

UNDERSTANDING THE BIOREACTOR WADDEN SEA: A GEOCHEMICAL AND PHYSICAL APPROACH

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Introduction

Tidal flats are a highly dynamic system and subject to short- and long-term fluctuations of biological, geochemical, and physical parameters. Although the study area forms the biologically productive transition zone between the terrestrial and the marine environment, the processes controlling the geochemical dynamics are so far poorly understood. Such processes, e. g. microbial activity in the sediment and in the water column, influence the geochemical composition of dissolved and particulate matter in the intertidal area and therefore also the elemental export to the North Sea.

Our major goal is the characterisation and quantification of dissolved and particulate matter and their flux between the Wadden Sea and the North Sea on a tidal, seasonal and annual scale. Additionally, the biogeochemical transformation of matter in the water column is investigated with a special focus on redox-sensitive trace metals.

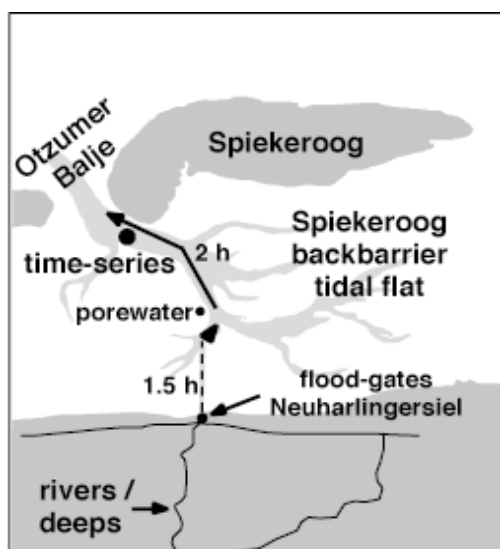


Fig. 1. Map of the study area showing the location of the time-series station in the major tidal outlet (Otzumer Balje), the flood-gate at Neuharlingersiel, and the porewater sampling site. Arrows mark the pathway of freshwater contributed via the flood-gates.

Geographical setting

Fig. 1 shows the sampling location in the major tidal outlet (Otzumer Balje; 53°44.9N, 7°40.0E) of the Speikeroo g island backbarrier tidal flat. Sampling was performed with research vessel FK Senckenberg during four time-series stations in February, May, August and November 2002 at spring tide.

Material and methods

Water column temperature, salinity, pH, oxygen, and redox potential were measured with a Seabird SBE 19-plus Seacat profiler. Sampling and filtration of surface water was done every hour for analysis of yellow-substance fluorescence (samples filtered with 0.7 μm glass fibre filters and analysed with a Shimadzu RF1501 spectrofluorometer), DOC (0.7 μm Whatman GF filters, multi N/C 3000, Analytik Jena), and particulate major and trace elements (0.4 μm polycarbonate filters). Major and trace elements were determined from

HNO_3 , HF, HClO_4 acid digestions by ICP-OES and ICP-MS. Dissolved trace metals (0.45 μm SFCA syringe filters, ICP-MS) were sampled every 15 to 30 min depending on the variation of physical parameters.

Results and discussion

Water column signatures

The tidal flats of the study area form the transition zone between the terrestrial (freshwater) and the marine (North Sea) realm. The varying influence of both end members is reflected in tidal and seasonal fluctuations in salinity, which are exemplified in Fig. 2 for February and August. Lowest salinity values and the most pronounced variation is seen in winter, whereas in summer salinity is on the highest level with only marginal differences between high and low tide.

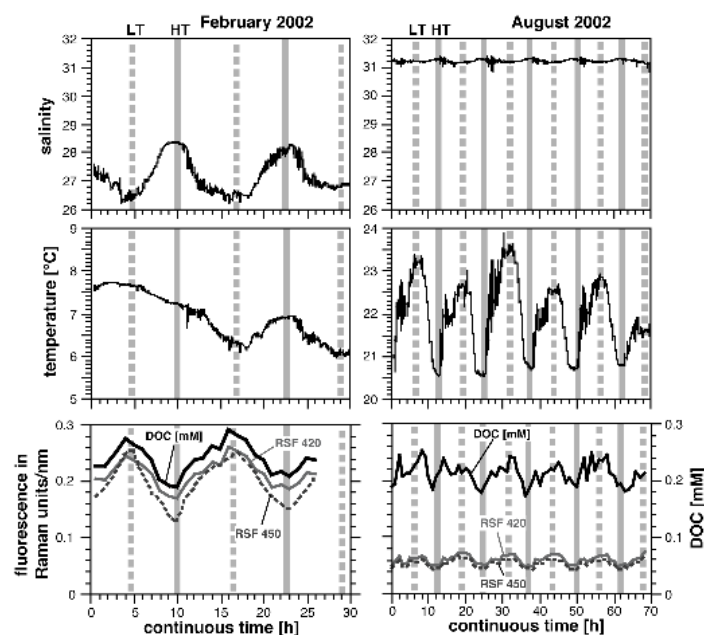


Fig. 2. Salinity, water temperature, yellow-substance fluorescence (308 nm excitation, 420 and 450 nm emission, normalised to the water Raman scatter band; DETERMANN *et al.*, 1994) and DOC during two time-series in 2002 in the Otzumer Balje (LT=low tide, HT=high tide).

The situation found in May and November (not shown) reflects transition stages between winter and summer. In May salinity shows an almost identical pattern to August, whereas in November a distinct trend towards higher variation on a lower mean salinity level is observed. This variation is presumably controlled by weather conditions, in particular precipitation. Freshwater input into the investigated area via the Neuharlingersiel flood-gate is essentially controlled by rainfall in the catchment area of the flood-gate. In February the freshwater discharge was distinctly higher than in May or August. Depending on water levels, freshwater is usually discharged about two hours before low tide. It reaches the central backbarrier area at low tide, as shown by drift experiments (arrow in Fig. 1), and then spreads mainly towards the eastern part of the backbarrier area with the following flood current. During the subsequent ebb current the time-series station in the Otzumer Balje (Fig. 1, black arrow) is reached within about two hours.

Although salinity values are almost constant in May and August (Fig. 2) the temperature shows a tidal cyclicity owing to sunlight-induced warming of the water column at low tide, which evidences the exchange of different water masses. In February the water temperature pattern was more monotonous under the influence of day and night air temperatures.

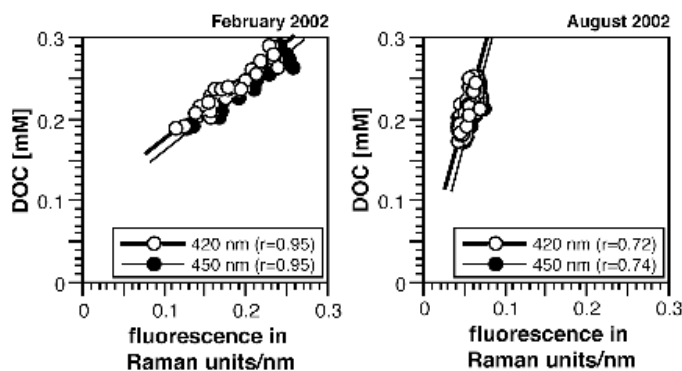


Fig. 3. Yellow-substance fluorescence (308 nm excitation) versus DOC.

Besides salinity a further parameter reflecting the freshwater influence on the Wadden Sea is yellow-substance fluorescence (Fig. 2). This parameter similar to the concentration of dissolved organic carbon (DOC) shows a tidal cyclicality with maxima at low tide in February and May. The mean level of yellow-substance fluorescence is distinctly higher in February when compared with the August data. Freshwater samples from the catchment area show a much higher level of yellow-substance fluorescence throughout the year than the Wadden Sea water (KÖLSCH *et al.*, this volume), which explains the observed higher level of yellow substance in February when the freshwater input was highest. Yellow-substance fluorescence is well correlated with the concentration of DOC for the individual cruises (Fig. 3). However, the specific relation of fluorescence versus DOC varies between cruises. This suggests a change in fluorophore concentration and/or composition of dissolved organic matter in the tidal flats, which may be caused by variations in DOC composition of the contributing water types or by chemical transformation during mixing.

In Fig. 4 we present the concentrations of dissolved Mn, Mo, and U for the cruises in February and August. Mn shows the most pronounced tidal pattern with maximum concentrations during low tide. However, the Mn concentrations in August are about 10-fold higher in comparison to the cruise in February. Again, the May and November (not shown) data show a transitional behaviour between both extreme situations. Whereas the changes of V in February are within the analytical accuracy, the samples taken during the cruise in August show a tidal pattern similar to that of Mn. Contrasting to Mn, Mo and U behave conservatively in February with maximum concentrations during high tide. This is also true for U in August, whereas Mo shows unexpected increasing concentrations towards low tide. This indicates a coupling of Mo to the Mn cycle in the Wadden Sea during summer.

Three major sources control the geochemical composition of the Wadden Sea waters and particulates: i) the German Bight, ii) the freshwater, and iii) the porewater which is drained from the tidal flat sediments during ebb tide. Whereas the water of the German Bight is relatively poor in Mn and rich in Mo (DELLWIG *et al.*, 2003), the freshwater reveals an opposite composition.

Nevertheless, the dominating Mn source seems to be porewater, which shows increasing Mn concentrations from winter to summer due to increasing microbial activity and a higher release of soluble Mn²⁺, respectively. Therefore, the Mn concentrations of the tidal creeks also increase towards summer (Fig. 5).

A similar but less pronounced seasonal behavior is seen for V as well. Mo concentrations of porewaters and creek water are almost identical to the German Bight, only in August a distinct increase is observed. This behavior is rather striking as Mo should be fixed in the sediments under reducing conditions.

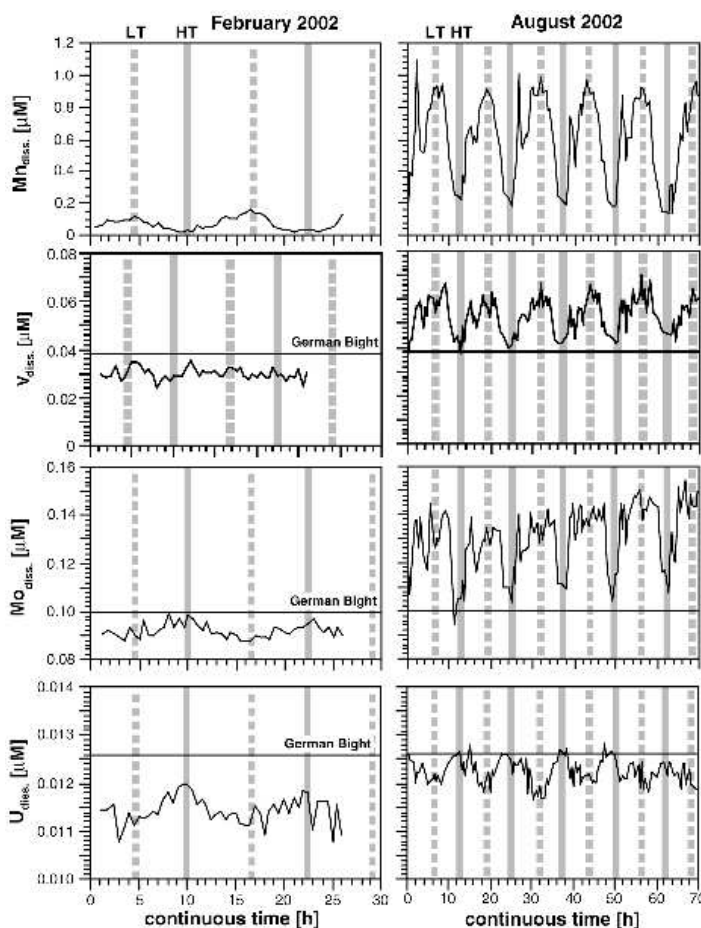


Fig. 4. Variations of dissolved Mn, V, Mo and U during two time-series stations in the Otzumer Balje

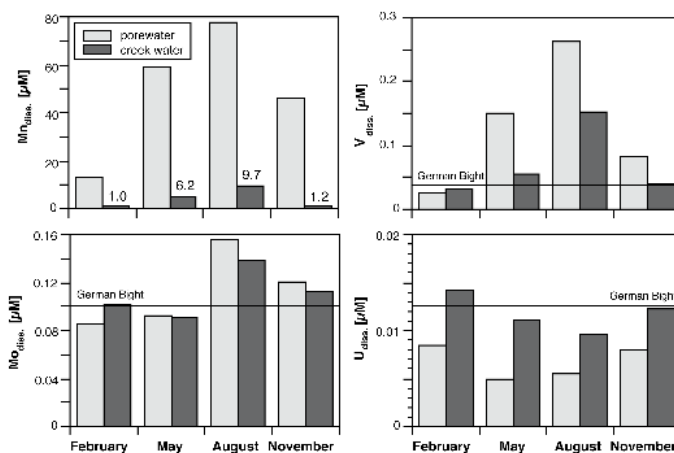


Fig. 5. Concentrations of Mn, V, Mo, and U in porewater and creek water for the individual cruises.

Hence, special conditions in summer must be responsible for this unusual observation. Taking into account the seasonal dependency, the involvement of biological processes has to be considered. In contrast, the sediments seem to be a sink for U, which shows distinctly lower pore water concentrations in comparison to the German Bight value.

Suspended particulate matter

Mn on SPM in most cases shows a tidal cyclicality for the individual cruises, with increasing concentrations towards high tide in February, whereas in May and August the maximum Mn load was observed during low tide. In addition, Mn shows

a distinct seasonality with increasing Mn contents towards summer by a factor of about 2 in comparison to the winter situation. In Fig. 6a we present the Mn/Al ratios versus Al₂O₃ of SPM of the four cruises in the Wadden Sea. It can be clearly seen that the Mn load of the individual particles increases towards summer due to increasing microbial and/or photo-oxidation of dissolved Mn (MOFFETT, 1994; NICO *et al.*, 2002). However, regarding the scatter plot of excess Mn versus Al of the particles per water volume (Fig. 6b) it is likely that the high SPM concentrations in winter and fall lead to a high concentration of particulate Mn in the water column.

In August particles are also strongly enriched in Mo, whereas U and V essentially reflect the geogenic background. Leaching experiments (1 N HCl, 24 h) with SPM from August showed that about 90% of the Mn and 70% of the Mo are adsorbed on particle surfaces which confirms the strong relation between Mo and Mn cycles in summer (Fig. 7). Thus, scavenging of Mo during the formation of particulate Mn in the water column may lead to enrichments of Mo on SPM. Such processes are favoured during the temperate conditions in summer. When such Mn- and Mo-rich particles reach the suboxic sediment surface, Mn-oxides will be partly redissolved and Mo will be released. Mo fixation under reducing conditions in surface sediments is possibly prevented by its strong affinity to DOC, which may act as a carrier for Mo until it reaches the water column during low tide.

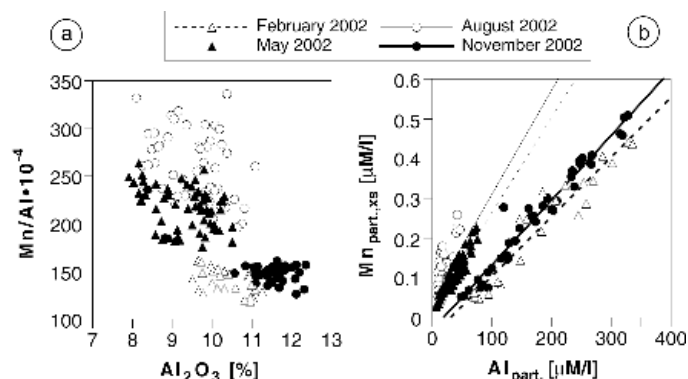


Fig. 6. Scatter plots of Mn/Al vs. Al₂O₃ of the particles and particulate Mn_{xs} vs. Al per water volume of the four time-series stations in the Wadden Sea.

Mn balance

As mentioned above the dominating Mn sources in the Wadden Sea system are the porewater and the freshwater environment. In Table 1 we present a simple balance calculation in order to illustrate the importance of both sources for the Mn budget of the Wadden Sea. Based on the assumption that the variation in salinity is caused by the freshwater contribution via the flood gates at Neuharlingersiel, the differences in salinity between the German Bight and the Wadden Sea allow estimating the freshwater and total Mn input (dissolved and particulate). The comparison of the total Mn input via freshwater with the observed mean concentration of Mn in the Wadden Sea shows that in February sufficient Mn is contributed by the freshwater and no additional sources are required. On the other hand, a distinct porewater input is needed to explain the observed Mn concentration in August. This is also true but less pronounced for the situation in May and November.

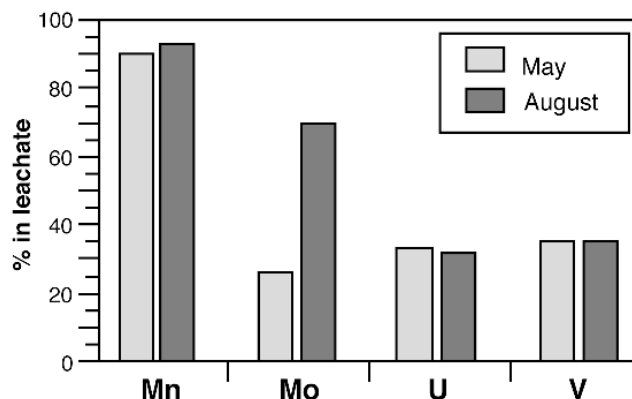


Fig. 7. Percentage of selected trace metals in leachate (1 N HCl) of suspended particulate matter of the Wadden Sea.

Table 1. Manganese mass balance of the Spiekeroog Island Wadden Sea water based on Mn input via freshwater and calculated porewater contribution (Mn concentrations are given in μM; total Mn = Σ dissolved and particulate Mn).

	February	May	August	November
mean salinity German Bight	33	33	33	33
mean salinity Wadden Sea	27.2	30.9	31.2	29.5
Δ salinity	5.8	2.1	1.8	3.5
% freshwater	17.7	6.3	5.4	10.6
total Mn freshwater	2.5	5.1	7.8	2.9
total Mn input via freshwater	0.44	0.32	0.42	0.31
total Mn Wadden Sea	0.35	0.40	0.75	0.39
calculated Mn input via porewater	-0.08	+0.07	+0.33	+0.08

Conclusions

- The observed changes in salinity in the Wadden Sea are controlled by freshwater input.
- Water temperature may indicate the tidal exchange of different water types even when salinity is almost constant, as it is strongly affected by heat input through solar radiation especially at low tide.
- Dissolved Mn shows a distinct tidal and seasonal variation with maximum concentrations during low tide in summer, due to enhanced microbial activity within the tidal flat sediments. A similar but less pronounced behaviour is seen for V. Mo and U behave conservative and follow salinity. Only during summer, Mo shows a coupling to the Mn cycle.
- Dissolved Mo and U behave conservatively and follow salinity. The only exception forms Mo during summer when increasing concentrations towards low tide are observed. This unusual behaviour indicates a coupling of Mo to the Mn cycle during summer.
- Porewater concentrations of Mn, Mo, and V increase towards summer, whereas the tidal flat sediments seem to be a sink for U in summer.
- Wadden Sea particles are distinctly enriched in Mn when compared with the geogenic background. Particulate Mn contents increase towards summer due to enhanced bacterial and/or photo-oxidation of Mn.
- Besides pore water, the freshwater contribution of the study area also forms an important Mn source. Although a distinct pore water contribution is necessary to explain the Mn budget of the Wadden Sea during summer, freshwater contributes sufficient Mn in winter.

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References

DELLWIG, O., HINRICHS, J., TERJUNG, F., REUTER, R. & BRUMSACK, H.-J. (2003). Tidal and seasonal variations of a backbarrier intertidal system near Spiekeroog Island and the adjoining German Bight, in prep.
 DETERMANN, S., REUTER, R., WAGNER, P. & WILLKOMM, R. (1994) Fluorescent matter in the eastern Atlantic Ocean: Part 1. Method of measurement and near-surface distribution. *Deep-Sea Res.*, **41**, 659-675.
 MOFFETT, J. W. (1994). A radiotracer study of cerium and manganese uptake onto suspended particles in Chesapeake Bay. *Geochim. Cosmochim. Acta*, **58**, 695-703.
 NICO, P. S., ANASTASIO, C. & ZASOSKI, J. (2002). Rapid photo-oxidation of Mn(II) mediated by humic substances. *Geochim. Cosmochim. Acta*, **66**, 4047-4056.

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METHANOGENESIS FROM METHYLAMINE AND METHANOL AT CHANGING HYDROGEN CONCENTRATIONS

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Methylotrophic methanogens in pure culture metabolize methylated substrates (e. g. methanol, methylamine, acetate) to CH₄ and CO₂ in a predictable ratio (KELTJENS & VOGELS, 1993). Detailed studies revealed, that the proportion of the two products can deviate from the predicted stoichiometry. PHELPS *et al.* (1985) showed that methanogenesis from acetate yielded more CO₂, if the methanogen was cocultured with a sulfate reducer oxidizing the hydrogen produced by the methanogen. The continuous leakage of reducing power (as H₂) from the methanogen, as a result of sulfate reducing

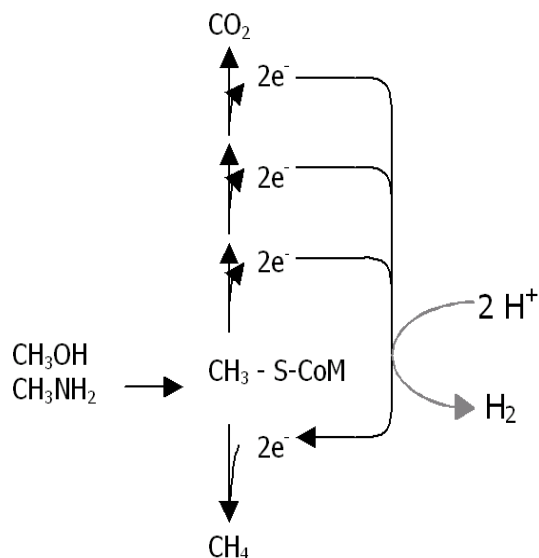


Fig. 1. Pathway of methanogenesis from methanol and methylamine. Dependent on the surrounding hydrogen concentration the methanogens can transfer more or less electrons to hydrogen instead of methane.

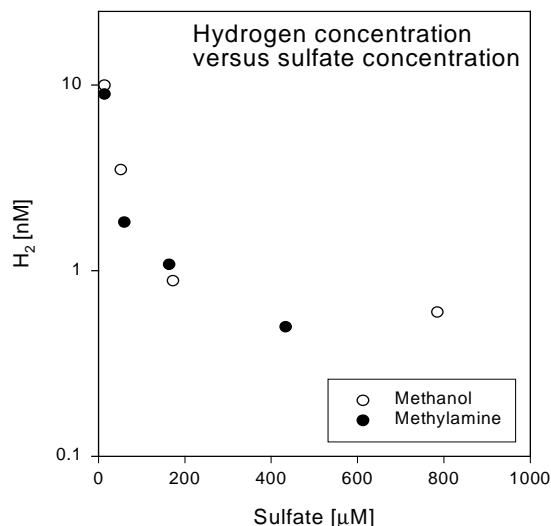


Fig. 2. Hydrogen concentration in dependence of the sulfate concentration in incubations with sediment from Dangast, Wadden Sea Germany

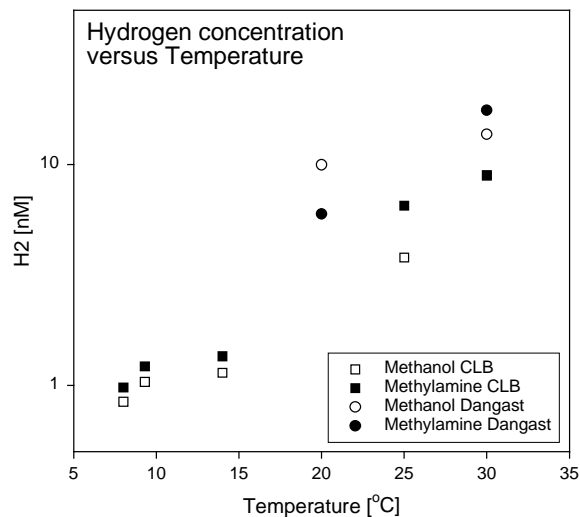


Fig. 3. Hydrogen concentrations as a function of the incubation temperature in sediments from Dangast, Wadden Sea Germany, and Cape Lookout Bight, USA.

activity, allows the methanogen to oxidize a greater proportion of the carbon to CO₂. We hypothesized that natural variations in H₂ concentrations in aquatic sediments might affect the degree to which H₂ liberation and oxidative metabolism of methylotrophic substrates occurs (Fig. 1). To test this hypothesis, we performed incubation experiments using methanogenic sediment in which H₂ concentrations were caused to vary as a function of temperature and sulfate concentration (HOEHLER *et al.*, 1998). In an additional experiment, lactate was added to the sediment to increase the hydrogen concentration due to increased fermentation activity. The conversion of methanol and methylamine to CH₄ and CO₂ in these treatments was quantified using radiotracer techniques. Increasing temperatures and decreasing sulfate concentrations both resulted in increasing H₂ concentrations, as well as the addition of lactate (Figs. 2, 3). With increasing H₂ concentrations, methanogenesis yielded less oxidized carbon (Fig. 4, Table 1). At the lowest H₂ concentrations, the fraction of electrons lost to H₂ leakage significantly exceeded that channeled into methane production. This was true even in the absence of sulfate (e. g., for the lowest temperatures). Thus, dependent on the hydrogen concentration, protons can represent a more important electron acceptor than the methyl carbon for methylotrophic methanogenesis.

Marine sediments are spatially separated according to the electron acceptor used for terminal oxidation. The decreasing