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SEDIMENT CARBON, NITROGEN AND PHOSPHORUS CYCLING IN AN ANOXIC FJORD, EFFINGHAM INLET, BRITISH COLUMBIA

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ABSTRACT. Sediment geochemistry, as well as benthic exchange of nutrients, was investigated in Effingham Inlet, a fjord located on the west coast of Vancouver Island in Barkley Sound. The effect of bottom-water oxygenation on sediment carbon, nitrogen and phosphorus cycling was compared at sites overlain by oxic and anoxic bottom waters. The sites, separated by only 3 kilometers, were similar in terms of key diagenetic parameters including mass accumulation rate and bulk sediment organic carbon content, thus allowing a focus on diagenetic effects attributable to depositional oxygen availability. Benthic flux chamber incubations, sulfate reduction rate measurements, measurements of solid-phase and pore water chemical profiles were compared for the sites. These comparisons reveal that diagenetic processes in the site overlain by oxic waters act to retain more phosphorus in the sediment relative to the anoxic site. Differences in phosphorus benthic fluxes and burial between the two sites most likely result from differences in organic matter cycling under aerobic versus anaerobic conditions and are not strongly influenced by cycling of P associated with metal oxide phases.

INTRODUCTION

Nitrogen (N) and phosphorus (P) are vital nutrients sustaining marine primary productivity. Nitrogen enters marine systems by N fixation, riverine input and rainfall, while P enters the system primarily via riverine transport (Berner and Berner, 1996). The supply of imported N and P is insufficient to solely support global primary production, thus recycling of nutrients is essential for sustaining primary productivity. Coastal sediments are characterized by intense nutrient recycling and organic matter decomposition because a large fraction of organic matter produced in the water column reaches the sediment surface. The exchange of dissolved nutrients across the sediment-water interface is particularly important in estuarine and coastal environments, where benthic nutrient regeneration can supply a significant fraction (10 – 80%) of water column nutrients required for biological productivity (Callender and Hammond, 1982; Dollar and others, 1991). Benthic nutrient regeneration can directly affect the availability and ratios of nutrients in the overlying water column. Consequently, insight into controls on the magnitude and elemental ratios of benthic fluxes is essential for understanding water-column nutrient dynamics and productivity. Recent research suggests that the global biogeochemical cycles of N and P may be affected in profoundly different ways by shifts in the extent of oxic/anoxic regions within ocean models (Van Cappellen and Ingall, 1994, 1996; Lenton and Watson, 2000a, 2000b; Hansen and Wallman, 2003; Wallmann, 2003). In particular, the release and benthic flux of these nutrients from sediments relative to carbon (C) remineralization may change significantly as a function of bottom-water oxygen availability.

Benthic fluxes of P are a complex function of the cycling of biogenic materials, metals such as iron and manganese, authigenic mineral formation and bottom-water

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oxygen concentration (Klump and Martens, 1981; Sundby and others, 1986; Ingall and Jahnke, 1997; McManus and others, 1997; Colman and Holland, 2000). Limited evidence derived either from direct measurement of benthic fluxes or fluxes calculated from pore water profiles suggests that the presence of anoxic bottom waters enhances the release of P (as compared to N and C) from organic matter (Ingall and Jahnke, 1994, 1997; McManus and others, 1997; Colman and Holland, 2000). In certain situations, suboxic bottom waters may also enhance the release of P from marine sediments (McManus and others, 1997; Colman and Holland, 2000). Preferential regeneration of P from sediments overlain by anoxic bottom waters is also suggested from studies of solid phase P distribution (Ingall and others, 1993; Petsch and Berner, 1998; Murphy and others, 2000a, 2000b). However, other studies suggest the net effect of anoxia on P release is not as significant (Ruttenberg and Berner, 1993; Filippelli and Delaney, 1996; Delaney, 1998; Anderson and others, 2001). Studies of N remineralization patterns under a range of bottom water oxygen concentrations show conflicting results. Some sediments overlain by oxic bottom waters have significantly higher C_{org}/N_{total} ratios than sediment trap material and average plankton, implying selective remineralization of N (Suess and Müller, 1980; Calvert and others, 1992; Calvert and others, 1996; van der Weijden and others, 1998). However, a reversal of this pattern has been noted in the Black Sea (Cowie and Hedges, 1992).

The potential consequences of enhanced P regeneration from sediments under anoxic bottom waters have been explored in several studies (Van Cappellen and Ingall, 1994, 1996; Lenton and Watson, 2000a, 2000b; Wallmann, 2003; Filippelli and others, 2003). One idea incorporated in these models is that increased benthic regeneration of P leads to increased primary production. Greater primary production intensifies respiratory oxygen demand in the water column, thus creating a positive feedback loop. Because atmospheric and oceanic oxygen concentrations are linked, a feedback between atmospheric oxygen levels and P-limited marine productivity was proposed. This feedback between the extent of ocean anoxia, P release and marine productivity has been hypothesized to act as a key control on global O_2 levels on geologic time scales (Van Cappellen and Ingall, 1994, 1996; Colman and Holland, 2000).

This paper focuses on the influence of bottom-water oxygen concentration on C:N:P remineralization and burial patterns. Carbon, N and P chemistry was characterized in the water column as well as the pore waters and solid phases of sediments at two sedimentologically similar sites within Effingham Inlet. Here we suggest that P is preferentially released from sediments relative to C and N based on (1) measurement of sediment solid phase chemistry, (2) *in situ* benthic chamber incubations and (3) pore water and water column chemical profiles.

METHODS

Study Site

Effingham Inlet was studied during a cruise aboard the *R/V Barnes* during May and June of 1997 (fig. 1). Effingham Inlet is a fjord on the southwestern coast of Vancouver Island, which opens into the Imperial Eagle Channel in eastern Barkley Sound. Effingham Inlet is approximately 17 km long and approximately 1 km in width along its entire length. Depth profiles for Effingham Inlet indicate the presence of two sills. The outer sill at 70 m water depth is found at approximately 49°00′ N (fig. 1). The outer basin, which reaches a depth of approximately 210 m, is located behind this sill (table 1; fig. 1). The inner sill is located at approximately 49°03′ N and 40 m water depth. Located behind this sill is the inner basin, which reaches a depth of approximately 120 m. There are no major rivers entering the inlet, thus freshwater surface outflow volume is low. Winds during the sampling cruise were very light, presumably due to the protection from the wind by steep topographical features surrounding the

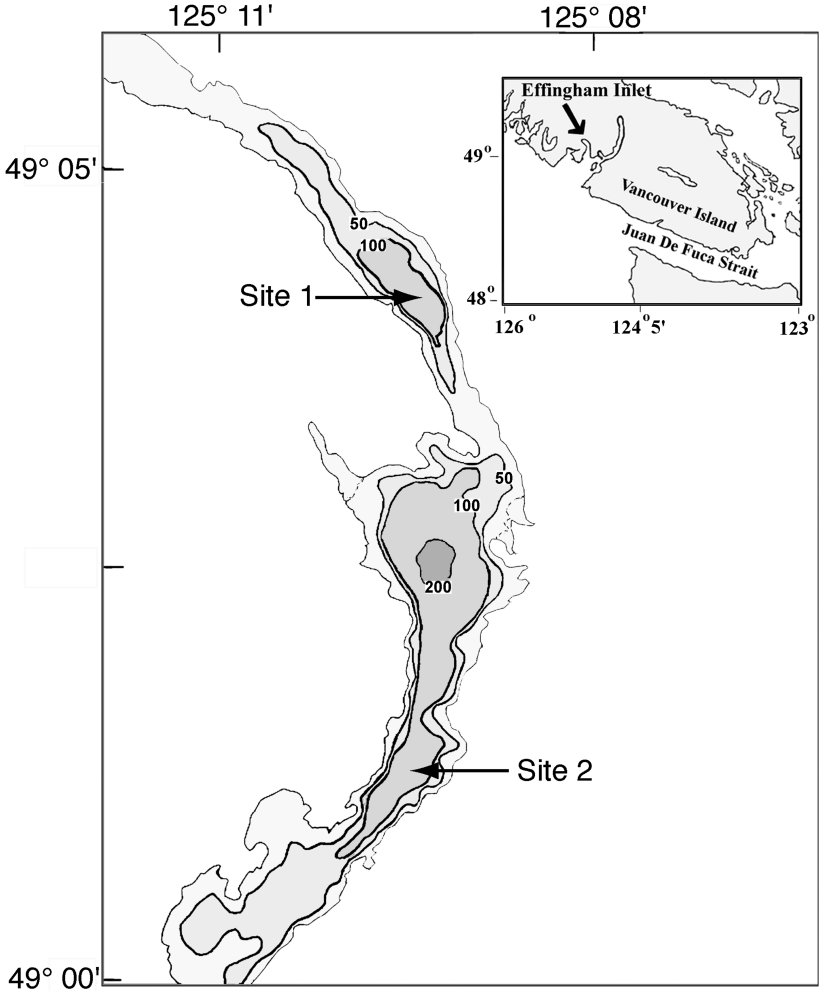

Fig. 1. Map of Effingham Inlet displaying inner basin sampling site 1 and outer basin site 2. Inset map shows the relation of Effingham Inlet to Barkley Sound on the west coast of Vancouver Island.

inlet. The shallow sills, low fresh water inputs, low wind mixing rates and cool dense saline waters of the deep portions of the inner and outer basins collectively inhibit ventilation of basin subsurface waters (Patterson and others, 2000). The reduced subsurface water replacement rates presumably lead to long deep-water residence

TABLE 1

Site locations and mass accumulation rate (MAR) measurements for Effingham Inlet

Site	Latitude	Longitude	Water Depth (m)	^{210}Pb MAR (mg/cm^2/y)	^{137}Cs MAR (mg/cm^2/y)
1	49°04.33N	125°09.56W	117	27	38
2	49°01.06N	125°09.62W	120	59	48

times, which are consistent with measurements of water column anoxia in the inner and outer basins (see Results).

Two sites at approximately 120 m water depth in Effingham Inlet were selected for detailed study (fig. 1). Site 1 is located in the deepest part of the inner basin. Sediment characteristics such as laminations coupled with measured accumulation rates suggest that bottom waters at this site have remained anoxic for at least the last 60 years (see Results). Site 2 is located at the southern edge of the outer basin. Waters at the sediment-water interface at this site had oxygen concentrations of 8 μM at the time of the cruise, and the sediments were clearly bioturbated and populated with macroscale infauna.

Sampling Procedures

All sediment cores were collected using a gravity corer. Sediment cores taken for solid phase analysis were sliced at 1 cm intervals under a N_2 atmosphere at ~8 °C, the ambient bottom-water temperature. These samples were placed in plastic dishes and frozen for later chemical analysis of the solids. Sediment samples were freeze-dried and then ground with an agate mortar and pestle before chemical and isotopic analyses. Pore waters were extracted by sectioning and centrifugation under a N_2 atmosphere. Water column samples were collected from 5L Niskin bottles. For oxygen analysis, water samples were collected directly from the Niskin bottle outlets into glass vials designed to greatly limit sample contact with the atmosphere. Additional water samples were collected in triple-rinsed polypropylene syringes. Both pore water and water column samples were immediately filtered through 0.45μm Whatman Puradisc 25mm polypropylene syringe filters into polypropylene vials and refrigerated. Samples taken for dissolved phosphate and iron analyses were acidified to pH 1 with trace metal grade hydrochloric acid before storage in acid cleaned polypropylene vials.

Mass Accumulation Rate Measurement and Porosity

Radionuclide activities necessary for calculations of ^{137}Cs and ^{210}Pb mass accumulation rates were determined by gamma spectroscopy using self-absorption corrections and methods described in Cutshall and others (1983) and Alexander and others (1993). ^{137}Cs is a pulse tracer produced in significant quantities during above-ground nuclear tests. Mass accumulation rates using ^{137}Cs assume that peak concentrations represent the above-ground nuclear testing zenith of 1963. Sediments were ground, sealed in 10 ml polycarbonate Petri dishes and equilibrated for a month to achieve secular equilibrium with ^{226}Ra daughters. Gamma energy spectral data were collected with a Canberra low background 2000 mm^2 N-type coaxial germanium detector connected to a computer-based multi-channel analyzer. Energy spectra were evaluated with Canberra analysis software. Total ^{210}Pb and ^{137}Cs activities were determined through measurement of the 46.5-KeV and 661.6 KeV gamma peaks, respectively. Excess ^{210}Pb was calculated by subtracting ^{226}Ra activity (determined through measurement of the gamma activity of ^{226}Ra daughters—^{214}Pb [295 and 352 KeV] and ^{214}Bi [609 KeV]) from total ^{210}Pb activity. Mass accumulation rates (g/cm^2/y) were determined from the slope of the least squares fitted line of the logarithm of excess ^{210}Pb activity versus cumulative down core sediment mass. Down core cumulative mass was calculated using the porosity data for each core. Porosity was calculated from sediment dry weight and chloride content measurements using the procedures outlined in Reimers and Smith (1986). Porosity calculations use an average bottom water salinity measurement of 35 permil and grain densities of 2.1 g/cm^3. The grain density value used (2.1 g/cm^3) is in the middle of the range (2.06 to 2.21 g/cm^3) determined for another Vancouver Island estuary, Saanich Inlet (Matsumoto and Wong, 1977). The bottom-water salinity of 35 permil was calculated through chlorinity titrations of

Effingham Inlet bottom waters and proportionality relations relating chlorinity to salinity (Pilson, 1998).

In Situ Benthic Flux Measurements

Two *in situ* benthic landers were deployed in this study. The two benthic landers are mechanistically similar, but one is designed as a free vehicle device for deep sea deployments; the second remains tethered and is designed for coastal deployments. Because of the shallow fjord depths (<230m), both benthic landers were deployed on a line tethered to a free-floating buoy during the incubation. The benthic landers consist of an aluminum tripod-shaped frame, which supports a PVC chamber (27 cm width x 27 cm length x 45cm height), the electronic components and a power supply. Water samples are independently withdrawn from the chamber during each lander deployment via spring-loaded, 60mL syringes. A cable attached to the top of the syringe piston holds the spring under tension, and the cable is placed around a solenoid pin such that the powering of the waterproof solenoid causes the pin to retract, the cable to release and the syringe to withdraw a sample. Electronic timing for triggering the syringes was programmed using ladder logic industrial controllers (IDEC MICRO-1). Power was provided by 24 volt rechargeable gelled electrolyte cells. As each sample is withdrawn from the chamber, samples pass through two 10 mL glass vials connected with Tygon tubing, which flushes the sample vials with chamber water before the actual sample is collected. The chamber is gently stirred during deployment via an electric motor in a watertight housing, which is magnetically coupled to a 5 cm teflon stir bar placed on the underside of the chamber lid and rotated at approximately 20 rpm. All electronic and battery components were encased in watertight pressure housings. Chamber volume was calculated from chamber penetration depth, which was determined by sediment markings on double-sided foam tape placed on the inside and outside surfaces of the chamber before deployment.

Two 10 ml samples were collected for each time point during a chamber deployment. Both vials were removed immediately and clamped off on both ends upon retrieval of the landers. One vial was used for alkalinity titrations, and the other vial was used for analyses of all other constituents. Samples were filtered through 0.45μm Whatman Puradisc 25mm polypropylene syringe filters into 2 polypropylene vials. One vial was acidified to pH 1 with trace-metal grade hydrochloric acid and the other was left unacidified. Both vials were refrigerated. Benthic fluxes were calculated from the changes in concentration observed in the time series of samples. During sampling a small volume of bottom water replaces the volume of the withdrawn sample. This results in a small (~0.5%) dilution of the chamber waters. Because the dilution of the chamber waters was insignificant relative to typical uncertainties in the chemical analyses, results have not been corrected for dilution.

Chemical Analyses

Oxygen concentrations were determined using Winkler titrations, and alkalinity was determined by Gran titration; both analyses were performed on board (Parsons and others, 1984; Grasshoff and others, 1999). Dissolved inorganic phosphate, iron, and ammonium were measured using colorimetric methods that have analytical uncertainties of approximately 3 percent. Specifically, the following colorimetric techniques were employed: 1) phosphorus was measured by formation of phosphomolybdate heteropoly acid, which is reduced by addition of ascorbic acid to form a highly colored blue complex (Parsons and others, 1984; Grasshoff and others, 1999); 2) iron was measured through the formation of a colored ferrozine complex (Stookey, 1970; Aller and Blair, 1996); ammonium was measured using the indophenol blue method (Parsons and others, 1984; Grasshoff and others, 1999). Sediment total C, organic C and N concentrations were measured using a Carlo Erba NC 2500 elemental analyzer

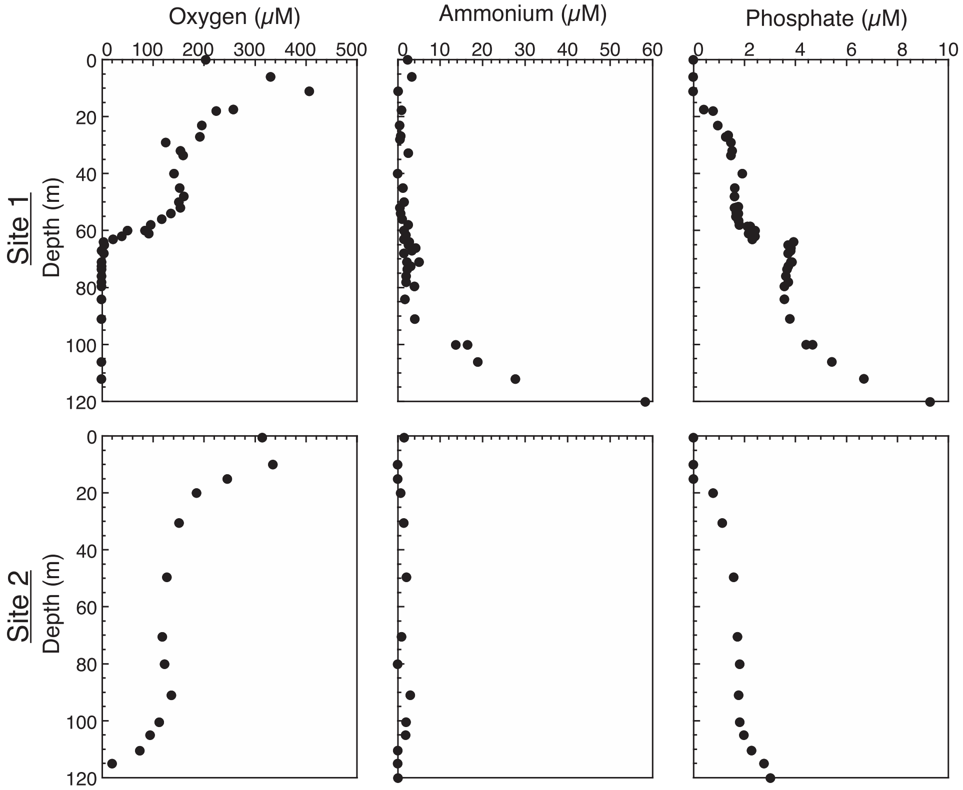

Fig. 2. Water column distributions of dissolved oxygen, ammonium and phosphate for sites 1 and 2 in Effingham Inlet.

using methods described in Hedges and Stern (1984). Total, inorganic and organic phosphate concentrations in sediments were measured according to the Aspila and others (1976) method. Sulfate reduction rates measurements are from the paper by Hurtgen and others (1999). These sulfate reduction rates were determined using ^{35}S radiotracer techniques described in detail in the Hurtgen and others (1999) paper. Additional, complementary data, including dissolved sulfide concentrations, are provided in Hurtgen and others (1999). Note that Sites 1 and 2 of this study are equivalent to sites designated as EF1 and EF2, respectively, by Hurtgen and others (1999).

RESULTS

Site and Sediment Characteristics

Water column oxygen, ammonium, and phosphate concentration profiles taken near Sites 1 and 2 are shown in figure 2. The Site 1 water column was anoxic below 65 m. Observable H_2S was recorded below 65 m, with concentrations reaching ~160 μM at the sediment-water interface (Hurtgen and others, 1999). Cores taken at Site 1 consisted of black fine-grained microlaminated muds (mm-scale) with laminations visible to the eye down to a depth of 30 cm. Below the microlaminated muds is a massive layer, which extended to the base of all cores taken at the site. The massive layer is interpreted to be a gravity flow originating from the steep walls of the basin margin (Hay and others, 2003). Sediment laminations are generally indicative of

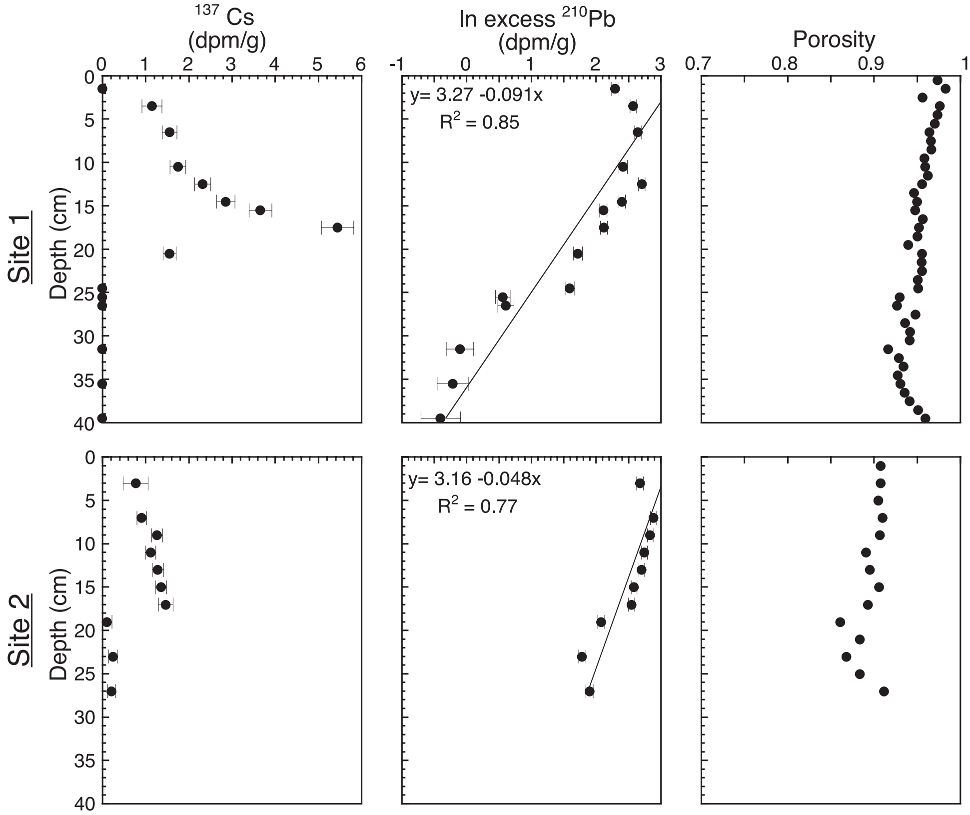

Fig. 3. Down-core distributions of ^{210}Pb, ^{137}Cs activity and porosity for sites 1 and 2 in Effingham Inlet. Lines through the ^{210}Pb data are linear regressions of the depth versus activity data used in the calculation of the linear sedimentation rates. Regressions of the activity data versus cumulative sediment mass (not shown) were used for calculations of mass accumulation rates presented in table 1.

deposition under anoxic or extremely low oxygen conditions. A simple calculation using the depth of laminations at Site 1 coupled with the sedimentation rate indicate that the site has remained anoxic for at least the last 60 years and perhaps much longer. The Site 2 water column was characterized by decreasing oxygen concentrations with depth. However in contrast to Site 1, bottom waters at Site 2 remained oxic with oxygen concentrations of approximately 8 μM at the sediment-water interface. Cores taken at Site 2 consist of homogenized, gray-brown, fine-grained muds. Consistent with the presence of bottom water oxygen, small infauna and mm-scale burrows were observed in Site 2 cores, and these cores had no visible evidence of lamination.

Mass Accumulation Rates and Porosity

Mass accumulation rates determined from profiles of ^{210}Pb, ^{137}Cs and porosity (fig. 3) are presented in table 1. Sedimentation rates derived for Sites 1 and 2 from ^{137}Cs profiles are similar, with rates agreeing within 26 percent. Peak ^{137}Cs concentrations are not as prominent in the Site 2 profile, which is consistent with the potential effects of bioturbation. It should be noted that as a pulse tracer only the magnitude but not the depth of the peak concentration of ^{137}Cs will be affected by bioturbation (Alexander and others, 1993). Hence, ^{137}Cs provides the best comparative measure of sedimentation rates at the two sites. ^{210}Pb profiles for both sites are near vertical with

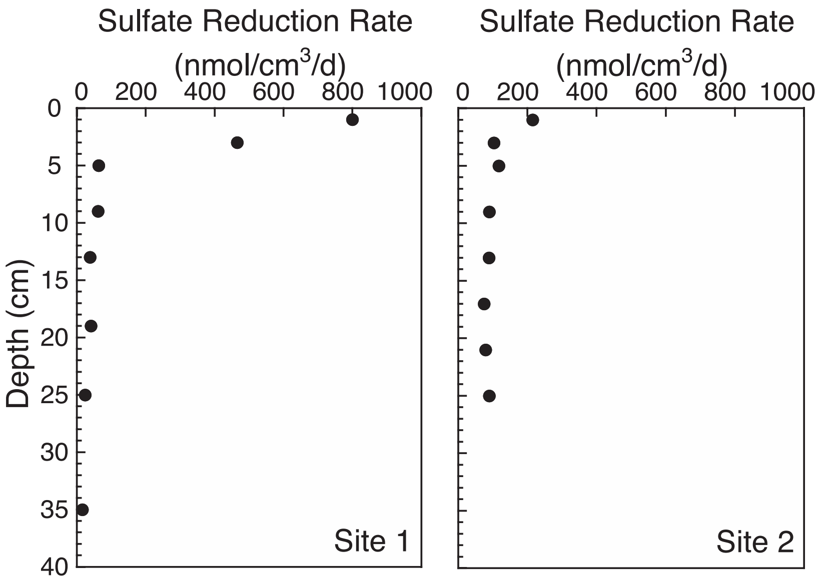

Fig. 4. Sulfate reduction rates vs. depth for sites 1 and 2 in Effingham Inlet. Data are from Hurtgen and others (1999).

depth in the first few centimeters below the sediment water interface (fig. 3). This may indicate the action of sediment mixing processes. Even with the potential for sediment mixing, simple linear regressions of the ^{210}Pb data yield mass accumulation rates within 30 percent to those determined by ^{137}Cs (table 1). Linear sedimentation rates calculated directly from the ^{210}Pb distributions with depth are 0.3 cm/y for Site 1 and 0.7 cm/y for Site 2. Linear sedimentation rates determined from ^{137}Cs peaks in each core are an identical 0.5 cm/y for both sites.

Sulfate Reduction Rates

Depth profiles for sulfate reduction rate measurements for cores from Sites 1 and 2 are presented in figure 4 using data from Hurtgen and others, (1999). Sulfate reduction rates are highest at the sediment-water interface in both cores and then decrease approximately by an order of magnitude at Site 1 and by a factor of 2 at Site 2 in the first few cm. At Site 1, sulfate reduction rates drop gradually with depth reaching a value of 13 nmol/cm^3/d at 36 cm. In contrast, sulfate reduction rates are relatively constant (average 90 nmol/cm^3/d) with depth in the Site 2 core after the initial decrease near the sediment-water interface. Depth integrated sulfate reduction rates are 13.6 mol/m^2/y for Site 1 and 9.5 mol/m^2/y for Site 2. It should be noted that these integrated rates are calculated for cores of different lengths. Unfortunately, longer cores were not obtained at Site 2. Given that sulfate reduction rates show no sign of decline at depth in the Site 2 core, an estimate for the purposes of site comparison may be obtained by extrapolation of the average rate at depth of 90 nmol/cm^3/d to 35cm. With this extrapolation, a depth integrated sulfate reduction rate of 12.8 mol/m^2/y is calculated for Site 2.

Benthic Fluxes

Concentration versus time results for three benthic chamber deployments at Site 1 are displayed in figures 5 and 6. Unfortunately, both *in situ* chamber deployments

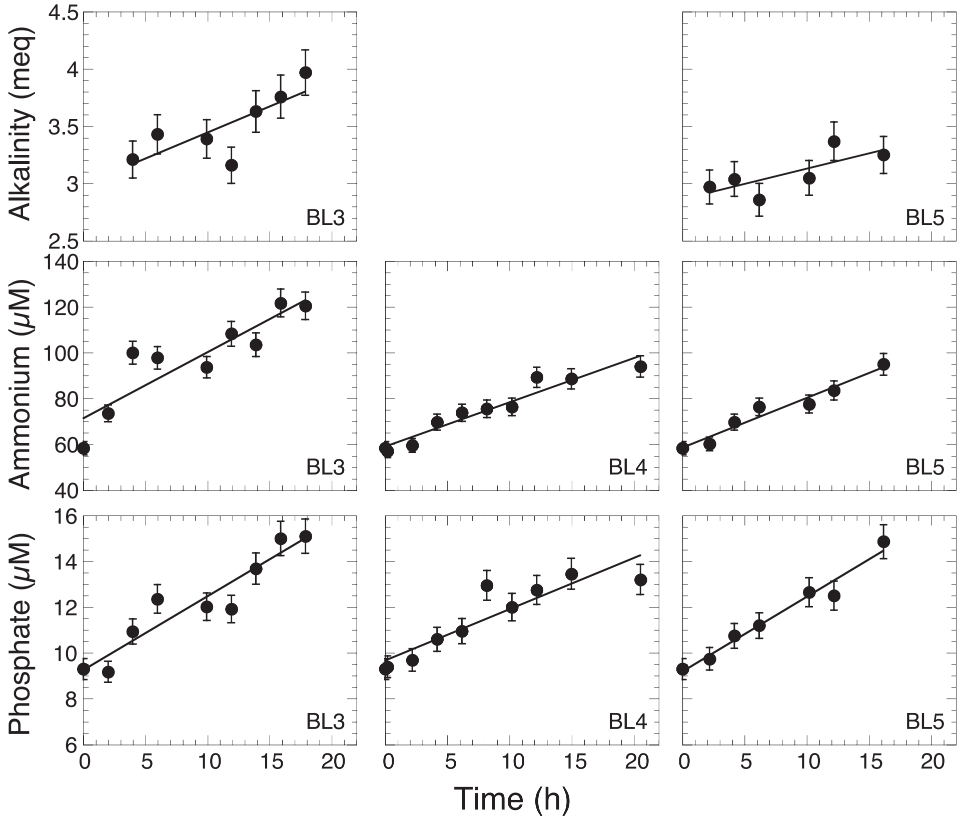

Fig. 5. Alkalinity, ammonium, and phosphate benthic chamber results for three chamber deployments for site 1, Effingham Inlet. Lines are linear regressions through the data points.

attempted at Site 2 failed. Alkalinity, phosphate and ammonium increase over the course of three benthic chamber deployments indicating a solute flux out of the sediment at Site 1 (fig. 5). In contrast, iron concentrations decrease with time in all three deployments indicating a solute flux into the sediments (fig. 6). Benthic fluxes presented in table 2 are calculated from chamber volume for each deployment, and

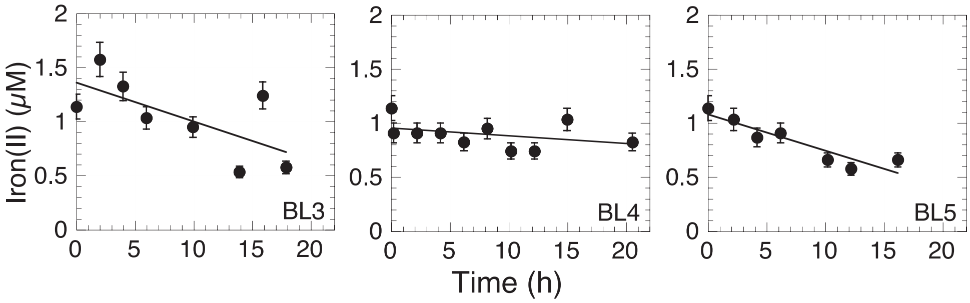

Fig. 6. Dissolved iron(II) benthic chamber results three chamber deployments for site 1, Effingham Inlet. Lines are linear regressions through the data points.

TABLE 2

Benthic fluxes for site 1. Positive fluxes denote a benthic flux out of the sediment, and negative fluxes denote a benthic flux into the sediment

Deployment	Alkalinity ($eq/m^2/y$)	Ammonium ($mol/m^2/y$)	Phosphate ($mol/m^2/y$)	Iron(II) ($mol/m^2/y$)
BL3	84	5.2	0.60	–0.066
BL 4		6.2	0.71	–0.023
BL 5	61	5.0	0.75	–0.076
Average	73	5.5	0.69	–0.055

the slope is determined by linear regression of the concentration versus time results. Linear regression of the chamber data assumes a constant flux during the chamber incubation, which is the assumption made in most chamber studies (Tengberg and others, 1995). Differences in the concentration versus time slopes result from differences in both the fluxes and chamber penetration depths of different deployments.

Sediment Pore Waters and Solids

Pore water ammonium and phosphate profiles are presented in figure 7. A significant feature in the profiles for dissolved phosphate and ammonium at both sites is the large difference between bottom-water concentrations taken just above the sediment-water interface and the concentration in the first measurable pore water interval. The steep concentration gradient is generally consistent with the high benthic fluxes observed in benthic chamber incubation experiments (see discussion). In general, pore water concentrations of ammonium and phosphate at Site 2 are significantly lower than those of Site 1. Site 1 pore water ammonium and phosphate profiles show increasing concentration trends with depth; in contrast, Site 2 profiles decrease with depth after the initially high values at the sediment-water interface.

Ammonium and phosphate fluxes were calculated from the pore water profiles using well-established procedures (see for example, Colman and Holland, 2000). Briefly, the diffusive flux of phosphate and ammonium across the sediment-water interface was determined using Fick's First Law of diffusion. The Fick's Law flux equation is the product of the concentration gradient of the species of interest and a diffusion coefficient appropriately modified for ambient conditions and application to sediments. A linear gradient was calculated using the bottom-water concentration and the concentration of the species of interest in the first measured pore water interval (0.5cm). Diffusion coefficients were corrected for temperature using the formulations of Li and Gregory (1974). Benthic phosphate and ammonium fluxes calculated from pore water profiles are 0.16 and 0.77 $mol/m^2/y$ for Site 1, respectively, and 0.034 and 0.20 $mol/m^2/y$ for Site 2, respectively. These flux values are several times less than fluxes measured during *in situ* chamber incubations at Site 1 (table 2). This discrepancy between flux determinations is likely a function of the extremely steep gradients at the sediment-water interface. These reactions in the top few mm of the sediment cannot be characterized spatially with the resolution of the pore water sampling techniques utilized in this study. Given the steepness of the gradients at the sediment-water interface, small spatial differences in the distribution of pore water species will drastically change the gradients, which in turn, will result in large differences in calculated fluxes. Additionally, the unknown potential effects of irrigation by organisms at Site 2 can influence fluxes calculated from pore water gradients.

Analyses of solid phase organic and inorganic C, organic and total P and total N in the sediments are presented in figure 8. Relatively high organic C, total N and organic

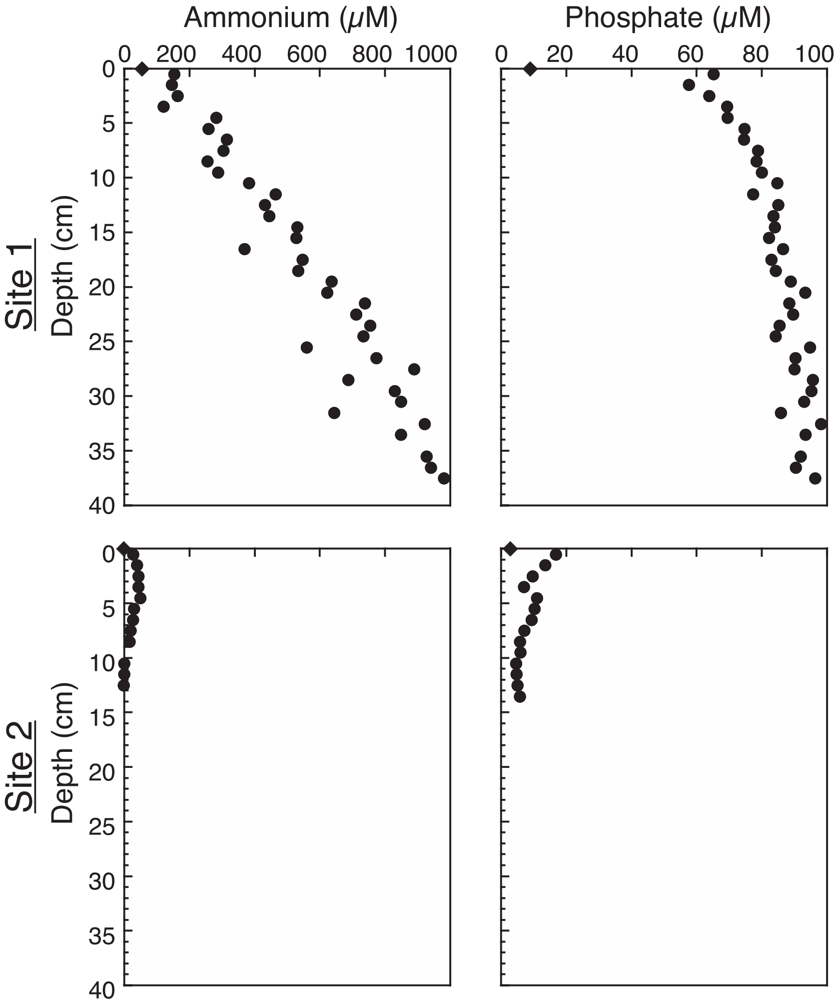

Fig. 7. Sediment pore water distributions of ammonium and phosphate for sites 1 and 2 in Effingham Inlet. Diamond symbols are concentrations measured in the bottom waters just above the sediment-water interface.

P concentrations were observed in the near-surface interval of the Site 1 core. The high surface concentrations are consistent with a seasonal pulse of sediment organic matter being delivered to the sediment-water interface. Although a similar seasonal pulse of organic material was likely delivered to Site 2, absence of high surface organic matter concentrations would be consistent with the effects of bioturbation. Organic and inorganic C and total N concentrations are similar for both sites. Averages of organic and inorganic C concentrations (wt%) are 6.3 ± 0.8 (± 1σ) and 0.4 ± 0.6 for Site 1 and 5.9 ± 0.3 and 0.6 ± 0.3 for Site 2, respectively. Total N (wt%) averages 0.4 ± 0.05 for Site 1 and 0.5 ± 0.02 for Site 2. In contrast to C and N, average organic and total P concentrations are distinct between sites. Average organic P concentrations (μmol/g) are 12.8 ± 2.8 at Site 1 and 17.5 ± 3.7 at Site 2. Total sediment P concentrations average 26.7 ± 3.7 at Site 1 and 37.1 ± 3.5 at Site 2.

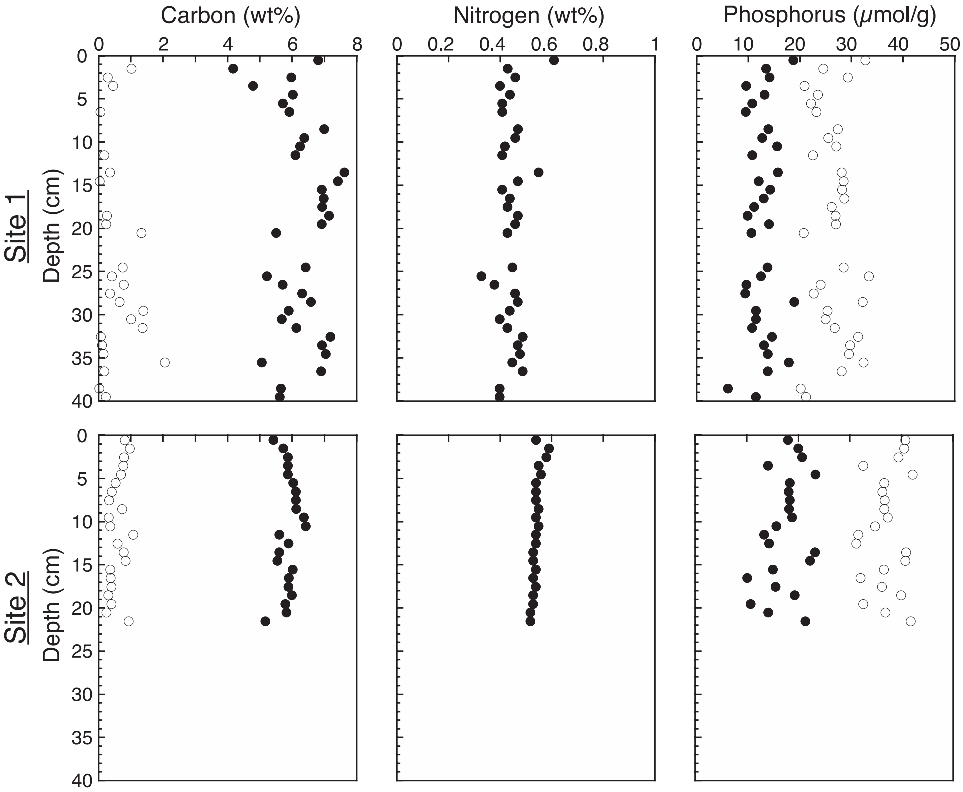

Fig. 8. Sediment solid phase inorganic carbon (open circles), organic carbon (closed circles), total nitrogen, organic phosphorus (closed circles) and total phosphorus (open circles) distributions for sites 1 and 2 in Effingham Inlet.

DISCUSSION

The global biogeochemical cycles of N and P may be affected in profoundly different ways by shifts in the extent of suboxic/anoxic conditions within the ocean. In particular, the release of these nutrients relative to C remineralization within sediments may change significantly as a function of bottom-water oxygen concentration. In addition to oxygen concentration, C, N and P diagenesis can be affected by variables such as sedimentation rate and organic matter quantity, source and reactivity. In order to focus on the role of oxygen in C:N:P remineralization it is advantageous to study sites where the role of oxygen can be isolated from the other controlling factors. The similarities of the two Effingham Inlet study sites, which include mass accumulation rates and organic C concentrations, are well suited to such comparisons.

Sediment accumulation rate has been shown in many studies to be an important factor in the preservation and resulting relative remineralization rates for C, N and P of sedimentary organic matter (Berner, 1980; Henrichs and Reeburgh, 1987; Canfield, 1989). In general, these studies indicate that C preservation in marine sediments increases with increasing sedimentation rates. In contrast, the relationship between P preservation and sedimentation rate is less clear. The organic C:P ratio of buried organic matter has been shown to be a complex function of sedimentation rate (Ingall and Van Cappellen, 1990). Low C:P ratios (<200) are found in sediments with sedimentation rates both less than ≈ 0.002 cm/y and greater than ≈ 1 cm/y. At sedimentation rates between these extremes, C:P ratios up to 600 are found (Ingall and Van Cappellen 1990). Thus, it is imperative to compare C and P regeneration at sites with similar accumulation rates, such as Effingham inlet Sites 1 and 2 (table 1). It should be noted that the sedimentation rate effects in studies cited above cover the entire 5 order of magnitude range of marine accumulation rates. Thus, differences much less than an order of magnitude, such as those observed between Sites 1 and 2 (table 1), are essentially insignificant in terms of the above factors.

Even in cases where there are many similarities between sites, small differences in elemental ratios could potentially be attributed to differences in organic matter source and composition rather than diagenetic effects specifically related to the availability of bottom-water oxygen. For example, elevated C/N and C/P ratios have been linked to terrestrial-derived organic matter (Likens and others, 1981). In Effingham Inlet, atomic organic C to total N ratios are 18.4 and 13.8 for Sites 1 and 2, respectively. Atomic ratios of the average organic C to organic P concentration are 410 for Site 1 and 281 for Site 2. Therefore, the elevated C/N and C/P ratios at Site 1 relative to Site 2 could indicate that Site 1 contains a higher proportion of terrestrial material. However, if Site 1 does contain higher proportions of terrestrially-derived material, which is often presumed to be less reactive than marine-derived organic matter, it is not reflected by the integrated rates of sulfate reduction, which are higher at Site 1 relative to Site 2. Given proximity of the two sites, the identical water depths and nearly identical sedimentation rates, we argue there is limited potential for large variations in the quantity, source and reactivity of organic matter delivered to the sediment-water interface. Rather we argue that differences in the elemental ratio data are caused by differences in organic matter diagenesis at the two sites.

Benthic fluxes of dissolved C, N, P and other elements across the sediment-water interface are one measure of net diagenetic effects on a particular species. It should be noted that phosphate and ammonium chamber fluxes at Site 1 are high relative to other low oxygen continental margin sites (McManus and others, 1997; Ingall and Jahnke, 1997) but similar to values seen in other anoxic fjords (Devol, 1987). It is very likely that the observed fluxes reflect a seasonal high resulting from late spring or early summer phytoplankton blooms followed by increased rates of organic matter sedimentation and decomposition. Fjords in the region are characterized by pronounced seasonal cycles in phytoplankton production, with peak production generally occurring in the late spring or early summer (Herlinveaux, 1962; Hay and others, 2003; Chang and Patterson, 2003). Temporal patterns in benthic phosphate fluxes from several other regions consistently show the highest values occur during the summer (Colman and Holland, 2000). Summer benthic phosphate fluxes often exceed those of other seasons by up to an order of magnitude. Indications of a seasonal pulse of organic matter may also be reflected in the phosphate pore water profiles (fig. 7), where sharp concentration increases at the sediment-water interface are followed by significant down core decreases. The likelihood of depositional seasonality makes extrapolation of these fluxes to annual rates imprudent. Nevertheless, it is still informative to compare flux ratios for the sampling period, as determined by chamber incubations and other techniques, among sites with differing oxygen concentrations.

Given the importance of organic matter remineralization on N and P cycling, comparison of P and N fluxes to integrated sediment C oxidation (a measure of organic matter remineralization) has been the approach of many studies. Sedimentary C oxidation can be estimated using integrated sulfate reduction rate measurements at both sites. Using integrated sediment sulfate reduction rates as a measure of C oxidation assumes (1) that other mechanisms of C oxidation such as iron and manganese oxide reduction are not significant and (2) that sulfate availability is not limiting. At Site 1 pore water sulfate concentrations decrease down core as a result of sulfate reduction but remain at sufficiently high concentrations so as to not be limiting ($>$11 mM) to 35 cm depth (Hurtgen and others, 1999). Similarly, pore water sulfate concentrations at Site 2 remain high throughout the length of the core ($>$26 mM). Reduction of Mn and Fe oxides during organic C oxidation are generally much less significant in comparison to other oxidation pathways, such as sulfate reduction (Canfield, 1989).

Assuming the average oxidation state of organic C undergoing remineralization can be approximated by carbohydrate, for every mole of sulfate reduced to sulfide two moles of organic C are oxidized to carbon dioxide. Thus, multiplying the integrated sulfate reduction rate for each site by 2 yields an estimate of C remineralization of 27.2 moles C/m^2/y for Site 1 and 25.6 moles C/m^2/y for Site 2. The ratio of this C oxidation estimate to the P flux determined from pore water profiles is 170 for Site 1 and 752 for Site 2. Comparison of these ratios shows that more P is remineralized per unit C, during diagenesis in sediments overlain by anaerobic waters. It is likely however that the value of 752 for site 2 is an overestimate because it does not incorporate the potential effects of irrigation on phosphate and ammonium fluxes. A more robust approach for calculating C remineralization to P flux ratios can be employed for site 1 using the average P flux determined during benthic chamber incubations. For site 1 the ratio of C oxidation determined from integrated sulfate reduction to P flux is 39. This ratio is well below the average ratio C/P ratio of planktonic marine organic matter of 106 (Redfield and others, 1963) and the C/P ratio of organic matter in the site 1 sediments of 410 (see below). Comparison of the measured C/P flux ratio of 39 with the much higher C/P ratios of average marine organic matter or organic C/P ratios of the sediments supports the idea of preferential remineralization of P relative to C during organic matter diagenesis in sediments overlain by anoxic bottom waters.

Taking the ratio of the average ammonium to phosphate fluxes determined from benthic flux chamber incubations (table 2) yields a value of 8, which is half the value determined by Redfield and others (1963) for average planktonic marine organic matter. Ammonium to phosphate flux ratios determined from Fick's law calculations of pore water profiles are 4.8 and 5.9 for Sites 1 and 2, respectively. Although the error in these flux estimates based on pore water profiles is potentially very high due to the steepness of the gradients at the sediment-water interface (see Results), the results are consistent with the low ammonium to phosphate flux ratio observed in the Site 1 incubations. The low ammonium to phosphate flux ratios can be explained in several ways: (1) preferential regeneration of P relative to N during remineralization of organic matter, (2) release during diagenesis of P from non-organic sources, and (3) removal of ammonium relative to phosphate during diagenesis.

The *in situ* flux measurements and pore water profiles may be influenced by a seasonal input of organic matter and reactions occurring at the sediment-water interface. A longer time scale perspective on P burial and mineralization relative to C and N can be obtained by looking at solid phase C, N and P profiles presented in figure 8. The main difference between Site 1 and 2 sediments is the concentrations of organic and total P. Molar ratios of the average organic C to organic P are 410 for Site 1 and 281 for Site 2. These ratios are consistent with the trends observed in the C/P ratios in modern sediments collected in regions with anoxic and oxic bottom waters (Van Cappellen and Slomp, 2002). In the Van Cappellen and Slomp (2002) study, it was shown that sedimentation rate and bottom water oxygenation are the major controls of the C/P ratio of organic matter preserved in marine sediments. At comparable sedimentation rates the C/P ratio of sedimentary organic matter is consistently higher in sediments deposited within low oxygen and anoxic water columns in comparison to those deposited from oxic waters. The difference in C/P ratios between low and high oxygen sites is greatest at sites with the lowest sedimentation rates (0.001 to 0.01 cm/y).

At sites with the high sedimentation rates (>1 cm/y) the differences in C/P ratios become less apparent (Van Cappellen and Slomp, 2002). At the relatively high sedimentation rates of the Effingham Inlet sites, large differences in C/P ratios between oxic and anoxic sites analogous to those observed in studies of ancient shales (see below) would not be expected.

In studies of ancient shale sequences, significant differences in the organic C/P ratios have been observed between shales deposited in oxygenated versus anoxic waters (Ingall and others, 1993; Murphy and others, 2000b). For example, in a study of Devonian-Mississippian shales average organic C/P ratios of 3900 and 150 were found in shales deposited from anoxic and oxic bottom waters, respectively (Ingall and others, 1993). A similar trend in organic C/P ratios has been observed in Black Sea sediments. Black Sea sediments deposited in portions of the basin with oxic waters have organic C/P ratios of 237, whereas anoxic portions of the basin have C/P ratios of 558 (Van Cappellen and Ingall, 1997). Significant down core increases in the organic C/P ratios of Saanich Inlet sediments (a seasonally anoxic basin of Vancouver Island) have also been observed (Filippelli, 2001). The above data all suggest that organic P is preferentially recycled and lost from sediments relative to organic C under reducing conditions. However, direct comparison of organic C/P ratios for sediments deposited under differing redox conditions may not represent a true picture of P preservation because some P regenerated from organic phases may be subsequently retained in authigenic mineral phases during diagenesis (Ruttenberg and Berner, 1993; Filippelli and Delaney, 1996; Delaney, 1998; Anderson and others, 2001). Retention of mineralized organic P in authigenic phases would be reflected in the molar ratios of average organic C to average total P (C/P_{tot}). C/P_{tot} ratios are 197 for Site 1 and 133 for Site 2. Conservatively assuming all remineralized P is converted to authigenic P and retained in the sediments, the higher C/P_{tot} ratios of Site 1 relative to Site 2 still support the observation of preferential remineralization of P relative to C.

Explanations of the sensitivity of P burial and preservation in sediments to bottom water oxygen concentration have centered on the cycling of P associated with reducible iron oxide phases and storage and release of P by bacteria. P release associated with the reduction of ferric oxyhyroxide particles is a widely observed phenomenon. This process is favored at sites with low bottom water oxygen concentrations. The importance of the ferric oxyhydroxide reduction mechanism relative to other potential mechanisms of P release is unclear. McManus and others (1997) showed that the cycling of P associated with ferric oxyhydroxides is a complex function of bottom water oxygen concentration, sediment organic C concentration and the depth to which oxygen penetrates a sediment. In the Santa Monica basin where oxygen concentrations are low, ferric oxyhydroxide reduction accounts for a maximum of 30 percent of the observed benthic P flux in this very low oxygen basin (Ingall and Jahnke, 1997). In the absence of a competing process such as iron sulfide formation, the reduction of ferric oxyhydroxides should result in a Fe(II) flux out of the sediment. At Site 1 the flux of dissolved Fe(II) is clearly from overlying waters into the sediment (fig. 6, table 2). The absence of a sediment to water dissolved Fe(II) flux at Site 1 most likely results from the precipitation of all dissolved Fe(II) liberated during ferric oxyhydroxide reduction as sulfide minerals. This is consistent with the results of Hurtgen and others (1999), who showed that precipitation of iron sulfides at Effingham Site 1 is limited by iron availability.

The benthic P flux resulting solely from the release of P from ferric oxyhydroxide particles can be estimated. Total reactive iron concentrations at the sediment-water interface are 1.51 and 2.35 weight percent at Sites 1 and 2, respectively (Hurtgen and others, 1999). Total reactive iron is a measure of total sulfidizable iron in the sediment. Assuming the iron in these sulfides ultimately originates from ferric oxyhydroxide reduction and dissolution, the difference in total reactive iron contents at the sediment-water interface at the two sites represents the total amount of iron liberated during reduction and then sequestered as sulfides at Site 1. Using the difference in total reactive iron concentrations between the sites of 0.84 weight percent and an average sedimentation rate of 32.5 mg/cm^2/y for Site 1, a reducible iron production of 0.05 mol/m^2/y is estimated for the sediment. Although poorly constrained, an average ratio of iron to P in reducible ferric oxyhydroxide particles of 10.8 has been previously reported (Ingall and Jahnke, 1997). Using this value, the benthic P flux due solely to the release of P associated with the reduction ferric oxyhydroxides would be 4.6×10^{-3} mol/m^2/y, which represents only 0.7 percent of the total P flux for Site 1. Using the much lower ratio of iron to P in reducible phases of 1.25 reported by Hyacinthe and Van Cappellen (2005) in the above calculations results in a benthic P flux of 4.0×10^{-2} mol/m^2/y. This benthic P flux would represent only 6 percent of the total P flux for Site 1. These calculations strongly suggest there must be other redox sensitive mechanisms that result in the preferential regeneration of P relative to C.

One alternative mechanism for redox sensitive P cycling is the storage and release of P by certain bacterial and protozoan genera (See Ingall and Jahnke, 1997, and references therein). The underlying mechanism for this process is the ability of some microorganisms to store and accumulate P as intracellular polyphosphate granules as the end result of oxidative phosphorylation. This phenomenon occurs under aerobic conditions when excess dissolved P is available. If these microorganisms are then exposed to an anoxic environment, the stored P is utilized as an energy source and is eventually released in dissolved form to the surrounding waters. The potential for redox sensitive cycling of polyphosphates in Effingham Inlet sediments is supported by recent ^{31}P nuclear magnetic resonance studies (Ingall and Sannigrahi, 2005). These studies showed that polyphosphates were found only in the surface sediments of site 2. In Effingham Inlet, high phosphate concentrations coupled with the availability of oxygen at the water column redox transition zone would provide an ideal environment for polyphosphate accumulation by microorganisms. Presence of polyphosphates in sediments from the oxic site 2 suggests that polyphosphate accumulating microorganisms are transported and sedimented from the redox transition zone. Rapid and complete utilization of the sedimented polyphosphates at the site 1 anoxic sediment-water interface may explain their absence at this site. Complete utilization at the sediment-water interface would be consistent with extremely high sulfate reduction rates indicating high levels of microbial activity in this region. At site 2, oxic conditions at the sediment water interface are not conducive for the utilization of polyphosphates. However, anoxic sediment conditions below a few cm at site would likely induce the utilization and subsequent disappearance of polyphosphates at depth.

SUMMARY

This study provides evidence for the enhanced regeneration of P relative to C and N during diagenesis in marine sediments deposited from anaerobic bottom waters. Although the exact mechanisms behind enhanced P fluxes under anaerobic conditions are not well understood, simple calculations show that cycling of P associated with reducible iron oxides is insufficient to account for the observed benthic P fluxes. The differences in P diagenesis and benthic fluxes under aerobic and anaerobic conditions are ultimately reflected in sedimentary organic C to organic P and the organic C to total P ratios preserved in the sediments. Given the relative rarity of sites with anoxic bottom waters in the modern ocean, this study also provides fundamental background information on an excellent site for further studies of diagenetic processes in sediments overlain by anoxic bottom waters.

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