Delayed immobilization of heavy metals in soils and sediments under reducing and anaerobic conditions; consequences for flooding and storage

Jos Vink

Venice, April 8 2011

Goal

1. Investigate and quantify the **mechanisms** and **kinetics** associated with redox transitions in soils and sediments

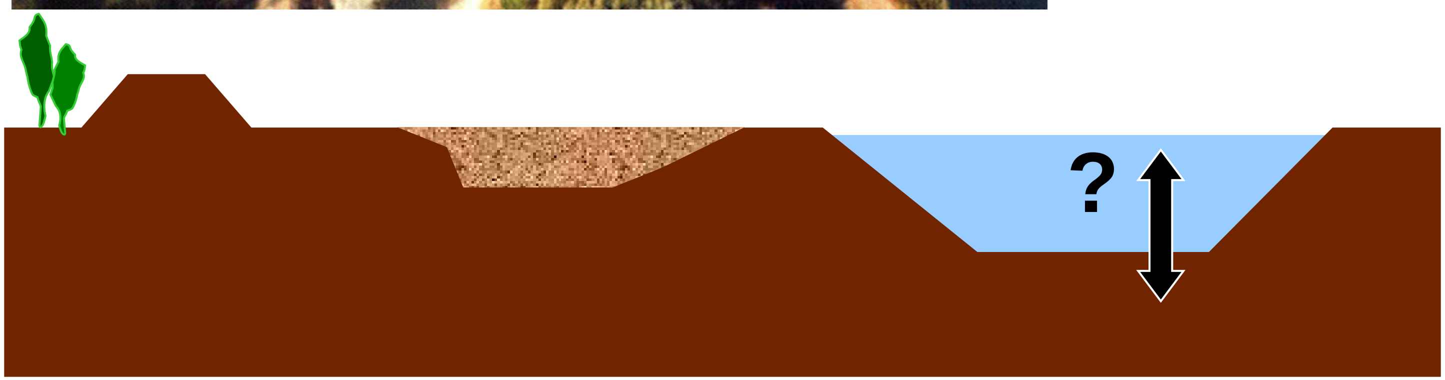
2. Evaluate the (large-scale) **practice** of dumping, storage or long term inundation in river restoration works

Redevelopment along rivers

Increase river discharge

Nature development

Sanitation




Analytical instruments?

For analytical purposes, we need instruments to measure in pore water…

.. metal speciation AND nutrients..

.. over redox gradients..

.. in undisturbed sediment..

.. repeatedly..

.. over small depth intervals and water-sediment interfaces..

.. that remain geochemical integrity..

.. and integrate exposure tests with biota..

.. that don’t cost an arm and a leg.

Methods

SOFIE®

Sediment Or Fauna Incubation Experiment
EU-patent 02077121.8

www.sofie.nl

Environ. Sci. Technol. 2002, 36, 5130–5138

Measurement of Heavy Metal Speciation over Redox Gradients in Natural Water–Sediment Interfaces and Implications for Uptake by Benthic Organisms

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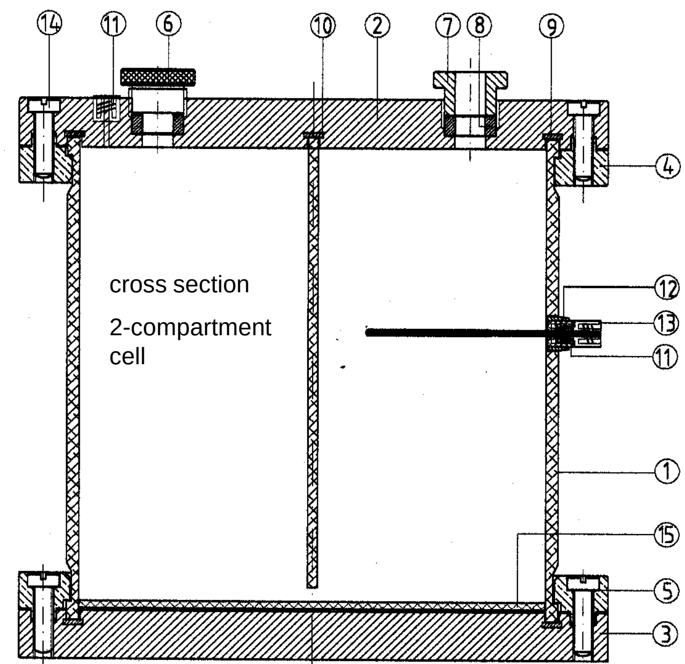
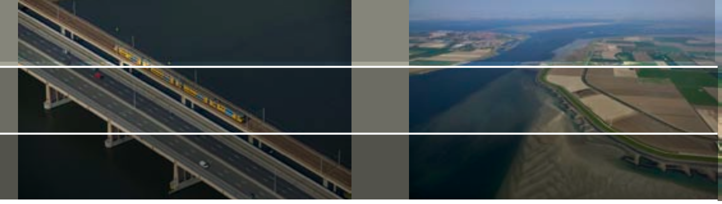
In past years, sur
chemical speciation
organisms) in natura
models, very few t
actually quantify (i.e
to measure these per
The concept of the f
that free aqueous m
total or dissolved
toxicological or bi
organisms that are e

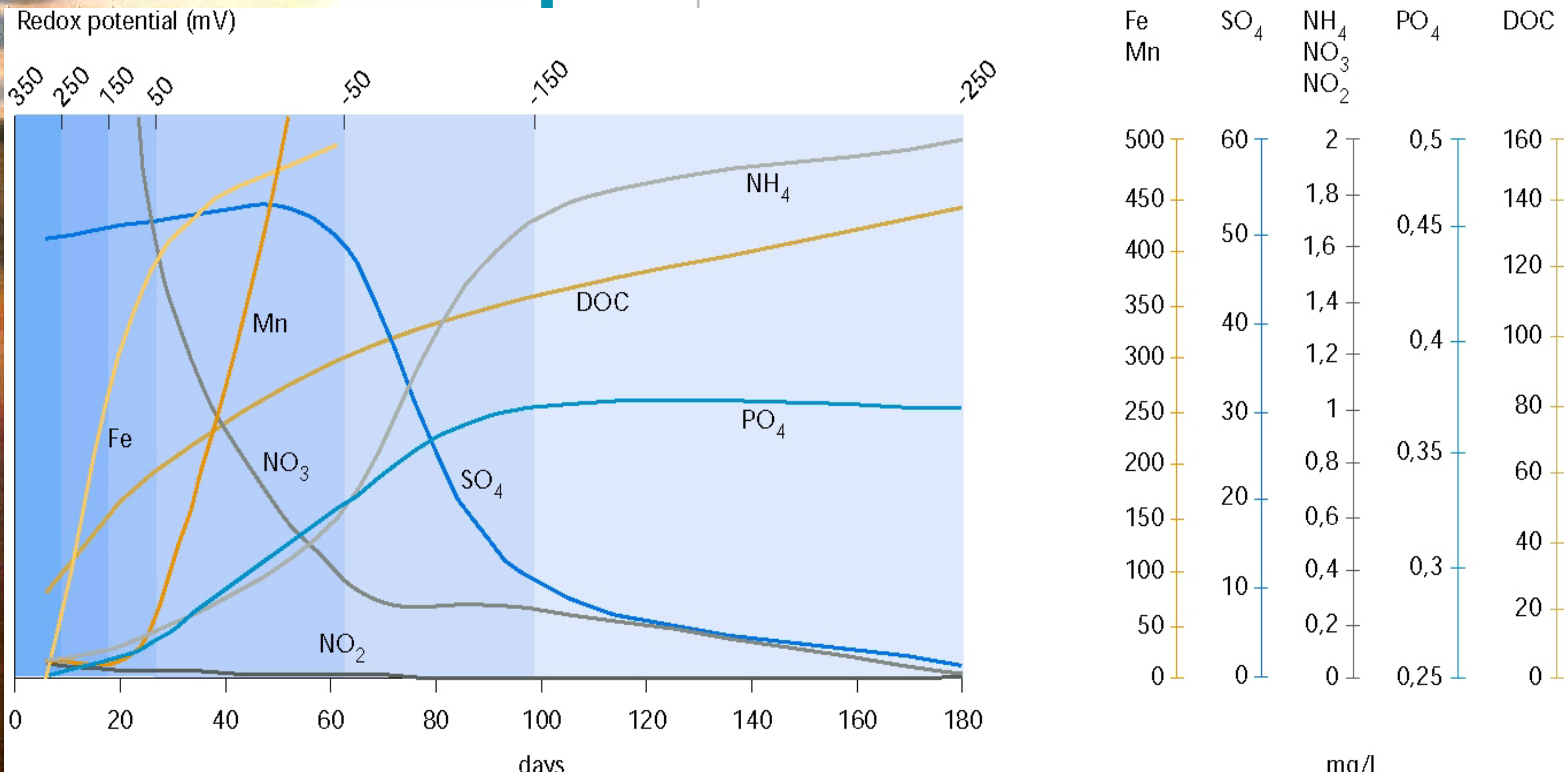


Methods (2)



Reduction in time

10



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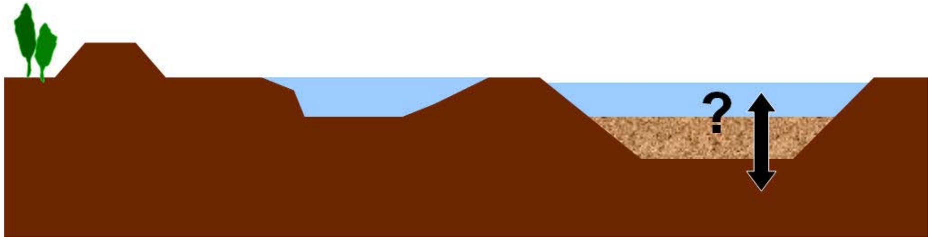
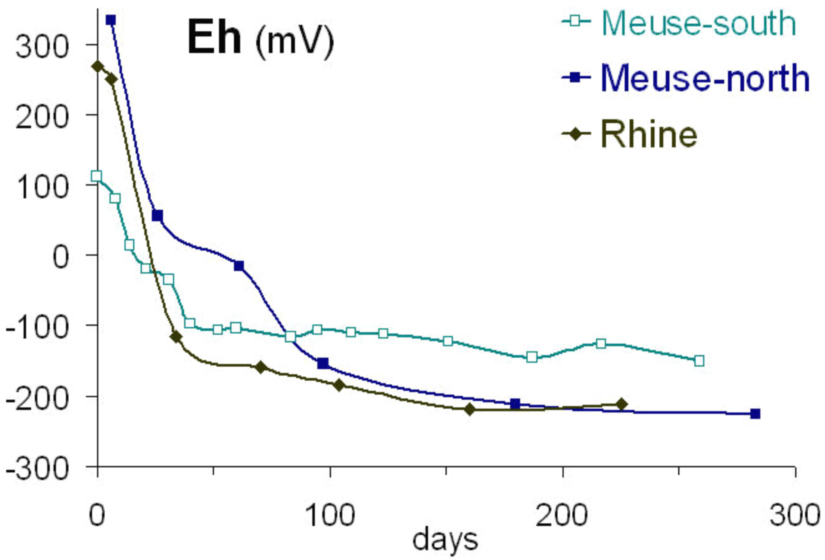
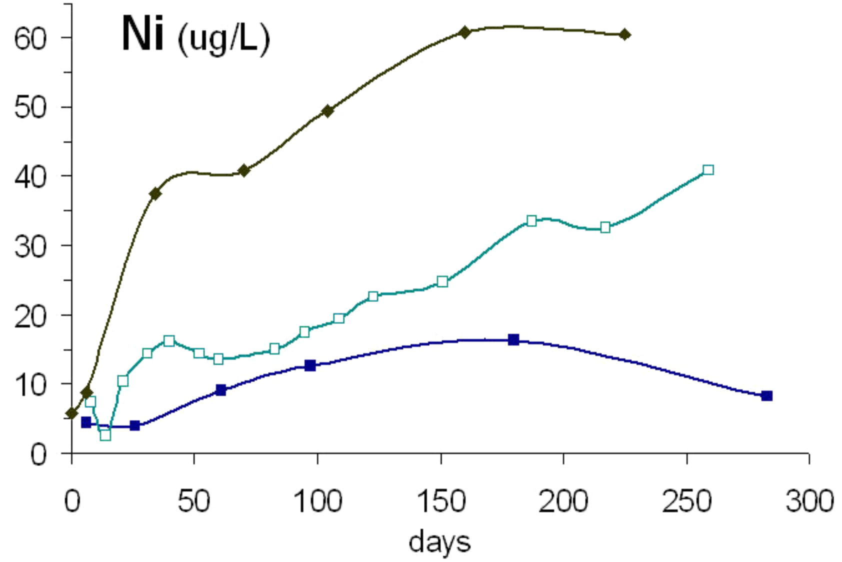
Reduction kinetics (2)







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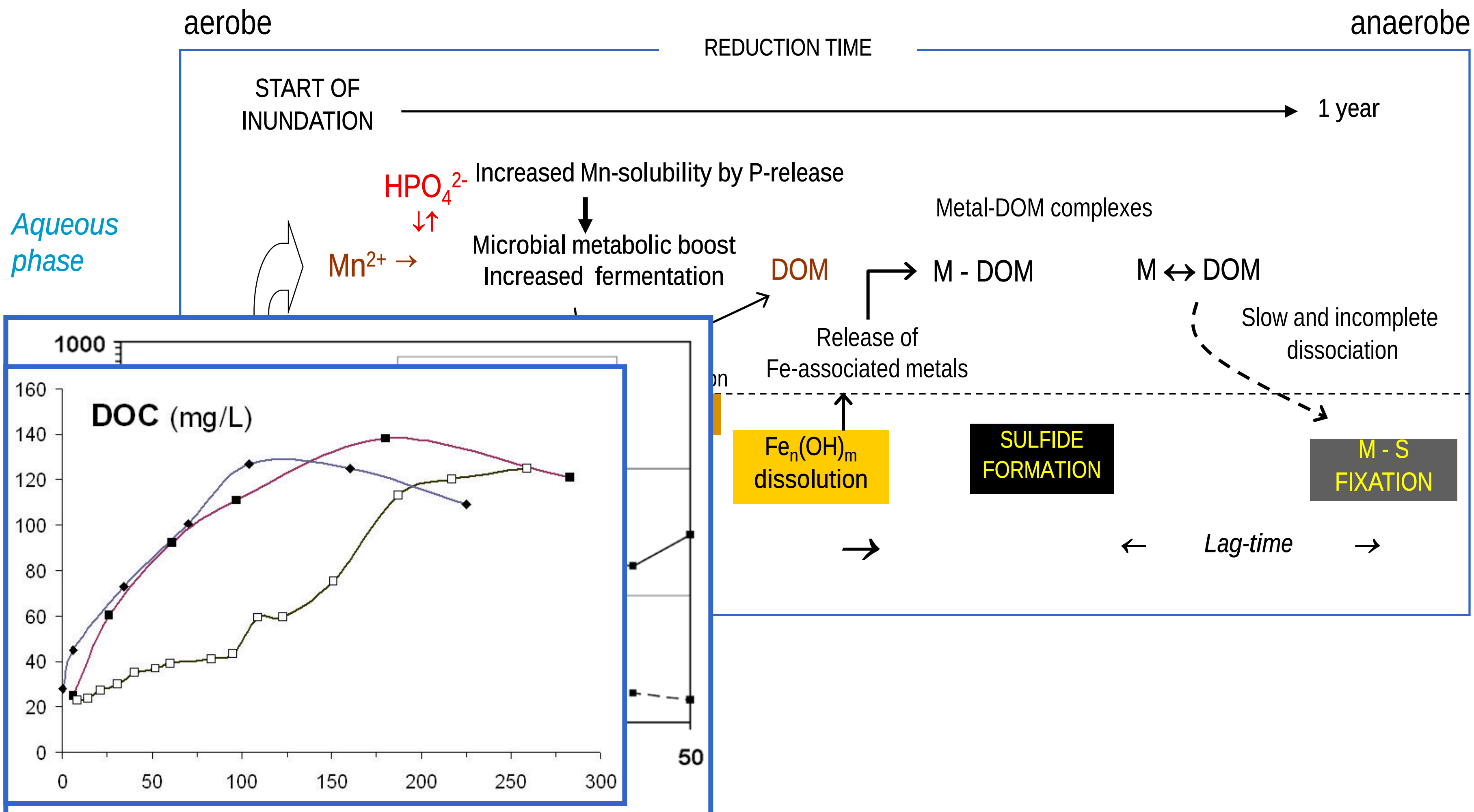
Sequence of processes



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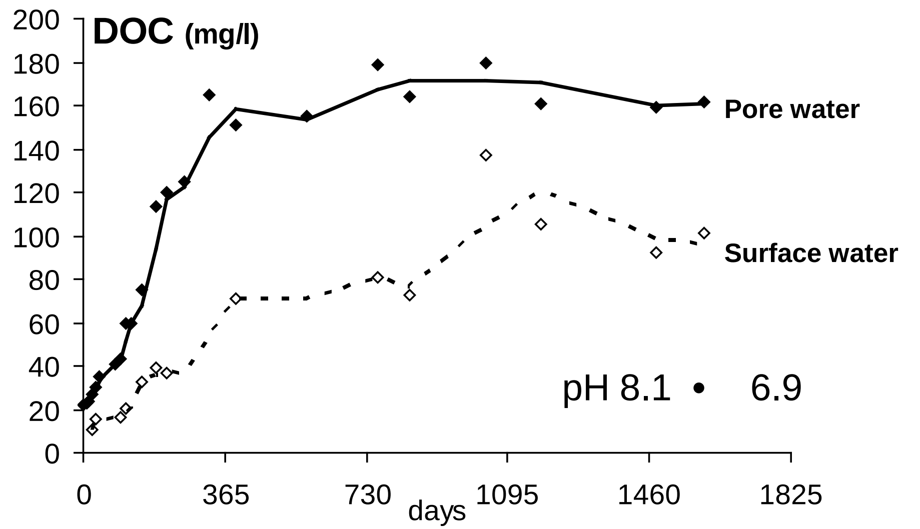
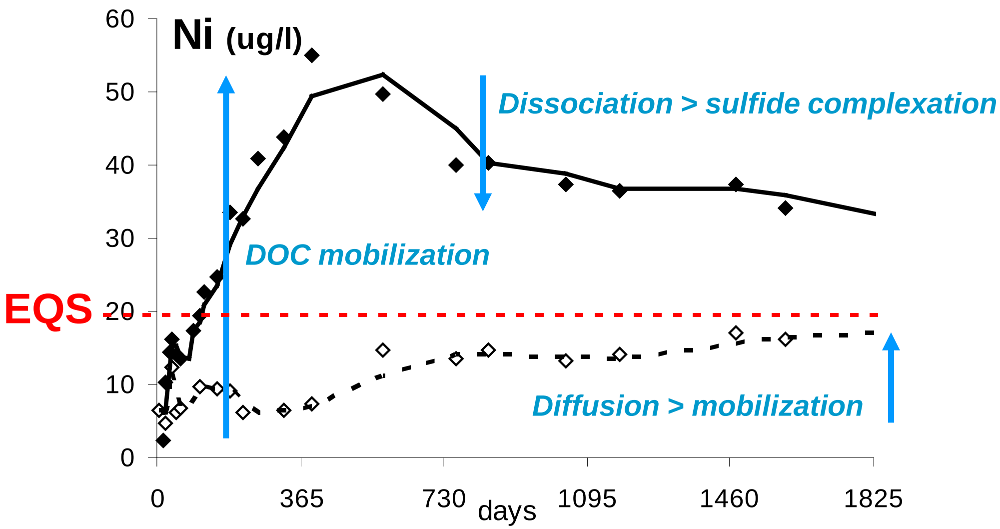
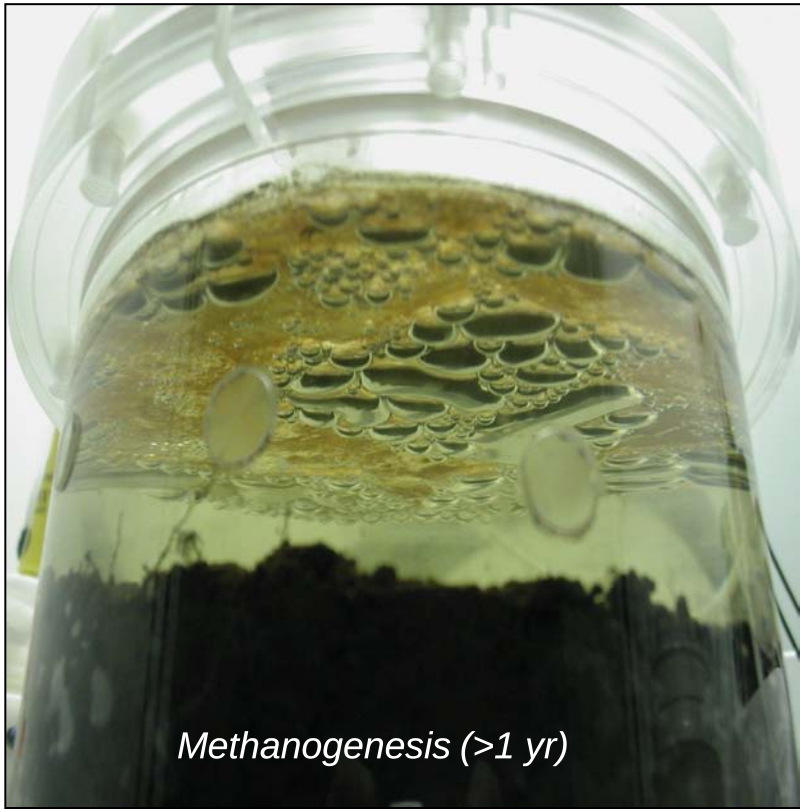
Long term reduction (5 yr)







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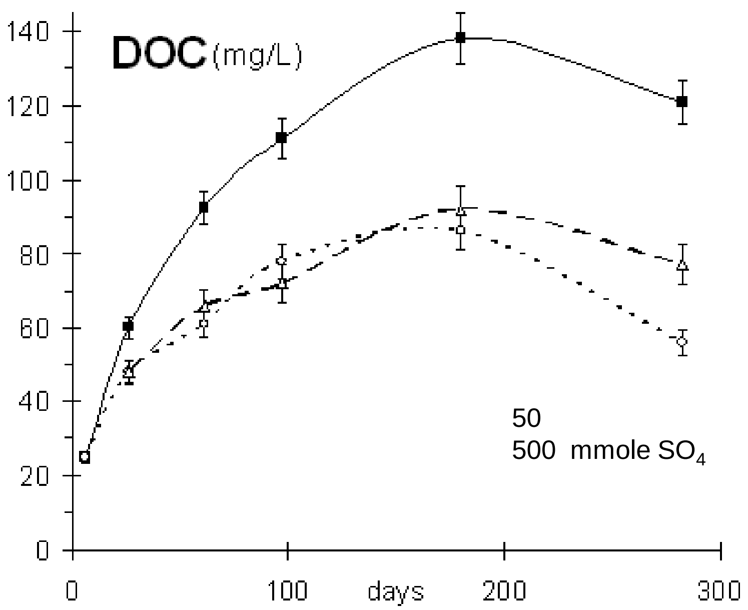
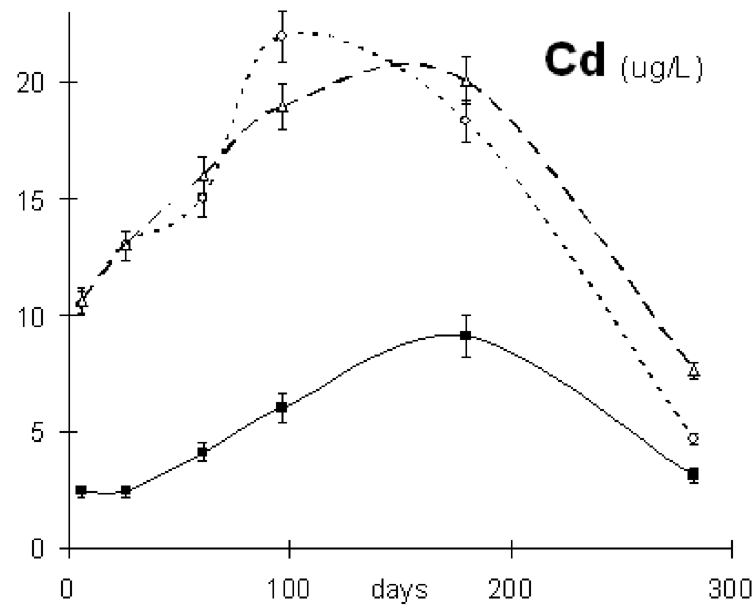
Enhanced sulfide precipitation by $CaSO_4$

SO_4^{2-} • sulfide • MetalSulfide precipitates

Can sulfide-pool be increased by adding an alternative source of SO_4^{2-} (gypsum)?



Ca competition + S binding



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Storage in depots

IJsseloog

Slufter

6 Depots:

Slufter
Amerikahaven
IJsseloog

} Aquatic origin ("sediments")

Moorlag
Asselt
Meers

} Terrestrial origin ("soils")

Measurements in storage sites

Table 1a Solid state characteristics of sediment cores collected from 6 storage sites

		Slufter	Amerika haven	IJsseloog	Moorlag	Asselt	Meers
Origin of sediment		Aquatic	Aquatic	Aquatic	Terrestrial	Terrestrial	Terrestrial
Depth	m	-12	-9	-8	-3	-5	-4
Dry wgt	%	44.0	77.2	84.3	65	79.3	59.2
<2μm	%	28.1	4.9	16.8	22.1	12.3	22.2
Org. C	%	4.3	8.4	9.5	1.5	3.6	4.4
$CaCO_3$	%	1.9	6.2	1.8	0.9	0.5	1.2
Fe	$g.kg^{-1}$	36.6	9.0	18.6	11	28.0	22.9
S	$g.kg^{-1}$	1.3	2.9	0.14	0.9	0.63	3.6
As	$mg.kg^{-1}$	23.0	6.7	6.6	27.3	15.5	33.3
Cd	$mg.kg^{-1}$	9.2	0.5	0.4	5.2	5.6	5.7
Cr	$mg.kg^{-1}$	151	20.0	15.2	105.2	38.9	120
Cu	$mg.kg^{-1}$	105	29.3	10.4	75.2	59.5	85.6
Ni	$mg.kg^{-1}$	43.8	9.7	16.6	37.8	25.4	27.7
Pb	$mg.kg^{-1}$	145	59.0	37.4	128	230	138
Zn	$mg.kg^{-1}$	807	368	103	466	758	724

Table 1b Dissolved characteristics of pore water collected from sediment cores (with standard deviations)

		Slufter	Amerika haven	IJsseloog	Moorlag	Asselt	Meers
pH	-	6.9	7.2	6.9	7.4	7.1	7.0
Eh	mV	-236	-127	-168	-169	-202	-244
DOC	$mg.l^{-1}$	$46^{\pm2}$	$43^{\pm1}$	$42^{\pm4}$	$168^{\pm3}$	$165^{\pm6}$	$215^{\pm7}$
NO3	$mg.l^{-1}$	$<0.04^{\pm0}$	$0.88^{\pm0.11}$	$0.22^{\pm0.08}$	$<0.04^{\pm0}$	$0.5^{\pm0.02}$	$<0.04^{\pm0}$
SO4	$mg.l^{-1}$	$0.3^{\pm0.02}$	$1.4^{\pm0.01}$	$0.65^{\pm0.02}$	$10.2^{\pm0.4}$	$0.4^{\pm0.06}$	$0.06^{\pm0}$
PO4	$mg.l^{-1}$	$<0.05^{\pm0}$	$1.8^{\pm0.2}$	$<0.05^{\pm0}$	$0.9^{\pm0.07}$	$0.05^{\pm0}$	$0.96^{\pm0.04}$
NH4	$mg.l^{-1}$	$184^{\pm11}$	$95^{\pm8}$	$0.5^{\pm0.2}$	$14^{\pm1}$	$9.3^{\pm0.3}$	$9^{\pm0.4}$
Ca	$mg.l^{-1}$	$375^{\pm14}$	$384^{\pm21}$	$217^{\pm17}$	$294^{\pm9}$	$333^{\pm16}$	$219^{\pm22}$
Fe	$mg.l^{-1}$	$60^{\pm4}$	$5^{\pm0.2}$	$1.2^{\pm0.2}$	$44^{\pm0}$	$27^{\pm8}$	$0.6^{\pm0.1}$
Mn	$mg.l^{-1}$	$7^{\pm0.2}$	$0.3^{\pm0.05}$	$4.4^{\pm0.1}$	$5.7^{\pm0.6}$	$21.7^{\pm0.8}$	$1.2^{\pm0.2}$
As	$\mu g/l^{-1}$	$30^{\pm4}$	$1^{\pm0.2}$	$7.3^{\pm1.2}$	$47^{\pm3}$	$100^{\pm12}$	$32^{\pm4}$
Cd	$\mu g/l^{-1}$	$0.26^{\pm0.04}$	$0.21^{\pm0.03}$	$0.20^{\pm0.01}$	$0.89^{\pm0.08}$	$0.98^{\pm0.12}$	$0.23^{\pm0.13}$
Cu	$\mu g/l^{-1}$	$3.8^{\pm0.2}$	$4.9^{\pm0.5}$	$7.5^{\pm0.3}$	$24^{\pm2}$	$26.3^{\pm1.8}$	$18.7^{\pm1.9}$
Cr	$\mu g/l^{-1}$	$90^{\pm11}$	$12^{\pm5}$	$5.1^{\pm1.3}$	$46^{\pm14}$	$6.1^{\pm0.9}$	$16^{\pm4}$
Ni	$\mu g/l^{-1}$	$13.4^{\pm1.2}$	$2.6^{\pm0.4}$	$20.1^{\pm1.8}$	$2.3^{\pm1.1}$	$49^{\pm4}$	$11.4^{\pm3.3}$
Pb	$\mu g/l^{-1}$	$1^{\pm0.6}$	$6.9^{\pm0.5}$	$1.2^{\pm0.8}$	$37^{\pm2.3}$	$23.2^{\pm2.2}$	$12.8^{\pm3.1}$
Zn	$\mu g/l^{-1}$	$37.4^{\pm5.1}$	$52.3^{\pm3.3}$	$22.9^{\pm3.1}$	$95^{\pm8}$	$266^{\pm22}$	$204^{\pm18}$

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Conclusions

- Reduction of aerobic soils releases essential nutrients Mn and P which facilitate microbial boost > production of DOC
- DOC retains heavy metals in pore water for prolonged periods of time (>1yr)
- Thermodynamic modelling seriously underestimes emission risks of heavy metals
- Addition of gypsum stimulates 1) coagulation of DOC
  2) formation of sulfides
  3) Ca^{2+} binding competition
- When storage or permanent inundation is considered, a distinction should be made between sediments of aquatic and terrestrial origin