DIAGENESIS IN SUBRECENT MARINE SEDIMENTS IN THE EASTERN SCHELDT, SOUTHWEST NETHERLANDS

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ABSTRACT

The diagenesis in fine-grained sediments from a 300 to 400-years-old Dunkirk deposit, exposed on the intertidal flat, was studied at a site in the Eastern Scheldt. A new *in situ* pore water sampling technique that allowed repeated sampling at exactly the same place was used to monitor the seasonal fluctuations in interstitial water composition.

Concentrations of organic carbon (1.5 to 2%), nitrogen (C/N=19), phosphorus (500 $\mu g \cdot g^{-1}$) and manganese (250 $\mu g \cdot g^{-1}$) in the subrecent anoxic sediments were low, probably because they had already been depleted during earlier stages of diagenesis. Rates of organic carbon mineralization by sulphate reduction (0.1 $Mole \cdot m^{-2} \cdot y^{-1}$) and rates of nutrient regeneration were 1 to 2 orders of magnitude lower than in recent fine-grained sediments elsewhere in the Eastern Scheldt.

Pore water NH_4^+ and ΣPO_4 concentrations were controlled by mineralization, uptake by *Zostera noltii* and sediment-seawater exchange. During the summer the uptake exceeded the mineralization rate at 0 to 5 cm. Mineralization and diffusional processes dominated the changes in the NH_4^+ and ΣPO_4 profiles in the other seasons.

Dissolved manganese and iron concentrations showed a typical subsurface maximum at 0 to 3 cm, and low (<5 $\mu Mole$) concentrations below this depth. Dissolved iron concentrations were probably controlled by the solubility of iron sulphides, and manganese probably by the solubility of Mn, Ca-carbonate.

1. INTRODUCTION

Before 1986, approximately 0.1 to 0.3 Tg of fine-grained sediment (silt + clay) accumulated annualy in sheltered places in the Eastern Scheldt, a tidal inlet in the southwest Netherlands (OENEMA, 1988). This sediment was a mixture of mainly quaternary marine deposits of marine origin, recent algal detritus and river-borne suspended material. The subrecent quaternary deposits locally outcrop in the Eastern Scheldt because of the scouring and deepening of tidal channels and the erosion of salt marshes and tidal flats during the last few centuries (VAN DEN BERG, 1986).

The accreting fine-grained sediments in the Eastern Scheldt are rapidly supplied with new, reactive material. Mineralization of organic matter through sulphate reduction is a dominant diagenetic process in these sediments, supporting high fluxes of C, N, P, Si and Mn from the sediments to the overlying water (OENEMA, 1988). In contrast, the subrecent sediments exposed on tidal flats and in tidal channels have lost their most reactive surface layers due to erosion. Initial diagenesis since its deposition several centuries ago will also have decreased the reactivity of these subrecent sediments (BERNER, 1980).

Within the context of studies on the early diagenesis in anoxic fine-grained sediment, we made measurements of sedimentation rates and of the composition of sediments and their pore waters, to assess the role of the sedimentary environment in the carbon and nutrient cycles of the Eastern Scheldt. This paper reports the investigations on the diagnesis in the subrecent marine sediments.

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2. METHODS

2.1. STUDY SITE

The Eastern Scheldt is a tidal inlet with a total surface area of 450 km^2. Approximately 30% of the area consists of intertidal flats. The tide range was 3.0 to 3.5 m and the tidal volume 1100 million m^3 before the recently completed Storm Surge Barrier and Compartment dams in 1986-1987 (KNOESTER et al., 1984). The fresh water and river-borne suspended matter inputs were relatively small (STORTELDER et al., 1984).

The study site was located on an intertidal flat in the Zandkreek (Fig. 1), where 20 to 30% of the surface area is covered by subrecent clayey deposits. These bluish-grey deposits (Revised Standard Soil Color Charts) of low porosity (0.55-0.65 cm^3 cm^{-3}) are remnants of eroded salt marshes, which probably began to form in the 16th and 17th centuries, according to historic maps (DE BRUIN & WILDEROM, 1961). No precise data for the formation and the erosion rate of these marshes are available. Topographic maps of 1856, 1902 (map 48) and 1933 (maps 617, 618, 637 and 638) indicate that the former marshes in the Zandkreek were almost completely eroded between 1856 and 1933. Since then little or no sedimentation has occurred at the study site. These subrecent sediments are easily distinguished from the highly unconsolidated (porosity is 0.70 to 0.85) dark grey muds of the rapidly accreting fine-grained sediments in abandoned channels and mussel plots in the Zandkreek and elsewhere in the Eastern Scheldt (OENEMA, 1988). Like most of the sheltered locations with clayey sediments in the Eastern Scheldt, the surface of the study site was covered in summer with a dense growth of eelgrass, Zostera noltii (NIENHUIS & DAEMEN, 1985).

2.2. SEDIMENT ANALYSIS

Sections of 2 to 10 cm of a 1 m deep sediment core (i.d. 10 cm) were freeze-dried immediately after sampling. All further sediment analyses, except for the determination of the grain-size distribution, were carried out on powdered samples. A summary of the methods used is given in Table 1.

2.3. PORE-WATER ANALYSIS

—The sampler. Pore water was sampled by in situ dialysis (e.g. CARRIGAN, 1984; HESSLEIN, 1976; HOWES, 1985), to avoid any artifacts of oxidation and temperature which might have occurred if squeezing or centrifuging techniques had been used. The sampler (Fig. 2a), a modified and extended version of the sampler described by HESSLEIN (1976), allowed
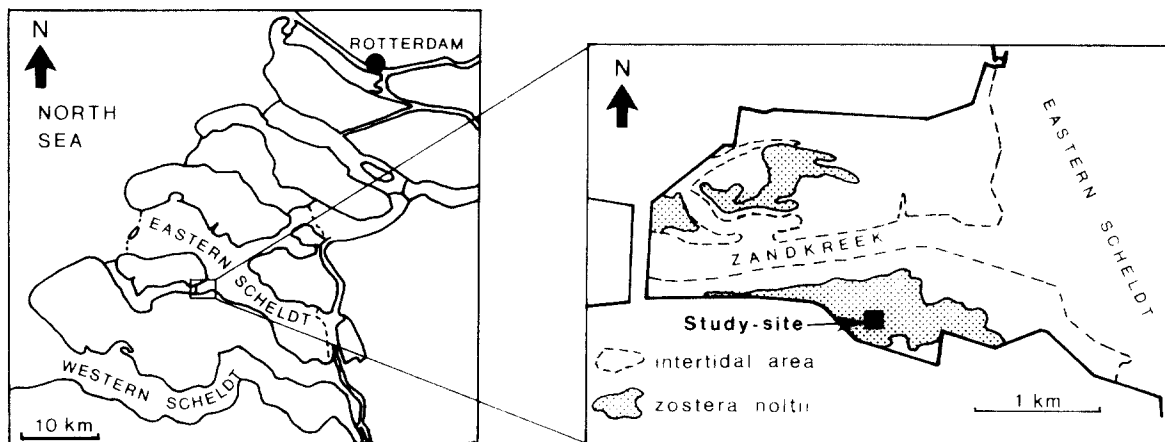

Fig. 1. The Zandkreek study-site in the Eastern Scheldt, with distribution of Zostera noltii in 1984 according to data of D.J. de Jong.

TABLE 1

Analytical methods for sediment analysis.

|	
Porosity:	from weight loss of known sediment volumes.
Grain-size distribution:	pipette method, after pre-treatment with H_2O_2 and HCl.
Loss on ignition:	ignition at 950°C.
Major elements:	determination of Si, Al, Fe, Ca, Mg, K, Mn and P by XRF after fusion of 0.5 g of ignited sediment with 5 g Spectroflux type 1100 (Johnson Matthey Chemicals, England).
Organic C.:	wet oxidation with $K_2Cr_2O_7$ and H_2SO_4 (PAGE et al., 1982).
Total N:	titrimetric, after digestion with H_2SO_4 and Se (PAGE et al., 1982).
Calcite:	acid dissolution and determination of the volume of liberated CO_2 (PAGE et al., 1982).
Fe, Mn oxyhydroxides:	extraction with NH_4-oxalate (1 M, pH 3); determination of iron and manganese with AAS (SCHWERTMANN, 1964).
Pyrite-iron:	selective dissolution with H_2SO_4 (96%), HF (48%) and HNO_3 (70%) (BEGHEYN et al., 1978); determination of iron with AAS.
Phosphates:	extraction scheme of HIELTJES & LYKLEMA (1980)
	—exchangeable and carbonate bound-P: 1 M NH_4Cl
	—Fe and Al oxyhydroxide bound-P: 0.1 M NaOH
	—Ca bound-P: 0.5 M HCl
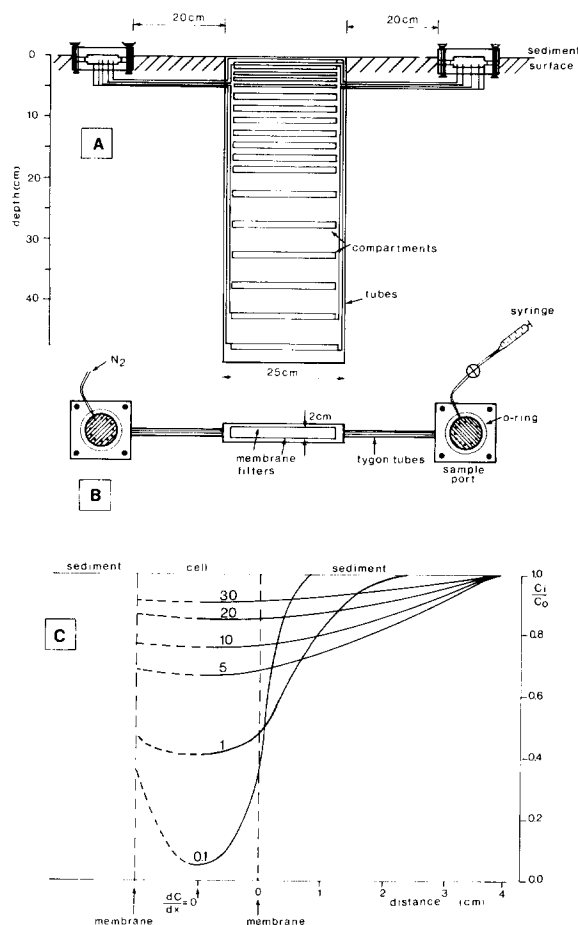
Fig. 2. The pore-water sampler: (A) cross-section in the sediment, (B) view from the top during sampling, and (C) development of equilibrium in the dialysis cell after 0.1 to 30 days (see text).

repeated sampling of pore water at exactly the same location. It had 5 compartments of 20 cm³ each in the top 5 cm, and 40 cm³ compartments at 1 to 5 cm depth intervals below. Both sides of the 2-cm-thick (PVC) sampler contained a biologically inert acrylic copolymer membrane filter (Versapor-200; Gelman Sciences) with a pore-size of 0.2 μm, attached to the sampler by a thin (1.5 mm) PVC sheet with notches at the level of each compartment. This membrane filter was so strong that after a period of two years in several types of sediments in the Eastern Scheldt, no visible degradation of the membrane filters was observed. Each compartment was connected by to tygon (PVC, Norton, Belgium) tubes (i.d. 0.8 mm; o.d. 4.0 mm) to two sample ports at the surface, one with the bottom of each compartment and the other with the top. The sampler was inserted in the sediment at a slight angle (1 to 2° to the vertical) and remained there permanently. The depth of the upper sample compartment varied irregularly between 0 to 0.5 cm depth in the sediment during the sampling period, due to temporal sedimentation and erosion of fine sand and silt.

—Sampling and analysis. Samples were withdrawn from the compartments by drawing the "pore water" through one sample port into a syringe and pumping nitrogen gas into the compartment via the second port (Fig. 2b). After sampling, all compartments were immediately refilled with filtered (0.2 μm), deoxygenated Eastern Scheldt water. The connections between the compartments and sample ports, and the slight inclination of the sampler in the sediment, allowed all nitrogen gas to escape during this replenishment.

Three successive samples with a total volume of about 15 cm^3 were drawn from each compartment. The sample volumes were calculated from the weight differences of the syringes before and after sampling. The first 1 to 2 cm^3 were always discarded via a 3-way valve (Fig. 2b). A 0.5 to 1.5 cm^3 portion was sucked into a syringe, prefilled with 2 cm^3 Zn-acetate (2%) and 0.5 cm^3 1 M NaOH, for dissolved sulphide (ΣS) determination. A 2 to 4 cm^3 portion went into a syringe prefilled with 5 cm^3 0.1 M H_2SO_4 for the determination of Fe^{2+} and Mn^{2+}. Another 8 to 12 cm^3 went into an empty syringe for the determination of pH, Cl^-, SO_4^{2-}, total inorganic carbon (ΣCO_2),NH_4^+, ΣPO_4, and dissolved reactive silica (H_4SiO_4). All samples were stored at 4°C and analysed within 36 h. The whole sampling procedure took approximately 2 h. Extreme care was taken not to disturb the sediment within 0.5 m of the sampler.

The analyses for Cl^-, SO_4^{2-}, ΣCO_2, NH_4^+, ΣPO_4, H_4SiO_4, Fe and Mn were done by routine auto-analyser techniques. Dissolved ΣS was measured on a Perkin Elmer 550 S spectrophotometer (670 nm). A summary of the analytical methods is given in Table 2.

—Sampling frequency. The equilibration time of the solution in the sampler was calculated according to Fick's second law and verified experimentally. When the sampler, filled with distilled water, was placed in the clayey sediment for 19 days, the Cl^- and SO_4^{2-} concentrations in the compartments were still only 90 to 95% of the concentrations in pore water squeezed from a core taken in the vicinity of the sampler. Complete equilibrium, i.e. less than 4% difference between Cl^- and SO_4^{2-} concentrations in the sampler and those in the pore waters squeezed from a core taken nearby, was attained after ≥ 25 days.

Calculations, based on the concept of one-dimensional diffusion from a constant source (e.g. KEPKAY et al., 1981), confirmed these results. Fick's second law holds for the dialysis cell:

$$\frac{dC_1}{dt} = D \frac{d^2C_1}{dx^2} \qquad (1)$$

and the sediment:

$$\frac{dC_2}{dt} = D_s \frac{d^2C_2}{dx^2} \qquad (2)$$

where C_1, C_2 =concentrations of ions in cell and sediment, respectively,

D =diffusion coefficient in seawater (cm^2·s^{-1}),

$D_s = D\Phi^{n-1}$ =diffusion coefficient in sediment corrected for porosity and tortuosity ($n \approx 2$ for sediments with $\Phi < 0.7$; ULLMAN & ALLER, 1982),

Φ =porosity

x =distance (cm),

t =time (s).

The diffusive fluxes match at the membrane so that at this site for $t > 0$

$$D\frac{dC_1}{dx} = \Phi D_s \frac{dC_2}{dx} \qquad (3)$$

The partial differential equations (1) and (2) were solved numerically by Gear's method (DEW & WALSH, 1981) for the following conditions:

initial conditions:

C_1 =0 (distilled water in the cell),

$C_2 = C_o$ (equilibrium concentration in the sediment),

boundary conditions:

TABLE 2

Analytical methods for pore-water analyses.

pH	with a micro-electrode within 3 h of sampling
ΣS	methylene-blue (GILBOA-BARBER, 1976)
Cl^-	mercury thiocyanate (ZALL et al., 1956)
SO_4^{2-}	methylthymol blue (MERKS & SINKE, 1981)
ΣCO_2	sulfuric acid-gas membrane-phenolphtalein (GRASSHOFF & HANSEN, 1979)
NH_4^+	sodium salicylate-nitro-prusside-hypochlorite (TELLOW & WILSON, 1964)
$NO_3^- + NO_2^-$	sulfanilamide-N- (1 naphtylethylene diamine) dihydrochloride, after cadmium reduction (ARMSTRONG et al., 1967)
ΣPO_4	molybdate-ascorbic acid (MURPHY & RILEY, 1962)
H_4SiO_4	molybdate-ascorbic acid-oxalic acid (BREWER & RILEY, 1966)
Fe^{2+}	2, 4, 6,-tripyridyl-(2)-1, 3, 5,-triazine-hydroxylamine (HENRIKSEN, 1967)
Mn^{2+}	formaldoxime (HENRIKSEN, 1966)

$$\frac{dC_1}{dx} = 0 \text{ (in the centre of the cell),}$$

$C_2 = C_o$ (in the sediment, at distance z from the cell membrane).

An example of these calculations is shown in Fig. 2c for z=4 cm, $D(Cl^-)=1.6*10^{-5}cm^2 \cdot s^{-1}$ and $\Phi=0.6$. After 30 days the concentration in the dialysis cell was 91% of the equilibrium concentration C_o in the sediment. Incomplete equilibration in the cell compartments after 30 days was calculated if the distance z of the second boundary condition exceeded 2 cm. Thus, when the second boundary condition held for z= ∞, the final concentration in the compartments was only 84% of C_o after 30 days; for z=1.5 cm equilibrium was attained after 21 days.

Comparison of results from these calculations with those obtained experimentally indicated that two- and three-dimensionsal diffusion played an important role in the replenishment of the ion-depleted pore waters in the sediment adjacent to the sampler. Production of ions in the sediment by, for example, the oxidation of organic matter will accelerate the equilibration process in the cell. On the basis of these considerations the sampling frequency was set at once per 1 to 2 months, to attain >95% equilibrium in the dialysis cells, also after repeated samplings.

3. RESULTS AND DISCUSSION

Results of the sediment analyses are shown in Table 3 and Fig. 3. Seasonal variations in the pore-water composition are indicated in Figs 4 to 8.

3.1. CALCULATION OF THE SEDIMENT DIFFUSIVITY

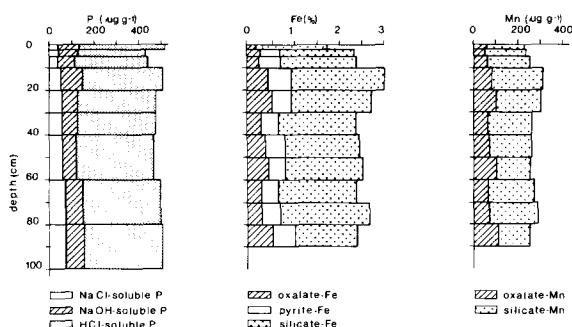The chlorosity (Fig. 4a) of the surface layers (0 to 20

Fig. 3. The speciation of phosphorus, iron and manganese in the sediment.

cm) responded to seasonal salinity variations in the Eastern Scheldt. These variations reflect real seasonal changes, because the sampler remained at exactly the same location throughout the study. This is a major advantage of the present *in situ* pore-water sampling technique for studying seasonal changes, because spatial variation does not obscure them.

The range of chlorosities (15 to 18 $g \cdot dm^{-3}$) in the surface layers exceeded the mean seasonal range in the overlying Eastern Scheldt water (STORTELDER *et al.*, 1984) by a factor of almost 2. A part of this increased variation may have been caused by brackish-water (8 to 13 g $Cl^- \cdot dm^{-3}$) discharges from the Zandkreek sluices in autumn. Infiltration of rainwater into the sediment in winter and evaporation of pore water from the surface layers during low tides in summer may also play a role. At depths greater than about 15 to 20 cm in the sediment, the chloride concentration converged to a seasonally averaged chlorosity of 16.4 $g \cdot dm^{-3}$. The thickness (L) of the

TABLE 3

Sediment composition at different depths. LOI=Loss on ignition.

| depth cm	porosity	clay (%)	clay+silt (%)	org. C (%)	N-tot (%)	LOI (%)	CaCO_3 (%)	Si (%)	Al (%)	Ca (%)	Mg (%)	K (%)
0- 2	0.65	11	33	1.4	0.08	9.8	9.8	31.8	3.09	4.07	0.53	1.35
2- 5	0.60	27	59	2.1	0.10	13.4	14.1	28.1	4.40	5.80	0.85	1.59
5-10	0.63	24	62	1.8	0.09	12.7	14.2	28.6	4.17	5.71	0.82	1.51
10-20	0.60	35	83	2.3	0.14	16.2	15.1	25.0	5.35	6.82	1.07	1.71
20-30	0.60	34	78	2.0	0.11	14.5	15.2	26.9	4.80	6.40	0.94	1.59
30-40	0.59	19	65	1.9	0.09	12.6	14.2	28.7	4.27	5.86	0.88	1.49
40-50	0.55	26	71	1.8	0.10	13.9	15.1	27.7	4.48	6.11	0.92	1.49
50-60	0.54	22	63	1.8	0.09	13.6	15.1	28.2	4.34	6.22	0.91	1.46
60-70	0.56	25	61	1.9	0.10	14.0	15.7	27.8	4.37	6.27	0.88	1.46
70-80	0.59	25	71	2.0	0.10	14.1	15.3	27.6	4.54	6.25	0.91	1.54
80-90	0.54	27	66	1.9	0.11	13.5	13.8	28.3	4.41	6.07	0.98	1.56
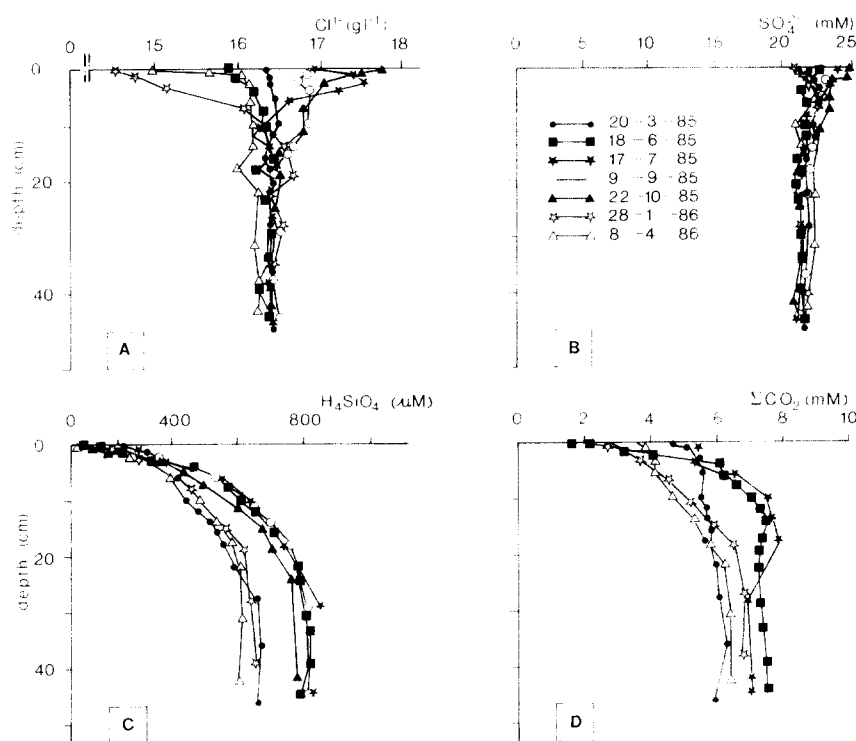
Fig. 4. Seasonal variation in pore-water concentrations of (A) chloride, (B) sulphate, (C)
reactive silica, and (D) total inorganic carbon concentrations.

surface layer responding to the diffusive transport
from the overlying water is related to the sediment
diffusion coefficient according to $L = (D_s t)^{0.5}$. If it is
assumed that the chloride concentration in the
superficial layer fluctuates seasonally about a mean
value, it follows that for a "damping depth" L=15 to
20 cm, the apparent sediment diffusivity of Cl^- is
225 to 400 $cm^2 \cdot y^{-1}$. Application of the harmonic dif-
fusion/advection model of HOLDREN et al. (1975) and
LORD & CHURCH (1983) predicted 4 of the 7 observed
Cl^- profiles to within 3%, using a sediment diffusion
coefficient for Cl^- of 300 $cm^2 \cdot y^{-1}$. An increase or
decrease in the sediment diffusion coefficient by a
factor of 1.5 gave significantly greater deviations from
the observed profiles at depth of 5 to 20 cm. The
predicted profiles of October, March and June gave
a somewhat wider variation (up to 8% in the upper 3
cm), suggesting that some discrete, temporal events
also affect the variation of Cl^- concentrations in the
surface layers. This limits the application of the
sinusoidal diffusion model for the estimation of the
sediment diffusion coefficient at this site, and
therefore the results have to be interpreted
cautiously.

A comparable value for the sediment diffusivity

was calculated from the molecular diffusion coeffi-
cient, corrected for porosity and tortuosity according
to the formula:

$$D_s = D\Phi^{n-1} = 270 \text{ cm}^2 \cdot y^{-1} \tag{4}$$

where D =440 $cm^2 \cdot y^{-1}$ (diffusion coefficient of Cl^-
adjusted to a mean annual temperature of 11°C (LI &
GREGORY, 1974), and n =2 (ULLMAN & ALLER, 1982).
These results suggest that the solute transport in the
pore waters takes place mainly by diffusion. Wave ac-
tion during rough weather conditions may temporari-
ly increase the diffusion coefficient in the surface
layer (e.g. RUTGERS VAN DER LOEFF, 1981), but ap-
parently have no great effect on the mean annual dif-
fusion coefficient. Effects of tides are also of minor
influence regarding the relatively quiescent
geographical location of the study site at present, the
small hydraulic gradient during low tide (<2
$m \cdot km^{-1}$) and the clayey composition of the sediment
(Table 3). Effects of bioturbation and irrigation are
restricted to the upper 2 cm, where high densities
(100 to 200 per m^2) of cockles, Cerastoderma edule,
were found. No deeper-burrowing fauna was observ-
ed at the study site (unpublished results).

3.2. ORGANIC MATTER OXIDATION

Organic carbon concentrations (1.5 to 2%) were related to the clay content ($R^2 = 0.76$) and were 1 to 2 times smaller than in the recent fine-grained sediments elsewhere in the Eastern Scheldt (OENEMA, 1988). The mineralization of metabolizable organic matter has proceeded continuously in the sediment since its deposition som 3 to 4 centuries ago, and has decreased the organic carbon-clay ratio.

The low Eh (-150 to -200 mV) below a depth of 1.5 cm and the low NO_3^- concentrations (<0.5 μMole) at all depths suggest that the reduction of O_2 and NO_3^- by organic matter oxidation was confined to the superficial sediment. Sulphate was the major electron acceptor below a depth of 0.5 to 1.5 cm. The bacterial sulphate reduction caused a slight decrease in the sulphate concentration in the top 20 cm (Fig. 4b).

A rough estimate of the sulphate reduction rate was made by calculating the diffusive sulphate flux into the sediment. First, exponential functions of the type:

$$C_x = (C_o - C_\infty) \exp(-bx) + C_\infty \qquad (5)$$

were fitted to measured pore-water sulphate profiles, normalized to an average chlorosity of 16.4 $g \cdot dm^{-3}$, to estimate C_o, C_∞ and the attenuation coefficient b. An exponentially decreasing SO_4^{2-} concentration with depth gave better fits than a linearly decreasing sulphate concentration, as has been shown (e.g. BERNER, 1980) for many marine sediments. However, the attenuation coefficient b is only a parameter fit; it has no mechanistic meaning in this particular case. Next, the flux was calculated from Fick's law:

$$F = \Phi D_s \frac{dC}{dx}\bigg|_{x=0} = \Phi D_s b (C_o - C_\infty) \qquad (6)$$

where $F = SO_4^{2-}$ flux ($\mu Mole \cdot cm^{-2} \cdot d^{-1}$),
$C_o = SO_4^{2-}$ concentration at zero depth $\mu Mole \cdot cm^{-3}$),
$C_\infty = SO_4^{2-}$ concentration below 20 cm
($\mu Mole \cdot cm^{-3}$), and
b=attenuation coefficient (cm^{-1}).

Mean porosity and tortuosity-corrected SO_4^{2-} diffusion coefficients were calculated from (4) and data from the literature (LI & GREGORY, 1974): $0.5 \cdot 10^{-5} cm^2 \cdot s^{-1}$ in summer (mean temperature 15.5°C) and $0.36 \cdot 10^{-5}$ $cm^2 \cdot s^{-1}$ in winter (at 6°C). The best fits of (5) to the measured SO_4^{2-} profiles were obtained with an attenuation coefficient b of 0.10 to 0.15 cm^{-1} and with $(C_o - C_\infty) = 0.5$ to 2.0

$\mu Mole \cdot cm^{-3}$. The calculated sulphate reduction rate varied from 230 to 680 $\mu Mole \cdot m^{-2} \cdot d^{-1}$ in summer to 50 to 160 $\mu Mole \cdot m^{-2} \cdot d^{-1}$ in winter. These rates were 1 to 2 orders of magnitude lower than those measured in other near-shore marine sediments (GOLDHABER et al., 1977; JØRGENSEN, 1977; BERNER & WESTRICH, 1985). Sulphate reduction rates in recent marine deposits in the Eastern Scheldt were also 10 to 100 times larger (OENEMA, 1988).

Similar calculations were made for ΣCO_2. Dissolved ΣCO_2 increased from about 2 mMole in the surface layer to about 6 to 8 mMole at depths >15 cm (Fig. 4d) due to organic matter oxidation. Most of the ΣCO_2 is present as HCO_3^- at a pH varying from 7.2 to 7.4 in the sediment (STUMM & MORGAN, 1981). Therefore, the sediment diffusivity of bicarbonate (LI & GREGORY, 1974; (4)) was adopted in the following calculations: $0.55 \cdot 10^{-5}$ $cm^{-2} \cdot s^{-1}$ in summer and $0.4 \cdot 10^{-5} cm^{-2} \cdot s^{-1}$ in winter. The calculated diffusive flux from the sediment (2500 to 3600 $\mu Mole \cdot m^{-2} \cdot d^{-1}$ in summer and 800 to 1600 $\mu Mole \cdot m^{-2} \cdot d^{-1}$ in winter) exceeded the opposite SO_4^{2-} flux by 5 to 10 times. A $\Sigma CO_2 / SO_4^{2-}$ flux ratio of minus 5 to 10 is far more than the expected minus 2 inferred stoichiometrically from bacterial sulfate reduction, assuming equal coefficients of molecular diffusion for HCO_3^- and SO_4^{2-} (e.g. ELDERFIELD et al., 1981a). This large ΣCO_2 excess relative to the SO_4^{2-} depletion suggests that other sources of ΣCO_2 are involved than bacterial sulphate reduction alone.

Organic matter oxidation by O_2 and NO_3^- reduction may increase the ΣCO_2 concentration in the pore water by approximately twice the O_2 (250 to 330 μM) plus NO_3^- (0 to 80 μM) concentrations present in the overlying seawater (ELDERFIELD et al., 1981a). Thus, at most 500 to 800 μM of the excess ΣCO_2 in the overlying seawater originates from O_2 and NO_3^- reduction in the surface sediment. Another minor portion of ΣCO_2 may come from microbial Mn and Fe oxihydroxide reduction (SØRENSEN & JØRGENSEN, 1987). The ΣCO_2 production by O_2 and NO_3^- reduction can explain the large ΣCO^2 excess relative to the SO_4^{2-} depletion in winter pore waters, but not in those of summer. Probably a major source of the ΣCO_2 excess relative to the SO_{2-}^4 depletion in summer is root respiration and oxygen release by Zostera noltii in the sediment (e.g. GLEASON & ZIEMAN, 1981; SAND-JENSEN et al., 1982). Root respiration increases the ΣCO_2 concentration in the sediment, and release of O_2 by the roots may oxidize sulphides to sulphate. Consequently, the root activity of Zostera noltii may increase the concentrations of both ΣCO_2 and SO_4^{2-} in the pore water, thereby increasing the ratio of the ΣCO_2 increase relative to the SO_4^{2-}

depletion. The possible oxidation of sulphides to sulphate in the rhizosphere also causes an underestimation of the calculated sulphate reduction rate. The calculated rates of 50 to 160 μmol·m^{-2}·d^{-1} in summer are therefore lower limits. Precipitation of Mn, Ca-carbonates (see below) may have slightly lowered the ΣCO_2 concentration.

In summary, several diagenetic processes, of which bacterial sulphate reduction, root respiration and sulphide oxidation in the rhizosphere appear to be of prime importance, have modified the ΣCO_2 and SO_4^{2-} concentrations in the pore waters.

3.3. NITROGEN AND PHOSPHORUS DIAGENESIS

A complex seasonal variation in NH_4^+ and ΣPO_4 concentrations occurred in the pore waters of the surface layers (0 to 20 cm) (Figs 5 and 6). These short-term variations were caused by nutrient uptake by *Zostera noltii* in the summer, superimposed on seasonally varying rates of nutrient regeneration and sediment-seawater exchange. Between May and August, the nutrient uptake clearly exceeded the nutrient regeneration at 0 to 5 cm, resulting in very low ΣPO_4 and NH_4^+ concentrations in the superficial sediment. Between September and April the opposite occurred. During the winter (*e.g.* data of January 1986), the rate of sediment-seawater exchange apparently exceeded the rate of nutrient regeneration, because the NH_4^+ and ΣPO_4 concentrations in the 0 to 5 cm depth interval were lower than in autumn.

The total nitrogen and phosphorus uptake by *Zostera noltii* at the study-site was calculated from the primary production and the elemental C:N:P composition. The total primary production above and below ground at the study site is 100 to 150 g C·m^{-2}·y^{-1} (NIENHUIS & DAEMEN, 1985; Daemen, pers. comm.). A mean C:N:P ratio in the shoots (180:15:1) and the roots (210:9:1) was calculated from data of DAEMEN (1979).

If the nutrients were taken up by the roots alone, the mean pore-water NH_4^+ pool (3 to 6 mMole·m^{-2}) in the upper 10 cm would have been replenished 150 to 200 times per year to account for the total nitrogen uptake (700 to 1100 mMole·m^{-2}·y^{-1}). Similar calculations for the total phosphorus uptake (50 to 70 mMole·m^{-2}·y^{-1} yield a turnover of 100 to 150 times per year for the pore-water ΣPO_4 pool. On the assumption that the relative changes of ΣCO_2, SO_4^{2-}, NH_4^+ and ΣPO_4 in the pore water follow the REDFIELD *et al.* (1963) ratio (106:$-$53:16:1), it can easily be calculated from the estimated sulphate reduction rate (50 to 150 mMole·m^{-2}·y^{-1}, or from the total ΣCO_2 production rate (580 to 990 mMole·m^{-2}·y^{-1}) that the sediment cannot meet this nutrient demand at all. There has been some dispute whether macrophytes take their nutrients and especially ΣPO_4, from the sediments or from the overlying seawater (*e.g.* CARRIGAN & KALFF, 1980; 1982; McRoy *et al.*, 1972). The results of the present study strongly suggest that the major part of the NH_4^+ and ΣPO_4 uptake by *Zostera noltii* must have taken place from the overlying seawater.

Below the zone of nutrient uptake a slight but steady increase in NH_4^+ and ΣPO_4 concentration was observed. However, the upwardly directed diffusive flux to the surface layers, calculated by Fick's law, was small, 1 to 3 mMole·m^{-2}·y^{-1} for NH_4^+ and 0.1 to 0.3 mMole·m^{-2}·y^{-1} for ΣPO_4.
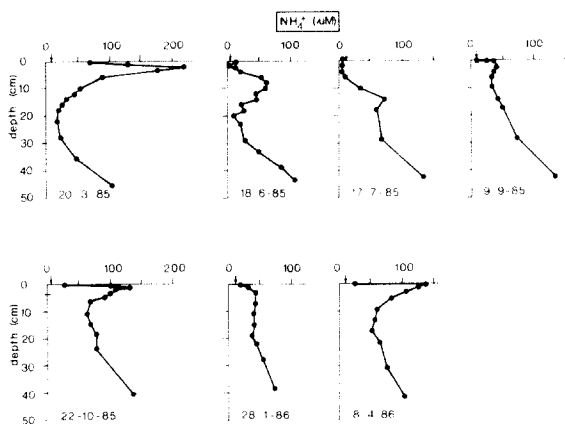

Fig. 5. Seasonal variations in pore-water ammonium concentrations.
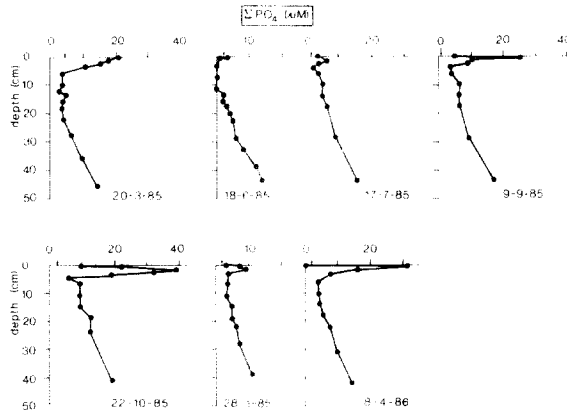

Fig. 6. Seasonal variations in pore-water ortho-phosphate concentrations.

Mineralization processes, and nutrient uptake by *Zostera noltii* and sediment-seawater exchange (*e.g.* CALLENDER & HAMMOND, 1982; ELDERFIELD *et al.*, 1981b) have selectively depleted the sediment. Thus the C/N ratio in the sediment is high (19±1.6), because protein-rich organic matter is oxidized preferentially (ROSENFELD, 1981). Results of the phosphoros fractionation (Fig. 3) indicate that only small amounts are exchangeable and carbonate bound-P (NH_4Cl soluble P: 10-15%) and iron and aluminium oxyhydroxide bound-P (NaOH soluble P: 10-15%). Apatites (HCl soluble P) are the dominant (70-80%) phosphorus containing compounds. This is in reasonable agreement with the result of the calculated saturation state of the pore waters; the ion activity products (IAPs) were calculated with a modified version of the Wateq programme (VAN GAANS, 1988; TRUESDELL & JONES, 1974). Effects of ionic strength (I=0.55), ion pairing and temperature (5 to 20°C) were included in these calculations. The necessary Ca^{2+}, Mg^{2+}, Na^+ and K^+ concentrations were calculated from the measured chloride concentrations and the ratio between these cations and Cl^- in standard seawater (STUMM & MORGAN, 1981).

The pore waters were highly supersaturated with respect to hydroxy-apatite, and undersaturated with respect to iron(3)phosphate (*e.g.* strengite) and also to iron(2)phosphate (vivianite). Thus iron oxydroxide bound phosphates are unstable in this reducing sediment and were probalby already liberated during the initial diagnosis (*e.g.* KROM & BERNER, 1981).

3.4. SILICA DIAGENESIS

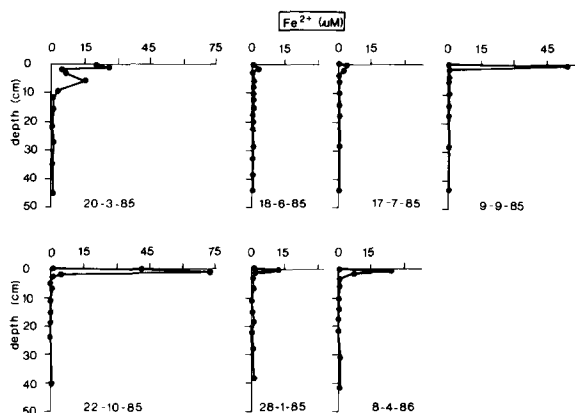Dissolved reactive silica concentrations increased exponentially with depth (Fig. 4c). This increase was the result of competition between dissolution, mainly of skeletal remains of diatoms, reprecipitation processes (HURD, 1972; 1973) and sediment-seawater exchange. The apparent equilibrium concentration (C_∞) in summer was approximately 150 μM higher than in winter because of the temperature-dependance of the dissolution process (HURD, 1972). The dissolution rate is generally considered to be proportional to the degree of undersaturation: $R = k(C_\infty - C_X)$ (HURD, 1973; LERMAN, 1979). Estimates of the rate constant k were obtained by fitting the following equation to the measured summer and winter profiles (LERMAN, 1979):

$$C_X = C_\infty - (C_\infty - C_0) \exp\{-x(k/D_s)^{0.5}\} \qquad (7)$$

assuming "quasi-steady-state" conditions during summer and winter. The diffusion coefficient, corrected for porosity and tortuosity (4.7·10^{-6}·cm^{-2}·s^{-1} in summer and 3.4·10^{-6}·cm^2·s^{-1} in winter) was calculated from (4) and data from the literature (WOLLAST & GARRELS, 1971). The best fits of (7) yielded k values of 7 to 8·10^{-8}·s^{-1} in summer and 4-5·10^{-8}·s^{-1} in winter.

Diffusive fluxes of H_4SiO_4 from the sediment to the seawater, calculated from Fick's law:

$$F = \Phi D_s (C_\infty - C_0)(k/D_s)^{0.5} \qquad (8)$$

varied between 0.2 mMole·m^{-2}·d^{-1} in summer and 0.1 mMole·m^{-2}·d^{-1} in winter. Actual fluxes to the overlying water are probably even lower, because part of the H_4SiO_4 is intercepted and consumed by benthic diatoms at the surface (RUTGERS VAN DER LOEFF *et al.*, 1981; Van Geldermalsen, pers. comm.). The calculated dissolution rates and fluxes are ap-

Fig. 7. Seasonal variations in pore-water iron concentrations.
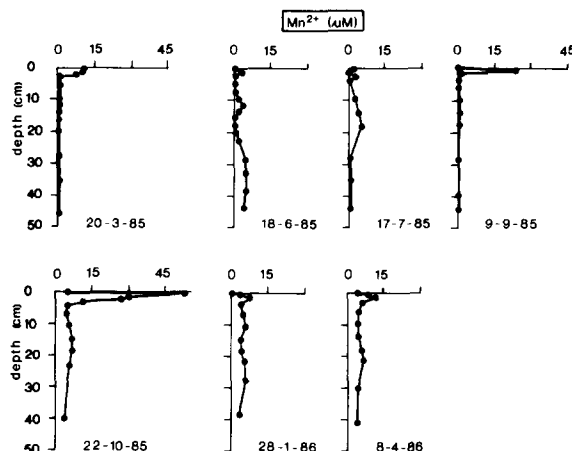

Fig. 8. Seasonal variations in pore-water manganese concentrations.

proximately 1 order of magnitude smaller than those reported for nearshore marine sediments elsewhere (VANDERBORGHT *et al.*, 1977; ELDERFIELD *et al.*, 1981b; BALZER, 1984). This suggests that the solid silica in the sediment has a low reactivity. The most reactive opaline silica from diatom skeletons has already been dissolved.

3.5. IRON AND MANGANESE DIAGENESIS

Dissolved iron and manganese profiles (Figs 7 and 8) are similar to those reported for other nearshore marine sdiments by ALLER (1980) and HOLDREN *et al.* (1975). Distinct maxima were observed in the upper 1 to 2 cm and very low concentrations at greater depths.

The absence of a sub-surface maximum in June and July coincided with the NH_4^+ and ΣPO_4 depletion in the surface layers during the summer. This suggests that the dissolved Fe^{2+} and Mn^{2+} removal from the pore waters was caused by precipitation of oxyhydroxides due to release of oxygen from the roots of *Zostera noltii* (see *e.g.* SAND-JENSEN *et al.*, 1982). However, no visible iron oxyhydroxide precipitate on the roots or any significant change in redox conditions were observed in the top 5 cm during the summer.

Downcore Fe^{2+} concentrations in the subrecent sediment of the investigated site and in the recent fine-grained sediments elsewhere in the Eastern Scheldt (OENEMA, 1988) are equally low, while downcore Mn^{2+} concentrations in the subrecent sediment are 10 to 100 times lower than in the recent sediments. There are two possible explanations for low dissolved Fe^{2+} and Mn^{2+} concentrations in anoxic pore waters:
—1. a low rate of Fe- and Mn oxyhydroxide reduction,
—2. precipitation of Fe- and Mn sulfides, phosphates and carbonates.
The reduction rate of Fe- and Mn oxyhydroxides in the subrecent sediment is severely limited, not only by their own low concentration but also by the low concentrations of metabolizable organic matter, which restricts the growth of heterotrophic microbes in the sediment. The likelihood of a dissolved Fe^{2+} and Mn^{2+} control by low concentration of Fe- and Mn oxyhydroxides and possibly by Fe^{2+} and Mn^{2+} precipitation is discussed in the following.

The calculated saturation indices indicate that the pore waters were close to saturation with greigite (Fe_3S_4) and mackinawite (FeS), with pK_{SP} values of 4.2 and 3.7, respectively (BERNER, 1967), and under-saturated with respect to amorphous ferrous sulphides (FeS; $pK_{SP} = 2.9$), vivianite

($Fe_3(PO_4)_2 \cdot 8H_2O$) and siderite ($FeCO_3$). This suggests that precipitation of greigite and possibly mackinawite is involved in the control of dissolved iron. Dissolved ΣS concentrations were low ($< 5 \mu M$) in the upper 3 to 5 cm, but increased to maxima of 300-400 μM at 20 to 40 cm in the bluish-grey sediment. Pyrite (FeS_2) is the ultimate sink of the reduced Fe and ΣS species in marine sediments (BERNER, 1970). FeS_2 concentrations varied between 0.4 and 1.1% (Fig. 3) and were linearly related to the organic carbon concentrations. Low concentrations of easily extractable iron (0.2 to 0.5% Fe) did not seem to control further pyrite formation, because the degree of pyritization (BERNER, 1970) of the easily extractable iron pool was only 54 $\pm$ 9%. In conclusion, the dissolved Fe^{2+} concentrations in the anoxic pore waters were most probably controlled by the precipitation of iron sulfides.

The pore waters were strongly undersaturated (1 to 3 orders of magnitude) with respect to pure manganese minerals such as rhodochrosite ($MnCO_3$; $pK_{SP} = 10.4$ MIDDELBURG *et al.*, 1987), alabandite (Mns; $pK_{SP} = 1.32$, MILLS, 1974) and reddingite ($Mn_3(PO_4)_2$; $pK_{SP} = 31.8$, POSTMA, 1981). This indicates that precipitation of these pure phases did not control the Mn^{2+} concentration in the pore waters.

Approximately 20 to 30% of the total solid Mn concentration (Fig. 3) was oxalate-extractable (50 to 100 $\mu g \cdot g^{-1}$). Equal quantities were extracted by an unbuffered 1 M NH_4Cl solution. It was found that NH_4^+-oxalate as well as NH_4Cl completely dissolved calcite, but according to GAMBRELL & PATRICK (1982) only NH_4^+-oxalate may dissolve manganese oxides to any great extent. This suggests that the extractable Mn in the sediment was predominantly carbonate-bound Mn, and that manganese reduction rates were severely slowed down by the very low concentration of Mn-oxides. The large differences between downcore Mn^{2+} concentrations in the pore waters of the investigated subrecent sediments and those in the recent fine-grained sediments elsewhere in the Eastern Scheldt are attributable to the very low manganese reduction rates in the subrecent sediments. The easily extractable manganese in the subrecent sediment (250 to 300 $\mu g \cdot g^{-1}$, Table 3) is probably present as a Mn, Ca carbonate with an estimated Mn mole fraction of $1 \cdot 10^{-3}$. Precipitation of such $Mn_{0.001}$, $Ca_{0.999}CO_3$ solid solutions may regulate downcore Mn^{2+} concentrations at 1 to 5 μM in marine sediments with pH values of 7.2 to 7.4 and 4 to 8 mM ΣCO_2 (MIDDELBURG *et al.*, 1987), as found in the sediment investigated.

In the surface 2 cm, freshly deposited manganese

oxides and organic matter (*e.g.* from diatoms and *Zostera noltii*) may become incorporated in the sediment by burrowing *Cerastoderma edule*. This promotes a rapid microbial manganese reduction, and consequently high dissolved Mn^{2+} concentrations appeared in the surface pore waters (*e.g.* SUNDBY & SILVERBERG, 1985).

4. CONCLUSIONS

The pore-water sampler proved to be useful for monitoring seasonal variations in the pore-water composition, because spatial variability as a disturbing factor could be ruled out. The use of this sampler is advised for unconsolidated sediments in salt marshes, intertidal flats and other shallow (< 0.5 m) water bodies.

Subrecent Dunkirk deposits, exposed on intertidal flats in the Eastern Scheldt, contain predominantly non-metabolizable organic carbon. Consequently, rates of organic carbon mineralization and nutrient regeneration in these sediments are low underneath the superficial 0 to 2 cm of sediment in which metabolizable organic matter may temporarily accumulate. The contribution of these sediments to the carbon and nutrient dynamics in the Eastern Scheldt is negligible, because of its restricted surface area and its refractory organic matter. The organic carbon from these types of sediments, after erosion, will behave as inert stuffing in the recent fine-grained deposits, accumulating elsewhere in the Eastern Scheldt.

The dissolved NH_4^+ and ΣPO_4 concentrations in the pore waters were controlled by mineralization, nutrient uptake by *Zostera noltii* and sediment-seawater exchange. Only a small percentage of the total nutrient uptake by *Zostera noltii* was derived from the sediment. The major part was taken up from the overlying seawater. Root-respiration probably accounted for a large part of the total dissolved inorganic carbon in the summer pore waters.

Total nitrogen, phosphorus and manganese concentrations in the sediment were low; mineralization and sediment-seawater exchange must have depleted these deposits during earlier stages of diagenesis. The low downcore Mn^{2+} concentrations, if compared to recent fine-grained sediments, must be attributed to the very low manganese oxide concentration and the low reduction rate in the subrecent sediment. Equilibrium with a Mn, Ca carbonate with an estimated manganese mole fraction of $1 \cdot 10^{-3}$ apparently controlled the pore water Mn^{2+} concentration at 1 to 5 μm.

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