.00010	0.28	0.27	0.36	0.10	
nZVI 12 months	0.00030	0.50	0.27	0.19	0.06	
nZVI 15 months	0.00006	0.54	0.14	0.26	0.09	
		nZVI-BC	Lepidocrocite	Ferrihydrite	Goethite	Magnetite
	R factor	weight	weight	weight	weight	weight
nZVI-BC 1 month	0.0000665	0.16	0.17	0.51		0.17
nZVI-BC 3 months	0.0001031			0.20	0.55	0.27
nZVI-BC 12 months	0.0001341	0.16	0.30	0.43		0.13
nZVI-BC 15 months	0.0000906	0.65	0.11	0.20		0.06
	54	Montmorillonite	Muscovite	Hematite	Goethite	Magnetite
	R factor	weight	weight	weight	weight	weight
Control soil average	0.00011	0.20	0.14	0.22	0.25	0.18
		Control	nZVI			
	R factor	weight	weight			
nZVI mix 1 month	0.00022	0.91	0.09			
nZVI mix 3 months	0.00111	0.90	0.10			
nZVI mix 12 months	0.00025	0.98	0.02			
nZVI mix 15 months	0.00064	0.96	0.04			
		Control	nZVI-BC			
	R factor	weight	weight			
nZVI-BC mix 1 month	0.00028	0.98	0.02			
nZVI-BC mix 3 months	0.00101	0.92	0.08			
nZVI-BC mix 12 months	0.00010	0.95	0.05			
nZVI-BC mix 15 months	0.00005	0.97	0.03			

Table S3a: Correlation matrices of soil extraction data based on the Pearson coefficient.

1 month	Zn	Pb	рН	Eh	Fe	Mn	DOC		
Zn		0.60	-0.86	0.79	-0.57	-0.96	0.03		
Pb	0.60		-0.12	0.03	0.11	-0.73	0.81		
рН	-0.86	-0.12		-0.99	0.65	0.69	0.42		
Eh	0.79	0.03	-0.99		-0.59	-0.59	-0.47		
Fe	-0.57	0.11	0.65	-0.59		0.55	0.63		
Mn	-0.96	-0.73	0.69	-0.59	0.55		-0.20		
DOC	0.03	0.81	0.42	-0.47	0.63	-0.20			
3 months	Zn	Pb	As	Cd	рН	Eh	Fe	Mn	DOC
Zn		0.36	0.59	0.98	-0.88	0.48	-0.82	-0.73	-0.63
Pb	0.36		0.91	0.19	-0.73	0.53	-0.57	-0.84	0.10
As	0.59	0.91		0.47	-0.80	0.82	-0.54	-0.80	0.11
Cd	0.98	0.19	0.47		-0.78	0.46	-0.72	-0.58	-0.64
рН	-0.88	-0.73	-0.80	-0.78		-0.47	0.93	0.96	0.50
Eh	0.48	0.53	0.82	0.46	-0.47		-0.12	-0.35	0.38
Fe	-0.82	-0.57	-0.54	-0.72	0.93	-0.12		0.92	0.75
Mn	-0.73	-0.84	-0.80	-0.58	0.96	-0.35	0.92		0.44
DOC	-0.63	0.10	0.11	-0.64	0.50	0.38	0.75	0.44	
12 months	Zn	Pb	As	Cd	рН	Eh	Fe	Mn	DOC
12 months Zn	Zn	Pb -0.08	As -0.09	Cd 0.94	pH -0.43	Eh -0.98	Fe -0.13	Mn 0.26	DOC -0.69
12 months Zn Pb	Zn -0.08	Pb -0.08	As -0.09 1.00	Cd 0.94 -0.39	pH -0.43 0.93	Eh -0.98 -0.13	Fe -0.13 0.99	Mn 0.26 -0.79	DOC -0.69 0.20
12 months Zn Pb As	Zn -0.08 -0.09	Pb -0.08 1.00	As -0.09 1.00	Cd 0.94 -0.39 -0.40	рН -0.43 0.93 0.93	Eh -0.98 -0.13 -0.12	Fe -0.13 0.99 1.00	Mn 0.26 -0.79 -0.78	DOC -0.69 0.20 0.19
12 months Zn Pb As Cd	Zn -0.08 -0.09 0.94	Pb -0.08 1.00 -0.39	As -0.09 1.00 -0.40	Cd 0.94 -0.39 -0.40	рН -0.43 0.93 0.93 -0.70	Eh -0.98 -0.13 -0.12 -0.85	Fe -0.13 0.99 1.00 -0.43	Mn 0.26 -0.79 -0.78 0.56	DOC -0.69 0.20 0.19 -0.78
12 months Zn Pb As Cd pH	Zn -0.08 -0.09 0.94 -0.43	Pb -0.08 1.00 -0.39 0.93	As -0.09 1.00 -0.40 0.93	Cd 0.94 -0.39 -0.40 -0.70	рН -0.43 0.93 0.93 -0.70	Eh -0.98 -0.13 -0.12 -0.85 0.23	Fe -0.13 0.99 1.00 -0.43 0.93	Mn 0.26 -0.79 -0.78 0.56 -0.86	DOC -0.69 0.20 0.19 -0.78 0.49
12 months Zn Pb As Cd pH Eh	Zn -0.08 -0.09 0.94 -0.43 -0.98	Pb -0.08 1.00 -0.39 0.93 -0.13	As -0.09 1.00 -0.40 0.93 -0.12	Cd 0.94 -0.39 -0.40 -0.70 -0.85	pH -0.43 0.93 0.93 -0.70 0.23	Eh -0.98 -0.13 -0.12 -0.85 0.23	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06	DOC -0.69 0.20 0.19 -0.78 0.49 0.61
12 months Zn Pb As Cd pH Eh Fe	Zn -0.08 -0.09 0.94 -0.43 -0.98 -0.13	Pb -0.08 1.00 -0.39 0.93 -0.13 0.99	As -0.09 1.00 -0.40 0.93 -0.12 1.00	Cd 0.94 -0.39 -0.40 -0.70 -0.85 -0.43	рН -0.43 0.93 0.93 -0.70 0.23 0.93	Eh -0.98 -0.13 -0.12 -0.85 0.23 -0.07	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06 -0.74	DOC -0.69 0.20 0.19 -0.78 0.49 0.61 0.16
12 months Zn Pb As Cd pH Eh Fe Mn	Zn -0.08 -0.09 0.94 -0.43 -0.98 -0.13 0.26	Pb -0.08 1.00 -0.39 0.93 -0.13 0.99 -0.79	As -0.09 1.00 -0.40 0.93 -0.12 1.00 -0.78	Cd 0.94 -0.39 -0.40 -0.70 -0.85 -0.43 0.56	pH -0.43 0.93 0.93 -0.70 0.23 0.93 -0.86	Eh -0.98 -0.13 -0.12 -0.85 0.23 -0.07 -0.06	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07 -0.74	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06 -0.74	DOC -0.69 0.20 0.19 -0.78 0.49 0.61 0.16 -0.70
12 months Zn Pb As Cd pH Eh Fe Mn DOC	Zn -0.08 -0.09 0.94 -0.43 -0.98 -0.13 0.26 -0.69	Pb -0.08 1.00 -0.39 0.93 -0.13 0.99 -0.79 0.20	As -0.09 1.00 -0.40 0.93 -0.12 1.00 -0.78 0.19	Cd 0.94 -0.39 -0.40 -0.70 -0.85 -0.43 0.56 -0.78	рН -0.43 0.93 0.93 -0.70 0.23 0.93 -0.86 0.49	Eh -0.98 -0.13 -0.12 -0.85 0.23 -0.07 -0.06 0.61	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07 -0.74 0.16	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06 -0.74 -0.70	DOC -0.69 0.20 0.19 -0.78 0.49 0.61 0.16 -0.70
12 months Zn Pb As Cd pH Eh Fe Mn DOC	Zn -0.08 -0.09 0.94 -0.43 -0.98 -0.13 0.26 -0.69	Pb -0.08 1.00 -0.39 0.93 -0.13 0.99 -0.79 0.20	As -0.09 1.00 -0.40 0.93 -0.12 1.00 -0.78 0.19	Cd 0.94 -0.39 -0.40 -0.70 -0.85 -0.43 0.56 -0.78	pH -0.43 0.93 0.93 -0.70 0.23 0.93 -0.86 0.49	Eh -0.98 -0.13 -0.12 -0.85 0.23 -0.07 -0.06 0.61	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07 -0.74 0.16	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06 -0.74 -0.70	DOC -0.69 0.20 0.19 -0.78 0.49 0.61 0.16 -0.70
12 months Zn Pb As Cd pH Eh Fe Mn DOC	Zn -0.08 -0.09 0.94 -0.43 -0.98 -0.13 0.26 -0.69 Zn	Pb -0.08 1.00 -0.39 0.93 -0.13 0.99 -0.79 0.20 Pb	As -0.09 1.00 -0.40 0.93 -0.12 1.00 -0.78 0.19 As	Cd 0.94 -0.39 -0.40 -0.70 -0.85 -0.43 0.56 -0.78 Cd	рН -0.43 0.93 0.93 -0.70 0.23 0.93 -0.86 0.49 рН	Eh -0.98 -0.13 -0.12 -0.85 0.23 -0.07 -0.06 0.61 Eh	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07 -0.74 0.16 Fe	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06 -0.74 -0.70 Mn	DOC -0.69 0.20 0.19 -0.78 0.49 0.61 0.16 -0.70 DOC
12 months Zn Pb As Cd pH Eh Fe Mn DOC 15 months Zn	Zn -0.08 -0.09 0.94 -0.43 -0.98 -0.13 0.26 -0.69 Zn	Pb -0.08 1.00 -0.39 0.93 -0.13 0.99 -0.79 0.20 Pb -0.02	As -0.09 1.00 -0.40 0.93 -0.12 1.00 -0.78 0.19 As 0.20	Cd 0.94 -0.39 -0.40 -0.70 -0.85 -0.43 0.56 -0.78 Cd 0.97	рН -0.43 0.93 0.93 -0.70 0.23 0.93 -0.86 0.49 рН -0.59	Eh -0.98 -0.13 -0.12 -0.85 0.23 -0.07 -0.06 0.61 Eh 0.26	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07 -0.74 0.16 Fe -0.80	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06 -0.74 -0.74 -0.70 Mn 0.44	DOC -0.69 0.20 0.19 -0.78 0.49 0.61 0.16 -0.70 DOC -0.65
12 months Zn Pb As Cd pH Eh Fe Mn DOC 15 months Zn Pb	Zn -0.08 -0.09 0.94 -0.43 -0.98 -0.13 0.26 -0.69 Zn -0.02	Pb -0.08 1.00 -0.39 0.93 -0.13 0.99 -0.79 0.20	As -0.09 1.00 -0.40 0.93 -0.12 1.00 -0.78 0.19 As 0.20 0.98	Cd 0.94 -0.39 -0.40 -0.70 -0.85 -0.43 0.56 -0.78 Cd 0.97 -0.22	рН -0.43 0.93 -0.70 0.23 0.93 -0.86 0.49 рН -0.59 0.11	Eh -0.98 -0.13 -0.12 -0.85 0.23 -0.07 -0.06 0.61 Eh 0.26 -0.08	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07 -0.74 0.16 Fe -0.80 -0.57	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06 -0.74 -0.70 Mn 0.44 -0.88	DOC -0.69 0.20 0.19 -0.78 0.49 0.61 0.16 -0.70 DOC -0.65 0.75
12 months Zn Pb As Cd pH Eh Fe Mn DOC 15 months Zn Pb As	Zn -0.08 -0.09 0.94 -0.43 -0.98 -0.13 0.26 -0.69 Zn -0.02 0.20	Pb -0.08 1.00 -0.39 0.93 -0.13 0.99 -0.79 0.20	As -0.09 1.00 -0.40 0.93 -0.12 1.00 -0.78 0.19 As 0.20 0.98	Cd 0.94 -0.39 -0.40 -0.70 -0.85 -0.43 0.56 -0.78 Cd 0.97 -0.22 -0.01	рН -0.43 0.93 0.93 -0.70 0.23 0.93 -0.86 0.49 рН -0.59 0.11 -0.01	Eh -0.98 -0.13 -0.12 -0.85 0.23 -0.07 -0.06 0.61 Eh 0.26 -0.08 -0.02	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07 -0.74 0.16 Fe -0.80 -0.57 -0.73	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06 -0.74 -0.70 Mn 0.44 -0.88 -0.76	DOC -0.69 0.20 0.19 -0.78 0.49 0.61 0.16 -0.70 DOC -0.65 0.75 0.60
12 months Zn Pb As Cd pH Eh Fe Mn DOC 15 months Zn Pb As Cd	Zn -0.08 -0.09 0.94 -0.43 -0.98 -0.13 0.26 -0.69 Zn -0.02 0.20 0.97	Pb -0.08 1.00 -0.39 0.93 -0.13 0.99 -0.79 0.20 Pb -0.02 0.98 -0.22	As -0.09 1.00 -0.40 0.93 -0.12 1.00 -0.78 0.19 As 0.20 0.98 -0.01	Cd 0.94 -0.39 -0.40 -0.70 -0.85 -0.43 0.56 -0.78 Cd 0.97 -0.22 -0.01	рН -0.43 0.93 0.93 -0.70 0.23 0.93 -0.86 0.49 рН -0.59 0.11 -0.01 -0.01 -0.47	Eh -0.98 -0.13 -0.12 -0.85 0.23 -0.07 -0.06 0.61 Eh 0.26 -0.08 -0.02 0.13	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07 -0.74 0.16 Fe -0.80 -0.57 -0.73 -0.67	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06 -0.74 -0.74 -0.70 Mn 0.44 -0.88 -0.76 0.58	DOC -0.69 0.20 0.19 -0.78 0.49 0.61 0.16 -0.70 DOC -0.65 0.75 0.60 -0.76
12 months Zn Pb As Cd pH Eh Fe Mn DOC 15 months Zn Pb As Cd pH	Zn -0.08 -0.09 0.94 -0.43 -0.98 -0.13 0.26 -0.69 Zn -0.02 0.20 0.97 -0.59	Pb -0.08 1.00 -0.39 0.93 -0.13 0.99 -0.79 0.20 Pb -0.02 0.98 -0.22 0.11	As -0.09 1.00 -0.40 0.93 -0.12 1.00 -0.78 0.19 As 0.20 0.98 -0.01 -0.01 -0.01	Cd 0.94 -0.39 -0.40 -0.70 -0.85 -0.43 0.56 -0.78 Cd 0.97 -0.22 -0.01 -0.47	рН -0.43 0.93 0.93 -0.70 0.23 0.93 -0.86 0.49 рН -0.59 0.11 -0.59 0.11 -0.01 -0.47	Eh -0.98 -0.13 -0.12 -0.85 0.23 -0.07 -0.06 0.61 Eh 0.26 -0.08 -0.02 0.13 -0.93	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07 -0.74 0.16 Fe -0.80 -0.57 -0.73 -0.67 0.30	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06 -0.74 -0.70 Mn 0.44 -0.88 -0.76 0.58 -0.52	DOC -0.69 0.20 0.19 -0.78 0.49 0.61 0.16 -0.70 DOC -0.65 0.75 0.60 -0.76 0.58
12 months Zn Pb As Cd pH Eh Fe Mn DOC 15 months Zn Pb As Cd pH Eh	Zn -0.08 -0.09 0.94 -0.43 -0.98 -0.13 0.26 -0.69 Zn -0.02 0.20 0.97 -0.59 0.26	Pb -0.08 1.00 -0.39 0.93 -0.13 0.99 -0.79 0.20 Pb -0.02 0.98 -0.22 0.11 -0.08	As -0.09 1.00 -0.40 0.93 -0.12 1.00 -0.78 0.19 As 0.20 0.98 -0.01 -0.01 -0.01 -0.02	Cd 0.94 -0.39 -0.40 -0.70 -0.85 -0.43 0.56 -0.78 Cd 0.97 -0.22 -0.01 -0.47 0.13	рН -0.43 0.93 0.93 -0.70 0.23 0.93 -0.86 0.49 рН -0.59 0.11 -0.01 -0.01 -0.47 -0.93	Eh -0.98 -0.13 -0.12 -0.85 0.23 -0.07 -0.06 0.61 Eh 0.26 -0.08 -0.02 0.13 -0.93	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07 -0.74 0.16 Fe -0.80 -0.57 -0.73 -0.67 0.30 -0.04	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06 -0.74 -0.74 -0.70 Mn 0.44 -0.88 -0.76 0.58 -0.52 0.39	DOC -0.69 0.20 0.19 -0.78 0.49 0.61 0.16 -0.70 DOC -0.65 0.75 0.60 -0.76 0.58 -0.37
12 months Zn Pb As Cd pH Eh Fe Mn DOC 15 months Zn Pb As Cd pH Eh Eh Fe	Zn -0.08 -0.09 0.94 -0.43 -0.98 -0.13 0.26 -0.69 Zn -0.02 0.20 0.97 -0.59 0.26 -0.80	Pb -0.08 1.00 -0.39 0.93 -0.13 0.99 -0.79 0.20 Pb -0.02 0.98 -0.22 0.11 -0.08 -0.57	As -0.09 1.00 -0.40 0.93 -0.12 1.00 -0.78 0.19 As 0.20 0.98 -0.01 -0.01 -0.01 -0.02 -0.73	Cd 0.94 -0.39 -0.40 -0.70 -0.85 -0.43 0.56 -0.78 Cd 0.97 -0.22 -0.01 -0.47 0.13 -0.67	рН -0.43 0.93 0.93 -0.70 0.23 0.93 -0.86 0.49 рН -0.59 0.11 -0.59 0.11 -0.11 -0.47 -0.93 0.30	Eh -0.98 -0.13 -0.12 -0.85 0.23 -0.07 -0.06 0.61 Eh 0.26 -0.08 -0.02 0.13 -0.93 -0.04	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07 -0.74 0.16 Fe -0.80 -0.57 -0.73 -0.67 0.30 -0.04	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06 -0.74 -0.70 Mn 0.44 -0.88 -0.76 0.58 -0.52 0.39 0.18	DOC -0.69 0.20 0.19 -0.78 0.49 0.61 0.16 -0.70 DOC -0.65 0.75 0.60 -0.76 0.58 -0.37 0.07
12 months Zn Pb As Cd pH Eh Fe Mn DOC 15 months Zn Pb As Cd pH Eh Fe Mn	Zn -0.08 -0.09 0.94 -0.43 -0.98 -0.13 0.26 -0.69 Zn -0.02 0.20 0.97 -0.59 0.26 -0.80 0.44	Pb -0.08 1.00 -0.39 0.93 -0.13 0.99 -0.79 0.20 Pb -0.02 0.98 -0.22 0.11 -0.08 -0.57 -0.88	As -0.09 1.00 -0.40 0.93 -0.12 1.00 -0.78 0.19 As 0.20 0.98 -0.01 -0.01 -0.01 -0.01 -0.02 -0.73 -0.76	Cd 0.94 -0.39 -0.40 -0.70 -0.85 -0.43 0.56 -0.78 Cd 0.97 -0.22 -0.01 -0.47 0.13 -0.67 0.58	рН -0.43 0.93 0.93 -0.70 0.23 0.93 -0.86 0.49 рН -0.59 0.11 -0.11 -0.01 -0.47 -0.93 0.30 -0.52	Eh -0.98 -0.13 -0.12 -0.85 0.23 -0.07 -0.06 0.61 Eh 0.26 -0.08 -0.02 0.13 -0.93 -0.04 0.39	Fe -0.13 0.99 1.00 -0.43 0.93 -0.07 -0.74 0.16 Fe -0.80 -0.57 -0.73 -0.67 0.30 -0.04	Mn 0.26 -0.79 -0.78 0.56 -0.86 -0.06 -0.74 -0.74 -0.70 Mn 0.44 -0.88 -0.76 0.58 -0.52 0.39 0.18	DOC -0.69 0.20 0.19 -0.78 0.49 0.61 0.16 -0.70 DOC -0.65 0.75 0.60 -0.76 0.58 -0.37 0.07 -0.97

Significant (p<0.05) correlations are represented by red coloured numbers.

Table S3b: Correlation matrices of pore water data based on the Pearson coefficient.

3 months	Zn	Pb	Cd	рН	Eh	Fe	Mn	DOC
Zn		0.45	0.46	-0.91	0.35	0.11	-0.51	0.14
Pb	0.45		0.94	-0.98	0.23	0.43	-0.63	0.39
Cd	0.46	0.94		-0.86	0.07	0.55	-0.53	0.39
рН	-0.91	-0.98	-0.86		-0.50	-0.23	0.50	-0.41
Eh	0.35	0.23	0.07	-0.50		-0.37	-0.03	0.30
Fe	0.11	0.43	0.55	-0.23	-0.37		-0.09	-0.47
Mn	-0.51	-0.63	-0.53	0.50	-0.03	-0.09		-0.12
DOC	0.14	0.39	0.39	-0.41	0.30	-0.47	-0.12	
15 months	Zn	Pb	Cd	рН	Eh	Fe	Mn	DOC
Zn		0.88	0.98	-0.37	0.07	0.47	0.43	-0.11
Pb	0.88		0.83	-0.59	0.21	0.75	0.24	-0.02
Cd	0.98	0.83		-0.27	-0.01	0.46	0.54	-0.15
рН	-0.37	-0.59	-0.27		-0.58	-0.61	0.25	-0.29
Eh	0.07	0.21	-0.01	-0.58		0.41	-0.22	0.14
Fe	0.47	0.75	0.46	-0.61	0.41		0.02	0.11
Mn	0.43	0.24	0.54	0.25	-0.22	0.02		-0.52
DOC	-0.11	-0.02	-0.15	-0.29	0.14	0.11	-0.52	

Significant (p<0.05) correlations are represented by red coloured numbers.

Figure S17: Concentrations of NO⁻₃ and SO⁻₄ in the soil H₂O extracts after 1, 3, 12 & 15 months of incubation.

Figure S18: The acid neutralisation capacity (ANC) of the studied treatments and control soil (*n*=2).

Table S4 Speciation of Cd, Pb and Zn in the pore water samples as calculated by the PHREEQC-3 geochemical code.

Time	Treatment	рН	Cd ²⁺	CdNO ₃ +	Pb ²⁺	PbNO ₃ +	PbHCO ₃ ⁺	Zn ²⁺	ZnSO ₄	ZnHCO ₃ +
	Control	5.05	95%	5%	77%	21%	1%	99%	1%	0%
3 months	BC	5.25	97%	3%	82%	14%	3%	96%	3%	1%
0 11011113	nZVI	5.82	97%	3%	78%	14%	7%	98%	1%	2%
	nZVI-BC	5.78	96%	4%	75%	19%	7%	97%	1%	1%
	Control	5.50	94%	6%	70%	27%	3%	98%	2%	1%
15	BC	5.69	96%	4%	77%	19%	4%	96%	3%	1%
months	nZVI	5.69	94%	6%	69%	26%	4%	98%	1%	1%
	nZVI-BC	5.76	95%	5%	69%	23%	8%	97%	1%	2%

Table S5 Saturation indices of selected phases found in the pore water as calculated by the PHREEQC-3 geochemical code.

			AI(SO₄)				KFe ³⁺					
	Formula	AI(OH) ₃	(OH)·5H₂O	CdCO ₃	Fe(OH) ₃	Fe ₃ (OH) ₈	₃ (SO ₄) ₂ (OH) ₆	MnCO ₃	PbSO ₄	PbCO ₃	Pb(OH) ₂	ZnCO ₃
Time	Treatment	Gibbsite	Jurbanite	Otavite	Fe(OH) ₃	Fe ₃ (OH) ₈	Jarosite	Rhodochrosite	Anglesite	Cerussite	Pb(OH) ₂	Smithsonite
	Control	1.17	-1.63	-2.82	-0.10	-6.31	-4.54	-1.91	-2.24	-2.52	-4.04	-2.65
3	BC	-	_	-2.74	-0.40	-6.98	-3.68	-1.47	-2.01	-2.26	-3.84	-2.63
months	nZVI	-	_	-2.21	0.37	-5.08	-4.56	-0.12	-2.89	-1.59	-2.97	-2.43
	nZVI-BC	_	_	-1.93	0.39	-5.03	-3.70	-0.11	-2.84	-1.77	-3.20	-2.01
	Control	1.23	-2.27	-1.86	0.24	-6.31	-1.82	-1.54	-2.61	-2.23	-3.70	-1.63
15	BC	1.86	-1.80	-1.80	-0.39	-8.23	-2.54	-3.54	-2.57	-2.18	-3.51	-1.60
months	nZVI	1.78	-2.35	-1.67	-0.40	-8.25	-1.57	-0.98	-3.08	-2.15	-3.55	-1.53
	nZVI-BC	1.73	-2.47	-1.39	-0.33	-7.97	-2.40	-1.29	-3.20	-2.00	-3.60	-1.23

Saturation indices in the interval <-1.5 - 1.5> are highlighted with grey background, values >0 are given in bold.

Table S6 Speciation of Cd, Pb and Zn in the soil extracts as calculated by the PHREEQC-3 geochemical code.

Time	Treatment	рН	Cd ²⁺	Pb ²⁺	PbCO ₃ 0	PbHCO ₃ ⁺	Zn ²⁺	ZnHCO₃⁺	ZnSO ₄ ⁰
	Control	5.80	_	69%	12%	19%	95%	4%	1%
1 month	BC	6.20	_	38%	38%	24%	90%	9%	1%
1 month	nZVI	6.24	_	43%	36%	21%	92%	7%	1%
	nZVI-BC	6.35	_	37%	43%	19%	92%	8%	1%
	Control	5.36	100%	95%	1%	4%	98%	1%	1%
2 months	BC	5.92	100%	90%	5%	6%	98%	1%	1%
3 months	nZVI	5.30	100%	97%	0%	2%	98%	0%	1%
	nZVI-BC	5.28	100%	97%	0%	2%	99%	0%	1%
	Control	5.74	100%	70%	10%	19%	95%	4%	1%
12 months	BC	5.92	100%	59%	19%	23%	93%	6%	1%
12 11011015	nZVI	5.56	100%	81%	5%	14%	97%	3%	1%
	nZVI-BC	5.73	100%	72%	10%	18%	95%	4%	1%
	Control	5.51	100%	95%	1%	4%	98%	1%	1%
15 months	BC	5.55	_	90%	3%	8%	98%	1%	1%
10 monuns	nZVI	5.53	_	92%	2%	6%	98%	1%	1%
	nZVI-BC	5.62	_	91%	3%	6%	98%	1%	1%

Table S7 Saturation indices of selected phases found in the soil extracts as calculated by the PHREEQC-3 geochemical code.

	Formula	AI(OH) ₃	AI(SO ₄)(OH) · 5H ₂ O	$CdCO_3$	Fe(OH) ₃	Fe ₃ (OH) ₈	KFe ³⁺ ₃ (SO ₄) ₂ (OH) ₆	MnCO₃	PbSO ₄	PbCO₃	Pb(OH) ₂	ZnCO₃
Time	Treatment	Gibbsite	Jurbanite	Otavite	Fe(OH) ₃	Fe ₃ (OH) ₈	Jarosite	Rhodochrosite	Anglesite	Cerussite	Pb(OH) ₂	Smithsonite
1 month	Control	1.11	-0.84	_	2.40	-0.28	1.34	-2.44	-2.47	-0.67	-2.43	-2.18
	BC	1.58	-1.11	_	2.92	1.16	1.60	-1.30	-2.56	-0.08	-1.78	-1.62
month	nZVI	1.30	-1.52	_	3.00	1.33	1.51	-0.41	-2.82	-0.35	-1.91	-2.01
Time 1 month 3 months 12 months	nZVI-BC	1.51	-1.52	_	2.95	1.17	1.04	-0.39	-2.85	-0.26	-1.73	-1.87
	Control	-0.06	-1.05	-3.45	1.54	-1.78	-0.03	-2.44	-2.32	-1.86	-3.24	-3.34
3	BC	0.70	-1.31	-3.19	2.52	0.09	1.25	-1.16	-2.40	-1.29	-2.29	-3.30
months	nZVI	-0.13	-0.90	-3.66	1.65	-3.07	0.71	-2.64	-2.31	-2.26	-3.45	-3.56
	nZVI-BC	-0.13	-1.13	-3.85	1.66	-3.13	0.18	-3.10	-2.43	-2.13	-3.34	-3.75
	Control	0.88	-0.87	-2.19	2.11	-0.01	0.85	-2.10	-2.56	-0.90	-2.72	-2.06
12 mantha	BC	1.05	-0.97	-2.11	2.34	-0.40	1.03	-2.60	-2.52	-0.64	-2.41	-2.02
monuns	nZVI	0.05	-1.36	-2.83	1.65	-1.86	-0.19	-1.98	-3.01	-1.72	-3.50	-2.72
	nZVI-BC	0.62	-1.10	-2.48	2.02	-1.08	0.59	-2.74	-2.74	-1.14	-2.92	-2.34
	Control	0.21	-1.03	-3.07	1.76	-1.51	0.60	-3.13	-2.30	-1.75	-2.98	-3.18
15 months	BC	0.24	-1.06	_	1.86	-1.29	0.64	-3.39	-2.29	-1.42	-2.89	-3.05
	nZVI	0.01	-1.28	_	1.91	-1.15	0.85	-2.82	-2.62	-1.84	-3.24	-3.15
	nZVI-BC	0.19	-1.28	_	1.88	-0.74	0.52	-3.11	-2.45	-1.56	-2.89	-3.06

Saturation indices in the interval <-1.5 - 1.5> are highlighted with grey background, values >0 are given in bold.

Figure S19: Total concentrations of the studied risk elements in the sand layer after 1, 3, 12 & 15 months of incubation and total concentration of As in the pure sand sample.

Figure S20: The amount of metal(loid)s extracted by H_2O extraction from the mixed soil samples after 15 months of incubation (expressed as % proportion of the total concentrations).