

## Continuous Eh-recordings in sediment columns\*

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**KURZFASSUNG: Kontinuierliche Messungen des Redoxpotentials in Sedimentsäulen.** Die Meßergebnisse von Redoxpotentialen in marinen Sedimenten sind oft schwierig zu interpretieren, weil neben vielen Störungen auch Potentialänderungen nach dem Einbringen der Elektrode in das Sediment auftreten. Zur Quantifizierung dieses Problems wurden Sande aus der Nordadria in Plexiglasrohre gefüllt und Laborversuche unter kontrollierten Bedingungen durchgeführt. Nachdem sich das mit Gold- bzw. Platinelektroden gemessene Redoxpotential stabilisiert hatte, die Elektroden herausgezogen und mechanisch gereinigt waren, konnten deutlich andere Potentiale als vor dem Reinigen festgestellt werden, die erst im Verlauf einiger Tage die alten Marken wieder erreichten. Dabei ändert sich das Eh-Profil in den Sandsäulen selber offensichtlich wohl nicht. Es zeigt sich aber, daß die gemessene Form des Redoxprofils von der Stabilisierungszeit abhängig ist. Durch kurzfristige Messungen kann allerdings die Lage der Redox-Potential-Diskontinuität festgestellt werden.

### INTRODUCTION

Basic work on redox-potentials was published by MORTIMER (1941, 1942) who studied the concentration of organic matter of mud and water in lakes, and by ZOBELL (1946) who discussed the theory and problems related with marine sediments. Beyond that, this field lies within the interest of geologists. MASON (1961), FYFE (1960), and MANHEIM (1961) deal with redox-potentials in connection with sediments and describe methods of measurement. Origin and limits of chemical sediments in terms of pH and redox-potentials are the interest of KRUMBEIN & GARRELS (1952) and BAAS-BECKING et al. (1960).

Now and again, the accuracy of Eh-measurements is discussed in the literature. Difficulties begin with the fact that an equilibrium, which, in a chemical sense, does not exist, is measured by definition. In addition, electrochemical processes at the electrodes influence the measurement. By introducing the probes, the sediment is changed mechanically, resulting in a change in chemical composition. When a reading is finally obtained, the relative contribution of each redox couple cannot be determined. Therefore, statements on the influence of one redox system, e. g. the sulfide system, should be avoided if the chemical composition of sand is not known. Possible difficulties in connection with actual measurements are discussed by WHITFIELD (1969).

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Current methods used to determine redox-potentials in sediments are: introduction of one or more electrodes into the sediment layer of interest (MACHAN & OTT, 1972); extraction of a sediment sample with a tube and insertion of electrodes through prefabricated holes from the side of the tube (RIEDL & OTT, 1970), and laboratory experiments (SCHMIDT & MACHAN, in press). Biologists turn to redox-potentials more and more as a convenient parameter to characterize distribution of the interstitial fauna (WIESER et al., 1974) and to describe the flow of energy (RIEDL, 1971; OTT & MACHAN, 1971). A drawback of field measurements is the difficulty associated with long-term observations. Usually a reading is taken as soon as the needle is stable. In addition it seems quite impossible to determine every quantity which influences the redox-potential, such as pH, temperature, tides or biological processes. Correct interpretation of long-term field-measurements is therefore difficult. On the other hand, most of the parameters can be kept constant or changed at will in the laboratory, so that long term recordings may become meaningful.

## MATERIAL AND METHODS

Figure 1 shows a setup well suited for long-term measurements in marine sediments. The central unit consists of two plexi-glass tubes (D), which can be closed at both ends by a lid. Through conical drillholes sealed with silicone rubber on the side of the tubes, electrodes may be inserted into the sediment at various depths from the sand surface. From reservoirs (A), water is pumped by pumps (B) through pipes (a) and (b) into containers (C). From (C), water flows via (d) over the sand surface and back to (A) or directly back to (A) through (c), thereby establishing a controllable hydrostatic head between (C) and (D) in order to keep the flow across (D) constant. Air or other gases may be pumped from input (E) through pipes (e) into reservoirs (A). Connections (f), (g) and (h) provide a path for pressure equalization between the airtight containers. Excess gas is allowed to escape in (F) against an adjustable hydrostatic head so that the pressure inside the system can be kept slightly above the ambient. Salt bridges (i) electrically link the sand columns to a common container (G) which houses the reference electrode. (G) is mounted below the water levels in (D) such that a constant slow outflow provides chemical separation. This water leaves the system through (k). Water and gas flow can be regulated at all connecting units. Also, water can be drained through the bottom of the sediment columns. The entire apparatus consists of two separate systems set up symmetrically to allow for control measurements. Further probes for monitoring other parameters, e. g. pH, temperature, and oxygen may be inserted through openings in the lids of the sediment columns.

The sand for our experiments was collected in the Northern Adriatic, near Strunjan (Porto Roz, Yugoslavia) and at the Lido of Venice (Italy). The sands from both locations had obviously been freshly deposited. Nevertheless, a well-developed redox-potential discontinuity could be observed. The sand from Strunjan contained very few species of interstitial fauna, mainly Nematodes, and no Gnathostomulida. The plexi-glass columns were filled on the spot in such a way that the layering roughly resembled

natural conditions. Some excess sand had to be added to allow for settling during the transport to Vienna.

The electronic equipment consisted of a twelve-position scanner, an electrometer, and a chart recorder for each column. By synchronous scanning of the electrodes with the falling bar of the recorder, twelve distinct tracks were produced. Application of

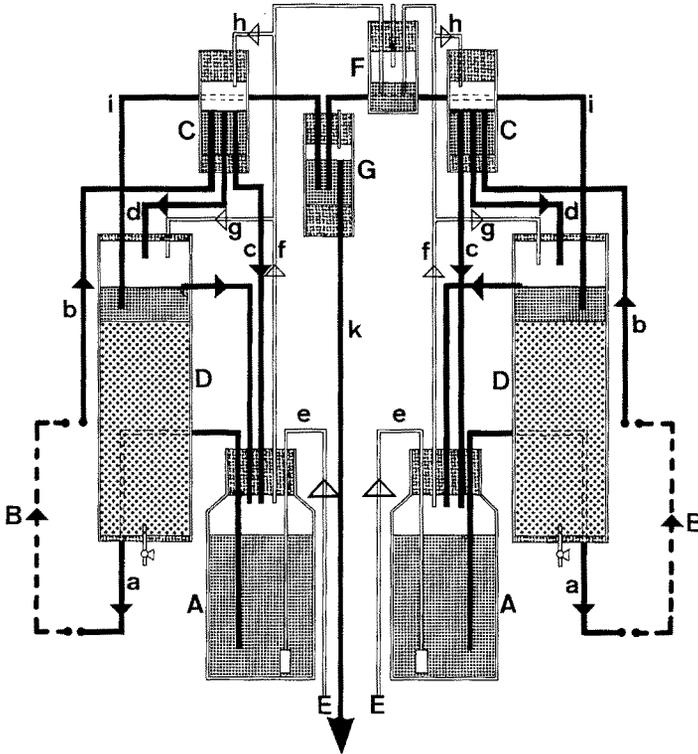


Fig. 1: Schematic diagram of the setup used for Eh monitoring. One half of the symmetrical unit can be used as a control. (For detailed explanation see text)

the start-stop principle to the paper transport enabled us to use very low chart speed, e. g. 20 mm per day. Even slow changes were then clearly visible. A more detailed description of the electronic circuit is given in MACHAN & OTT (1972) and SCHMIDT & MACHAN (in press).

The terms Eh and redox-potential will not be applied here with the same exactness as they should be in electrochemical literature. Here they symbolize the potential of a metal electrode compared to a standard hydrogen electrode, without implying that the actual measurement was carried out with an accuracy essential for chemical interpretation. We used a calomel electrode as reference, adding 230 mV electronically to get a reading on the Eh-scale. Pieces of platinum and gold wire were used for the metal electrodes. Measured potential or electrode potential usually means the voltage between metal electrode and reference electrode, without correction, but is the same

as Eh in this case. In order to differentiate between changes in measured potential resulting from changes in the redox profile and those simulated by electrode processes, we repeatedly removed the metal electrodes, cleaned them mechanically and reinserted them into the sediment. This procedure will be called an experiment.

## RESULTS

Before starting any experiments in a specific column, we had to wait for the redox profile to become stable. This process took about four weeks, even if the columns had been left standing undisturbed without electrodes. The process was considered terminated when the measured values remained constant for several days. Experiments of the kind described are therefore very time-consuming. We repeated all our experiments with gold electrodes but did not find significant variations in general behaviour.

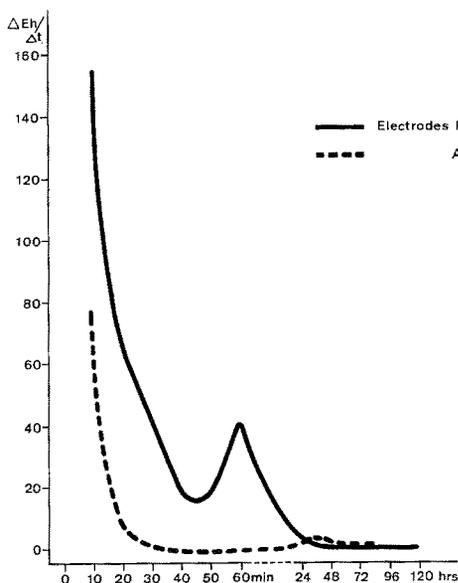


Fig. 2: Rate of change of recorded potential as a function of time. The Pt-electrodes exhibit a pronounced step during stabilization. Gold electrodes reach equilibrium a little bit more rapidly

Another surprising result was the observation that the potentials measured immediately after an experiment, that is after cleaning and reinserting the electrodes, differed considerably from those measured before the experiment. Practically all the values came close to the zero-point of the system, from positive as well as from negative regions. A few days are required until the original values are attained again. Occasionally an electrode potential does not return to its pre-experiment reading (SCHMIDT & MACHAN, in press). In these cases the electrode was ignored.

Figure 2 shows the rate of potential change,  $\Delta Eh/\Delta t$ , as a function of the time elapsed after an experiment. Stabilization proceeds rather rapidly during the first

hours. It is worth noting that the process of stabilization occurs in steps, as clearly demonstrated by the platinum electrodes. Taking all our experiments together we can say that it takes from three to six days to re-attain the original potential readings. To some extent the steepness of the slope during the first hours justifies limited statements for biological purposes based on quick measurements. Three to four hours may be sufficient, depending on sand quality, but for accurate measurements ample time should be allowed for equilibration.

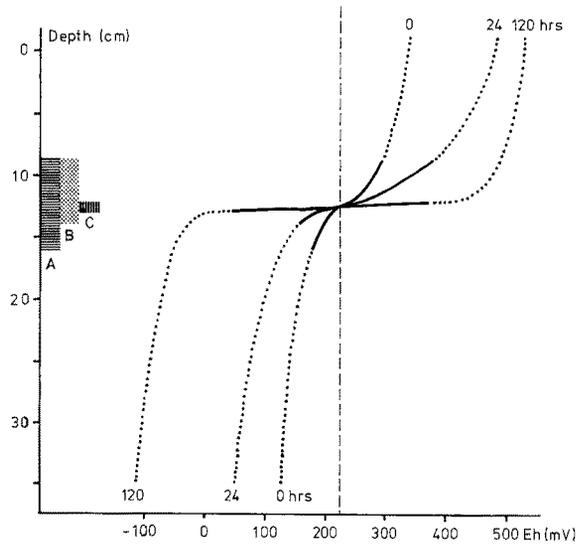


Fig. 3: Eh as a function of depth for different times of stabilization. Depth of discontinuity hardly changes with time. Thickness of the RPD-layer strongly depends on the time of stabilization: *A* immediately after insertion of the electrodes; *B* 24 hours, and *C* 120 hours later

Another possible application of short-time measurements can be derived from Figure 3 where the redox-potential is plotted versus depth for different spans of reequilibration. If one defines the redox-potential-discontinuity-layer (RPD-layer) by the point of inflection in the curve, one can see that the apparent depth of that layer is remarkably independent of the time that the electrodes are left in the sediment. In other words, an experiment (in the sense of this paper) does not influence the measured position of the RPD-layer. Only the shape of the curve changes. The further a value lies off the 230 mV-mark, which is the electrical zero of the electrode system on the Eh-scale, the bigger the associated potential change and the longer it takes to reach the original values again.

## DISCUSSION

The process of reequilibration has been mentioned in MACHAN & OTT (1972). They found that the time needed for this process could be quite variable, but had no knowledge of the conditions before inserting the probe. The quality of the sediment prob-

ably significantly influences the time required. We can make no statement on this problem here because the sands we took at three different locations in the Northern Adriatic Sea were quite similar in this respect. Mechanical disturbance by the electrode and electrochemical influence in their vicinity might again be important factors but are difficult to define quantitatively. Biological investigations are altogether impossible during the measurements. Even under controlled conditions in the laboratory, factors which are hard to quantify may influence the results. As the measurement of the redox-potential turned out to be a convenient method to separate biomes for those working on meiofauna, a standardized method should be defined for measurements of redox-potential, especially in the field. The outcome might be called "Eh" in the literature. The time elapsed between the insertion of an electrode and the taking of the reading will have to be an essential part of such a definition. One hour seems to be a practical compromise but a lot of field experiments have to verify it.

An exception to this requirement might be permitted solely for determining the depth of the RPD-layer if the layer is defined by the point of inflection of the curve depth versus Eh. Figure 3 clearly shows that no appreciable change occurs, even if the electrodes are cleaned and reinserted. According to FENCHEL & RIEDL (1970), the RPD-layer is "a layer where oxidizing processes become displaced by reducing processes" or, defined more closely, as "the flattest part of the Eh-curve". Thickness is then determined by one half of the total Eh-change within a core. This definition, unfortunately, not only makes the thickness of the RPD-layer dependent on the length of the core taken, but, as we have seen, also dependent on the time elapsed after inserting the electrodes. The vertical extension of the RPD-layer apparently decreases with time (Fig. 3). The time allowed for a measurement of redox-potentials should therefore be included in a definition of the redox-potential-discontinuity, especially if the layer itself and its finite thickness are of interest to the biologists.

#### SUMMARY

1. Long-term recordings of redox-potential in marine sediments performed under laboratory conditions show that the drift of the measured potential after inserting the electrode cannot be neglected.
2. Cleaning and reinserting an electrode considerably changes the measured potential. This change may reach several hundred mV, depending on the position of the electrode and the composition of the sediment.
3. It takes several days until the potentials observed before cleaning are obtained again.
4. The overall Eh-profile in the sediment column is not changed by successive experiments. An electrode at a certain position in the sediment normally will return to the same potential if enough time is allowed for stabilization.
5. Quick measurements of single Eh-values in systems such as marine sediments must be handled with caution.
6. The measured shape of the redox-profile strongly depends on the time allowed for stabilization.

7. The position of the redox-potential-discontinuity defined as the point of inflection of the curve Eh versus depth seems to be the only meaningful parameter derived from quick measurements.

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