

An apparatus for temporal sampling without air contact of pore water from swamp sediments

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Nielsen, S. and Postma, D.: An apparatus for temporal sampling without air contact of pore water from swamp sediments. *Danm. geol. Unders., Årbog 1979*, : 31-39, København, 1. december 1980.

An apparatus has been designed which allows temporal sampling without air contact of pore water from swamp sediments. The system consists of a PVC filterprobe containing a glassfiber filter, a Pyrex glass sampling system and an arrangement for pressure filtration through a membrane filter. Sample recovery occurs in a N₂-filled glove box in which analyses sensitive to oxidation are carried out. The field operation of the system is described, and practical problems that may occur are dealt with. The preliminary results could be reproduced and shows little data scatter.

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In most geochemical studies, the pore water is extracted from the sediment by squeezing or centrifugation. However, these methods only allow temporal sampling when the sediments are homogeneous such as those found mostly in marine and lake sediments (for example Thorstenson and Mackenzie 1974; Matisoff et al. 1975).

For studying seasonal variations of oxidation/reduction processes in the pyrite and siderite containing swamp sediments of the Skjernå delta (Jutland, Denmark), pore water extraction by squeezing or centrifugation is not suitable. This is due to the fact that the sediments here are far from homogeneous, and sampling at exactly the same spot is therefore desirable. This can be accomplished by permanent installation of filters in the sediments, from which samples are drawn by suction. Sampling by suction always involves a risk of degassing, particularly of CO₂, which may lead to erroneously high pH measurements. It is a further complication that many samples from deeper layers contain high Fe²⁺ concentrations at a near neutral pH. As the oxidation of Fe(II) is extremely fast at near neutral pH (Stumm and Lee 1961), great care must be taken to prevent the admittance of air of the sample (Troup et al. 1974).

Precipitation of Fe(III) oxyhydroxides in the sample leads to erratic phosphate analyses (Bray et al. 1973) and may also affect alkalinity determinations. Hydrogen sulfide is present in some of the samples, and here there is a risk of degassing as well as of oxidation.

Oxidation during sampling and analysis should thus be rigorously prevented, while degassing should be limited to an absolute minimum. Finally, as the sampling rate proved to be low at several locations, sampling times of up to 12 hours should be permitted.

Through experimentation with different equipment, a system for temporal sampling of pore water by suction has been developed which satisfies the requirements for minimal disturbance of the sediment layering, no admittance of air and minimal degassing. The system consists of a filterprobe for permanent installation in the sediment, a portable sampling system, and an arrangement for subsequent membrane filtration and immediate analyses without air contact.

Apparatus

The filterprobes (fig. 1). The filterprobe is constructed in PVC and consists of a filterhead (A), lengths of one meter piping (B), pipe connections (C) and a terminal cap (D). The filterhead is pointed and perforated with approximately 50 holes, 3 mm Ø, drilled obliquely in order to prevent clogging when inserting the probes into the sediment. The head can be opened for attaching a glassfiber filtertube (E) (Whatman, size A1, 60 × 12 mm, poresize 2 µm).

The sample is drawn from the filterhead through flexible PVC tubing (F) (3 mm i.d.) which passes through the piping, pipe connections and terminal cap. The end of the tubing is equipped with a brass tubefitting (G) and a plug for sealing between sampling (Kuhnke screwed tube joint, sleeve and plug).

The sampling system (fig. 2). The sampling system is constructed in Pyrex glass with ground joints and stop cocks. It consists of a sample flask (A) (250 ml) equipped with a gas washing head with a stop cock (B) in the inlet and a vacuum reservoir flask (C) (1000 ml) that is closed with a 3-way stop cock (D). The sample flask and the vacuum reservoir are connected by flexible PVC tubing. Flexible PVC tubing is connected to the inlet of the sample flask with brass fittings.

In this investigation we use 5 filterprobes at each location, therefore 5 sampling systems are placed together in a plywood box.

The filtration system (fig. 3). The samples are filtrated by using a stainless steel pressure filtration cartridge (E) equipped with a 2-way switching valve

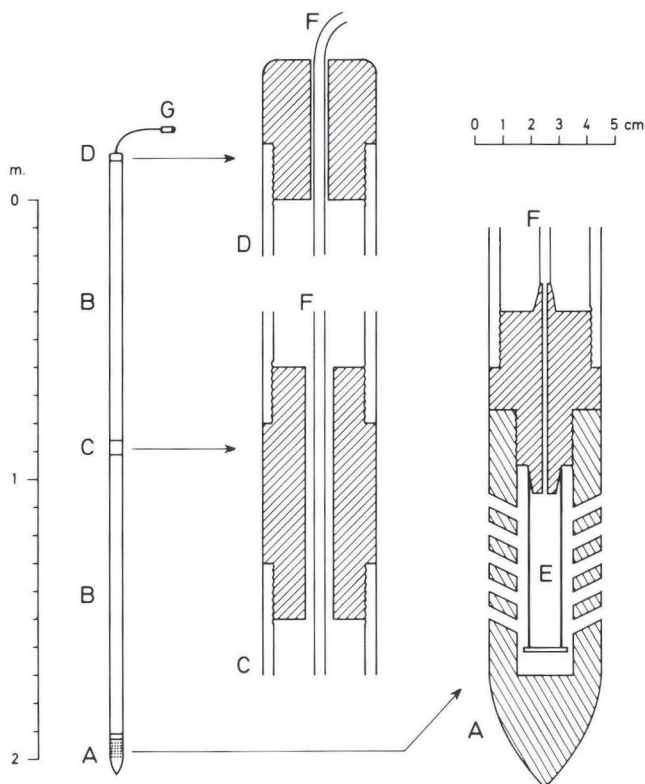


Fig. 1. The filterprobes. A: Filterhead. B: Piping. C: Pipe connection. D: Terminal cap. E: Filtertube. F: Flexible sample tubing. G: Tube fitting.

(F) at the inlet, and a toggle valve (G) for air venting and overflow. The outlet is led through a 2-way stop cock (H) into a N_2 -filled glove box. Analyses which are sensitive to oxidation are carried out in the glove box.

Operation

The filterprobes are installed by pre-drilling with a Hiller sampler (West 1968) of slightly smaller diameter than the filterprobe until about one meter above the desired sampling depth. The filterprobe is subsequently placed in the hole and pushed down to filter depth.

Before sampling, the PVC tubing from the filterprobes is connected to an evacuated glass flask in order to remove the water accumulated in the filterhead and the tubing (approximately 40 ml).

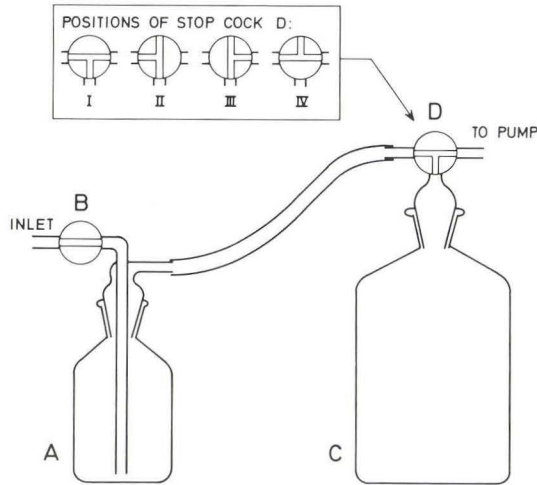


Fig. 2. The sampling system. A: Sample flask. B: Stop cock. C: Vacuum reservoir. D: 3-way stop cock.

A filterprobe is then connected to the sampling system, which is pre-flushed with N_2 . The sampling system is evacuated to 200 mm Hg using a portable peristaltic pump (stop cock B closed, stop cock D in position I). The system is checked for leaks after a few minutes by using a manometer on the peristaltic pump.

After moving stop cock D to position II, the sampling is started by opening stop cock B, and the equipment is left overnight. Nighttime sampling is preferred since strong solar irradiation may cause photoreduction of Fe(III) compounds (Stumm and Morgan 1970). Even though the sample flasks are protected from light as they are mounted in plywood boxes, some light may penetrate the PVC tubing which connects the sample flasks with the filterprobes. Connection tubing should therefore be kept as short as possible.

When sampling is terminated the following morning, the sampling system is disconnected from the filterprobes (B closed, D in position III), and the samples are brought to a van equipped as field laboratory.

The sample flask is connected to the filtration system as shown in fig. 3. Membrane filters with a poresize of $0.1 \mu m$ are used since Kennedy et al. (1974) showed that these filters yield more correct results than $0.45 \mu m$ filters for dissolved Fe and Al, and show little tendency for clogging.

Before each sample is introduced into the filter cartridge, the cartridge is fitted with a new membrane filter and flushed with N_2 (G closed, F in position I, H in position I).

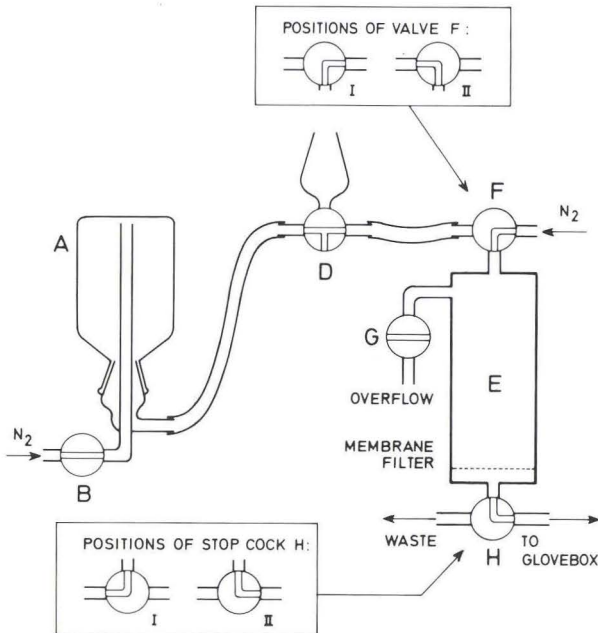


Fig. 3. The filtration system. A: Sample flask. B: Stop cock. D: 3-way stop cock. E: Filtration cartridge. F: 2-way valve. G: Toggle valve. H: 2-way stop cock.

The sample is then transferred to the filter cartridge by applying a gentle N_2 -pressure through stop cock B into the inverted sample flask (G open, F in position II, D in position IV). N_2 -pressure of about 2 atmospheres is applied to the filter cartridge, and the sample is recovered in a N_2 -filled glove box after discarding the first 10 ml (G closed, F in position I, H in position II).

In the glove box, pH is measured, alkalinity determined and reagents added for spectrophotometric determination of H_2S , Fe^{2+} and PO_4-P . The analytical procedures have been described by Postma (1980).

Filterprobes have been installed at 3 locations in the Skjernå delta (Jutland, Denmark). The sediments vary from wood peat to reed peat with a significant content of silt and clay. At each locality filterprobes have been placed at depths of 0.5, 1.0, 1.5, 2.0 and 2.5 m below the surface.

The filterprobes at a depth of 0.5 m were above the groundwater level during the summer months and could not be sampled. At a greater depth, sample recovery in most cases exceeded the volume of the sample flask (250 ml) by 250–500 ml. As the inlet of the sample flask is placed at its bottom, the content of the sample flask will be flushed with at least its own volume. This

minimizes the contact area between the sample and the overlying gas phase, and the risk of degassing the sample is hereby reduced.

Several problems had to be dealt with during field operation. Some probes, placed in clay-rich sediments, showed a sampling rate too slow for filling the sample flasks overnight. The sampling rate was improved by attaching quartz glass wool to the entrance holes of the filterhead. The glass wool served as a »wick« and increased the contact area with the sediment, ensuring a sufficiently high sampling rate.

In earlier tests, attempts were made to pump directly on the filterprobes through a hypodermic needle to a vial with silicone rubber septum. The N₂-filled vial was then evacuated through another hypodermic needle connected to the peristaltic pump. This method had to be abandoned due to an inacceptably low sampling rate.

Attempts were also made at placing membrane filters in the sampling system between the filterprobes and the sample flask. However, the membrane filters, when wet, proved to be impermeable to small gas bubbles. After accumulation of sufficient bubbles at the filter surface, the vacuum in the sampling system was not transmitted to the filterprobe.

Operation during the winter proved to be a problem due to the freezing of water in the sample tubing. The tubing and the sampling system above ground were kept slightly over the freezing point by insulating with glass wool bats and heating with a small catalytic oven. Within the upper end of the filterprobes, the water in the sample tubing was thawed by removing the terminal caps of the PVC outer tubes and lowering a U-formed piece of copper tubing. Hot water was circulated through the copper tubing by a peristaltic pump, and the frozen water was thawed within a few minutes. After discarding the first volume the filterprobes were connected to the sampling system, and no further problems were encountered.

A somewhat unexpected problem was an invasion of larva of sawfly (*Tenthredinidae*, *selandriini*) in the PVC tubing of the filterprobes between sampling periods. Even though the tubing was sealed at the end, the larva proved to be capable of rasping through the soft tubing. The problem was solved by protecting the tubing with hard plastic caps.

Discussion

The features of the equipment can be illustrated with some preliminary results, collected over a period of 8 months.

Measurements of pH at one locality are shown in fig. 4. At depths of 0.5 and 1.0 m the pH varies considerably as would be expected, since in this zone

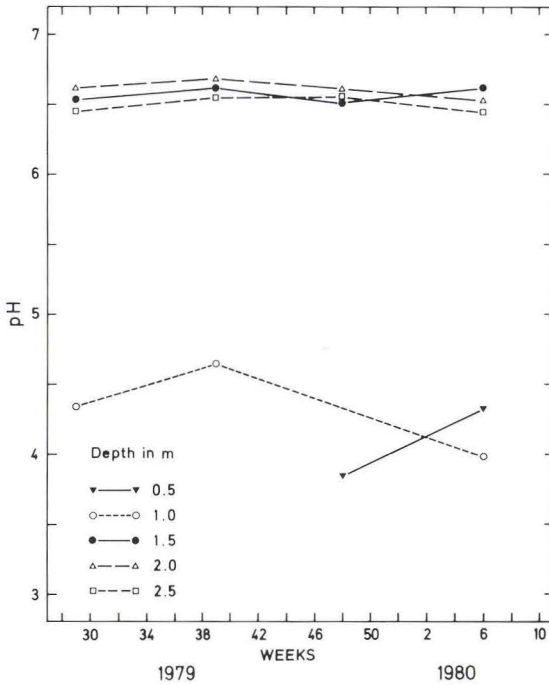


Fig. 4. The seasonal variation of pH at different depths. Data collected over a period of 8 months in Skjernå delta swamp sediments (locality C).

the redox conditions show seasonal variation. However, at a depth of 1.5 m a very constant pH is found, which indicates that no sample contamination from higher levels occurs. At depths of 1.5, 2.0 and 2.5 m the pH variations at each level are well within a range of 0.2 pH units. This indicates that sampling procedures can be reproduced.

Some results for Fe^{2+} concentrations at another locality are displayed in fig. 5. The extremely high Fe^{2+} concentrations at depths of 1.0 and 1.5 m are related to pyrite oxidation. At 1.5 m the corresponding pH ranges from 5.38 to 5.75, while at 2.5 m a still high Fe^{2+} concentration (0.72–0.88 mM) is found at a pH range of 6.32 to 6.63. Considering that the oxidation rate of Fe^{2+} at this pH is very fast (Stumm and Lee 1961), the measured Fe^{2+} concentrations are unlikely to be reproducible if sample oxidation takes place.

Compared with other descriptions of apparatus for sampling by suction from soil sediments, the reported apparatus has several advantages. First, the filterprobes do not contain ceramic cups (Wagner 1962), since it has been shown that they may produce erratic results for phosphate and cations

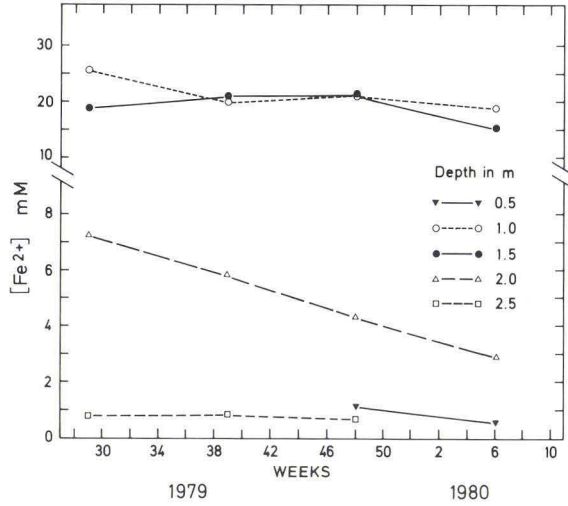


Fig. 5. The seasonal variation of Fe²⁺ concentration at different depths. Data collected over a period of 8 months in Skjernå delta swamp sediments (locality B).

(Stevenson 1978; Quin and Forsythe 1976). Secondly, there is no need for pre-drilling down to sample depth with subsequent backfilling as in other apparatus (Stevenson 1978; Quin and Forsythe 1976; van Breemen 1976), and this reduces the risk of sample contamination. The present instrumentation also compares favourably to the apparatus of Quin and Forsythe (1976) due to a significantly lower risk of degassing and a much lower sample volume in the filterprobe. Finally, the supplemental instrumentation described here enables sampling and analysis without air contact, which is of major importance when dealing with anoxic sediments.

Conclusion

The apparatus described in this report has in practice proved to be suitable for temporal sampling of pore water without air contact. Furthermore, it has several advantages compared to the apparatus described earlier for similar purposes.

Acknowledgements. For valuable assistance during the evaluation and testing of the apparatus in the field, we would like to thank laboratory technician Ellen Zimmer Hansen. Furthermore, we would like to thank tool maker Peder Skogstad for fruitful discussions during the manufacturing of the filterprobes, and the staff of the Geochemical Department for performing the laboratory analyses. A useful review of the manuscript by Jens Jacobsen is kindly acknowledged. The project has benefited from a grant of the Danish Natural Science Research Council.

Dansk sammendrag

Der er udviklet et apparatur, som gør det muligt at udtage porevandsprøver fra forskellige niveauer i inhomogene mosesedimenter. Apparaturets udformning tilstræber prøvetagning uden kontakt med luftens ilt og med en minimal afgasning af prøven.

Prøven udtages fra et PVC-rør, hvori der er monteret et glasfiberfilter (fig. 1). Da røret kan forblive i sedimentet er det muligt at følge sæsonvariationer af kemiske parametre. Prøven bliver opsamlet i Pyrex-glas flasker (fig. 2) og trykfiltreret ind i en N₂-fyldt handskekasse gennem et membranfilter (fig. 3). I handskekassen udføres analyser som kan påvirkes af oxidation.

Anvendelsen af apparaturet i felten er beskrevet, og problemer som kan opstå bliver behandlet. Nogle foreløbige resultater vist i fig. 4 og 5 tyder på god reproducerbarhed og lille spredning.

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