Pore Water Chemistry of Intertidal Mudflat Sediments: 1. Seasonal Variability of Nutrient Profiles (S, N, P).

CHANG-BOK LEE AND DONG-SEON KIM

Dept. of Oceanography, Seoul National University, Seoul 151-742, Korea

조간대 퇴적물의 공극수 지구화학:
1. 용존 영양염(S, N, P)의 계절변화

이창복 · 김동선
서울대학교 해양학과

A series of pore water data were obtained during the different time over one year period between October 1987 and October 1988, from a site on a muddy intertidal flat, located in the Kyeong-gi Bay, west coast of Korea. The results have revealed that the tidal flat is an environment of active nutrient regeneration. The sulfate reduction is so rapid that, throughout the year except some winter months, the sulfate supplied by the overlying seawater is almost completely removed from the pore water at depth of about 10 cm below the sediment surface. The nutrients such as ammonium and phosphate are produced through this process and subsequently accumulated in the pore water forming steep gradients near the sediment surface. Below the main sulfate reduction zone, a secondary peak of dissolved sulfate was often observed.

Great seasonal variation of the pore water nutrient profiles was observed, which was particularly clear in their maximum concentration as well as in their concentration gradient. The rate constants of sulfate reduction and nutrient regeneration, estimated by using a diagenetic model (Berner, 1980), differ by an order of magnitude between the summer and winter seasons. The difference in sediment temperature may account for most of the calculated variation. The C:N:P ratio, calculated from the pore water nutrient gradients, also exhibits a slight seasonal difference. The organic matter being decomposed by sulfate reduction appears to be depleted in nitrogen, compared to the average marine organic matter.

조간대 퇴적물의 공극수 화학과 초기 속성작용을 연구하기 위하여, 경기만 남동부의 반월지역 조간대의 한 정점에서 1987년 10월 -1988년 10월 사이에 6차의 공극수 시료가 채취·분석되었다. 시료채취 지점은 세립질 뻘 퇴적물이 분포하며 무산소 환경으로 인해 생물교란이 없는 곳으로서, 미생물에 의한 유기물 분해와 영양염의 재생이 매우 활발하였다. 공극수 내의 황산염 환원은 매우 급속히 이루어져, 해수로부터 공급된 황산염이 10 cm 깊이 이내에서 일차적으로 제거되는 현상이 겨울철을 제외한 전 시기에 관찰되었다. 황산염 환원과 유기물 분해의 산물로서 생겨난 암모니아와 인산염은 공극수 내에 축적되어 수직적으로 심한 농도구배를 나타냈다. 봄철에서 초여름에 걸친 시기에는, 한편, 일차적인 황산염 환원대 아래쪽으로 2차적인 농도 증가 현상이 관찰되었다.

공극수 내 황산염, 암모니아 및 인산염 농도의 수직 분포에서는 계절적인 차이가 나타났다. Berner (1980)의 속성모델을 적용하여 황산염 환원과 영양염류 재생의 반응속도를 정량화시킨 결과 여름철과 겨울철 사이에 약 10배의 차이를 나타냈으며, 이 차이는 계절적인 온도의 차이에 기인한 것으로 해석되었다. 영양염 농도구배로부터 계산된 C : N : P 비도 계절적인 차이를 나타냈다.

INTRODUCTION

Microbial degradation of organic matter during shallow burial of marine sediments exerts major control on the chemistry of pore waters (Berner, 1980). When molecular oxygen is present, organic decomposition is dominated by organisms using oxygen as an electron acceptor (Presley and Trefry, 1980). When molecular oxygen has been used up, organic matter decomposition continues, mediated by microorganisms which use progressively less efficient electron acceptors such as nitrate, manganese and iron oxides, sulfates, etc. Sulfate is especially important in the marine system, due to its high concentration in seawater and the high toxicity of its reduced product, H_2S, to most forms of life. The consequence of these reactions is a build-up of metabolites such as ammonium, phosphate and silicate within the pore water and a subsequent release of these metabolites into the overlying water column. Nutrient regeneration through these early diagenetic processes is essential to the maintenance of marine ecosystem (Berner, 1979; Suess, 1976).

The pore water chemistry has been extensively studied from various depositional environments, including the deep-sea, continental shelves, estuaries and salt marshes. A relatively limited number of researches have been reported from the intertidal mudflat sediment (El Ghobary and Dumon, 1984; Lyon and Fitzgerald, 1978; Watson et al., 1985). Intertidal mudflats are extensively developed along the western coast of Korea, forming a dominant coastal depositional feature in this area. They are distinguished from other sedimentary environments by their periodic exposure to the atmosphere, their susceptibility to the seasonal temperature changes, and their generally fine-grained nature.

In spite of the unique characteristics and extensive areal distribution, our understanding of the intertidal mudflat and its role in the coastal ecosystem is limited. Since the primary production in the tidal flat is known to be remarkably high (Cadée and Hegeman, 1974; Cho and Kim, 1988), its role as an organic carbon supplier in the ecosystem must be important, especially in an environment like the Yellow Sea where the biological production in the water column is limited by high turbidity. The high level of primary production supports not only secondary producers but also various heterotrophic microorganisms, which, in turn, support the primary producers via regeneration of nutrients fixed in the organic materials. Therefore, the knowledge of early diagenetic processes is essential to the understanding of local ecosystem.

In the present paper we report a series of pore water data determined over four seasons at a station located in the middle of a tidal mudflat. The seasonal variabiltiy of pore water sulfate, ammonium, and phosphate concentrations was estimated in terms of rate constants, calculated by using the general diagenetic model of Berner (1974, 1980).

DESCRIPTION OF THE STUDY SITE

Sediment cores were collected in an intertidal mudflat area, located on the southern part of Kyeonggi Bay. Kyeonggi Bay is characterized by a semi-diurnal, macrotidal regime with a mean springtidal range of about 8 m. The intertidal surface sediment shows a typical, shoreward-fining grain-size distribution pattern (Lee et al., 1985). Locally, a narrow belt of halophyte, Sueda japonica, is found along the coastline, near the high-water line, which waxes and wanes seasonally. An apparent sedimentation rate of this intertidal sediment was estimated at between 0.2-0.6 cm/yr, by means of the ^{210}Pb method (Park and Nittrouer, unpublished data).

The temperature of the intertidal surface sediment is very susceptible to that of the air and shows a distinct seasonality, with a difference in daily mean temperature of up to 30 °C between the summer and winter seasons (Koh and Shin,
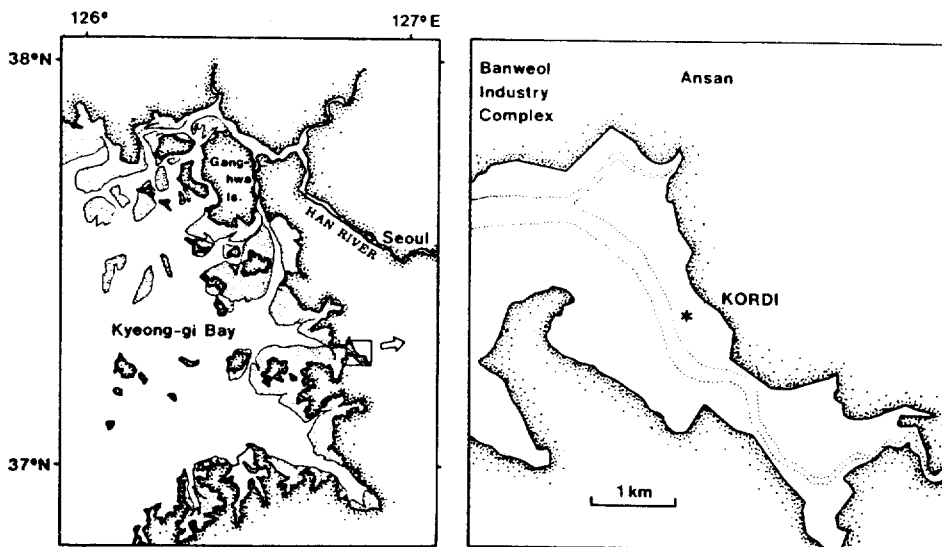
Fig. 1. Location of the study area and pore-water sample site(*).

1988). The intertidal zone in this area is in general heavily populated with various benthic animals (Koh and Shin, 1988; Lee et al., 1985). Nevertheless, the site where the sediment cores were collected has been apparently devoid of any type of macrobenthos, most probably because of the hydrogen sulfide and methane produced within the sediment. We could actually smell hydrogen sulfide from sediments during the core collection.

SAMPLING AND ANALYTICAL METHODS

A series of core samples were collected seasonally during the period between October 1987 and October 1988 at the same location in the middle part of the intertidal mudflat near Banweol (Fig. 1). The cores were taken by driving an acryl liner, with 50 cm of length and 11 cm of diameter, into the sediment, capping it at the sediment interface, and withdrawing the liner. The cores were extruded and sectioned into predetermined intervals in a glove box filled with pure nitrogen gas. Still in the glove box, each sectioned sediment was transferred into a 50 ml centrifuge tube. The pore waters were

then extracted by centrifugation at 5000 rpm for 20 minutes under the refrigerated condition.

Analyses were done within 3 days after the pore water extraction. Ammonium was measured by the indophenol blue spectrophotometric technique (Strickland and Parsons, 1972). Phosphate was determined by the molybdate spectrophotometric method (Murphy and Riley, 1962). Sulfate was determined by the indirect back-titration method (Howarth, 1978). Particulate organic carbon in sediment was analyzed by the back-titration method after treating of the sample with a sulfochromic mixture (Jackson, 1967). The precision of analysis was all within 5%. In addition to the above constituents, other dissolved pore water species, such as silicate, hydrogen sulfide, calcium, iron, and manganese, were also determined at the same time, but these results will be treated in a seperate paper.

RESULTS AND DISCUSSIONS

Pore Water Profiles

Concentrations of the dissolved constituents are plotted against depth in Fig. 2. In all the six
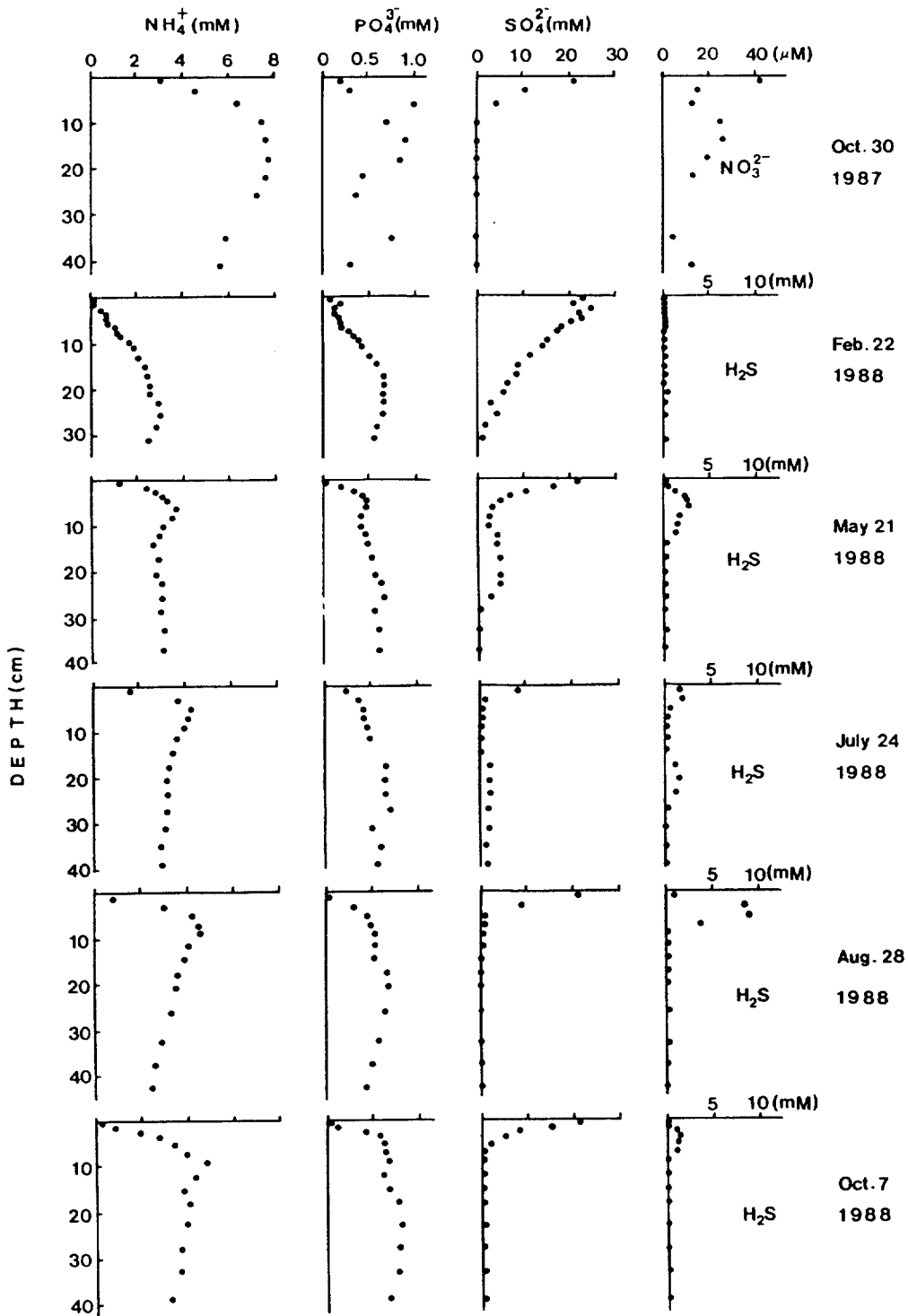
Fig. 2. Pore water profiles of ammonium, phosphate, sulfate, nitrate and hydrogen sulfide concentrations, observed in the six cores which were collected on different time of the year.

cores a rapid decrease of sulfate below the sediment surface was observed along with the increases of ammonium and phosphate. The sulfate reduction in this intertidal sediment is so effective that virtually no sulfate can be detected in the pore waters below 10 cm from the sediment surface except in the winter season when the microbial activity is greatly reduced due to the lowered sediment temperature. The release of the metabolites from this microbially mediated reaction is reflected in the ammonium and phosphate contents increasing rapidly below the sediment surface. The ammonium content attains maximum at a certain depth, generally between 5-25 cm below the sediment surface, and then decreases downward slightly. The characteristic features of pore-water constituents observed in each core, collected on different time of the year, will be briefly described below.

Core of October 30, 1987: The ammonium concentration showed a maximun value of 7.7 mM at depth interval of 16-20 cm below the sediment surface. The nitrate content was determined only on this core, and showed a maximum value of 42.5 μM at surface and decreased downward with some minor fluctuation in the sediment column. The amount of nitrate in pore-water was on the whole negligible compared to that of ammonium which was up to 200 times more abundant than nitrate. The phosphate concentration varied between 0.2 and 0.99 mM. The sulfate concentration decreased rapidly from the surface value of 21.1 mM downward to the depth of about 10 cm where it was totally depleted.

Core of February 22, 1988: In this wintertime core the vertical gradients of ammonium, phosphate, and sulfate concentrations were greatly reduced compared to those observed in other cores. The maximum ammonium content occurred at a depth of about 25 cm with a value of 3.02 mM. The maximum phosphate content was 0.67 mM. The sulfate reduction began at about 5 cm below the sediment surface and still at a depth of 30 cm the total depletion of pore-

water sulfate did not occur.

Core of May 21, 1988: The maximum ammonium content occurred at a depth of 6 cm with a value of 3.74 mM. The Phosphate maximum value was 0.65 mM. The complete depletion of pore water sulfate occurred at 30 cm below the sediment surface. One special feature worth to noting in this core is the secondary increase in contents of the pore-water constituents below the initial increases of ammonium and phosphate, and below the initial decrease for sulfate. The increase of sulfate below the main sulfate-reduction zone suggests that there have been some lateral transport of sulfate-laden water in this depth (between 10 and 25 cm below the sediment surface), probably through nearby burrows or other holes.

Core of July 24, 1988: In this core the ammonium maximum occurred at 5 cm below the sediment surface, with a value of 4.23 mM. The maximum phosphate value was 0.70 mM. The sulfate content of the surface layer, representing that of the uppermost 2 cm of sediment, was as low as 8.30 mM only. This indicates that extensive sulfate reduction (about 60% of the sulfate initially present) has been already occurring within the top 1 cm. A secondary increase of pore-water sulfate was observed also in this core. The pH of pore solution was determined only on this core and showed that the pore water was slightly acidic, within the range of 6.56-6.90, with no appreciable vertical change.

Core of August 28, 1988: The maximum ammonium content was 4.55 mM, which occurred at a depth of about 9 cm, and that of phosphate was 0.67 mM. The sulfate reduction proceeded very rapidly and a depth of 5 cm below the sediment surface, only 1.0 mM of sulfate has remained from the surface layer value of 21.0 mM. But the complete removal of pore-water sulfate did not occur until at a depth of 13 cm below the surface.

Core of October 7, 1988: The maximum concentrations of ammonium and phosphate were 4.7 mM and 0.8 mM in this core and occurred at

depth intervals of 8-10 cm and 20-26 cm below the sediment surface, respectively. The sulfate was completely removed from the pore water below 6 cm from the sediment surface and the hydrogen sulfide occurred at a depth between 2-8 cm.

Diagenetic Model

The vertical distributions of pore-water constituents can be treated quantitatively by the use of theoretical models. According to the general diagenetic equation of Berner (1980), the concentration of a pore-water species under steady-state condition can be expressed mathematically as follows:

$$D\frac{\partial^2 C}{\partial x^2} - (1+K) \ w\frac{\partial C}{\partial x} + R = 0 \qquad (1)$$

where C = concentration of dissolved species in terms of mass per unit volume of pore-water,

x = depth measured positively downward from the sediment surface,

w = dx/dt = the net rate of sediment deposition,

D = diffusion coefficient for dissolved species in the sediment,

R = reaction terms (mole cm^{-3} sec^{-1}) which affect the concentration of the dissolved species, including decomposition of organic matter, mineral dissolution and precipitation,

K = equilibrium adsorption constant.

In order to simplify solution of the above equation, the values of K and D (as well as w) are assumed constant with depth. According to Berner (1974), the use of average values for K and D, over the depth interval represented by early diagenesis, introduces errors which are negligible compared to errors resulting from other assumptions. In additon, the effect of bioturbation will also be ignored in this diagene-

tic model. Although the activity of benthic organisms may greatly increase the value of D in most coastal deposits, it seems not to be so important in the study site since sulfate reduction occurs just below the sediment surface. The reaction term R in equation (1) comprises different processes for each pore-water species. For sulfate it represents consumption through bacterial sulfate reduction while for ammonium and phosphate it represents production as a result of organic matter decomposition.

Sulfate:

Sulfate ion in pore-water is not involved in quantitatively important precipitation or dissolution reaction, nor does it undergo appreciable ion exchange (Berner, 1974). Hence, the processes affecting its concentration are diffusion, advection, and bacterial sulfate reduction. If it is assumed that organic matter decomposition accompanying bacterial sulfate reduction follows simple first order kinetics (the one-G model of Berner, 1980), the steady-state diagenetic equation from equation (1) with K = 0 is, accordingly:

$$D\frac{\partial^2 C}{\partial x^2} - w\frac{\partial C}{\partial x} - LFkG = 0 \qquad (2)$$

where C = concentration of dissolved sulfate;

G = concentration of metabolizable organic carbon (in moles per unit mass of total solids);

k = rate constant for sulfate reduction;

L = stoichiometric coefficient relating the number of moles of sulfate reduced per moles of organic carbon oxidized to CO_2 (normally = 1/2);

F = $[(1-\phi)/\phi]\rho$.

With the boundary conditions:

where x = 0, C = C_0 and G = G_0;

when x = ∞, C = C∞ and G = 0,

the solution of equation (2) is:

$$C = (Co - C\infty) \ exp[(-k/w)x] + C\infty \qquad (3)$$

$$SO_4^{2-} \text{ (mM)}$$

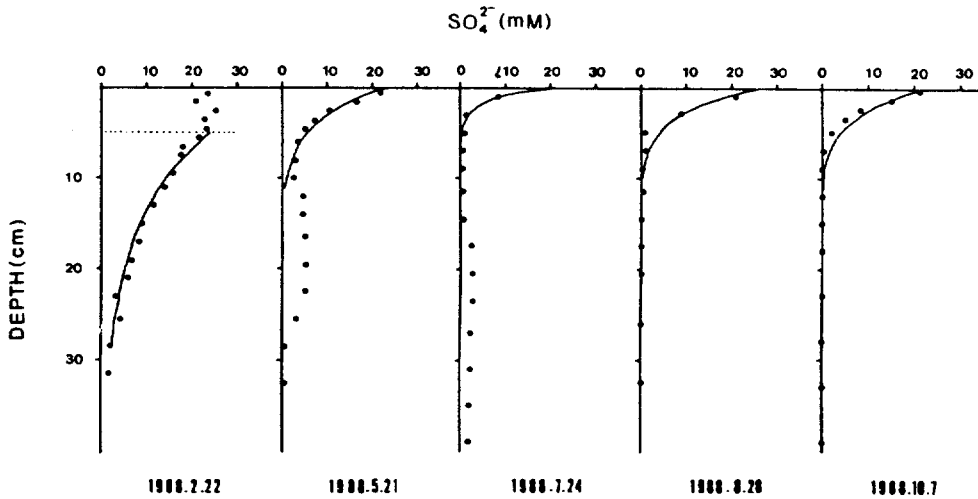

Fig. 3. Fits of one-dimensional steady-state model to pore-water sulfate profiles. The best fit non-linear equations for C (in mM) are:
24.1 exp(−0.10x) for February, 24.4 exp(−0.30x) for May, 21.0 exp(−0.93x) for July, 27.0 exp(−0.40x) for August, and 22.0 exp(−0.35x) for October.

Using $w = 0.4$ cm/yr and $\phi = 0.65$, the above equation was fitted to the sulfate data of Fig. 2 by non-linear regression method (Fig. 3), and the value of k, which represents the rate constant for sulfate reduction was estimated for different period of pore-water data obtained during the year 1988. Since L, F and G in equation (2) are all known constants in the Banweol tidal flat sediment and do not vary measurably over one year period, k can be served as a quantitative mean in comparing the difference in the sulfate reduction rate between different seasons.

The estimated k values (yr^{-1}) were 0.04 for February, 0.12 for May, 0.37 for July, 0.16 for August, and 0.14 for October 1988. So, the rate of sulfate reduction in the Banweol tidal flat sediment is up to ten times more rapid during the summer season than during the winter season. Aller and Yingst (1980) reported from the Long Island Sound a increase of about 3 times in the sulfate reduction rate when the sediment temperature increased by 10 °C. Crill and Martens (1987), on the other hand, found that the sulfate reduction rate in the Cape Lookout Bight sediment varied seasonally by a factor of

seven, which they attributed primarily to the seasonal temperature variation. The seasonal variability in the sulfate reduciton rate by a factor of ten, determined in the Banweol tidal flat, is thus an appropriate amount of variation that can be explained solely by the seasonal temperature change in this environment.

Ammonium and Phosphate:

Both ammonium and phosphate in pore-waters are derived from the bacterial decomposition of organic compounds, and undergo appreciable adsorption on the surfaces of particles (Berner, 1980). Phosphate differs from ammonium in that it commonly forms authigenic minerals, mainly apatite and vivianite. However, in the absence of appreciable $CaCO_3$ surface, the precipitation of apatite is strongly hindered by Mg^{2+} ions. For vivianite precipitation, the pore solution must attain sufficiently high concentrations of Fe^{2+} and PO_4^{3-} for supersaturation to occur (Berner, 1980). In the Banweol tidal flat, the above two situations of phosphate mineral precipitaiton are not probable and, therefore, will be ignored in the early
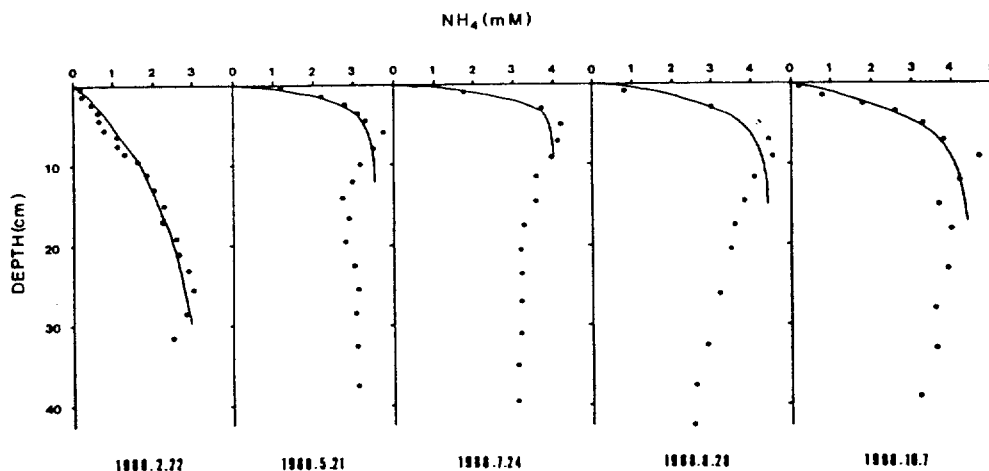
NH₄(mM)

Fig. 4. Fits of one-dimensional steady-state model to pore-water ammonium profiles. The best-fit non-linear equations for C (in mM) are:
3.50[1-exp(-0.063x)] for February, 3.50[1-exp(-0.60x)] for May, 4.03[1-exp(-0.62x)] for July, 4.37[1-exp(-0.40x)] for August, and 4.50[1-exp(-0.25x)] for October.

PO₄(mM)

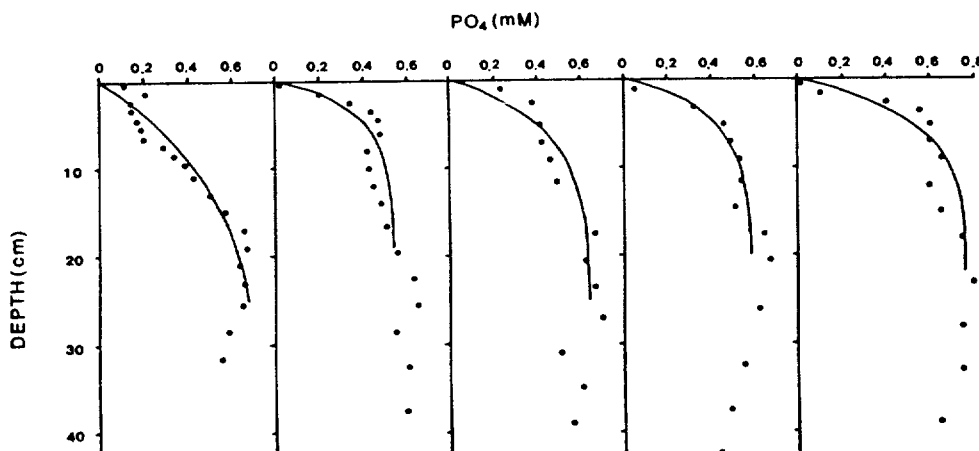

Fig. 5. Fits of one-dimensional steady-state model to pore-water phosphate profiles. The best-fit non-linear equations for C (in μM) are:
814.8[1-exp(-0.069x)] for February, 532.7[1-exp(-0.30x)] for May, 650.0[1-exp(-0.19x)] for July, 584.91[1-exp(-0.26x)] for August, and 750.0[1-exp(-0.25x)] for October.

diagenetic model. Then, the reaction term R in equation (1) can be expressed as FkN and FkP for ammonium and phosphate respectively, where N and P refer to the concentration of organic nitrogen and phosphorus, respectively, expressed in terms of mass per unit mass of total sediments solids. The boundary conditions for the solution of the equations are:

when $x = 0$, $C = C_0$, $N = N_0$, and $P = P_0$;

when $x = \infty$, $C = C\infty$, $N = 0$, and $P = 0$.

With these boundary conditions, the concentration vs depth equations for both ammonium and phosphate can be solved as:

$$C = (C\infty - Co)\{1 - exp[(-k/w)x]\} + Co \quad (4)$$

Fitting the above equation to the measured concentration profiles of ammonium and pho-
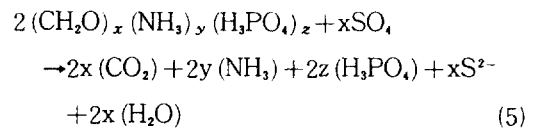
sphate of Fig. 2, as was done for the sulfate data, the rate constant, k, could be estimated (Fig. 4 and 5). For ammonium production, the estimated k values (yr^{-1}) were 0.025 for February, 0.12 for May, 0.28 for July, 0.16 for August, and 0.10 for October. And for phosphate these values were: 0.028 for February, 0.12 for May, 0.076 for July, 0.10 for August, and 0.10 for October. The rate constant thus varied seasonally by a factor of ten for ammonium, and of four for phosphate. The seasonal variation observed in the ammonium production is consistent with that of sulfate reduction rate, which indicates that the nutrient regeneration in the Banweol tidal flat is dominated by microbial sulfate reduction. On the other hand, the relatively subdued seasonal variability of phosphate may result from the inorganic precipitation of phosphatic minerals which was neglected in the model of reaction rate calculation.

The rate of sulfate reduction and nutrient regeneration can also be affected by the amount and nature of organic material present in the sediment (Jorgensen, 1978; Westrich and Berner, 1984). But, since we deal with temporal variation observed in the same site, and since we assume a steady-state condition, at least in a time scale of several months, it is not appropriate here to mention those effects as a possible source of seasonal variation in the microbially mediated reaction rates. Klump and Martens (1987) reported from the Cape Lookout Bight that the nutrient regeneration was dominated by a temperature dependent seasonal cycle and that the ammonium benthic flux varied by a factor of more than 40 between summer and winter. They also reported that the kinetics of nutrient regeneration are rapid, with a mean residence time of several months for recycled nutrients in the sediment. Our steady-state assumption in the diagenetic model will be justified if such rapid kinetics in the nutrient regeneration can be proved also in the Banweol tidal flat. For the cause of temporal variation in the reaction rate, the

seasonal change in sediment temperature and its effect on the microbial activity would be most responsible. The reported seasonal difference of up to $40\,°C$ in the daytime surface sediment temperature (Koh and Shin, 1988) can account for all of the amount of variation observed in the Banweol tidal flat.

Stoichiometry of Nutrient Regeneration

By using the diagenetic equations, it is possible to deduce the stoichiometric C:N:P ratio of decomposing organic matter from pore water data for dissolved sulfate, ammonium, and phosphate. In an area like the Banweol tidal flat where the organic matter decomposition is proceeded mainly by bacterial sulfate reduction, the decomposition process can be written simply as:

$$2\,(CH_2O)_x\,(NH_3)_y\,(H_3PO_4)_z + xSO_4$$
$$\rightarrow 2x\,(CO_2) + 2y\,(NH_3) + 2z\,(H_3PO_4) + xS^{2-}$$
$$+ 2x\,(H_2O) \tag{5}$$

From this relationship, the C:N:P ratio of the decomposing organic matter can be estimated directly from the $2\,\Delta SO_4^{2-}: \Delta NH_4^+: \Delta H_3PO_4$ ratio in pore waters within the sulfate reduction zone (Sholkovitz, 1973). The calculated C:N:P ratio in the Banweol tidal flat was 106: 6.7:1.6 for the February data, and 106:6.0:1.2 for the May data.

Berner (1977, 1979) has pointed out that the calculation of C:N:P ratio from pore water data alone may lead to an erroneous result due to different degrees of adsorption, as well as to different rates of diffusion, between phosphate, ammonium and sulfate. Further, he proposed a more sophisticated formula in which the effects of differential adsorption and diffusion were included. But this new formula appears not to be appropriate to our data because its assumed prerequisite of $k_S = k_N = k_P = k$ is not fulfilled in our results. Our calculation of the C:N:P ratio, which has been made by using the pore water
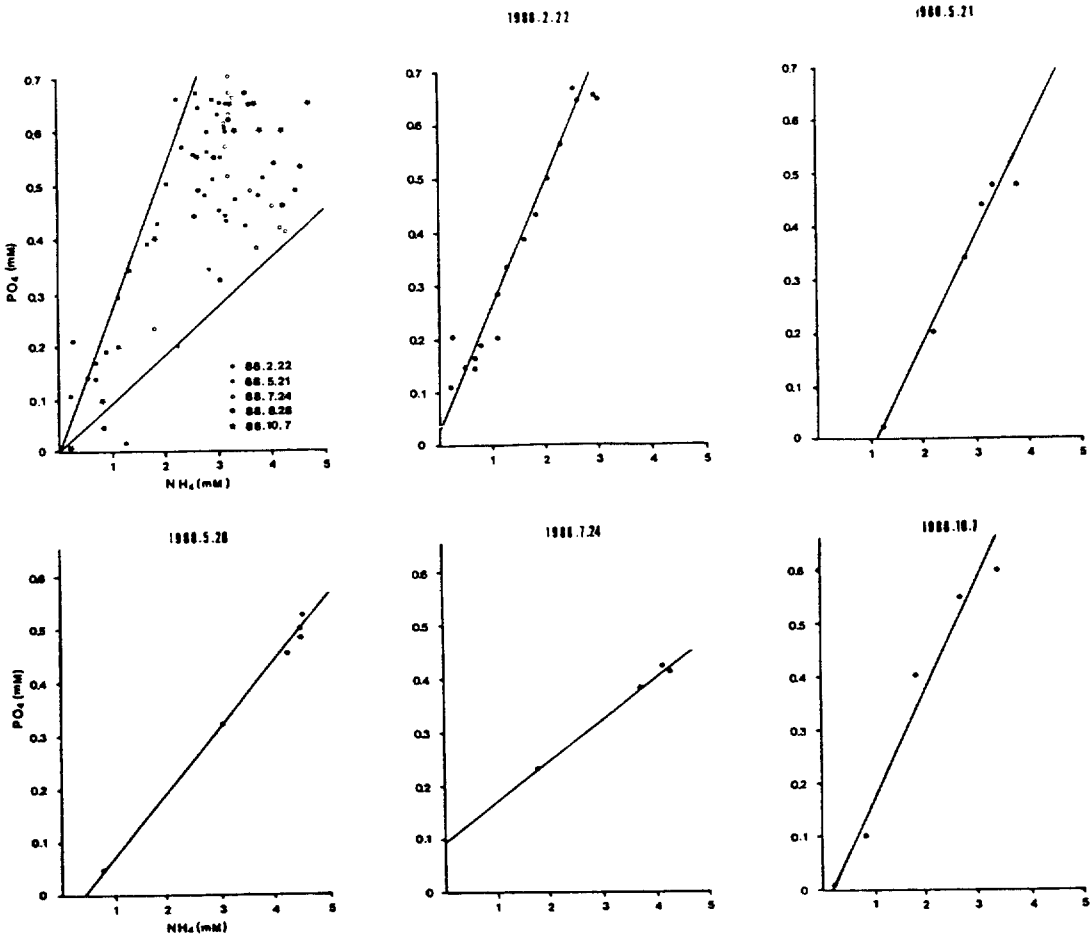
Fig. 6. Ammonium vs phosphate plots observed within the main sulfate reduction zone.

data alone, seems, however, still to be valid in the Banweol tidal flat sediment when the linear relationship between the pore water ammonium and phosphate contents within the sulfate reduction zone is considered (Fig. 6). Below the sulfate reduction zone, on the other hand, the ammonium vs phosphate plot was not linear, suggesting that some processes other than bacterial organic decomposition, such as the dissolution of inorganic compounds, might have been occurring.

The Problem of the Secondary Sulfate Peak: Methane Ebullition or Temperature Differences?

As was described earlier, the pore water sulfate profile often exhibited a secondary peak below the main sulfate reduction zone, especially during the spring and summer seasons. The pore water ammonium and phosphate concentrations on the other hand decreased downward, after a rapid initial increase and attainment of their maximum contents. Such phenomena, particularly for the ammonium decrease in the deeper part of the sediment column, was attributed to the effect of bioturbation by Aller (1980) in his study of Long Island Sound. However, the trace of burrowing organisms could not detected in our sample site in the Banweol tidal flat. Instead, we could observe

some holes with diameters up to several milli-meters, formed most probably by gas ebullition from below, around the sample site.

Sulfate reduction being completed within the upper 10 cm of the sediment column, methane will be produced in the deeper part, through a fermentative breakdown of organic matter, and transported upward and out of sediment surface via diffusion and gas bubble ebullition (Martens and Klump, 1980). Martens and Klump (1980) reported from the Cape Lookout Bight that the methane gas ebullition was more active during the ebb tide compared to the flood. It may also be controlled by the sediment temperature as the latter determines the rate of microbial degrada-tion processes (Martens and Klump, 1984), and by the spring-neap tidal cycle as the pressure variation over the tidal cycle influences the gas ebullition through the sediment surface (Thames Survey Committee, 1964). The gas holes formed during the low water will be filled during the subsequent high water period by the overlying seawater which contains plenty of sulfate and is depleted of ammonium and phosphate compar-ed to the pore solution. The lateral diffusion from (or into) this gas hole of pore water consti-tuents, a mechanism successfully applied to the burrow hole by Aller (1980) using his two-di-mensional model, will also explain the an-omalous profiles of sulfate, ammonium and phosphate in the Banweol tidal flat. The tem-perature dependency in the magnitude of me-thane gas ebullition, as was suggested by Mar-tens and Klump (1984), can also explain the ob-served seasonality in the anomalous pore water profiles.

Another possible way of explaining the se-condary peak of sulfate is to relate it to the changes in the temperature and the accompany-ing microbial activity. As the temperature rises in the spring season, the upper part of the sedi-ment becomes heated and the sulfate reduction in this near-surface layer is greatly enhanced. In the lower part of the sediment, however, a rela-tive coolness of temperature is maintained and

the microbial activity remains still low. As the season changes from winter to spring and sum-mer, the lower part of the sediment sees a relatively slow increase in the sulfate reduction compared to the upper part, and this results in the formation of the secondary peak which is the remnant from the cold winter season of incompletely consumed sulfate. The secondary sulfate peak is, therefore, a temporary pheno-menon which can be observed only during the spring and early summer seasons. This seasonality of secondary peak occurrence is in accordance with the observed pore-water pro-files described above. Furthermore, the concen-tration of sulfate in the secondary peak is lower in the July core compared to that of May, which is another support of this model.

CONCLUSIONS

The present study shows clearly that a tidal mudflat is an environment where active nutrient regeneration occurs through microbially mediat-ed early diagenetic processes. The rapid sulfate reduction, which often accompanies a secon-dary sulfate peak below the main sulfate reduc-tion zone, and the pronounced seasonal vari-ability in the porewater nutrient profiles make this environment unique and deserving of fur-ther detailed studies.

The seasonal variability was estimated quan-titatively in terms of rate constants of sulfate reduction and ammonium production, by using the general diagenetic model of Berner (1980). This seasonal variability, which was shown to be a factor of ten between the summer and winter seasons, can be attributed to the differences in sediment temperatures.

The secondary sulfate peak below the main sulfate reduction zone, which was observed in the May and July cores, is still an enigmatic phenomenon which has not yet been observed elsewhere. Though not yet fully understood, the secondary peak of pore-water sulfate, and pos-sibly part of the observed decreases of am-

monium and phosphate, in the deeper zone could be explained by the process of lateral transport via nearby located holes, produced by methane gas ebullition. Another possible way of explaining the secondary peak of sulfate is to regard it as a remnant of incompletely consumed sulfate from the cold winter season, which remain there for a while due to the different rates in microbial activity between the near-surface and deeper part of the sediment.

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