

Appendix A. Supplementary data

Use of iron-coated sand for removing soluble phosphorus from drainage water

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S1. Stock of Mn and Fe in Fe-coated sand versus leaching via drains

When enveloped drains were installed, Fe-coated sand was used that contained both Fe and Mn. Both elements are present in solid form, and are insoluble in that form but can be reduced under anaerobic conditions and may leach as bivalent ions.

Here we calculate for both Fe and Mn which stock was present in the Fe-coated sand after installing the enveloped drain, and which amount is leached during the experiment. The calculation was made for an enveloped drain of 1 m length.

Content of Fe and Mn in Fe-coated sand (see Groenenberg et al., 2013, Table 2): Fe content = 232 g kg⁻¹, Mn content Mn = 3.1 g kg⁻¹.

Estimated amount of Fe-coated sand (density taken from column study by Chardon et al., 2012) = 0.14 m³ (m drain)⁻¹ * 2000 [density, kg m³] = 280 kg.

Thus Fe in Fe-coated sand = 232 g kg⁻¹ * 280 kg = 65 kg Fe, and for Mn = 3.1 g kg⁻¹ * 280 kg = 0.87 kg Mn.

The amounts of Fe and Mn leached can be calculated as the volume of water from the rainfall surplus passing the drain, times the average concentration measured.

Volume of water = rainfall surplus * surface of rain entrance above drain

$$= 0.3 \text{ m yr}^{-1} [\text{surplus}] * 4.5 [\text{yr}] * 5 \text{ m} [\text{width}] * 1 \text{ m} [\text{length}] = 0.3 * 4.5 * 5 * 1 = 6.75 \text{ m}^3.$$

Groenenberg et al. (2013) estimated that the amount of seepage in the experimental area is equal to the amount of rainfall surplus, which implicates that the total volume of water that has passed the 1 m drain during the experiment can be estimated as 13.5 m³.

Table S1 shows the amounts of Fe and Mn around the drain, the average concentrations of Fe and Mn in the water from the enveloped drain during the experiment, and the calculated yearly loss via leaching of both elements, both as total amount and as fraction of the amounts initially present. However, the water entering the enveloped drain also contains Fe and Mn. If the concentrations of Fe and Mn (taken from Table 2 in the main text) are corrected by subtracting the average concentration of Fe and Mn measured in the effluent of the reference drains, smaller relative amounts leached are calculated.

Table S1

Calculated fraction of stock of Fe and Mn leached during experiment; all data are calculated for 1 m drain length.

Element	Stock	Volume water	Average concentration	Leached	Fraction stock
	kg	m ³	g m ⁻³	kg	%
Fe	65	13.5	12.6	0.170	0.26
Mn	0.87	13.5	4.9	0.066	7.6
Fe [corrected]	65	13.5	9.8	0.132	0.20
Mn [corrected]	0.87	13.5	3.9	0.053	6.1

From the table it can be concluded that less than 1 % of the Fe initially present around the enveloped drain was lost during the 4.5 year of the experiment, and circa 8 % of the Mn initially present.

For the first 14 months (1.17 yr), it can be calculated that 3.5 m³ water had passed the enveloped drain. The average concentration of Fe in the enveloped drain effluent during this period was 0.60 g m⁻³. Thus, 0.0021 kg Fe was leached during this period, or 0.003 % of the stock.

S2. Sampling of pore water in Fe-coated sand using a SOFIE® cell

Method

At t_{32} , the iron sand was sampled *in-situ* with a SOFIE® cell (Sediment Or Fauna Incubation Experiment; Vink, 2002, 2009; Engerling and Vink, 2016), as can be seen in Fig. S1 below. The location was visited on 21 November 2013. The drain was dug up and an Fe-coated sand core was collected in such a way that the core contained Fe-coated sand from below the drain, beside the drain, and above the drain. Thus, once the sample was collected no disturbances took place and measurements could be performed on the intact sediment core. The SOFIE® cell was stored in a dark room at approximately 18 °C until the measurements started. PES probes (PolyEtherSulfone) were installed at several heights in the sediment core: one probe was installed just under the surface of the Fe-coated sand, another in the middle of the column, and the third one near the bottom. The PES-probes enabled the direct sampling of pore water at the redox conditions preserved from the field. The mesh size of the probes was 0.1 μm (Vink, 2002), which meant that the samples were sterile and relatively insensitive to microbial redox alterations. Both pH and redox potential were measured directly in the SOFIE® cell. After sampling, the pore water was analysed using ion chromatography for the measurement of the concentrations of F, Cl, Br, $\text{NO}_3\text{-N}$, and $\text{SO}_4\text{-S}$. Using an auto-analyser, concentrations of $\text{NH}_4\text{-N}$ and DRP were determined and ICP-MS was used to determine the concentrations of Fe, Mn, and TDP.

Results

Table S2

Redox potential (Eh), pH, and composition of the pore water in three different layers of an undisturbed Fe-coated sand core, measured within the SOFIE® cell.

Layer	Depth	Eh	pH	Cl	Br	F	NO ₃ -N	SO ₄ -S	DRP	TDP	NH ₄ -N	Fe	Mn	Na	Ca
	cm	mV		mg L ⁻¹											
U ¹	0.5	-107	7.9	71.5	0.44	0.50	0.23	136	<0.01	0.61	0.5	5.6	1.9	12.7	351
M ¹	5	-219	n.d. ²	72.1	0.47	0.47	<0.02	108	<0.01	<0.01	4.5	9.4	3.4	12.2	106
L ¹	10	-233	7.9	75.1	0.48	0.37	<0.02	62	<0.01	<0.01	7.4	15.8	6.1	18.9	112

¹Measurements were done in pore water collected from PES probes installed at several heights in the sediment core: one probe was installed just under the surface of the Fe-coated sand, denoted as the upper layer (U), another in the middle of the column, denoted as the middle layer (M), and the third one near the bottom, denoted as the lower layer (L).

²Not determined.



Fig. S1. *In-situ* field sampling of the Fe-coated sand envelope with the SOFIE® cell.

S3. Conditions used for characterization of Fe-coated sand using acid ammonium oxalate

An extraction using acid ammonium oxalate can be used for determining the concentrations of amorphous Fe, Al, and Mn (hydr)oxides in soil samples (Schwertmann, 1964; McKeague and Day, 1966). Using these data, the phosphate saturation degree can be calculated (Schoumans and Chardon, 2015). During the extraction, a solution-to-solid ratio (SSR) of 20 L kg⁻¹ and an extraction time of 2 hours are often used (Schoumans, 2009).

Solution-to-solid ratio: Schwertmann (1964) mentions the use of a range of 20 to 100 L kg⁻¹, and McKeague and Day (1966) used either 40 or 80 L kg⁻¹. Schwertmann (1964) refers to the work of Tamm (1922, 1932), who also used the range of 20 to 100 L kg⁻¹, using two consecutive extractions on the same sample. For a sample from an iron-cemented hard pan an even wider ratio of 200 L kg⁻¹ was used by Tamm (1922).

Extraction time: The extraction time was also extended, when compared to Tamm (1922, 1932), who used two consecutive extractions of 1 hr, and to Schwertmann (1964) and Schoumans (2009), who both used an extraction time of 2 h.

Preliminary research on both Fe-coated sand from the same source as used in the field experiment and on iron oxide sludge showed that both the acid ammonium oxalate-extracted amount of Fe and the amount of P increased when the SSR increased from 20 to 200 L kg⁻¹. A further increase of the SSR up to 400 L kg⁻¹ for iron oxide sludge gave no further increase (Table S3). For characterization of the Fe-coated sand, we therefore used a SSR of 200 L kg⁻¹. We used an extraction time of 4 h, as was also used by McKeague and Day (1966). This combination was shown by Koopmans et al. (2020) to be sufficient for a complete extraction of both Fe_{ox} and P_{ox} from iron oxide sludge, that has an even higher Fe_{ox} content than our Fe-coated sand (Chardon et al., 2012).

Table S3

Acid ammonium oxalate-extractable amounts of Fe and P and the molar P/Fe ratio in Fe-coated sand or iron sludge at different values of the solution-to-solid ratio (SSR) after an extraction time of 4 hours.

By-product	SSR L kg ⁻¹	Fe mg kg ⁻¹	P mg kg ⁻¹	P/Fe mole/mole
Fe-coated sand	20	59	0.88	0.027
Fe-coated sand	100	176	3.24	0.033
Fe-coated sand	200	199	3.53	0.030
Iron oxide sludge	200	336	2.82	0.015
Iron oxide sludge	300	328	2.68	0.015
Iron oxide sludge	400	329	2.66	0.015

S4. Concentrations in the 0.01 M CaCl₂ extracts of the Fe-coated sand

Table S4

Results of the 0.01 M CaCl₂ extraction method of the Fe-coated sand, sampled from three different layers of the Fe-coated sand envelope wrapped around the pipe drain, after 32 and 59 months (denoted as t₃₂ and t₅₉).

Sampling	Layer	pH	Al	Fe	Mg	Mn	TDP	DRP	S	Si	DOC	As	Cd	Cu	Ni	Pb	Zn
			mg L ⁻¹														
t ₃₂	U ¹	7.3	<0.01	<0.09	7.1	2.78	<0.1	<0.03	3.08	1.85	4.4	0.174	<0.005	<0.010	0.36	0.07	0.02
t ₃₂	M ¹	7.3	<0.01	<0.09	6.5	2.74	<0.1	<0.03	3.00	2.00	5.1	0.144	<0.005	<0.010	0.38	<0.04	<0.02
t ₃₂	L ¹	7.2	<0.01	<0.09	6.6	2.07	<0.1	<0.03	1.51	2.25	5.7	0.109	<0.005	<0.010	0.65	<0.04	<0.02
t ₅₉	U	6.7	0.01	0.02	14.1	3.72	<0.1	<0.03	2.18	5.51	8.0	0.207	0.010	0.001	1.02	<0.04	<0.02
t ₅₉	M	6.7	<0.01	0.02	13.9	3.79	<0.1	<0.03	2.21	5.25	8.2	0.208	0.008	0.001	0.87	<0.04	<0.02
t ₅₉	L	6.9	0.01	0.02	17.5	2.72	<0.1	<0.03	1.90	4.61	9.4	0.305	0.007	0.002	1.19	<0.04	<0.02

¹Samples were taken from three different layers of the Fe-coated sand envelope wrapped around the pipe drain where U denotes the upper layer, M the middle layer, and L the lower layer.

S5. Calculation of P retention by enveloped drain and resulting P/Fe ratio in Fe-coated sand

Over the experimental period of 54 months ($n = 32$), the average concentration of TDP was 3.304 mg L^{-1} for the reference pipe drains. For the enveloped pipe drain, the average TDP concentration was 0.138 mg L^{-1} . The difference can be used for calculating the amount retained $= 3.17 \text{ mg L}^{-1} = 3.17 \text{ g m}^{-3}$.

According to Section S1, during the experimental period 13.5 m^3 water had passed per meter drain, with an infiltration area of ($5 \text{ m} * 1 \text{ m} =$) 5 m^2 .

Thus, per m drain: $13.5 \text{ m}^3 * 3.17 \text{ g m}^{-3} = 42.7 \text{ g TDP}$ was retained $= 0.043 \text{ kg P}$. This retention was calculated for 5 m^2 , during 4.5 yr, which corresponds with ($2000 * 0.043/4.5 =$) $19 \text{ kg P ha}^{-1} \text{ yr}^{-1}$.

Also according to Section S1, per m drain we have 65 kg Fe, so per mole Fe, the following amount of TDP was retained: $(0.043/31) / (65/55.85) \text{ mole TDP/mole Fe} = 0.0014 \text{ mole/mole}$. According to Table 4 (more precisely calculated), the molar P/Fe-ratio at t_0 was 0.0296 mole/mole , and on t_{59} it was 0.0335 mole/mole (upper layer); 0.0314 mole/mole (middle layer), and 0.0341 mole/mole (lower layer). This gives an average molar P/Fe ratio at t_{59} of 0.0330 mole/mole (± 0.0014). Adding the calculated increase due to TDP retention to the ratio at t_0 gives ($0.0296 + 0.0014 =$) 0.0310 mole/mole , which is rather close to the value of 0.0330 mole/mole (± 0.0014).

S6. Composition of Fe-coated sand and structural characterization of Fe in Fe-coated sand

Table S6

Composition of Fe-coated sand measured using an 0.2 M acid ammonium oxalate extraction. The Fe-coated sand samples were taken after 32 and 59 months (denoted as t_{32} and t_{59}).

Sampling	Fe _{ox}			Mn _{ox}			P _{ox}			P _{ox} /Fe _{ox}		
	U ¹	M ¹	L ¹	U	M	L	U	M	L	U	M	L
	g kg ⁻¹			g kg ⁻¹			g kg ⁻¹			mole/mole		
t_{32}	173	166	132	1.83	1.69	1.05	3.22	3.16	2.36	0.034	0.034	0.032
t_{59}	83	113	134	1.23	1.34	1.19	1.68	2.18	2.54	0.037	0.035	0.034
ox/AR t_{32}^{\ddagger}	89%	88%	79%	87%	91%	70%	91%	91%	78%			
ox/AR t_{59}	56%	60%	74%	70%	73%	65%	61%	67%	74%			

¹Samples were taken from three different layers of the Fe-coated sand envelope wrapped around the pipe drain where U denotes the upper layer, M the middle layer, and L the lower layer.

[‡]Acid ammonium oxalate extractable F_{ox}, Mn_{ox}, and P_{ox} as a % of the so-called "pseudo-total" contents as determined by Aqua Regia digestion (see Table 4), denoted as ox/AR.

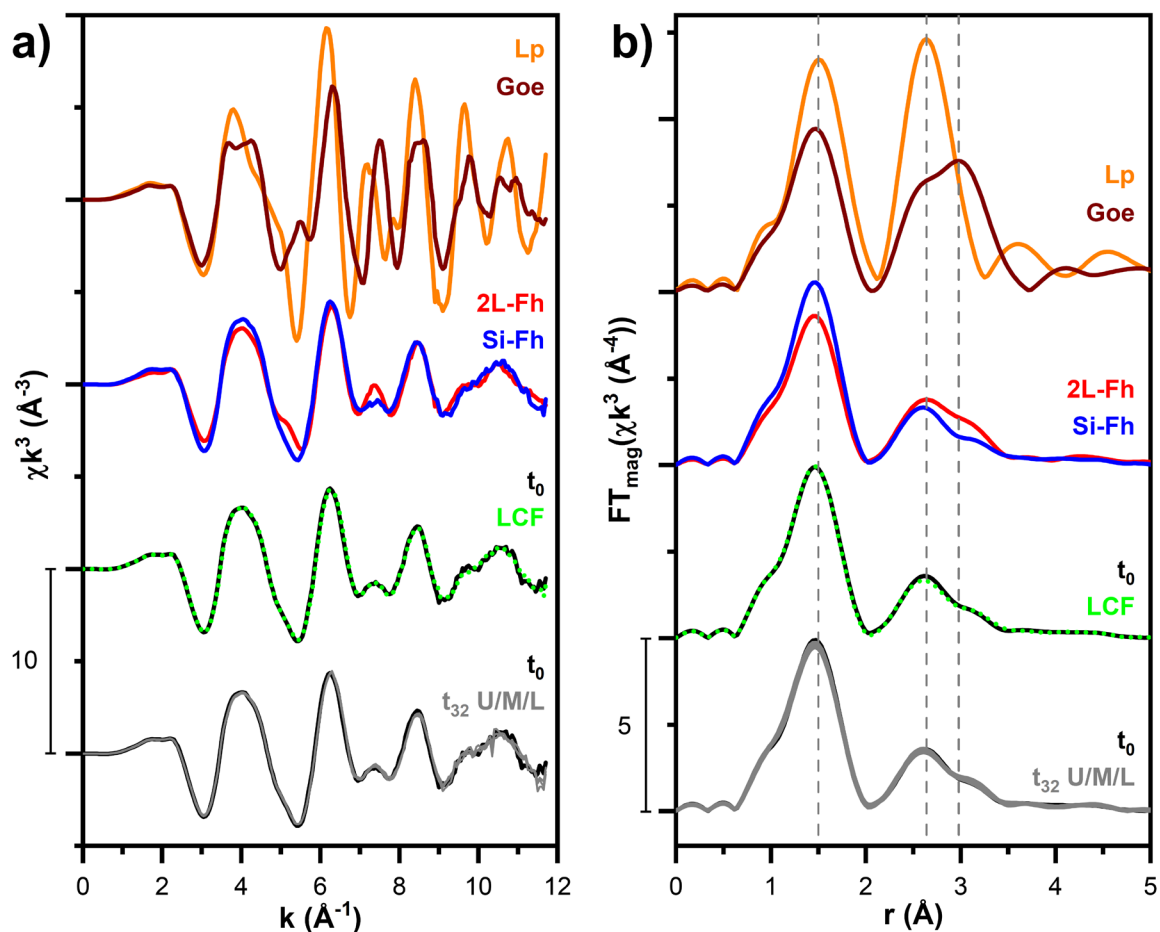


Fig. S2. Fe K-edge EXAFS spectra in k-space and r-space for (i) lepidocrocite (Lp, orange) and goethite (goe, brown), (ii) 2-line ferrihydrite (2L-Fh, red) and silicate-ferrihydrite (Si-Fh, blue), (iii) the Fe-coated sand sampled at t_0 (black) in comparison to a linear combination fit reconstruction (green; 0.20 2L-Fh + 0.78 Si-Fh) and (iv) the Fe-coated sand sampled at t_0 (black) and the spectra of Fe-coated sand sampled at t_{32} from three different levels around the enveloped pipe drain (U: upper layer; M: middle layer; L: lower layer; gray). The vertical lines in Figure S2 denote the peaks arising from (left to right) first-shell Fe-O, second-shell edge-sharing Fe-Fe, and second-shell corner-sharing Fe-Fe contributions.