OCEANOLOGICA ACTA 1983 - VOL. 6 - N° 4

Redox-turnover at the sediment/water interface studied in a large bell jar system

Redox turnover
Sediment/water interface
Bell jar system
Organic matter degradation
Nutrient release
Transition d'oxydo-réduction
Interface eau-sédiment
In situ en cloche
Minéralisation de la matière organique
Flux des composés nutritifs

W. Balzer[a], K. Grasshoff[a*], P. Dieckmann[b], H. Haardt[b], U. Petersohn[b]
[a] Institut für Meereskunde, Düsternbrooker Weg 20, 2300 Kiel, FRG.
[b] Institut für Angewandte Physik, Olshausenstr. 40-60, 2300 Kiel, FRG.
* Deceased March 11, 1981.

Received 16/8/82, in revised form 14/3/83, accepted 22/4/83.

ABSTRACT

To study the degradation of organic matter and the release of nutrients from the sediment/water interface under different environmental conditions, a large bell jar system was designed to minimize the effects of spatial inhomogeneities in benthic fauna distribution. The system encloses 2 094 l bottom water over 3.14 m^2 of its original sediment, and is equipped with probes for oxygen, temperature, redox potential and pH, and with a remotely controlled stirrer. During late summer (t = 12°C) a redox turnover was simulated at a water depth of 20 m in Kiel Bight, Western Baltic. Subsequent periods of oxygen consumption (161 ml $m^{-2}d^{-1}$), denitrification and sulphate reduction were clearly reflected in the redox potential; measured potentials of about 510 mV in the first part support prior findings that the O_2/H_2O_2 couple exerts redox control over oxic conditions; Eh = —265 mV during sulphate reduction is the same as that predicted from equilibrium calculations for the system SO_4^{2-}/HS^-. Phosphate release rate increased from 73 μM $m^{-2}d^{-1}$ during oxic conditions to 677 μM $m^{-2}d^{-1}$ in the anoxic milieu, mainly due to reductive dissolution of iron-hydroxo-phosphates. Concentration of dissolved inorganic nitrogen also increased significantly after the onset of anoxic conditions, partly due to rapid decomposition of dying organisms. Comparison of the release rates with the N/P ratio of the organic matter revealed a preferential release of phosphorus. After reaeration, phosphorus is rapidly sorbed by the sediment surface, while ammonia is converted to nitrite and more slowly to nitrate. Silicate exhibited no clear dependence on either pH or Eh and was released at a mean rate of 1 576 μM $m^{-2}d^{-1}$.

Oceanol. Acta, 1983, **6**, 4, 337-344.

RÉSUMÉ

Étude *in situ* du cycle d'oxydo-réduction à l'interface eau-sédiment

Pour étudier *in situ* la dégradation de la matière organique et les échanges de sels nutritifs à l'interface eau-sédiment dans différentes conditions du milieu, un système de « cloche » a été construit. La « cloche » devait être suffisamment grande, de manière à réduire les effets de l'hétérogénéité de la distribution de la faune benthique. Le système permettait d'enfermer 2 094 l d'eau au-dessus du sédiment sur une surface de 3,14 m^2. Il était équipé de capteurs pour mesurer l'oxygène, la température, le potentiel d'oxydo-réduction et le pH; elle était aussi équipée d'un agitateur télécommandé. A la fin de l'été (t = 12°C), un cycle Redox fut simulé sur les fonds de 20 m de la baie de Kiel en Mer Baltique occidentale. Les phases successives de consommation d'oxygène (161 ml.$m^{-2}.j^{-1}$), de dénitrification et d'utilisation des sulfates, puis de réoxygénation après une période de 50 jours, se reflétaient dans l'évolution du potentiel d'oxydo-réduction. La valeur de 510 mV environ, mesurée pendant la première phase, confirme les résultats précédemment obtenus, c'est-à-dire que le milieu oxygéné est contrôlé par le couple Redox O_2/H_2O_2. Pendant la période d'utilisation des sulfates, le potentiel

---

Contribution No 418 of the Sonderforschungsbereich 95 of the University of Kiel.

Redox (Eh = -265 mV) était le même que celui déduit, par calcul, de l'équilibre du système SO$_4^{2-}$/HS$^-$. La libération du phosphate est passée de 73 µM m^{-2}j^{-1} en milieu oxygéné, à 677 µM m^{-2}j^{-1} en conditions anoxiques, en raison, pour une bonne part, de la réduction des phosphates ferriques. La concentration des sels azotés dissous a ainsi beaucoup augmenté après l'établissement des conditions anoxiques, en raison vraisemblablement de la décomposition rapide d'organismes morts. La comparaison des taux de libération avec le rapport N/P de la matière organique, montre un relargage préférentiel du phosphate. Après la réoxygénation, les phosphates sont adsorbés rapidement à la surface du sédiment, tandis que l'ammoniaque est transformée d'abord en nitrite puis, plus lentement, en nitrate. Le silicate ne manifeste de dépendance, ni vis-à-vis du potentiel d'oxydo-réduction, ni vis-à-vis du pH.

Oceanol. Acta, 1983, **6**, 4, 337-344.

INTRODUCTION

Benthic metabolism is an important component in the cycling of organic matter and the regeneration of inorganic nutrients; especially in coastal environments, where input of organic substance by sedimentation is large, microbially mediated remineralization at the sea floor is a major recycling pathway and nutrient release from near-shore bottom areas can supply a significant portion of the nutrient requirements of the primary producers in the overlying water column (see recent reviews by Zeitzschel, Davies, 1978; Hinga *et al.*, 1979; Zeitzschel, 1980, and Pamatmat, 1977).

The intensive decompositional processes at the sediment/water interface may create oxygen depletion whenever its supply cannot balance consumption. This situation is often encountered in semienclosed sea areas where a strong pycnocline exists (Richards, 1965; Grasshoff, 1975). Seasonal stagnation of the bottom water is most pronounced during summer due to the seasonal build-up of a thermocline, eventually supported by a halocline as in Kiel Bight, the area of this investigation (Bodungen, 1975). Oxygen depletion leads to the utilization of other available electron acceptors in the sequence of decreasing free energy yield for the bacteria involved (Martens, 1978; Billen, 1978; Froelich *et al.*, 1979): Mn-oxides and nitrate, iron oxides, sulfate and eventually bicarbonate. Further consequences of suboxic or anoxic conditions in the bottom water are drastic changes in the rates of nutrient release as compared to well oxygenated conditions (Mortimer, 1971; Hallberg *et al.*, 1972). Nutrient regeneration within the sediments and nutrient fluxes through the interface have been treated in a number of recent publications (Aller, 1980; Berner, 1980; Elderfield *et al.*, 1981; Klump, Martens, 1981; and literature cited therein) by evaluation of sophisticated stoichiometric and kinetic models with respect to pore water concentration profiles; calculated fluxes partly were compared to direct determinations of release rates.

There are various techniques available to quantify benthic community metabolic activity: oxygen uptake (Zeitzschel, Davies, 1978), sediment dehydrogenase activity (Pamatmat, Bhagwat, 1973), electron transport system (Christensen, Packard, 1977), glucose uptake and adenylate energy charge ratio (Hanson, 1980), and direct calorimetry (Pamatmat, 1975; 1980). Among these measurements oxygen uptake has been the most widely used technique, although it appears to have serious limitations (Pamatmat, 1980).

Apart from those involving the measurement of oxygen uptake and nutrient release, most of these methods were employed *in vitro*, and it is conceivable that sediment core retrieval, temperature and pressure changes, transport and eventually the segmentization of the core material itself may cause significant alteration of the original metabolic activity (Smith, 1978). An *in situ* bell jar system was constructed (Hallberg *et al.*, 1972) to avoid these artifacts and to minimize wall or "bottle" effects. The system employed is large enough to include low abundant macrofauna in a representative way.

This investigation forms part of an interdisciplinary programme of Kiel University (SFB 95) to study the interaction between sea and sea bottom, and was conducted in the "Hausgarten", a 0.6 km by 1 km wide sea area in Kiel Bight reserved for research purposes (Fig. 1). The bell jar system was set up at a water depth of 20 m, which is about the average depth of Kiel Bight. Situated in the transition zone between North Sea and the Baltic, the Kiel Bight is characterized by frequent short term salinity fluctuations. During summer, the season of this study, a strong thermo-halocline develops, leading almost regularly to anoxic conditions in the bottom water of the deep furrow (28 m) adjacent to the area of investigation. It was therefore intended to simulate the transition from oxic to anoxic conditions by enclosing bottom water over its original sediment in the bell jar.

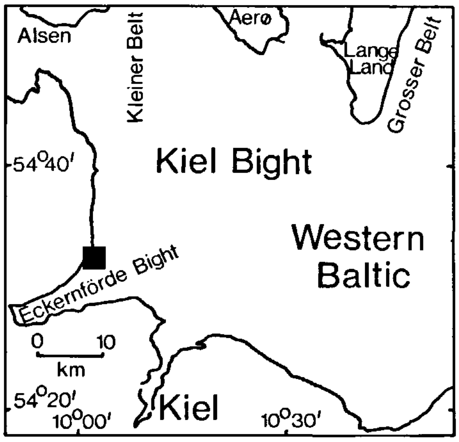


Figure 1

The area under investigation: Kiel Bight.

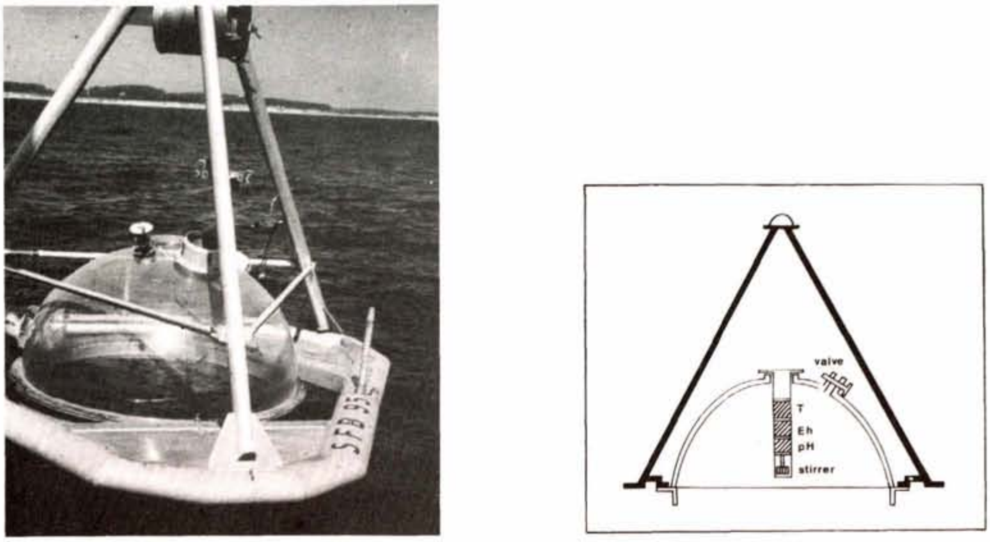


Figure 2
Bell jar system: ready for deployment and schematic view including probes and sampling port.

MATERIALS AND METHODS

The bell jar system

The bell jar is a half-sphere made of plexiglass and held by an aluminium frame (Fig. 2). When lowered to the bottom, a 20 cm deep plexiglass rim penetrates into the sediment thus enclosing 2 094 l of bottom seawater over 3.14 m^2 of its original sediment without contact with any metal components. To prevent the build-up of concentration gradients in the bell jar, homogenization of the enclosed water body was ensured by a remotely controlled stirrer. Prior to use, divers checked that the rotor speed was sufficient to homogenize the water but was not strong enough to disturb the sediment surface.

Dissolved oxygen, redox potential (Eh), pH, and temperature were monitored using automatic probes (Dieckmann *et al.*, 1976). The data from the probes were either recorded on a tape unit placed near the bell jar or transmitted directly from the "Plankton-Tower" (Bodungen *et al.*, 1976), positioned in the same area, to the land based station for rapid processing.

Regular sampling of the bell jar water was performed by Scuba divers once a week through a sample port by means of 300 ml air-tight glass syringes which were prerinsed with sample before use. In addition, samples were taken by an automatic sampler attached to the bell jar by flanges; evacuated glass ampoules remove water from inside when its capillary tip is cut in a pre-selected time sequence; approximately once a week the sampler with the filled ampoules has to be replaced by a new one. Since electronic reliability was poor, only a few samples were obtained by this system; furthermore data from the ampoules seemed to have a bias to low values indicating alteration of the sample due to contamination or subsequent reactions in the ampoules. Thus the use of the automatic system is very limited and data are reliable only if corroborated by direct sampling. Rates calculated from the concentration data were not corrected for the sampled amount of water withdrawn from the bell jar because the ratio of sample to total bell jar volume was very low and the water was either replaced (syringes) by surrounding waters of lower concentration or replaced (ampoules) through the sediments of higher concentration thus matching one another to a certain extent.

Sensors

Redox potential

Potentials which developed between a platinum ring electrode and an Ag/AgCl reference electrode ("Lazaran") were recorded and are reported as Eh with respect to the standard hydrogen electrode. The probe was calibrated with a redox standard solution yielding an Eh = +625 mV at 25°C (Light, 1972). Recalibration yielded a reading 30 mV lower, and it was shown that electrodes of this type react rapidly and accurately to standard solutions even after months of exposure to anoxic sediments (Kohr, 1976).

pH

The pH-probe consists of a glass electrode (Fa. Ingold) and an Ag/AgCl reference electrode with solidified electrolyte and ceramic diaphragm which is hydrogen sulphide resistant ("Lazaran", Fa. Beckman). The response of the electrode is pressure independent down to 250 m. To check the probe against drift, the pH of syringe samples was measured once a week on board ship using a standard combination electrode (Fa. Ingold). Both systems were standardized against at least two NBS-low ionic strength buffers.

Oxygen

O_2 was recorded by an electrode of the Clark' type which was calibrated in air saturated and oxygen depleted (Na_2SO_3) water. To check the probe against drift oxygen was measured by Winkler titration weekly. Electrode readings were adjusted to results from titration.

Hydrochemical parameters

H_2S was determined spectrophotometrically using the methylene-blue method, or iodometrically in case of higher concentrations (Fonselius, 1976). Chloride was titrated argentometrically (Grasshoff, 1976). Nutrients were determined following the procedures given by Grasshoff (1976); ammonia was corrected for the salinity dependence of the calibration curve, and the formation of the yellow silicomolybdic acid was used in case of higher silica concentration. Alkalinity (TA) was determined by standard acid addition (Anderson, Robinson, 1946). To obtain carbonate alkalinity, proteolytic species contributing significantly to TA (borate and sulphide) were subtracted following standard methods (Gieskes, 1974).

Sediment

A detailed description of the sedimentary regime of the area is given by Wefer and Tauchgruppe Kiel (1974). The sediment underlying the bell jar water was a muddy sand having a carbonate content of 0.2% dw, an average of 0.49% dw organic carbon in the top 5 cm, and a C:N:P composition of 106:8.9:0.87 (by atoms) at the time of the investigation (Balzer, 1978).

RESULTS

Consumption of oxidants

The bell jar system was deployed at 20 m from the beginning of August to October to study the transition from oxic to anoxic conditions at the season of maximum oxygen consumption. After establishing anoxic conditions for 5 weeks, air from a diving gear was bubbled through the bell jar water to study whether release processes were reversible. Since persistent oxic conditions were not established within a few hours, the water body was continuously aerated from the 55th to the 60th day of the experiment. Because the air had to escape through an opened top valve, there was considerable exchange with surrounding water, as reflected in a chlorinity increase from Cl = 10.59 ‰ before the 55th day to Cl = 11.89 ‰ after the 60th day of experiment. Once the system is closed, therefore nutrient data cannot be fitted directly to those of the former period. Temperature rose from 9.5°C to 13.9°C by the end of the experiment. Subsequent periods of oxygen consumption, denitrification and sulphate reduction, and their relation to redox potential are clearly seen in Figure 3. From its initial low oxygen value of 1.50 ml/l O_2 ($\underline{\Omega}=21\%$ saturation) due to natural stagnation, oxygen was consumed at a rate decreasing from 161 ml $m^{-2}d^{-1}$ to 83.3 ml $m^{-2}d^{-1}$. Oxygen was exhausted by the 13th day of the experiment. From Eh = 380 mV, redox potential rose after a few days to Eh > 500 mV; this effect may be attributed to achievement of a certain equilibrium state at the electrode surface. Model calculations led Breck (1974), following suggestions of Bockris and Oldfield (1955) and Sato (1960), to propose that the redox couple O_2/H_2O_2 exerts control over oxic redox conditions. From the equation of redox equilibrium for this reaction

$$Eh = Eh^0 + 0.030 \log P_{O_2} - 0.059\,pH - 0.030 \log C_{H_2O_2},$$

using data of Breck (1974) for Eh^0 and $C_{H_2O_2}$ and

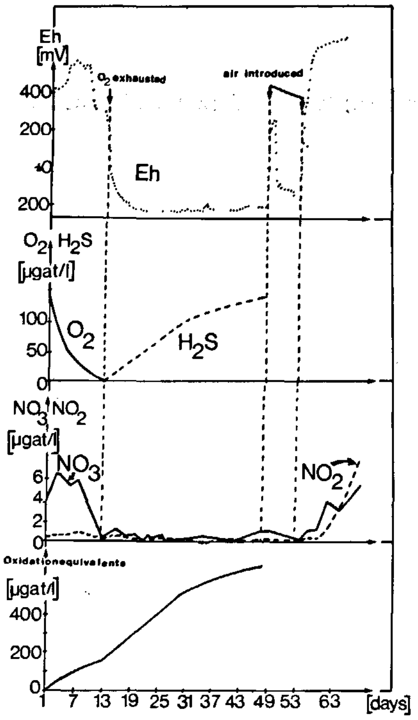


Figure 3

Variations of redox potential (Eh), O_2 and H_2S, NO_3^- and NO_2^-, and oxidation equivalents (for definition: see text) during the bell jar experiment (summer).

taking $P_{O_2} = 0.01$ atm $\underline{\Omega}$ 0.33 ml/l and pH = 7.43 at the 6th day a redox potential of Eh = 510 mV is calculated, in reasonable agreement with experimental data. The calculation for the redox couple O_2/H_2O yields far higher potentials.

The rapid decrease of the redox potential coincides with the onset of denitrification at the 8th day as reflected by the nitrate concentration drop. Interpolated oxygen concentration at that time is $C_{O_2} = 0.22$ ml/l, in agreement with Deuser *et al.* (1978) who stated that O_2 concentrations between 0.11 and 0.22 ml/l must apparently be reached before denitrification can start. Intermediate stabilization of Eh during denitrification (Fig. 3) is not a true effect, but a consequence of insufficient homogenization of the bell jar water.

After the end of oxygen consumption and denitrification at the 13th day, redox potential further fell from Eh = +130 mV to Eh = —265 mV, indicating the onset of sulphate reduction; according to Stumm and Morgan (1970) considerable sulphate reduction cannot occur before a redox potential Eh less than —51 mV (at 25°C) is reached. Thermodynamic calculations for the redox couple SO_4^{2-}/HS^- at the prevailing pH = 7.9, a sulphate concentration $C_{SO_4} = 15.4$ mM/l and $C_{HS^-} = 50$ µM/l, yield a potential of Eh = —268 mV. Since SO_4^{2-} is not electroactive, the observed potential is not a reflection of the Eh calculated for this redox couple (Berner, 1971).

The re-aeration of the anoxic bell jar water at the 48th day resulted in a sudden increase of the redox potential to Eh = +220 mV, thus suggesting that poisoning of the platinum electrode surface has little influence on the response time; however, from the increase to only Eh = +220 mV (although oxic conditions were attained), it may be inferred that poisoning prevents short-term equilibration or creates mixed potentials at the surface. It is interesting to note that there were measurable concentrations of nitrite and nitrate at the 50th day. Since aeration was too short to oxidize all reduced substances at the sediment surface, redox potential dropped again, but only to Eh = —150 to —180 mV. The couple S_x°/H_2S (aq), e.g., yields a potential of Eh = —156 mV from equilibrium calculations at pH = 7.6 and $C_{H_2S} = 10$ µM/l. Berner (1963) has found that the measured Eh of many sulfidic sediments is the same as predicted for the S°/HS^- couple.

Sufficient air delivery between the 55th and 60th day created oxygen saturation of about 89% and the redox potential rose up to Eh = +650 mV. The high oxygen level and the ammonia concentration of nearly 170 µM/l provided excellent conditions for rapid nitrification: nitrite and nitrate increased to 8.58 µM/l and 5.9 µM/l, respectively, after a few days. The faster increase (after the 65th day) of nitrite over nitrate concentration supports the idea that in the two-step process of nitrification the first step to nitrite is favoured either kinetically or by the activity of bacteria.

Carbon dioxide system

Due to strong stratification and the intensive oxygen consumption during late summer, pH was only 7.47 when the experiment was started. Contrary to the common observation of a strong pH drop during intensive oxygen consumption, under the conditions of this experiment the pH decreased only slightly. From the 6th day on, the pH even increased and stabilized after the 20th day at pH = 7.89. The buffering of the enclosed water body against strong pH drops is caused by calcium carbonate dissolution and by consumption of protons during anoxic conditions as described in detail by Balzer (1980) for another experiment in the same area. From measured calcium, pH, and alkalinity data at the beginning of the experiment, a saturation state with respect to calcite of less than 30% is obtained when using the procedure of Edmond and Gieskes (1970).

Nutrient release

Phosphate

From the initial value of 1.3-1.4 µM/l which is usual for oxic conditions in this area (Bodungen, 1975), phosphate concentration rose steadily to 2.9 µM/l at the end of the denitrification period (Fig. 4). After a few days of slow increase as before (possibly due to oxidation artifacts during sampling), phosphate concentration rose sharply during anoxic conditions. It is important to note that the phosphate release rate increased with time, thus ruling out the possibility that all of this phosphate is released from organisms dying at the sediment surface. The most important source is probably the reductive dissolution of iron-hydroxo-phosphates (Krom, Berner, 1981).

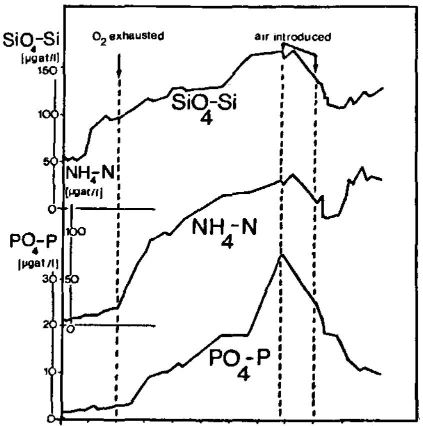


Figure 4
Nutrients released during the bell jar experiment (summer).

Possible consequences (cf. Nixon *et al.*, 1980) for the relationship between phytoplankton production and nutrient availability may be inferred from a comparison of the release rates during oxic and anoxic conditions: 73 $\mu Mm^{-2}d^{-1}$ during the first 13 days contrast with a mean rate of 677 $\mu Mm^{-2}d^{-1}$ between the 16th and 48th day, respectively.

The decrease in phosphate after the first aeration is partly due to water exchange; during oxic conditions after the 60th day, however, dissolved phosphate is removed from the bell jar water and fixed to the bottom at a mean rate of 726 $\mu Mm^{-2}d^{-1}$. Unfortunately the experiment ended before an eventual stabilization of concentration could occur.

Ammonia

From the onset of denitrification (8th day) ammonia is the most abundant nitrogen species; but also in first period ammonia increased steadily at a rate of 667 µM $m^{-2}d^{-1}$ while nitrate showed no systematic increase. The data suggest that under conditions of low oxygen tension and intensive remineralization, ammonification is faster than subsequent oxidation to nitrate (provided that NO_3^- removal by diffusion into the sediment may be neglected). Ammonia concentration rose sharply after the beginning of sulphate reduction at a rate decreasing from 6 799 µM $m^{-2}d^{-1}$ in the first week to 1 238 µM $m^{-2}d^{-1}$ just before aeration. A part of this ammonia probably results from the decay of sedimentary organisms which could not withstand the anoxic conditions (cf. Koelmel, 1976). When again closing the bell jar after aeration ammonia was further released at a rate of 857 µM $m^{-2}d^{-1}$ somewhat similar to the rate at the very beginning of the experiment. All rates given for nitrogen species are net rates of release into the bottom water and should not be confounded with production rates. At the interface there are sites where production of nitrate via nitrification and (nearby) consumption via denitrification result in a removal of ionic nitrogen from the system.

Silicate

The high initial concentration of 50 µM/l reflects the intensive dissolution of diatom tests and the relatively stable layering of the water column. Concentration changes of silicate were neither connected to the pH changes which should not have any effect below pH 9.5 (Stöber, 1967) nor to the redox cycle. The release rate averaged over the whole experimental time until aeration was 1 576 µM $m^{-2}d^{-1}$.

DISCUSSION

There is still a controversy in the literature whether in situ experiments are generally preferable to laboratory incubation of sediments. Contrary to the results of Pamatmat (1971) who found no difference in rates of O_2 uptake when comparing results from in situ bell jars and box core incubation experiments (see also: Elderfield *et al.,* 1981), some information has been obtained that lab incubation of cores can yield considerably higher results than in situ investigations (Smith, 1978; Dye, 1979). Despite the relatively costly equipment required, Hargrave and Connolly (1978) stated that in situ incubations are preferable to lab measurements. Even in situ benthic flux determinations, however, differ from the natural situation in certain other respects, which include the so-called "bottle-effect", i.e. the increase in the number of bacteria after inclusion of small volumes of natural waters (Kunicki-Goldfinger, 1974); this effect should be minimized by the high volume to artificial surface ratio of the system described here. The large area of sediment covered by the system (3.1 m^2) should also reduce the spacial variability of results which has been attributed to heterogeneity in macrofauna distribution (Hargrave, Connolly, 1978); the area covered by the chambers of these authors (0.070 m^2) lies in the general range reported for those experimental systems by Zeitzschel and Davies (1978). Whatever the form and size of the system, the approximation to the true natural conditions is more seriously limited by the insufficient reproduction of natural water motions (Davies, 1975) and the fact that closed systems tend to approach an "equilibrium state" by exclusion of inputs and outputs rather than a "steady state" that is maintained more or less in the open natural system (Morgan, 1967). The effect from preclusion of inputs, however, should not be great in this experiment, since sedimentation of primary material in this area is low during summer months due to high consumption within the pelagic food web (Smetacek, 1980).

On the other hand, there will be a tendency for measured fluxes to decrease with time as concentrations in the overlying water approach those in sediment pore waters if pore water flux is the dominant source of released nutrients. There is evidence from pore water profiles taken in the same area (Balzer, 1978) that diffusive fluxes contribute only a part to the total observed release rate.

Pamatmat *et al.* (1981) recently demonstrated a good agreement between in situ oxygen consumption of a marine sediment and results from direct calorimetry, indicating that oxygen consumption may represent total metabolic activity under certain circumstances. The rate of 161 ml $O_2m^{-2}d^{-1}$ obtained at low oxygen tensions in the bottom water overlying reduced subsurface sediment layers, however, is not likely to reflect the total benthic activity from theoretical considerations (Pamatmat, 1977). Under conditions encountered in this experiment, macrofauna partly switch over to anaerobic metabolism (Dries, Theede, 1976) which cannot be accounted for adequately through oxygen consumption studies. In addition, products of sulphate reduction may accumulate during summer, leaving an oxygen debt in the sediment that is not necessarily compensated for by increased oxygen consumption during winter time but may be sustained by the permanent deposition of reduced compounds like pyrite or certain sulphur associations with humic materials (Pamatmat, 1977). Experimental evidence for a significant contribution of anaerobic processes to total benthic metabolism was presented by Hargrave and Phillips (1981) who found that the ratio of total carbon dioxide released to oxygen consumed at the bottom was well above unity.

In order to evaluate the portion of the nutrient release originating from actual decomposition of organic matter, the total consumption of oxidants (O_2, NO_3^-, SO_4^{2-}) was calculated as a function of time . According to model calculations for the degradation of organic matter during subsequent periods of oxygen consumption, denitrification and sulphate reduction (Richards, 1975; Hartmann *et al.,* 1973), it was assumed that the utilized oxidants are equivalent to each other in the form of oxidation equivalents (ox.eq., in µgat/l): ox.eq. = $\Delta O_2 + 2.5 \Delta NO_3^- + 4 \Delta SO_4^{2-}$ where Δ_i denote absolute changes in concentration (NO_3^- was only included after the onset of denitrification; the low amount of sulphate reduced was incorporated into the model as the corresponding production of sulphide). This calculation is only a rough approximation because is relies on the assumptions that: 1) consumption of oxidants takes place mainly at the interface; that 2) diffusion of oxidants into the sediments is counterbalanced by a respective upward diffusion of remineralized nutrients; and 3) that scavenging of sulphide as FeS (Balzer, 1982) is negligible. The plot of oxidation equivalents in Figure 3 shows a relatively low rate of consumption in the oxic period as compared to the anoxic region. This is probably due to the reduced respiration rate of the macrofauna as a consequence of the low oxygen saturation during late summer and especially during the first part of the experiment. In Figure 5 the concentrations of phosphate and ammonia are plotted versus the oxidation equivalents consumed. Assuming that the decomposition of organic nitrogen does not proceed further than ammonia, the oxidation of 1 mol of the model organic substance (Almgren *et al.,* 1975) having a composition of C:N:P = 106:8.9:0.87 in the top sediment layer should consume 212 oxidation

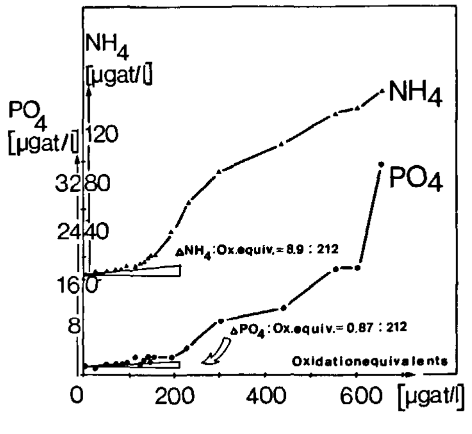


Figure 5
Nutrients released as a function of oxidants consumed.

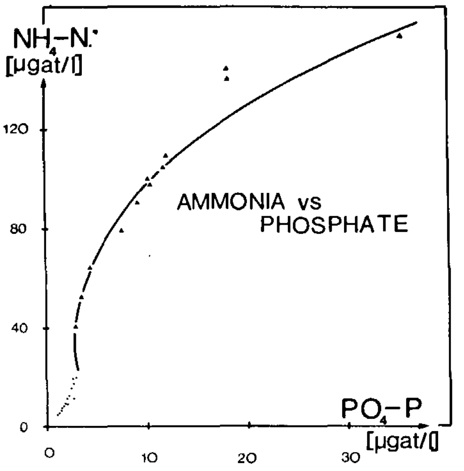
equivalents, and should release 8.9 moles ammonia and 0.87 mol phosphate according to the equation:

$$(CH_2O)_{106}(NH_3)_{8.9}(HPO_4^{2-})_{0.87} + 212 \text{ ox.eq.}$$
$$= 106\ CO_2 + 8.9\ NH_3 + 0.87\ HPO_4^{2-}.$$

During the first stage of the experiment, the products of decomposition are released only slightly in excess of the oxidants consumed. At the end of the oxic period, the release of nutrients deviate increasingly positive from the predicted values, suggesting already a contribution from dying organisms which cannot tolerate the developing anoxic conditions. After the onset of anoxic conditions in the bottom water, the relation between released products and consumed oxidants no longer holds. Enhanced phosphate release is due to fast autolytic production (Hoffmann, 1956) from organisms dying under anoxic conditions and to reductive dissolution of iron-hydroxo-phosphates. From the top 2 cm sediment of the bell jar area, with an average inorganic phosphorus content of 0.05% dw and a mean porosity of $\varphi = 0.62$ (Balzer, 1978), 954 µM/l phosphate could be released potentially into the enclosed water if all is bound to iron, released by reductive dissolution and evenly distributed in the water mass. Consequently, it cannot be determined which portion is released from organisms and which is due to the dissolution of sedimentary solids. Since nitrogen is not known to be involved in interaction with inorganic solids—except for low amounts sorbed to clay materials (Rosenfeld, 1979)—most of the excess ammonia release under anoxic conditions should originate from decaying organisms. To check whether one of the components is released preferentially, ammonia and phosphate were correlated in Figure 6. The justification for this plot relies on the assumption that the deviation from (natural) steady state conditions does not alter significantly the release behaviour of the two nutrients (via changing adsorption coefficients in the sediment and by accumulation of the species in the overlying water). During the oxic period, both nutrients are released at a nearly constant ratio of N:P = 8:1. Comparison with the sedimentary organic matter having a ratio of N:P = 10.25 suggests a slight preferential release of phosphate. Under lasting anoxic conditions, phosphate is released far in excess of ammonia, thus suggesting inorganic sources.

Figure 6

Plot of ammonia versus phosphate during oxic (small dots) and anoxic conditions (triangles).



Acknowledgements

We are indebted to Dieter Schorsch for taking care of the technical and electronic equipment and to Ingolf Keller for laboratory assistance. Theo Kollatschni and the SFB diving group helped during sampling; Captain Ohl and his crew provided shipboard facilities during the experiment. Ursula Seiffert drafted the figures. Valuable criticism and suggestions by the referees are gratefully acknowledged.

REFERENCES

Aller R. C., 1980. Diagenetic processes near the sediment-water interface of Long Island Sound. I. Decomposition and nutrient element geochemistry, *Adv. Geophys.*, **22**, 237-350.

Almgren T., Danielson L. G., Dyrssen D., Johannson T., Nyquist G., 1975. Release of inorganic matter from sediments in a stagnant basin, *Thalassia Jugosl.*, **11**, 19-29.

Anderson D. H., Robinson R. J., 1946. Rapid electrometric determination of the alkalinity of seawater using a glass electrode, *Ind. Eng. Chem. Anal. Ed.*, **18**, 767-773.

Balzer W., 1978. Untersuchungen über Abbau organischer Materie und Nährstoff-Freisetzung am Boden der Kieler Bucht beim Übergang vom oxischen zum anoxischen Milieu, *Ph. D. Dissert., Univ. Kiel*, 129 p.

Balzer W., 1980. Calcium carbonate saturometry by alkalinity difference measurement, *Oceanol. Acta*, **3**, 2, 237-243.

Balzer W., 1982. On the distribution of iron and manganese at the sediment/water interface: thermodynamic versus kinetic control, *Geochim. Cosmochim. Acta*, **46**, 1153-1161.

Berner R. A., 1963. Electrode studies of hydrogen sulfide in marine sediments, *Geochim. Cosmochim. Acta*, **27**, 563-575.

Berner R. A., 1971. *Principles of chemical sedimentology*, Mc Graw-Hill, New York, 240 p.

Berner R. A., 1980. *Early diagenesis: a theoretical approach*, Princeton Univ. Press, Princeton, 241 p.

Billen G., 1978. The dependence of the various kinds of microbial metabolism on the redox state of the medium, in: Biogeochemistry of estuarine sediments, *Proc. UNESCO/SCOR workshop, Melreux, Belgium*, 254-261.

Bockris J. O'M., Oldfield L. F., 1955. The oxidation-reduction reactions of hydrogen peroxide at inert metal electrodes and mercury cathodes, *Trans. Faraday Soc.*, **51**, 249-259.

Bodungen B., 1975. Der Jahresgang der Nährsalze und der Primärproduktion des Planktons in der Kieler Bucht unter Berücksichtigung der Hydrographie, *Ph. D. thesis, Univ. Kiel.*

Bodungen B., Bröckel K. v., Smetacek V., Zeitzschel B., 1976. The Plankton Tower. I. A structure to study water/sediment interactions in enclosed water columns, *Mar. Biol.*, **34**, 369-372.

Breck W. G., 1974. Redox levels in the sea, in: *The sea, vol. 5*, edited by E. D. Goldberg, Marine Chemistry, Wiley, New York, 153-180.

Christensen J. P., Packard T. T., 1977. Sediment metabolism from the Northwest African upwelling system, *Deep-Sea Res.*, **24**, 331-343.

Davies J. M., 1975. Energy flow through the benthos in a Scottish Sea loch, *Mar. Biol.*, **31**, 353-362.

Deuser W. G., Ross E. H., Mlodzinska Z. J., 1978. Evidence for and rate of denitrification in the Arabian Sea, *Deep-Sea Res.*, **25**, 431-445.

Dieckmann P., Haardt H., Petersohn U., 1976. Messungen zum Planktonschlauchexperiment 1975 mit dem Fernmeßsystem "OBS", Rep. Sonderforschungsbereich 95, Univ. Kiel, No. 17.

Dries R.-R., Theede H., 1976. Stoffwechselintensität und Reservestoffabbau einiger mariner Muscheln bei herabgesetzter Sauerstoffspannung des Mediums, *Kiel. Meeresforsch., Sonderheft 3*, 37-48.

Dye A. H., 1979. Measurement of biological oxygen demand in sandy beaches, *S.-Afr. Tydskr. Dierk.*, **14**, 55-60.

Edmond J. M., Gieskes J. M., 1970. On the calculation of the degree of saturation of seawater with respect to calcium carbonate under *in situ* conditions, *Geochim. Cosmochim. Acta*, **34**, 1261-1291.

Elderfield H., Luedke N., McCaffrey R. J., Bender M., 1981. Benthic flux studies in Narragansett Bay, *Am. J. Sci.*, **281**, 768-787.

Fonselius S. H., 1976. Determination of hydrogen sulphide, in: *Methods of seawater analysis*, edited by K. Grasshoff, Verlag Chemie, Weinheim, 71-78.

Froelich P. N., Klinkhammer G. P., Bender M. L., Luedke N. A., Heath G. R., Cullen D., Dauphin P., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis, *Geochim. Cosmochim. Acta*, **43**, 1075-1090.

Gieskes J. M., 1974. The alkalinity-total carbon dioxide system in seawater, in: *The Sea, Vol. 5*, edited by E. D. Goldberg, Marine Chemistry, J. Wiley, New York, 123-152.

Grasshoff K., 1975. The hydrochemistry of land locked basins and fjords, in: *Chemical oceanography, Vol. 2*, edited by J. P. Riley and G. Skirrow, Academic Press, London, 456-598.

Grasshoff K. (Ed.), 1976. *Methods of seawater analysis*, Verlag Chemie, Weinheim, 317 p.

Hallberg R. O., Bågander L. E., Engvall A. G., Schippel F. A., 1972. Method for studying geochemistry of sedimentwater interface, *Ambio*, **1**, 71-73.

Hanson R. B., 1980. Measuring microbial activity to assess detrital decay and utilization, in: *Marine benthic dynamics*, edited by K. R. Tenore and B. C. Coull, Univ. South Carolina Press, 347-358.

Hargrave B. T., Connolly G. F., 1978. A device to collect supernatant water for measurement of the flux of dissolved compounds across sediment surfaces, *Limnol. Oceanogr.*, **23**, 1005-1010.

Hargrave B. T., Phillips G. A., 1981. Annual in situ carbon dioxide and oxygen flux across a subtidal marine sediment, *Estuarine Coastal Shelf Sci.*, **12**, 725-737.

Hartmann M., Müller P., Suess E., Weijden C. H. van der, 1973. Oxidation of organic matter in recent marine sediments, *"Meteor" Forschungsergeb., Reihe C*, **12**, 79-86.

Hinga K. R., Sieburth J. McN, Heath G. R., 1979. The supply and use of organic material at the deep-sea floor, *J. Mar. Res.*, **37**, 557-579.

Hoffmann C., 1956. Untersuchungen über die Remineralisation des Phosphors im Plankton, *Kiel. Meeresforsch.*, **12**, 25-36.

Klump J. V., Martens L. S., 1981. Biogeochemical cycling in an organic rich coastal marine basin. II. Nutrient sediment-water exchange processes, *Geochim. Cosmochim. Acta*, **45**, 101-121.

Koelmel R., 1976. Ökosysteme im Wechsel zur Anaerobiose. Die Entwicklung von Zoobenthos und Abbau in zeitweise anoxischen Biotopen der Kieler Bucht, *Ph. D. thesis, Univ. Kiel*, 403 p.

Kohr P., 1976. Ein Meßverfahren zur Bestimmung der Tiefe der Redoxdiskontinuität über lange Zeiten, *Kiel. Meeresforsch., Sonderheft 3*, 11-15.

Krom M. D., Berner R. A., 1981. The diagenesis of phosphorus in a nearshore marine sediment, *Geochim. Cosmochim. Acta*, **45**, 207-216.

Kunicki-Goldfinger W. J. H., 1974. Methods in aquatic microbiology. A story of apparent precision and frustrated expectations, *Pol. Arch. Hydrobiol.*, **21**, 3-17.

Light T. S., 1972. Standard solutions for redox potential measurements, *Anal. Chem.*, **44**, 1038-1039.

Martens C. S., 1978. Some of the chemical consequences of microbially mediated degradation of organic materials in estuarine sediments, in: Biogeochemistry of estuarine sediments, *Proc. UNESCO/SCOR workshop, Melreux, Belgium*, 266-278.

Morgan J. J., 1967. Applications and limitations of chemical thermodynamics in water systems, in: Equilibrium concepts in natural water systems, edited by R. F. Gould, *Adv. Chem. Ser.*, **67**, 1-29.

Mortimer C. H., 1971. Chemical exchanges between sediments and water in the Great Lakes-speculations on probable regulatory mechanisms, *Limnol. Oceanogr.*, **16**, 387-404.

Nixon S. W., Kelly J. R., Furnas B. N., Oviatt C. A., Hale S. S., 1980. Phosphorus regeneration and the metabolism of coastal marine bottom communities, in: *Marine benthic dynamics*, edited by K. R. Tenore and B. C. Coull, Univ. South Carolina Press, 219-242.

Pamatmat M. M., 1971. Oxygen consumption by the seabed, IV: Shipboard and laboratory experiments, *Limnol. Oceanogr.*, **16**, 536-550.

Pamatmat M. M., 1975. *In situ* metabolism of benthic communities, *Cah. Biol. Mar.*, **16**, 613-633.

Pamatmat M. M., 1977. Benthic community metabolism: a review and assessment of present status and outlook, in: *Ecology of marine benthos*, edited by B. C. Coull, Univ. South Carolina Press, 89-111.

Pamatmat M. M., 1980. Facultative anaerobiosis of benthos, in: *Marine benthic dynamics*, edited by K. R. Tenore and B. C. Coull, Univ. South Carolina Press, 69-90.

Pamatmat M. M., Bhagwat A. M., 1973. Anaerobic metabolism in Lake Washington sediments, *Limnol. Oceanogr.*, **18**, 611-627.

Pamatmat M. M., Graf G., Bengtson W., Novak C. S., 1981. Heat production, ATP concentration and electron transport activity of marine sediments, *Mar. Ecol. Progr. Ser.*, **4**, 135-143.

Richards F. A., 1965. Anoxic basins and fjords, in: *Chemical oceanography, Vol. 1*, edited by J. P. Riley and G. Skirrow, Academic Press, London, 611-645.

Richards F. A., 1975. The cariaco basin (trench), *Oceanogr. Mar. Biol. Ann. Rev.*, **13**, 11-67.

Rosenfeld T. K., 1979. Amino acid diagenesis and adsorption in nearshore anoxic sediments, *Limnol. Oceanogr.*, **24**, 1014-1021.

Sato M., 1960. Oxidation of sulfide ore bodies. 1. Geochemical environments in terms of Eh and pH, *Econ. Geol.*, **55**, 928-961.

Smetacek V., 1980. Annual cycle of sedimentation in relation to plankton ecology in Western Kiel Bight, *Ophelia, Suppl.*, **1**, 65-76.

Smith K. L., 1978. Benthic community respiration in the N.W. Atlantic Ocean: *in situ* measurements from 40-5200 m, *Mar. Biol.*, **47**, 337-347.

Stöber W., 1967. Formation of silicic acid in aqueous suspensions of different silica modifications, in: Equilibrium concepts in natural water systems, edited by R. F. Gould, *Adv. Chem. Ser.*, **67**, 161-181.

Stumm W., Morgan J. J., 1970. *Aquatic chemistry*, Wiley-Interscience, New York, 583 p.

Wefer G., Tauchgruppe Kiel, 1974. Topographie und Sedimente im "Hausgarten" des Sonderforschungsbereiches 95 der Universität Kiel (Eckernförder Bucht, westl. Ostsee), *Meyniana*, **26**, 3-7.

Zeitzschel B., 1980. Sediment-water interactions in nutrient dynamics, in: *Marine benthic dynamics*, edited by K. R. Tenore and B. C. Coull, Univ. South Carolina Press, 195-218.

Zeitzschel B., Davies J. M., 1978. Benthic growth chambers, Rapp., *P.-V. Réun. Cons. Int. Explor. Mer*, **173**, 31-42.