

Pore water probing - Polyethersulfon is used as a semi-permeable polymer from which small tubes (1 mm diameter, 50 mm length) were manufactured. Polymer micropores discriminate colloidal fractions > 0.1 µm. This mesh size is impermeable to bacteria, so pore water that passes the polymer is sterile. A 0.5 mm fiberglass needle is mounted inside the probe for robustness. The probe is mounted on an impermeable HDPE tube (1 mm diameter, 20 mm length), so the area adjacent to the interior cell wall is avoided during probing.

By applying small under-pressure to the probes, pore water passes the polymer. Adhesive force along the fiberglass core guides the sample to the outlet.

Micro ion-exchange columns (MIC) - MICs are connected directly onto the outlet of the probes. In this way, ion exchange is practically instantaneous and is therefore executed at the reigning geochemical status of the probed sediment layer. To separate free metal ions from other forms of organic and inorganic metal ligands in solution,

use was made of styrene divinylbenzene copolymers containing paired iminodiacetate ions which act as chelating groups in binding positively charged metal ions. Preconditioned MICs (1 mm diameter, 20 mm length) were tested extensively on dimensions, preconditioning methods, metal affinities, contact time, and extraction procedures. Free metal ion activities $[M^{2+}]$ are quantified by step-wise, sequential extraction of the MICs.

Advantages

SOFIE® has at least eight major advantages over existing methods:

1. Experiments are carried out in undisturbed samples, including overlying surface water, which are taken with the body core of the cell.
2. Characteristic in-situ redox conditions and gradients are maintained.
3. Measurements can be carried out in 5 mm layer increments.
4. The method is non-destructive to the sample, so pore water can be monitored repeatedly.

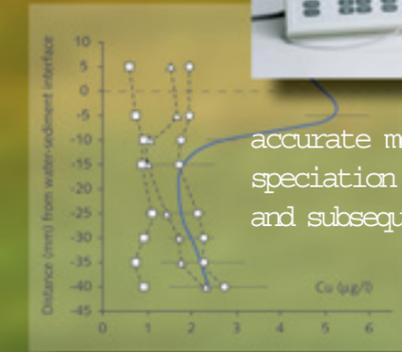
5. Pore water is micro-filtrated over 0.1 µm while sampling.
6. Free metal ions are separated from solution during sampling.
7. Bioassays are carried out simultaneously, thereby accounting for time dynamic exposure concentrations.
8. Aerobic or anaerobic conditions of the sample can be manipulated by flushing the atmospheric head space with a gas. In this way, various oxidation or reduction scenarios can be tested.

Future developments

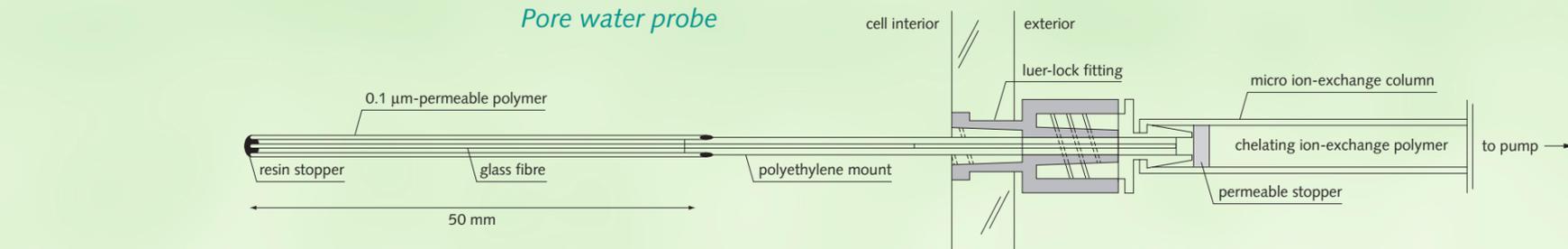
SOFIE® provides the necessary experimental tool to support, in a mechanistic way, environmental risk assessments of contaminants. Two-compartment cells are being developed to effectively carry out scenario experiments. Descriptive models are developed and improved to explain differences in bioavailability in various sediments. This knowledge may be incorporated in the derivation of specific quality criteria for sediments. Vink, J.P.M. *Environ. Sci. Technol.* 36/23, 2002.

SOFIE

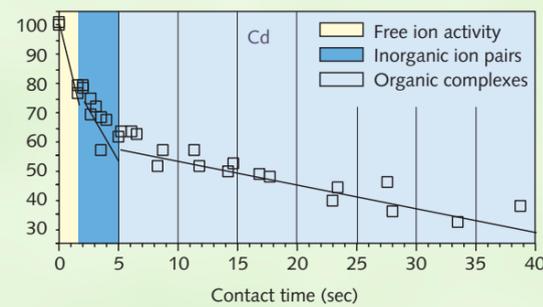
Sediment or Fauna Incubation Experiment



accurate measurement of chemical speciation in sediment pore water and subsequent uptake by organisms

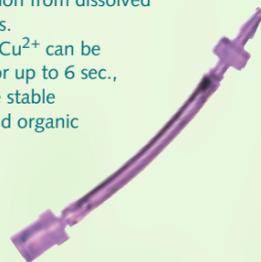


Remaining concentration (%) after column passage



Dissociation kinetics and contact time in MICs.

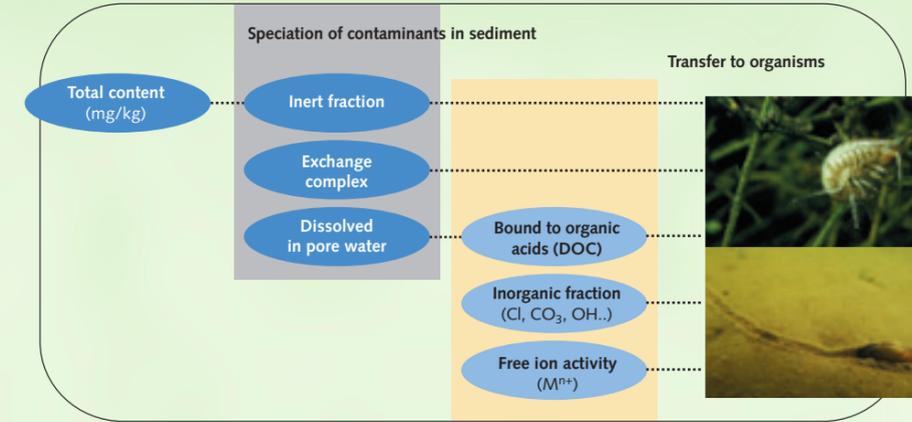
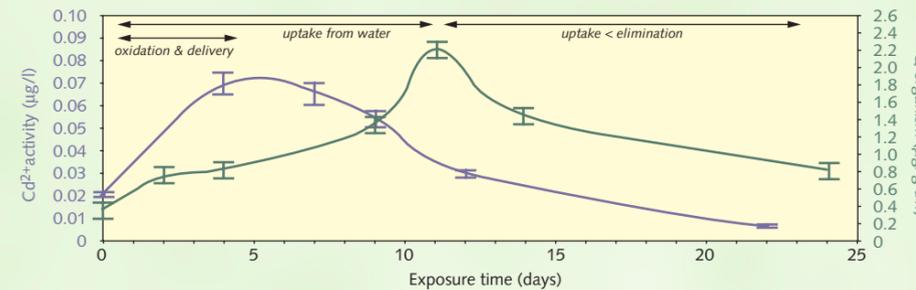
Free ions of cadmium $[Cd^{2+}]$ are exchanged against NH_4^+ ions in the micro column. This occurs within 2 seconds of contact time, and is rapidly followed by dissociation of inorganic ion pairs (e.g., $CdOH^+$, $CdCl_2$), and desorption from dissolved organic acids. In contrast, Cu^{2+} can be measured for up to 6 sec., due to more stable inorganic and organic complexes.



Chemical-biological interaction

Kinetic interaction between Cd^{2+} activities (blue line, left axis) and body concentration in oligochaetes *Limnodrilus* (green line, right axis). This simultaneous presentation of C_{act} and Q shows that interactions between chemical

availability and biological uptake actually takes place. Release to and simultaneous uptake from the water phase are, in terms of concentrations, antagonistic processes: body concentrations rise and free ion activities decline.



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What is SOFIE®?

SOFIE® (Sediment Or Fauna Incubation Experiment; patent nr. 02077121.8) is an experimental research tool or "cell", developed to study chemical speciation of heavy metals in pore water of natural, undisturbed sediments or water-sediment interfaces over time, while simultaneously conducting exposure tests (bioassays) with sediment-dwelling organisms. In this way, concentrations of chemical species are directly linked to accumulation by biota.

Why was it developed?

Sediments of rivers, river banks and flood plains are commonly characterized by elevated levels of heavy metals such as Cd, Cu, Cr, Ni, Pb, Zn. Organisms that inhabit these sediments are known to accumulate these metals, which, in turn, are passed on via the food web of the biotope.

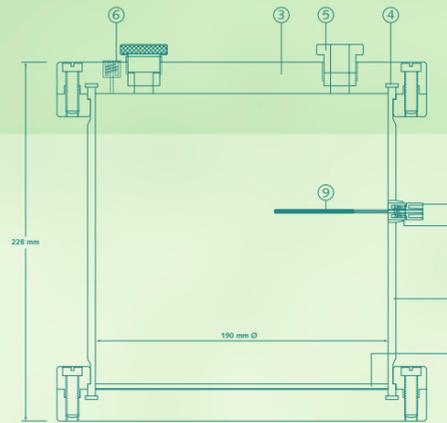
However, the development of well-defined quality criteria for (aquatic) sediments is seriously hindered mainly because of three reasons:

- 1) Laboratory exposure tests conducted with organisms (bioassays) do not adequately reflect the geochemical composition of the sediment in-situ, and do not link time-dynamic, chemical speciation with toxicological effects.
- 2) It is unclear which exposure and uptake routes contribute to accumulation in organisms and dictate the adverse effects.
- 3) There is disagreement over the relative contributions of various metal species to these effects.

In past years, surprisingly little has been achieved to link chemical speciation to bio-availability in natural systems. Beside some useful chemical models, very few techniques have become available to actually measure free ion activities, let alone to measure these periodically during exposure of organisms. The concept of free ion activity assumes that ions in the M^{n+} form, rather than total content or total dissolved, largely determine the toxicological or biological effect which is observed in organisms that are exposed to water or sediment containing heavy metals.

Experimenters that expose test organisms to contaminated water or water-sediment systems often assume constant external concentrations. It is highly questionable however to do so, since many processes may disrupt equilibrium conditions during the test. In those cases where time varying concentrations are recognized and/or modelled, speciation, again, is not accounted for. SOFIE® was developed to tackle these difficulties. For the first time, it is possible to quantify free metal ion activities in pore

water, repeatedly, and in a non-destructive manner to the sample. Bioassays are conducted simultaneously in the same setting. Sediment samples are taken in an undisturbed manner, including the overlying surface water. Gradients of metal species and micro/macro nutrients can be accurately measured over layer increments as low as 5 mm.



Method

Sampling - SOFIE® consists of a main body core, 200 mm radius, 200 mm height, which is used as a sampling device to obtain undisturbed sediment. Field samples are taken including the overlying surface water. After sampling, the core is closed at the bottom edge with a shutter plate and is mounted on a base socket. A top plate is attached, ensuring a gas-tight fitting with the body core with an internal silicone seal. The top plate has four gas tight connectors for electrodes to perform, for example, pH,

Eh, EC or O_2 measurements. These are inserted vertically in the sample. The sample does not leave the body core but is now part of the cell. The cell wall contains 15 gas tight connectors for probes.

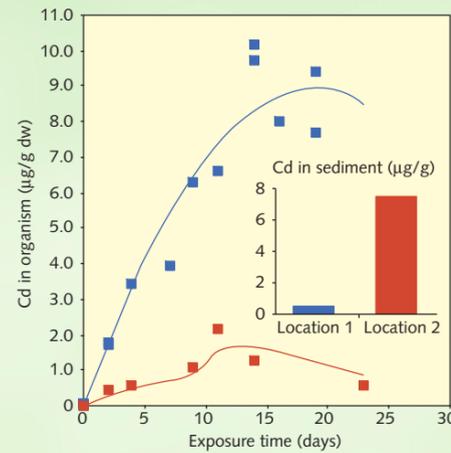
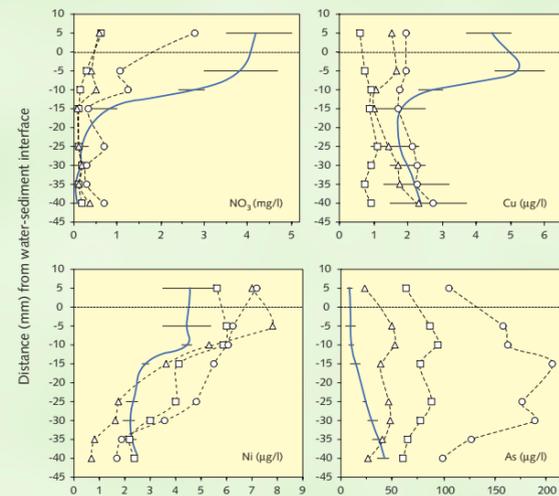
For experimental scenario purposes, aerobic or anaerobic conditions in the water-sediment system may be manipulated by flushing the atmospheric head space in the cell with gas (O_2 , N_2 , CO_2 or mixture) using a valve.

Time dynamic exposure concentrations

Examples of time-depth dynamic concentrations over a water-sediment interface of a redox sensitive macronutrient (top left), an essential metal (top right), a non-essential metal (bottom left) and a non-metal (bottom right). The blue solid line represents the mean steady state concentration.

The dotted lines are concentrations at 7 (triangle), 9 (square) and 13 (circle) days after introduction of oligochaetes to the system. These organisms oxidize their environment and therefore directly affect the chemical conditions, i.e. speciation.

In many cases, uptake kinetics of metals by organisms is inhibited by the supply rate from the sediment.

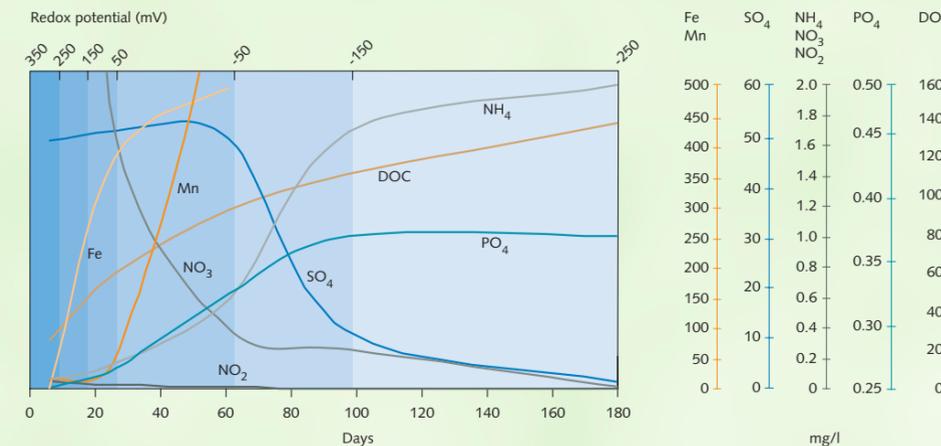


The chemical paradox

Oligochaetes that were exposed to undisturbed sediment and its surface water from two different locations show seemingly counterintuitive uptake behaviour, at least when looking at total amounts in the sediment. In this case, this phenomenon could be explained by the bioavailable fractions, which showed opposite trends compared to total sediment contents. Concentrations of free ion activities (Cd^{2+}) proved to be the best descriptor for uptake.

Redox scenarios

Example of an inundation experiment with a river flood plain sediment. Redox dynamic (upper x-axis) and time dynamic (lower x-axis) concentrations of Fe(II), Mn(II), nitrite, nitrate, ammonium, sulfate, phosphate and dissolved organic carbon (DOC) in reducing pore water can accurately be studied, and provide useful information on transformation processes and rates.



Differences in uptake: amount and rate

Exposed to the same sediment, chironomids (solid marker) accumulate cadmium faster and in larger amounts than the oligochaete *Limnodrilus* (open marker). After 15 days of exposure, chironomids even face lethal body burdens, possibly due to a low rate of elimination.

