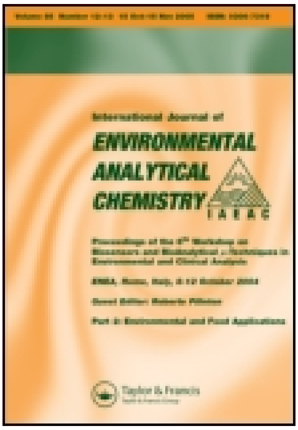
This article was downloaded by: [East Carolina University]
On: 20 February 2012, At: 00:15
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

An improved datalogger and novel probes for continuous redox measurements in wetlands

Michel Vorenhout [a] [b], Harm G. van der Geest [c] & Ellard R. Hunting [c]

[a] MVH Consult, Beukenrode 19, 2317 BD Leiden, The Netherlands

[b] Institute for Geo- and Bioarchaeology, VU University Amsterdam, De Boelelaan 1085, 1081 HV Amsterdam, The Netherlands

[c] Department of Aquatic Ecology and Ecotoxicology, University of Amsterdam, Science Park 904, 1098 XH, Amsterdam, The Netherlands

Available online: 16 May 2011

To cite this article: Michel Vorenhout, Harm G. van der Geest & Ellard R. Hunting (2011): An improved datalogger and novel probes for continuous redox measurements in wetlands, International Journal of Environmental Analytical Chemistry, 91:7-8, 801-810

To link to this article: http://dx.doi.org/10.1080/03067319.2010.535123

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [East Carolina University] at 00:15 20 February 2012

Intern. J. Environ. Anal. Chem.
Vol. 91, Nos. 7–8, 15 June–15 July 2011, 801–810

Taylor & Francis
Taylor & Francis Group

An improved datalogger and novel probes for continuous redox measurements in wetlands

Michel Vorenhout[a,b]*, Harm G. van der Geest[c] and Ellard R. Hunting[c]

[a]*MVH Consult, Beukenrode 19, 2317 BD Leiden, The Netherlands;* [b]*Institute for Geo- and Bioarchaeology, VU University Amsterdam, De Boelelaan 1085, 1081 HV Amsterdam, The Netherlands;* [c]*Department of Aquatic Ecology and Ecotoxicology, University of Amsterdam, Science Park 904, 1098 XH, Amsterdam, The Netherlands*

(*Received 15 January 2010; final version received 11 October 2010*)

In soils and sediments, the redox potential (Eh) is an important parameter controlling the persistence of many organic and inorganic compounds. Especially in wetlands, fluctuations in redox potential values can be very large and depth dependent. For this reason, field deployable logging systems have previously been developed, yet these systems were limited in several aspects. Here we report the development of an improved multichannel datalogger (HYPNOS) and two novel probes for continuous monitoring of Eh profiles, and briefly illustrate the potential applications. The combination of a multichannel logger with different types of probes allows characterisation of spatial and temporal variability of redox potential in relation to environmental and ecological parameters, and we expect this will greatly enhance our knowledge of the functioning of wetlands.

Keywords: wetland functioning; biogeochemistry; redox measurements

Downloaded by [East Carolina University] at 00:15 20 February 2012

1. Introduction

In soils and sediments, the redox potential (Eh) is an important parameter controlling the persistence of many organic and inorganic compounds [1]. The redox potential is a value for the ability of a medium to take up or release electrons [2]. The redox potential, given in mV, ranges from approximately +800 mV to −600 mV, with lower values for reducing conditions [3]. Its value can be determined by a precise voltage measurement between an inert probe, and a reference. In many cases, a pH meter is used, together with a single platinum-tipped probe and an Ag/AgCl reference probe [4]. Recent research shows that, especially in wetlands, fluctuations in redox potential values can be very large and depth dependent [5–7]. Previous work has shown that daily variations of 200 mV are not exceptional and can occur within hours [7]. These short-term variations cannot be measured using the manual measurement methods.

Seasonal variation is expected to occur in wetlands owing to temperature changes, different activities of microbiota and variations in the abiotic environment [8,9]. These variations in time are often overlooked in studies, when the redox potential is only described by making single-point measurements. Single-point measurements, for instance by installing one probe at one depth in a wetland soil and performing the measurement

*Corresponding author. Email: m.vorenhout@mvhconsult.nl

ISSN 0306–7319 print/ISSN 1029–0397 online
© 2011 Taylor & Francis
DOI: 10.1080/03067319.2010.535123
http://www.informaworld.com

with a pH meter [4], will give short-term information, but are influenced strongly by local and temporal conditions. Many authors report about the drifts in Eh measurements [4], or the significant difficulty in obtaining standardised readings [10].

A solution to these difficulties is to install a permanent measuring device, that can take automated readings from multiple locations. Also, probes should be used that can be installed at different depths, at multiple locations. Previously, we developed the datalogger Hypnos 2.0 for continuous redox potential and temperature measurements. It was developed to enable measurements at two locations, at various depths in the soil and sediments without disturbance of the site. The Hypnos 2.0 datalogger was field deployable, relatively cheap, and run autonomous on batteries [7]. However, critical issues remained the relative low impedance, limited number of channels, the requirement of a computer to operate the logger and a lack of probes that could measure differences in redox potentials at a small (below centimetre) scale.

Here we report the development of an improved multichannel data logger and complementary novel redox potential probes, and illustrate potential applications under both natural and laboratory conditions.

Downloaded by [East Carolina University] at 00:15 20 February 2012

2. Experimental

2.1 *Datalogger*

An overview of the improved datalogger (HYPNOS III) properties is provided in Table 1. The logger has an impedance for each separated redox channel of over 10 TOhm each, providing extreme stable measurement conditions and removing any drift from the measurements. This extreme impedance, the resistance against flow of current, is needed to remove any influence of the sediment by the probes. With a lower impedance of the measuring device, a small current can occur between the reference probe and the measuring probe. Hence, the actual measurement would generate reduction and/or oxidation processes in the medium under study by alteration of the number of electrons in the medium. This is also suggested by Rabenhorst [11] who found that redox potentials are more stable with higher impedances for the measurement channels.

In many cases, the spatial variability of the redox conditions in soils and sediments is the subject of study. This means that multiple probes will need to be installed and more loggers will be needed. In these cases, one datalogger can serve as a central measurement

Table 1. Technical properties HYPNOS III.

Property	Value	Remarks
Redox channels	48	
Temperature channels	50	Digital temperatures
Storage medium	SD card, RS232 output	1 Gb SD card
Datapoints	$>$11 million	Shared for both redox and temperature
Impedance per redox channel	$>$1 TOhm	Necessary for stable operation and low battery consumption
Sampling interval	1–60 mins	In logical steps

Downloaded by [East Carolina University] at 00:15 20 February 2012

device for a large sampling area if cable lengths to the probes can be large enough. The cost reduction by using one logger can be large. The maximum cable length for the HYPNOS datalogger was tested by adding various lengths of cable between the logger and a probe (probes are described later). The measurements of the redox potential in standard solutions was not influenced by lengths of up to 100 m (data not shown). Although we did not measure electric induction, we expect that Eh measurements remain unaffected owing to the high impedance and absence of current for most of the time.

Data collection from the HYPNOS is done by downloading the data on flash memory (SD cards). These SD cards are easy to replace in all weather conditions, so data can be safely transported. The use of the SD cards removes the need to connect a laptop to the datalogger, but also removes the option to program the datalogger with a portable computer like the previous version. Another option is the RS232 connection, which will provide raw data during measurement. A user menu was added to the HYPNOS datalogger, which allows for easy programming. Options that can be set from the menu include sampling interval and number of redox channels to use. The menu also allows for easy programming of temperature sensors.

The datalogger can be connected to up to 48 redox sensors and 50 temperature sensors. Temperature sensors should be included in the measurement as temperature is (a) needed for full calculation of the redox potential and (b) of potential influence on the soil processes involved in reduction of soil [12]. The redox potential measurement is performed by measuring the potential between the inert metal tip, and a reference electrode. In the presented studies, a Ag/AgCl reference probe QM710X from Q–I–S was used. This general-purpose probe is readily available.

All devices are waterproof and electronically autonomous. The datalogger runs on a 9-V battery providing a life span of at least one year at a sampling interval of 6 min (U9VL by Ultralife).

2.2 *Probes*

The redox potential is measured with an inert material that can conduct current. It has to be inert so there is no influence from the environment on the functioning of the probe. In most cases, the inert metal platinum is chosen. Depending on the probe's design, also other inert materials (e.g. gold) can be used. Below two different probe designs will be described: (a) a fibreglass probe with platinum sensor tips for large scale measurements under field conditions and (b) a probe made of printed circuit board with gold-plated tips for small-scale laboratory measurements. Of both probe types, the first applications will be described.

2.2.1 *Deep applications (meter scale)*

The first probe design consists of a fibreglass shell, equipped with platinum wire tips that are partly buried in the fibreglass (PaleoTerra, Amsterdam, The Netherlands) (Figure 1). The probe has a diameter of 8 mm with a small point at the end. It is very well suited for deep deployment owing to the strength of the material. Temperature sensors can be added to the probe (Model DS18B20, +/−0.5°C accuracy from 10°C to 85°C; Dallas Semiconductor, Dallas, TX). The probe can be extended by adding lengths of fibreglass or similar material.

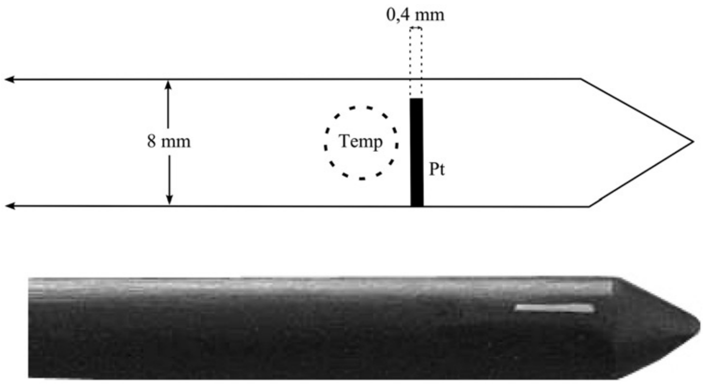


Figure 1. Fibreglass probe design and photographic details. The Pt wire is located on the side of the probe, lowered into the fibreglass. Average length: 12 mm. Temp: Inner temperature sensor. Not shown: cable connections inside.

Downloaded by [East Carolina University] at 00:15 20 February 2012

Probes should be placed in undisturbed soil. This will minimise the time needed for readings to become stable. A pushing device is available for placement of the fibreglass probes (PaleoTerra, Amsterdam, The Netherlands). In that case, the probes need to be extended in length with the same diameter fibreglass. The extension has been tested to lengths of 3 m. Probes have been placed at depths as great as 15 m below surface level. These great depths require some predrilling of a small diameter hole. The tip of the probe is still pushed into the soil. This way it is ensured that the deeper soil near the measuring tip is as undisturbed as possible. After placement, the hole is refilled with original soil material.

Preliminary results of two different field campaigns will be presented here. First, the HYPNOS datalogger was installed at site KW12 at the Araihazar village in Bangladesh [13]. This site (previously described by Radloff *et al.* [14] as site K240) has a sandy aquifer with a fluctuating groundwater table. The groundwater table can be as low as 6 m below surface, or reach surface level during storm events. The site shows a high occurrence of arsenic (As) species in groundwater and soil. The redox behaviour of the As species is well described [15] but the local fluctuations in redox potential at greater depths in depth and time had not been monitored. The HYPNOS system, together with an array of eight probes at various depths were installed in the spring of 2008. Glass fibre redox probes were installed to a depth of up to 8 m below surface. The probes were each equipped with one platinum tip, and one temperature sensor (Figure 1). The probes were extended with fibreglass, for the depths up to 3 m, and with PVC tubing for deeper allocations.

In the second field campaign, fibreglass probes were installed in a site in the Northern part of the Netherlands, Peizermade. The site consisted of a wet grassland area with local soil anomalies that are human made and of archaeological importance. The anomalies consist of a clay soil layer that was deposited on top of natural occurring peat as part of home building [16]. The redox potential is a proxy for the intrusion of oxygen in the soil layers and was monitored in order to gain insight in degradation processes of the peat layer and organic archaeological remains.

Fibreglass probes were installed at depths between 19 and 119 cm below soil surface in April 2009 and the redox potential was recorded every 15 min using a HYPNOS III logger.

Downloaded by [East Carolina University] at 00:15 20 February 2012

2.2.2 *Shallow applications (millimetre scale)*

The second probe was designed to study the variations in redox potential at below centimetre scales over time, for example to gain insight in biogeochemical processes and functioning of the top layers of sediments, measurements in and under biofilms, or to describe redox sensitive processes in the root zone of plants. These types of measurements require a probe with multiple redox measurement points at distances of about 1 mm. To this purpose we have developed a probe made of printed circuit board with gold-plated contacts (each 3×0.5 mm) that can be positioned in any required spatial arrangement. The first prototype of this microelectrode consisted of eight gold-plated sensortips, each 1 mm apart (Figure 2). Preliminary evaluation suggests that the microelectrodes can be used repetitively up to six months before measurements become affected by the development of an organic coating on the electrodes.

To illustrate the potential use of the microelectrode, we measured changes in the redox conditions in the top layer of an aquatic sediment induced by biomechanical reworking of the sediment by the aquatic oligochaete *Tubifex* spp. To this purpose, organic rich sediment was collected in the field (to include natural bacterial communities and organic matter) and transported to the laboratory. The collected sediments were mixed with clean river sand (ignited quartz; grain size 0.5–1.0 mm; ratio 1 : 5) and homogenised prior to experimentation. The experimental unit was made of plastic cores (2.5 cm diameter) that were incubated at 20°C under continuous light conditions (40 μmol photons $m^{-2} s^{-1}$) and overlying water (Dutch Standard Water) was continuously oxygenated. Next to a control, in which the process of redox stratification in the top 10 mm of the sediment was monitored over a period of 5 days, *Tubifex* spp. (±5 individuals cm^{-2}) was added to one core to rework the sediment. Eh was measured every 15 min.

2.3 *Calculations*

The redox potential (E_h) was calculated by adding the potential from the reference electrode (E_{ref}) to the measured potential (E_m):

$$E_h = E_m + E_{ref}$$

3. Results and discussion

From the first applications with the different redox probes developed in this project, connected to HYPNOS III, the dynamic behaviour of redox conditions in wetland soils and sediments becomes evident. Figure 3(a) and 3(b) show the results from the first 2 month-period of measurements at KW12 site in Bangladesh at −2 m and −8 m below surface, respectively. These depths represent the two distinct trends in time of the redox potential at this site. At −2 m, the redox potential shows anoxic conditions, with daily variations of ±50 mV and larger variations (about 300 mV) between months. The temperature at this depth is increasing over time (Figure 3(a)) and is directly related to the increase in air temperature at the site (data not shown), but these parameters showed no relationship with redox potential during the measurement period. At −8 m (Figure 3(b)), it is striking that the redox potential is higher compared with the redox potential at 2 m depth. It shows oxic conditions, with a slowly decreasing value over time (ca 200 mV decrease). Furthermore, at 8 m below surface, a daily variation in redox potential similar

Downloaded by [East Carolina University] at 00:15 20 February 2012

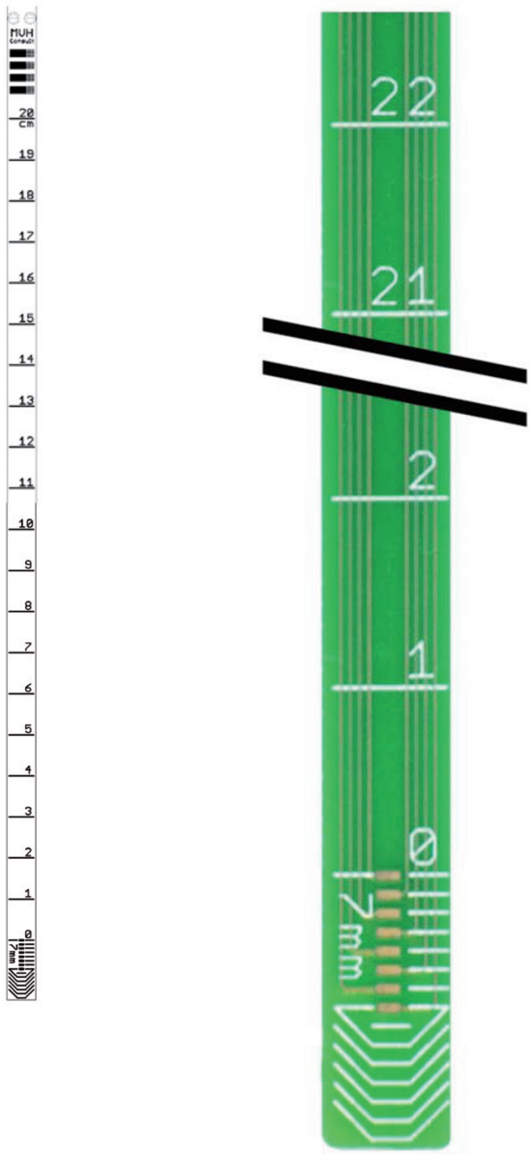


Figure 2. Millimetre probe, with photographic details.

to that in the higher layer is observed. The reason for this behaviour remains speculative and is subject for further investigation. One possible explanation is the lower solubility of oxygen and related species at higher temperatures at −2 m compared with the deeper layers. However, the temperatures at −8 m are also relatively high (26°C and above) and not likely to influence the solubility of the oxygen at that depth. It is also possible that an increased Eh is a result of introducing oxygen during installation, but this oxygen is likely to be removed by oxidation processes quickly. Future research efforts should resolve this issue.

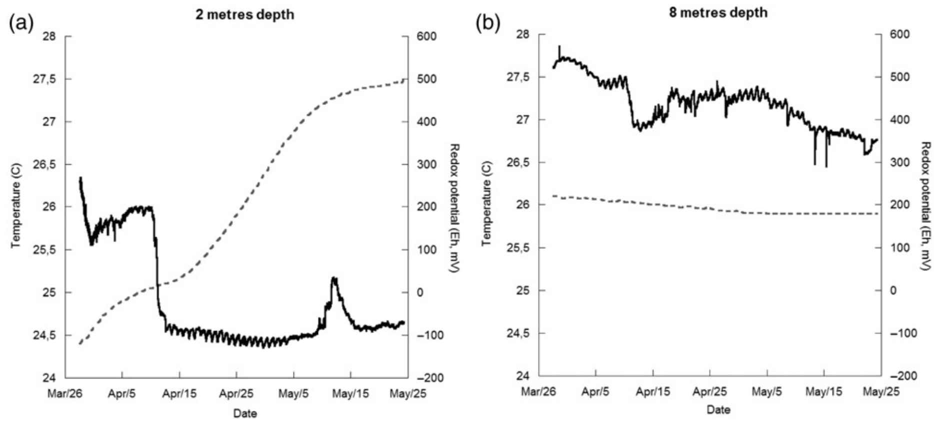


Figure 3. Redox potential and temperature at 2 m and 8 m depth. Note the higher Eh at higher depths and the daily variation in values. Temperature has been smoothed for clearness.

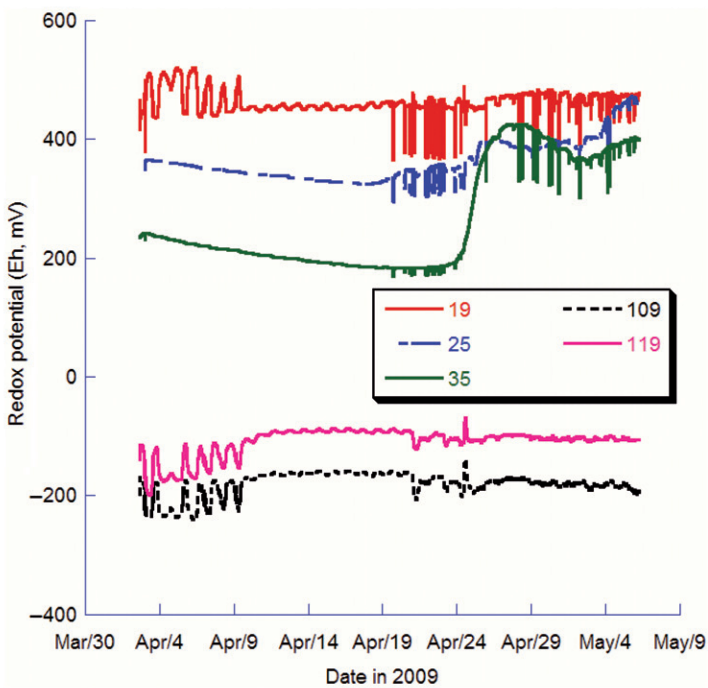


Figure 4. Redox potential at five depths in a peatmound (legend indicates measured depths in centimetres below surface).

In the wet grassland area in the Netherlands (Peizermade), the variations in redox conditions in the top 120 cm of the soil are two-fold (Figure 4). At −109 cm and below the soil consists of well-preserved peat, with expected redox conditions of −100 mV and lower. On top of the peat layer, the soil consists mainly of clay. In this clay layer, a distinct redox

Downloaded by [East Carolina University] at 00:15 20 February 2012

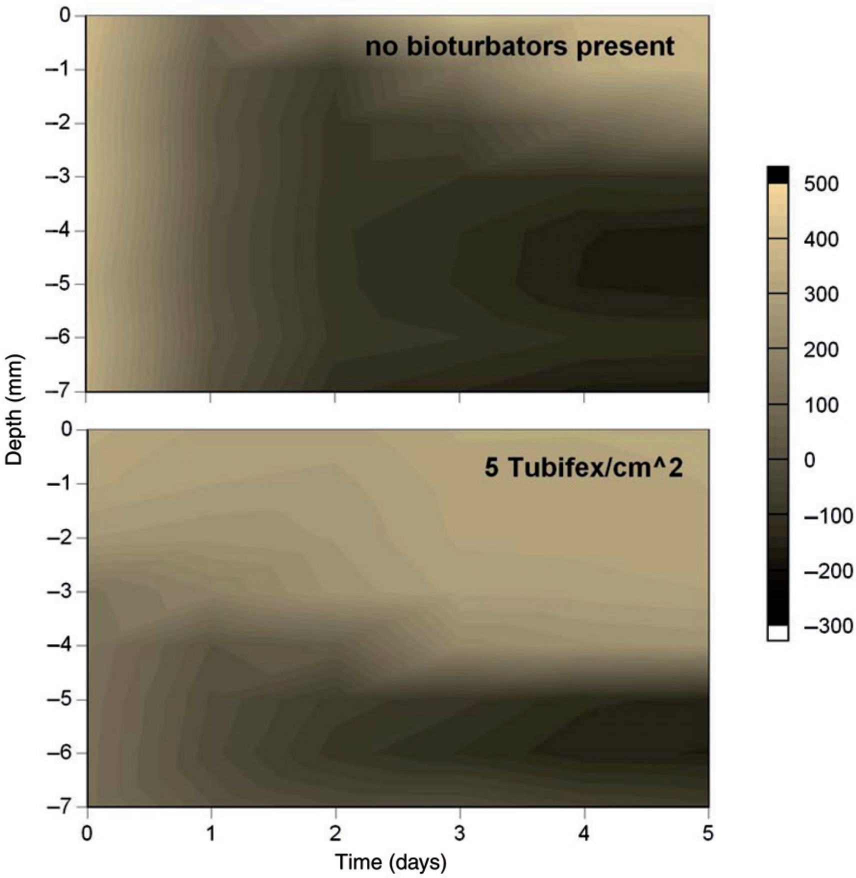


Figure 5. Changes in redox conditions measured with gold-plated micro redox sensors connected to HYPNOS III in homogenised organic rich sediments during 5 days after homogenisation in a control treatment (top) and a treatment in which 5 bioturbating oligochaetes (*Tubifex* spp.) per cm^2 were added (bottom graph). The redox contour plots are based on Eh values measured every 15 min at eight different depths (0–1 cm).

Downloaded by [East Carolina University] at 00:15 20 February 2012

stratification is measured during the first month of this monitoring campaign, but at the end of April stratification in the clay layer becomes less as redox potentials at −35 cm were increased. The daily variation is different at different depths, and ranges from 10 mV to 50 mV. This variation might be attributable to the local movement of soil water in the soil layers. Similar to the deep applications described above, also here an inversion of the vertical redox profile is observed in which redox potential at a certain depth increases.

First results from the measurements at the millimetre scale in the top layer of an aquatic sediment using the gold-plated microprobes are presented in Figure 5. The contour plots describe the variations in the redox conditions (with different colours) in a vertical profile over time, induced by biomechanical reworking of the sediment by the aquatic oligochaete *Tubifex* spp. In the control treatment (without bioturbating organisms), the development of redox stratification is clearly visible: at the start of the experiment, the sediment is completely homogenised and redox potentials show no vertical profile and reflect oxygenised conditions. During 5 days of incubation, oxygen disappears below 3 mm due to mineralisation of the organic matter, and the sediment becomes stratified with differences in Eh of 600 mV over a vertical distance of only 5 mm. The addition of *Tubifex* resulted in an enhanced redox potential in the top 5 mm of the sediment caused by the increased oxygen penetration. Since many biogeochemical processes are related to changes in redox conditions, these types of continuous measurements with a high spatial resolution may be used to serve as an easy-to-measure proxy for the biogeochemical functioning of sediments.

4. Conclusions

The newly developed HYPNOS datalogger, together with different dedicated probes, is highly suitable to measure variations in the vertical profile of redox conditions in wetland soils and sediments over time. A total of 48 extremely stable redox channels allow measurements of high resolution redox potentials that will provide insight in the dynamic biogeochemical behaviour of soils and sediments. The newly developed fibreglass probes with the sturdy tip and platinum contacts, are highly suitable for measurement of redox potential in deeper layers, while the gold-plated printed circuit board probes allow measurements at the millimetre scale. Results from three different applications with these probes have shown that variations in redox conditions occur at different scales in space (from metres to millimetres) and time (from daily to seasonal variations). It is expected that the development of the new datalogger and the new set of probes will greatly improve our knowledge on the functioning of wetlands.

Acknowledgements

The authors acknowledge the manufacturer of the sturdy probes, Sander Smit of Paleo Terra (http://www.paleoterra.nl) for all his work on probe design. The work in Bangladesh was funded by a National Science Foundation of USA award 0738888 to Yan Zheng, City University of New York. The measurements at Peizermade were funded by Projectbureau Herinrichting Peize.

More information on the HYPNOS datalogger can be obtained from MVH Consult via info@mvhconsult.nl. The READY project publishes manuals, design ideas, experiences and more on the web: http://www.redoxpotential.info/

Downloaded by [East Carolina University] at 00:15 20 February 2012

References

[1] T. Borch, R. Kretzschmar, A. Kappler, P. Van Cappellen, M. Ginder-Vogel, A. Voegelin, and K. Campbell, Environ. Sci. Technol. **44**, 15 (2010).
[2] W.J. Mitsch and J.G. Gosselink (Eds), *Wetlands* (Van Nostrand Reinhold, New York, 1993).
[3] S. Fiedler, M.J. Vepraskas, and J.L. Richardson, Adv. Agronomy **94**, 1 (2007).
[4] A.C. Rabenhorst, W.D. Hively, and B.R. James, Soil Sci. Soc. Am. J. **73**, 668 (2009).
[5] C.A. Seybold, W. Mersie, J. Huang, and C. McNamee, Wetlands **22**, 149 (2002).
[6] T. Mansfeldt, J. Plant Nutr. Soil Sci.-Z. Pflanzenernahr. Bodenkd **166**, 210 (2003).
[7] M. Vorenhout, H.G. van der Geest, D. van Marum, K. Wattel, and H.J.P. Eijsackers, J. Environ. Qual. **33**, 1562 (2004).
[8] M. Vorenhout, N.M. Van Straalen, and H.J.P. Eijsackers, Environ. Toxicol. Chem. **19**, 2161 (2000).
[9] C.R. Thomas, S.L. Miao, and E. Sindhoj, Wetlands **29**, 1133 (2009).

[10] E. Van Bochove, S. Beauchemin, and G. Thériault, Soil Sci. Soc. Am. J. **66**, 1813 (2002).
[11] A.C. Rabenhorst, Soil Sci. Soc. Am. J. **73**, 2198 (2009).
[12] K.L. Vaughan, M.C. Rabenhorst, and B.A. Needelman, Soil Sci. Soc. Am. J. **73**, 663 (2009).
[13] Y. Zheng, A. van Geen, M. Stute, R. Dhar, Z. Mo, Z. Cheng, A. Horneman, I. Gavrieli, H.J. Simpson, R. Versteeg, M. Steckler, A. Grazioli-Venier, S. Goodbred, M. Shahnewaz, M. Shamsudduha, M.A. Hoque, and K.M. Ahmed, Geochim. Cosmochim. Acta **69**, 5203 (2005).
[14] K.A. Radloff, A.R. Manning, B. Mailloux, Y. Zheng, M.M. Rahman, M.R. Huq, K.M. Ahmed, and A. van Geen, Appl. Geochem. **23**, 3224 (2008).
[15] Y. Zheng, M. Stute, A. van Geen, I. Gavrieli, R. Dhar, H.J. Simpson, P. Schlosser, and K.M. Ahmed, Appl. Geochem. **19**, 201 (2004).
[16] M. Schepers, Een archeologische inventarisatie van de staat van veenterpen in de polders Matsloot-Roderwolde en Peizer- & Eeldermaden, gemeente Noordenveld (Dr.). ARC-Publicaties, ARC, Groningen, p. 115, 2008.

Downloaded by [East Carolina University] at 00:15 20 February 2012