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A biogeochemical survey of the anoxic basin Golfo Dulce, Costa Rica

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Abstract: The waters and surface sediments of a 200 m deep tropical fjord were investigated with respect to chemical zonation, rates of respiratory processes, and benthic fluxes. Oxygen was found to *ca.* 100 m water depth, but only the upper part of the oxycline was associated with the pycnocline, which was situated above the sill located at 60 m. Nitrate-rich water entered the bay at sill depth, and denitrification was indicated at anoxic depths. Hydrogen sulfide was only found in low concentrations near the bottom, and nitrate was a possible oxidant for the hydrogen sulfide. The observations reproduced those of a survey in 1969 to a large extent. This suggests that water exchange is frequent enough to prevent the development of strongly reducing conditions in the bottom water. High rates of dark oxygen uptake indicated intense carbon cycling within the euphotic zone. The rates decreased rapidly with depth, and at anoxic depths, rates of denitrification and sulfate reduction were more than 100-fold lower than the surface oxygen uptake. The chemical zonation as well as x-radiographs indicated that sediments underlying oxic bottom water were strongly irrigated and bioturbated while anoxic sediments were laminated and composed of turbidites. The rates of carbon oxidation were 5 - 10 times higher in the sediments underlying oxic bottom water than in those at the bottom of the basin. Sulfate reduction was a dominating process, accounting for about 50% and 100% of the carbon oxidation at the oxic and anoxic sites respectively. Even at the anoxic sites, hydrogen sulfide did not accumulate in the pore water and a high sedimentation of reactive iron phases is suggested as a contributing cause.

Key words: Water column, sediment, microbial processes, carbon cycling, denitrification, sulfate reduction.

The supply of oxygen to the oceanic water masses is generally large enough to prevent degradative processes from causing the development of anoxia, but permanently anoxic waters are found in a number of basins with restricted circulation. The vertical chemical zonation of anoxic water columns provides a basis for general studies of chemical and microbiological processes under different redox conditions, and at redox boundaries such as the oxic/anoxic interface. Both the temporal stability of the zonation, and its extension over depth scales of decimetres or metres, facilitates such investigations in comparison to studies of the analogous redox zonation in sediments, that is restricted to millimetres or centimetres. Many biogeochemical studies have been carried out in anoxic basins at temperate latitudes such as the Black Sea, Framvaren Fjord, Norway, and Saanich Inlet, British Columbia (e.g. Richards 1965, Skei 1988, Murray *et al.* 1989).

In the absence of oxygen, the bacterial degradation of organic matter reduces the alternative oxidants nitrate, oxides of manganese and iron, and sulfate, releasing dissolved inorganic carbon, nutrients, and inorganic metabolites according to the general reaction (*e.g.* Froehlich *et al.* 1979):

$$\text{Organic matter} + NO_3^- / MnO_2 / FeOOH / SO_4^{2-} \rightarrow$$
$$CO_2 + NH_4^+ + PO_4^{3-} + N_2 / Mn^{2+} / Fe^{2+} / H_2S.$$

In most anoxic basins, NO_3^- and suspended Mn and Fe oxides are depleted close to the

oxic/anoxic interface due to low inputs, and sulfate reduction dominates in the anoxic bottom water leading to the build-up of hydrogen sulfide (e.g., Lewis and Landing 1991). A main characteristic of anoxic basins is, thus, the O_2/H_2S interface (Anderson and Devol 1987).

Golfo Dulce is one of only five anoxic basins described from the tropics. The others are the Cariaco Trench and Golfo de Cariaco, Venezuela, Kau Bay, Indonesia, and Darwin Bay, Galapagos Islands (Richards 1960, Richards and Broenkow 1971, Middelburg *et al.* 1988). The hydrography of Golfo Dulce was first described by Richards *et al.* (1971) based on two visits in March 1969. At that time, a pycnocline was centred well above the sill-depth of *ca.* 60 m and O_2 was found to about 150 m in the 200 m deep basin. The bottom water was sulfidic but the H_2S concentration only reached a few μmol L^{-1}. Based on a rise in the pycnocline, and changes in water column chemistry in the bay between the two visits, Richards and coworkers (1971) suggested that the basin was maintained at a relatively oxidized state through frequent flushing associated with upwelling events along the Pacific coast (see also Anderson and Devol 1987).

A brief description of the sediments has been given by Nichols-Driscoll (1976) who studied the faunal distribution in relation to bottom water O_2 concentrations. She found an organic carbon content of about 2% throughout the basin and observed large leaves and coconuts on the sediment surface of the inner basin. Infauna was found to 100 m depth which corresponded to approx. 40 μmol L^{-1} O_2 in the bottom water.

We here summarize the results of the biogeochemical investigations carried out during the second leg of the Costa Rica Expedition of RV Victor Hensen, January 1994. In view of the limited information published on the basin, the study was designed as a general biogeochemical survey. We focused on the degradative part of the carbon cycle, identifying and quantifying pathways of carbon mineralization in relation to the chemical zonation of the water column and sediments. In a parallel study, microbiological and molecular ecological analyses of the bacterial community were performed which are presented in a separate paper (Kuever *et al.* 1996). The investigations included:

- a description of the physical and chemical zonation of the water column through the bay
- direct determination of aerobic and anaerobic planktonic respiration rates
- analysis of the chemical zonation in the sediment pore waters and solids along a transect from oxic to anoxic bottom water
- quantification of rates of carbon mineralization in the sediments and of the rates of solute exchange between sediments and water column.

MATERIAL AND METHODS

Stations: Sampling took place 6 - 12 January 1994 at the positions given in Table 1. The hydrographical survey was carried out along the central axis of the bay with CTD casts at all stations and water-column chemistry at stations GD1, 2, 3, 89, 11, and 12 (Fig. 1; stations of Nichols-Driscoll 1976). Rates of respiration were measured in the water column at station GD1. Sediments were studied along a transect perpendicular to the coast of from GD30 to GD1.

TABLE 1

Stations occupied during the cruise

Station	Position	Depth (m)
GD1	8°41,7'N 83°23,7'W	205
GD1a	8°40,0'N 83°21,9'W	207
GD2	8°36,6'N 83°18,0'W	208
GD2a	8°36,6'N 83°18,0'W	200
GD3	8°34,9'N 83°15,9'W	194
GD3a	8°33,2'N 83°14,0'W	192
GD89	8°31,5'N 83°13,0'W	101
GD11	8°27,2'N 83°13,0'W	75
GD11a	8°23,8'N 83°13,3'W	75
GD12	8°20,5'N 83°13,8'W	205
GD30	8°38,9'N 83°25,6'W	42
GD9	8°39,0'N 83°25,5'W	53
GD160	8°39,9'N 83°25,1'W	163

Water column: Salinity and temperature were measured with a CTD (ME-Meerestechnik-Elektronik, Kiel, Germany). Light was measured at 10 m intervals from the surface with a spherical quantum sensor (Licor, Lincoln, Nebraska). Water samples were obtained in 5 l Go-Flo and Niskin bottles and expressed anoxically by applying a slight N_2 overpressure. For O_2 determinations, water was subsampled in Winkler-bottles under a N_2 atmosphere and analyzed by the Winkler method using reagents degassed with N_2. For samples from the deep, expectedly anoxic and sulfidic zone, the method of Ingvorsen and Jørgensen (1979) was used.

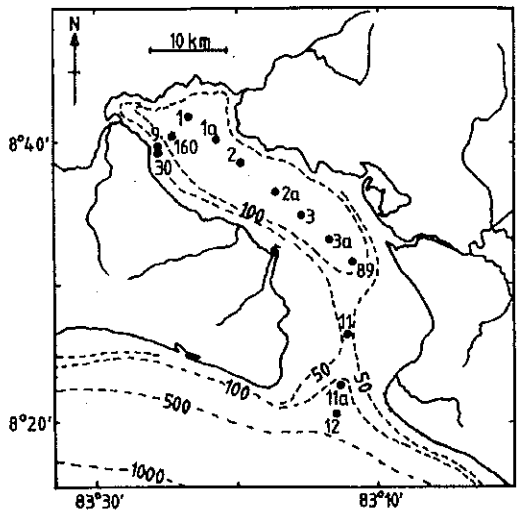

Fig. 1. Locations of sampling sites in Golfo Dulce.

Samples for NO_3^- + NO_2^- and NH_4^+ were stored frozen and analyzed with an autoanalyzer (APHA 1992). As NO_2^- concentrations were expected to be negligible compared to NO_3^-, the NO_3^- + NO_2^- measurements will be referred to as NO_3^- (see also Córdoba and Vargas 1996). Samples for H_2S were preserved with Zn^{2+} and analyzed with the methylene blue technique (Cline 1969). For analysis of dissolved and particulate Mn and Fe, water was filtered through N_2- flushed glassfiber filters (Whatman GF/F) and the filtrate was immediately acidified. Particulate Mn and Fe on the filters was extracted by dithionite-citrate-acetic acid extraction (Lord 1980). Manganese in filtrates and extracts was analyzed by flame atomic absorption spectroscopy (Perkin Elmer, Norwalk, Connecticut), and Fe was analyzed spectrophotometrically with Ferrozine (Stookey 1970). Phosphate was analyzed in the filtered, acidified samples by the phosphomolybdate blue method (APHA 1992).

Oxygen consumption was measured on water collected at 20 m intervals from the surface by incubation in Winkler bottles in the dark at *in situ* temperature. Incubation time was 12 h at 1 and 20 m and otherwise 24 or 36 h. Denitrification was measured in similar incubations of samples taken at 20 m intervals from 60 m depth. Quantification was by the isotope pairing technique with addition of $^{15}NO_3^-$ and mass spectrometric analysis of the N_2 produced (Nielsen 1992). The detection limit was estimated from the standard deviation of the mass spectrometric analyses of blanks. Likewise, SO_4^{2-} reduction was measured by addition of $^{35}SO_4^{2-}$ to the water samples from 200 and 205 m depth with 6 h incubation (Jørgensen 1978, Jørgensen *et al.* 1991). The production of reduced ^{35}S was quantified with the acidic Cr^{2+} distillation method (Fossing and Jørgensen 1989) and SO_4^{2-} was determined by non-suppressed anion chromatography (Fossing and Jørgensen 1990). The detection limit for SO_4^{2-} reduction was estimated from the background of the scintillation counting procedure.

Sediments: Sediments were obtained with a 50 x 50 cm box corer using only those deployments where the sediment surface appeared undisturbed. The box cores were subcored into acrylic tubes. For flux determinations and O_2 microelectrode measurements, cores were incubated with bottom water at *in situ* temperature and O_2 concentration, as described by Rasmussen and Jørgensen (1992). Fluxes were determined from concentration changes in the overlying water during incubations of 4 - 6 h at GD30 and GD9, and 28 h at GD1. The same setup was used for determination of denitrification rates, that were quantified by the isotope pairing technique (Nielsen 1992). Fine-scale profiles of pore-water NO_3^- were obtained by whole-core squeezing (Bender *et al.* 1987) with quantification by reduction to NO_2^- with spongy cadmium and spectrophotometric detection (Jones 1984).

Rates of $\sum CO_2$ and NH_4^+ production as well as SO_4^{2-} reduction were determined as described by Canfield *et al.* (1993a). In brief, sediment was sectioned in discrete depth intervals and incubated anoxically at *in situ* temperature in gas tight plastic bags. The sediment was sampled under N_2 five times during an incubation of approx. 30 h, and pore water for $\sum CO_2$, NH_4^+, Mn^{2+}, Fe^{2+}, H_2S, and SO_4^{2-} analysis was obtained by centrifugation. The initial T_0 sample from the incubations provided our initial pore water and solid phase data. Rates of SO_4^{2-} reduction were determined in subsamples twice during the incubations using $^{35}SO_4^{2-}$ with quantification as in the water-column samples.

Additional pore-water distributions of $\sum CO_2$ and NH_4^+ to 30 cm depth were obtained by sectioning and centrifugation of a separate core. Rates of SO_4^{2-} reduction were also deter-

mined in intact sediment cores by the whole-core $^{35}SO_4^{2-}$ injection method (Jørgensen 1978).

In the pore waters, ΣCO_2 and NH_4^+ were determined by flow injection analysis with gas exchange and conductivity detection (Hall and Aller 1992), with rates of accumulation during the bag incubations determined by linear regression. Organic C and total N in the sediments were determined on an elemental analyzer (Carlo Erba). Particulate Mn oxides were extracted as described for the water column and, additionally, poorly crystalline Fe(III) and easily extractable Fe(II) were extracted with an oxalate extraction assay (Canfield *et al.* 1993a). Pore water SO_4^{2-}, H_2S, Mn^{2+}, Fe^{2+}, and Mn and Fe in extracts were analyzed as in the water column. X-radiographs were obtained of sediment sampled in 3.5 x 30 cm acrylic boxes, 20 cm high using 2 min exposure at 80 kV and 2 mA.

RESULTS

Hydrography: The hydrographical survey along the central axis of the bay revealed steep gradients in both temperature and salinity below a shallow mixed surface layer, to about 60 m depth (Fig. 2). At station GD12 outside the bay, the pycnocline was centered at 40 - 50 m, roughly 10 - 20 m above the sill depth of 60 m, and the isopycnic surfaces were tilted slightly, rising about 10 m through the bay from GD12 to station GD1 at the head. Below the pycnocline at GD12, the potential density anomaly, σ_t, increased from 25.33 at 80 m to 26.52 at 200 m, whereas it only increased to 25.88 inside the basin. Thus, from 80 m, the water outside the bay was denser than the basin water at the same depth. The bottom water in the basin was only about 0.05‰ less saline and 1 °C warmer than in March 1969 (Richards *et al.* 1971).

The photic zone extended to 30 - 40 m depth, determined as the depth where the incoming light was attenuated to 1% of the surface value at both GD1 and GD3. Surface O_2 concentrations were 190 - 200 µmol L^{-1} (9 -11 AM) and a strong oxycline was associated with the pycnocline at all stations (Fig. 2). Outside the bay, the O_2 concentration dropped to 25 µmol L^{-1} at 200 m, but inside, O_2 was not detectable (< 3 µmol L^{-1}) below 100 m depth. Parallel to the decrease in O_2, NO_3^- increased at GD12 reaching 30 µmol L^{-1} at 200 m (Fig. 2). In the Golfo Dulce basin (GD1 - 3), however, NO_3^- increased with depth from the deple-

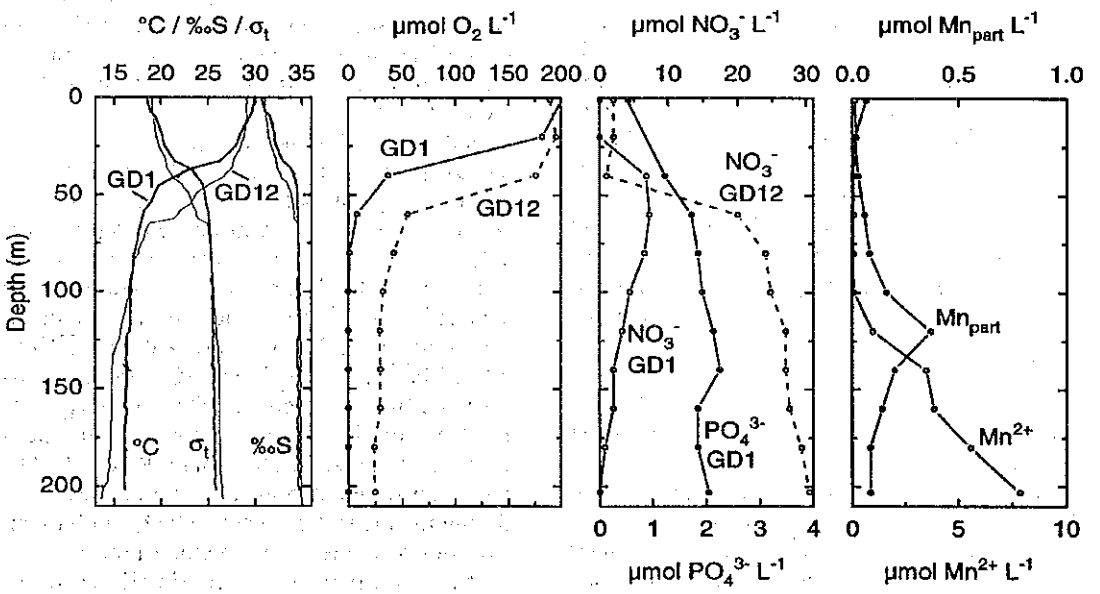

Fig. 2. Physical and chemical data from the water column at the head (GD1, 7 January 1994) and mouth (GD12, 9 January 1994) of Golfo Dulce. Far left: CTD data, fat lines GD1, thin lines GD12. Center left: Oxygen concentrations at GD1 and GD12; Center right: Nitrate+nitrite concentrations at GD1 and GD12, and soluble reactive P at GD1 (note separate scale). Far right: Dissolved and particulate Mn at GD1 (note separate scales).

ted surface water but reached a maximum of only 10 µmol L^{-1} at the bottom of the pycnocline, and below this the concentration decreased to less than 1 µmol L^{-1} at the basin floor. Ammonia was generally < 1 µmol L^{-1} except for a small peak of 2 µmol L^{-1} observed at 40 or 60 m depth at GD1 - 3 and single sporadic higher values in the bottom water (data not shown). Phosphate was determined at GD1 - 3 and increased through the pycnocline from ≤ 0.5 µmol L^{-1} at the surface to about 2 µmol L^{-1} in the bottom water (Fig. 2).

An active Mn redox cycle in the bottom waters of the basin was indicated by an increase in dissolved reduced Mn from 100 m depth to the sediment surface, and by a peak in particulate Mn, assumed to be Mn oxides, situated at 120 m. Dissolved Fe^{2+} was not detectable (< 0.5 µmol L^{-1}) and H_2S was never detected (< 0.5 µmol L^{-1}) above 180 m. On 6 January, H_2S concentrations of 1, 5, and 7 µmol L^{-1} were measured at 180, 200, and 203 m depth at GD1, respectively, whereas a barely detectable 0.7 µmol L^{-1} maximum was measured at 203 m at the same site on 12 January.

Water-column respiration rates: The surface water at GD1 showed a very high O_2 consumption in the dark of 64 µmol L^{-1} d^{-1} but it decreased rapidly to 11 µmol L^{-1} d^{-1} at 20 m and < 3 µmol L^{-1} d^{-1} at 40 m. Interpolation of these measurements yield an estimate of the depth-integrated rate of 0.7 mole m^{-2} d^{-1}. Denitrification was not detected at any depth, and likewise sulfate reduction was undetectable in the bottom water. The detection limits for these processes are estimated to 0.08 and 0.01 µmol L^{-1} d^{-1}, respectively. For denitrification, this limits the depth-integrated rate between 60 and 205 m depth to < 11 mmol N m^{-2} d^{-1}, i.e. much less than the oxic respiration.

Sediments, physical characteristics: Sediments were investigated near the head of the bay along a SW - NE transect from the Osa peninsula. Close to the shore, the sediment contained much coarse sand, pebbles, and shell and coral debris, and the station GD30 at 42 m was chosen as the shallowest site with a fine-grained texture suitable for our incubation techniques. The sediment there was silty with some sand and gravel-sized particles, and the bottom water contained 54 µmol O_2 L^{-1}. Live snails were observed at the surface, and burrows evidenced the activity of infauna. The sediment at the slightly deeper GD9, with 22 µmol O_2 L^{-1} in the bottom water, appeared similar to GD30. Burrows were present, but no living organisms were observed. At the anoxic GD160, a 1 - 2 cm thick brown-black fluff-layer covered the very fine-grained sediment. At the surface, 0.5 cm long bacterial filaments of the genus *Beggiatoa* were observed. Immediately below the fluff, the sediment was black, and below this, there was a sequence of horizons varying in color between light brown and black, and in thicknesses of 1 - 5 cm. Around 17 cm depth a prominent pink layer was observed. The sediment at the deepest station GD1 was covered by 2 - 4 cm fluff. Apart from one black band below the fluff layer and another about 15 cm depth, the sediment here was light brown. At all stations, pieces of coconuts, large leaves, and wood could be found both on and within the sediments.

Observations of sediment structure were corroborated by x-radiographs of the sediments (Fig. 3). Whereas the sediments at GD30 and GD9 (not shown) appeared uniformly mixed and contained worm burrows in the upper 5 cm, the differently colored horizons observed at GD160 were paralleled by changes in sediment density revealed by the x-radiographs. Below the fluff at GD1, a 12 cm thick layer was observed, with only slight laminations but grading from low to high density from top to bottom. At the base of this, a very dense, approx. 1 cm thick layer followed, abruptly succeeded by a more x-ray-transparent zone similar to that near the sediment surface. This observation is in good agreement with the results from long cores, which showed that the basin floor is comprised of a series of turbidites, each grading from fines at the top to a sand horizon at the bottom (Hebbeln 1994). From the x-radiographs the youngest turbidite is estimated to be about 13 cm thick, not including the surface fluff. It seems probable that the visible black band at 15 cm depth is a relict from the previous surface similar to the black band observed under the fluff layer, and that the thinner graded laminations on the slope station GD160 may represent a sequence of turbidite depositions of which the bulk deposited at the bottom of the basin.

Sediment chemistry: At both GD30 and GD9, the organic carbon content was about 2.4 % by

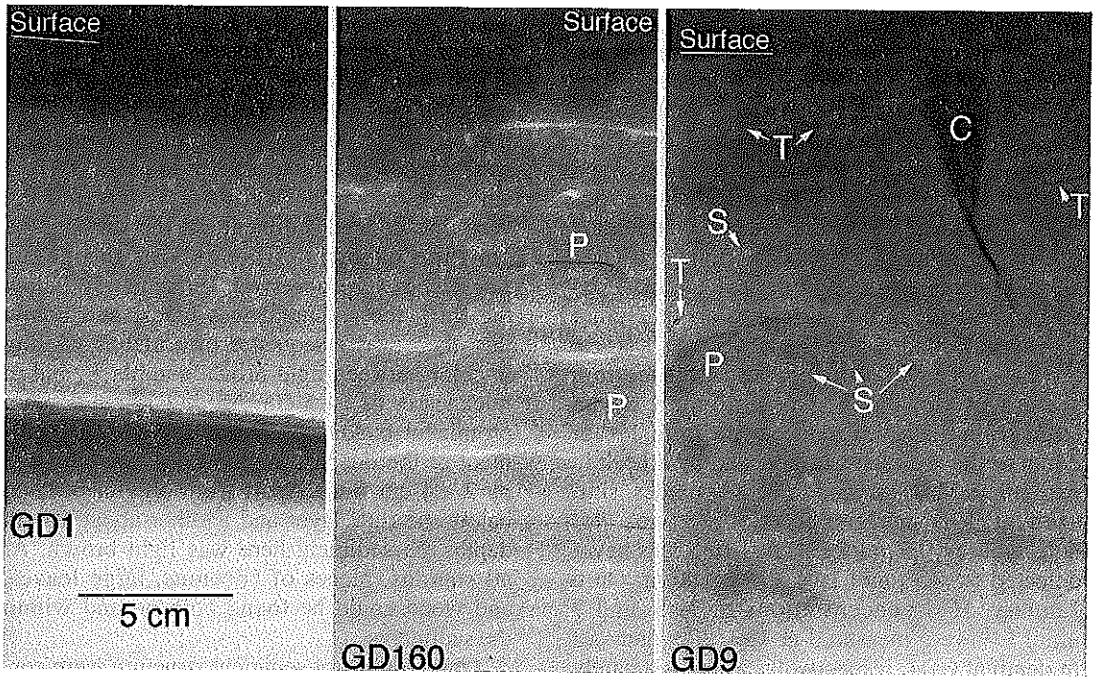

Fig. 3. Representative sections of sediment x-radiographs. Darker areas represent higher x-ray transparency, i.e. zones of higher porosity. P: plant debris (tentative identification); C: crack in the sediment surface created during coring; T: worm burrows; S: shell debris. The contrast of the images has been digitally enhanced after recording.

weight and varied little with depth to 15 cm, whereas at GD1, C_{org} decreased from 2.8% in the fluff layer to 1.9% below (Fig. 4). Due to the strong decrease in porosity from the fluff layer to the sediment below at GD1, however, the volume-based C_{org} content actually increased with depth from 0.35 to 0.65 mmol cm^{-3} between 0 - 0.5 and 8 - 10 cm. Similarly, the total C_{org} pool from 0 - 10 cm depth was 55, 128, and 124 mol m^{-2} at GD1, -9, and -30, respectively. The lowest C_{org}/N ratio (mole/mole) was observed at GD1, where it increased from 9.2 at the surface to 13.0 at 8 - 10 cm (Fig. 4). At both GD9 and GD30 the N content decreased markedly with depth leading to increases in C_{org}/N from 11-13 near the sediment surface to 15-18 at 8 -10 cm depth.

The mineralization of organic matter in the sediments led to a build-up of ΣCO_2 (= H_2CO_3 + HCO_3^- + CO_3^{2-}) and NH_4^+ in the pore waters (Fig. 5). Whereas the concentration profiles at GD1 were convex up reaching high values already near the sediment surface, the distributions at both GD9 and GD30 were concave up with steeper gradients below 10 cm. Also with respect to other aspects of pore-water and solid-phase chemistry stations GD30 and GD9 were quite similar, and hence, only results from GD30 are shown below.

To examine which electron acceptors were available for the oxidation of organic matter, the distribution of the possible oxidants, O_2, NO_3^-, Mn and Fe oxides, and SO_4^{2-} was determined. Microelectrode measurements showed that O_2 was only available in the upper 1 - 2 mm at both GD30 (Fig. 6) and GD9, and the whole-core squeezing indicated that NO_3^- was only present to 5 mm depth or less in the sediment pore water (data not shown). Chemical extractions revealed an enrichment of reactive manganese oxides in the upper 5 mm at these stations (Fig. 6; ct. Aller 1994). At GD1, Mn levels were high and stable with depth (approx. 10 µmol g^{-1}) and most likely represented an unreactive Mn phase as no surface maximum could be discerned. In agreement with these observations, Mn reduction in the upper 1 - 2 cm was indicated by Mn^{2+} maxima at 0 - 0.5 cm depth in the pore waters of GD30 (Fig. 6) and GD9. Conversely, at GD1 pore water Mn^{2+} was stable around 30 µmol L^{-1}, which, together with the bottom water level of 8 µmol

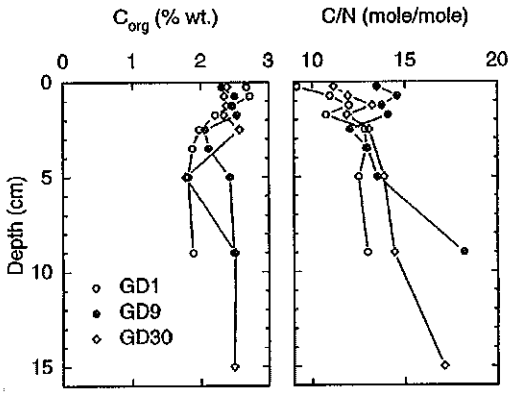

Fig. 4. Organic carbon content and C_{org}/N ratios in the sediments.

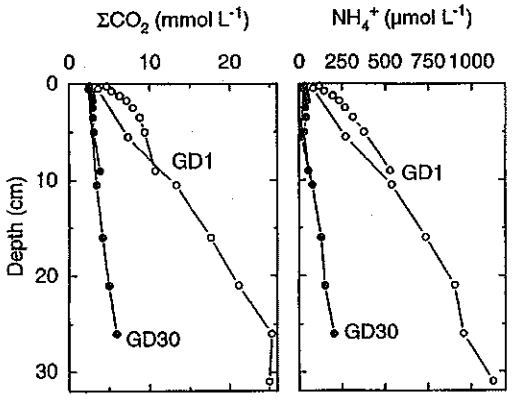

Fig. 5. Total inorganic C (ΣCO_2) and NH_4^+ in the pore water at stations GD1 and GD30. Data from both bag incubations (0 - 10 cm) and separately sectioned longer cores (0 - 30 cm).

L^{-1} (Fig. 2), indicated that Mn reduction was restricted to the surface of the fluff layer at this site.

As was the case for Mn oxides, the sediments at GD30 (Fig. 6) and GD9 showed a strong enrichment of poorly crystalline Fe(III) oxides near the surface and Fe reduction was indicated by maxima of dissolved Fe^{2+} at 1 - 1.5 cm depth. Most Fe(II) produced by Fe reduction was, however, extracted from the solid fraction and its distribution mirrored that of Fe(III) (Fig. 6). The concentration of Fe(III) was almost 100 times higher than that of Mn oxides, and significant levels of Fe(III) persisted deeper in the sediments. No enrichment was observed at GD1, but a small maximum of dissolved Fe^{2+} below the fluff layer indicated some Fe reduction (data not shown). The porewater concentration of SO_4^{2-} decreased with depth from the bottom water level of 28 mmol L^{-1}, reaching 26.0, 24.2, and 8.8 mmol L^{-1} at 30 cm depth at GD30, -9, and -1, respectively. Hydrogen sulfide was only detected in the pore water at GD1, where a small peak of < 10 µmol L^{-1} was observed in the fluff layer (data not shown).

Benthic fluxes and mineralization rates: The benthic fluxes of ΣCO_2, NH_4^+, O_2, and NO_3^- measured in our whole-core sediment incubations are given in Table 2. The fluxes of ΣCO_2 from the shallow oxic sediments were similar, and 10 times larger than that from the anoxic GD1. The NH_4^+ fluxes were small compared to ΣCO_2 with C/N mole/mole ratios of 22 and 49 at GD30 and GD9, respectively. The O_2 uptake was similar at GD30 and GD9 averaging about 50% of the ΣCO_2 efflux, whereas the NO_3^- uptakes were quite small.

The rates of ΣCO_2 accumulation in the upper 10 cm of the sediment determined by incubation of sediment after sectioning into discrete depth intervals were about twice the ΣCO_2 fluxes from the sediments, but showed a similar decrease from the oxic stations to GD1 as did the benthic fluxes (Table 2). The depth integrated rates of NH_4^+ accumulation in the pore water were much higher than the NH_4^+ fluxes, and the ratio with which ΣCO_2 and NH_4^+ accumulated in the incubations was close to 10 at all stations and hence similar to the C_{org}/N ratio of the sediments (Fig. 4). Ammonia adsorbs onto sediment particles (Rosenfeld 1979), however, and the measured rates of NH_4^+ accumulation, thus, underestimate the actual rates of NH_4^+ production from the decomposition of organic matter. Assuming that the adsorption coefficient for NH_4^+ in Golfo Dulce sediments was in the range reported from other marine sediments (Mackin and Aller 1984) the rates of NH_4^+ production were roughly twice the measured accumulation rates, and the production ratio of ΣCO_2 to $NH_4^+$was accordingly about 5 (assuming no precipitation of ΣCO_2; see also Canfield *et al.* 1993a). Similar values have been reported for mineralization of young organic matter in other coastal marine sediments (e.g., 4 - 6, Kristensen and Blackburn 1987).

Bacterial sulfate reduction was an important pathway of carbon mineralization at all sta-

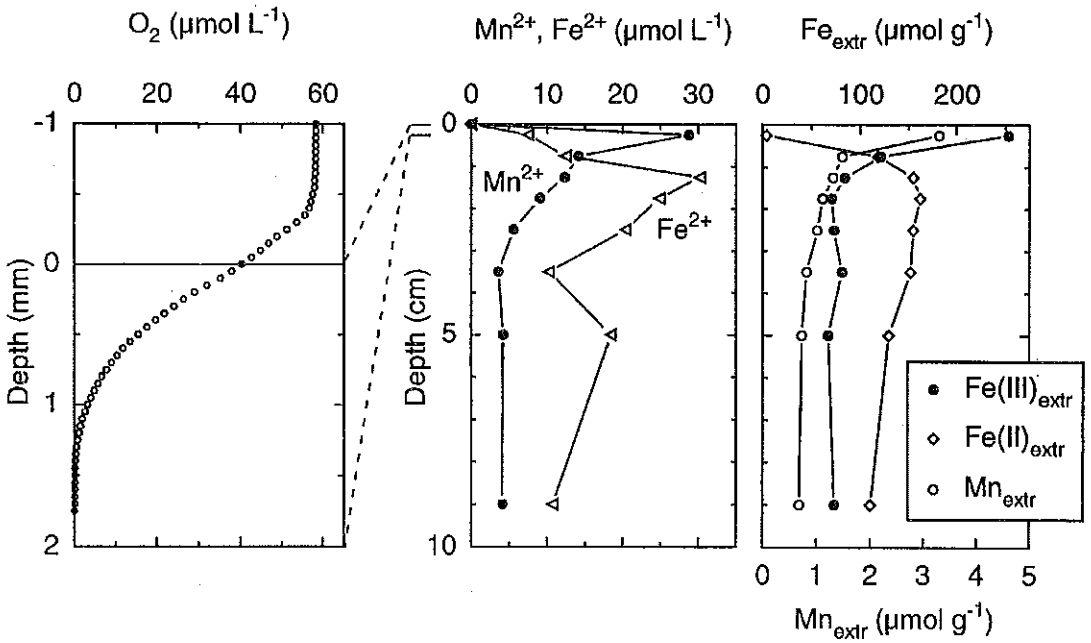

Fig. 6. Pore-water and solid-phase analyses from Station GD30. Left: Typical O_2 microprofile. Middle: Pore-water Mn^{2+} and Fe^{2+}. Right: Extractable, poorly crystalline Fe(III), extractable Fe(II), and extractable Mn (note separate scales).

TABLE 2

Fluxes over the sediment water interface (positive up) and rates intergrated over 0 - 10 cm depth in the sediment (mmol m^{-2} d^{-1})

	GD30	GD9	GD160	GD1
Benthic fluxes)*				
ΣCO_2	21.6 ± 0.2	18 ± 9	n.m.	1.9 ± 0.4
NH_4^+	0.82 ± 0.02	0.44 ± 0.02	n.m.	n.m.
O_2	-13.8 ± 2.5	-7.9 ± 2.4	n.m.	0.0
NO_3^-	- 0.12 ± 0.03	-0.60 ± 0.05	n.m.	0.0
Rates 0 - 10 cm				
ΣCO_2 accumulation	30	38	n.m.	4.8
NH_4^+ accumulation	3.1	3.4	n.m.	0.48
SO_4^{2-} reduction, bag incubations	7.0	10	n.m.	4.8
SO_4^{2-} reduction, whole cores	n.m.	4.8	2.4	6.0
ΣCO_2 production from				
SO_4^{2-} red., bag incub.	14.0	20	n.m.	9.6
Denitrification	0.28 ± 0.02	0.43 ± 0.07	n.m.	0.0

*) Mean ± SE of 2 - 6 determinations
n.m.: Not measured

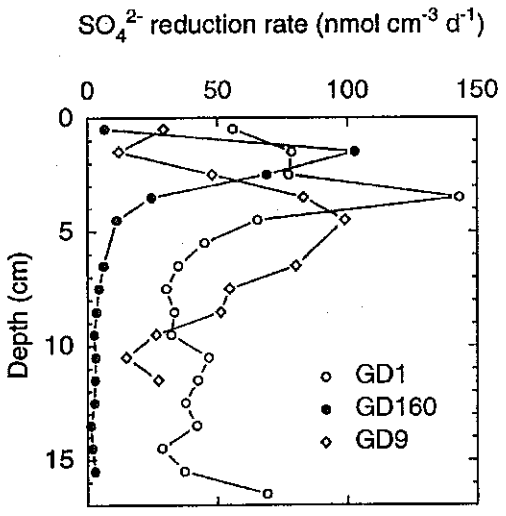

Fig. 7. Rates of SO_4^{2-} reduction at stations GD1, GD160, and GD30, as determined in intact cores of sediment.

tions. Similar rates were measured in the sediment incubations used for determination of ΣCO_2 and NH_4^+ accumulation rates, and in whole sediment cores injected with the $^{35}SO_4^{2-}$ radiotracer (Table 2, Fig. 7). The contribution of SO_4^{2-} reduction to ΣCO_2 production can be calculated by multiplying SO_4^{2-} reduction rates by 2 according to the overall stoichiometry (Richards 1965):

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 53SO_4^{2-} = 106HCO_3^- + 16NH_4^+ + HPO_4^{2-} + 53HS^- + 39H^+. \quad (1)$$

At GD1, the calculated ΣCO_2 production was twice the measured accumulation, and all C oxidation could, thus, be attributed to SO_4^{2-} reduction. The discrepancy between the ΣCO_2 accumulation rate and the calculated ΣCO_2 production at GD1 was most likely explained by difficulties in quantifying small changes in ΣCO_2 during the incubations with very high initial concentrations (Fig. 5). At GD30 and -9, SO_4^{2-} reduction accounted for about 50% of the ΣCO_2 production (Table 2). Direct measurements of denitrification showed that this process contributed little to C oxidation at all stations (Table 2). At GD9 and -30, approximately half of the NO_3^- consumed by denitrification came from the water column while the other half was produced by nitrification in the sediment (data not shown).

DISCUSSION

The hydrographic survey of Golfo Dulce reproduced the observations from the first survey by Richards and coworkers (1971) to a large extent. The centering of the pycnocline above the sill depth and the weak stratification of the waters below facilitates the exchange of water between the basin and the Pacific Ocean. The poor stratification of the sub-sill waters is similar to the other known tropical anoxic basins (Richards 1960, Richards and Broenkow 1971, Middelburg *et al.* 1988). Water of the same potential density as the densest water in the basin was found at 110 - 120 m depth outside the sill (Fig. 2). This situation is similar to the first of the two transects sampled by Richards *et al.* (1971) in March 1969. In a second transect one week later, they observed a 35 m rise in the pycnocline outside the bay (at GD12) lifting water of similar density as the bottom water to a depth of only 70 - 80 m, i.e. close to the sill depth. Simultaneously, they measured chemical changes in the basin to 160 m depth, which were attributed to the introduction of new O_2 -poor, NO_3^- -rich water over the sill. Seasonal upwelling was suggested as a driving force in the flushing of Golfo Dulce which maintains it in an intermediate stage between oxic and strongly sulfidic conditions.

Although 26 years had passed since the visit of Richards and coworkers (1971), the water column chemistry showed only minor differences from those reported then. Whether this reflects true stability, implying a steady rate of exchange over the sill, or the similarity was coincidental, can only be determined through a seasonal study.

Richards and coworkers (1971) found that NO_3^- disappeared at the same depth as, or even slightly above O_2 (around 150 m) and inferred that denitrification took place under oxic conditions. In the present study, the depths at which the two oxidants were depleted were clearly separated with anoxia already from 100 m depth and NO_3^- reaching close to the bottom (Fig. 2). Hence, in the present survey, part of the denitrification occurred under anoxic conditions, either in the water column or in the contacting sediments. Still, the decrease in NO_3^- concentration in the oxic zone below the pycnocline from the mouth to the head of the bay could be due to denitrification at low O_2 levels

(Fig. 2). The depletion of NO_3^- over the anoxic zone at GD1 could be explained by oxidation of typical organic matter by denitrification according to the equation (Richards 1965):

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 84.8NO_3^- = 106HCO_3^- + 16NH_4^+ + HPO_4^{2-} + 42.4N_2 + 7.2H^+ + 42.4H_2O. \quad (2)$$

With a decrease in NO_3^- of 5 µmol L^{-1}, the predicted increases in PO_4^{3-} (0.06 µmol L^{-1}) and NH_4^+ (0.9 µmol L^{-1}) would not be detectable.

Manganese had not previously been measured in Golfo Dulce, and we found a significant accumulation of dissolved Mn^{2+} in the anoxic portion of the water column (Fig. 2). Reduced Mn^{2+} is formed by reduction of Mn oxides either in abiotic reactions with, e.g., H_2S or Fe^{2+}, or by dissimilatory bacterial reduction coupled to oxidation of organic matter (Canfield *et al.* 1993a, Aller 1994). The reduction of Mn could occur as Mn oxide particles sink through the water column, but the Mn^{2+} distribution could also be due to a flux from the sediment as predicted by the pore-water distribution of Mn^{2+}. Dissimilatory Mn reduction is associated with a release of ΣCO_2 and inorganic nutrients:

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 212MnO_2 + 332H^+ = 106HCO_3^- + 16NH_4^+ + HPO_4^{2-} + 212Mn^{2+} + 212H_2O. \quad (3)$$

The accumulation of 8 µmol L^{-1} Mn^{2+} at the bottom of the basin is thus equivalent to a slightly smaller carbon mineralization, and associated release of NH^{4+} (8/212*16 = 0.6 µmol L^{-1}) and PO_4^{3-} to the water column, than that calculated for denitrification.

The depth distribution of Mn^{2+} suggested that it was oxidized by O_2 and this was supported by a peak of particulate Mn oxides just below the oxic/anoxic interface. In agreement with the findings of Froehlich *et al.* (1979) in hemipelagic sediments, there were no indications of Mn^{2+} oxidation by NO_3^-. The Mn oxidation was most likely bacterially catalyzed as this is generally the case in aquatic environments (cf. Thamdrup *et al.* 1994b). This mode of reaction[1] was also suggested for a similar maximum of suspended Mn oxides found at the oxic/anoxic interface in Kau Bay, Indonesia (Middelburg *et al.* 1988).

Richards and coworkers found low but significant levels of H_2S (> 1 µmol L^{-1}) below 180 m throughout the basin, whereas we only found such concentrations at GD1 and, more significantly, only at one of two dates. The general absence of H_2S as well as the undetectable levels of SO_4^{2-} reduction in the bottom water were in agreement with the deeper penetration of NO_3^- which could both be preferred to SO_4^{2-} as electron acceptor by heterotrophic bacteria, and could serve as an oxidant for any H_2S formed (e.g.; Sørensen 1987). Also the PO_4^{3-} concentrations (Fig. 2) were considerably lower than the 3.8 µmol L^{-1} maximum reported from 1969 which is another indication that the bottom water had not developed as far towards reduced conditions as during the 1969 survey. The drop in H_2S concentration near the sediment over a week may be explained as the dispersion or oxidation of a local H_2S plume which could have developed over a small area with particularly high rates of SO_4^{2-} reduction at the sediment surface. Thus, the maximum bottom-water concentration of 7 µmol L^{-1} was higher than any of the pore water analyses. Conspicuous sulfide-oxidizing bacteria, that might oxidize H_2S with NO_3^- were observed in the bottom water (Kuever *et al.* 1996).

In the traditional description of anoxic marine basins, the existence of a chemocline is assumed where opposed gradients of O_2 and H_2S meet (Anderson and Devol 1987). The existence in Golfo Dulce of a 100 m deep suboxic (i.e. anoxic and H_2S-free; Froehlich *et al.* 1979) zone containing NO_3^- is parallelled only by the small Darwin Bay in the Galapagos Islands where a similar zonation was found in 1969 (Richards and Broenkow 1971). Both bays are situated in upwelling regions and can thus receive water low in O_2 and high in NO_3. Transient separation of O_2 and H_2S zones, possibly due to the injection of an intermediate water mass, has been observed in other anoxic basins such as the Black Sea (Murray *et al.* 1989, Jørgensen *et al.* 1991). Since a suboxic zone was not identified during the first investigations of Golfo Dulce (Richards *et al.* 1971), the stability of this phenomenon still needs to be assessed.

The maximum planktonic O_2 respiration rate of 64 µmol L^{-1} d^{-1} measured at the surface was high compared to rates measured in temperate regions which typically have maxima of 10 - 20 µmol L^{-1} d^{-1} (Williams 1984, Kruse 1993). The high rates near the water surface suggested a high degree of internal cycling of carbon in the warm and calm photic zone. Although denitrification was not detectable, a small contribution from this process was still possible when integrating over the entire water column. Richards and coworkers (1971)attributed a NO_2^- maximum < 1 µmol L^{-1} near the bottom of the oxic zone to active denitrification but we did not separately analyze NO_2^-.

As denitrification and SO_4^{2-} reduction rates were not detectable in the anoxic water column, we can not accurately determine a turnover time for the bottom water. Division of the mean NO_3^- concentration in the anoxic water column (2 µmol L^{-1}; Fig. 2) by the detection limit of the denitrification rate determinations (0.08 µmol L^{-1} d^{-1}) yields a minimum depletion time of 25 days. Thus, disregarding benthic denitrification, the observed NO_3^- levels could be maintained with bottom water exchange on the order of once per month.

Sediments: The organic carbon contents of the sediments showed only small variations between the stations and were similar to those reported earlier from Golfo Dulce (Nichols-Driscoll 1976). The C_{org}/N ratios were relatively high but also similar to the earlier report. The high ratios could be due to the input of terrestrial organic matter with a high content of structural N-poor material, such as the leaves and coconut parts observed in the sediments.

The chemical zonation of the sediments at GD30 and GD9 followed the pattern known from coastal sediments at higher latitudes (e.g., Canfield *et al.* 1993b) with a successive depletion of the oxidants for organic matter in the order $O_2 > NO_3^- \geq MnO_2 > FeOOH > SO_4^{2-}$. This sequence represents a decreasing energy yield from carbon oxidation (Froehlich *et al.* 1979), and is established in part through microbial interactions, where bacteria utilizing energetically more favorable electron acceptors may outcompete other bacterial groups for common substrates (e.g. Lovley and Goodwin 1988). In many marine sediments, however, the competitive exclusion is only partial, and, e.g., SO_4^{2-} reduction has been demonstrated within the oxic zone and within the zone of dissimilatory Fe reduction (Jørgensen and Bak 1991, Canfield and Des Marais 1991, Canfield *et al.* 1993a). It therefore appears that the redox zonation is just as much maintained through a chain of abiotic or microbially catalyzed reoxidations that consume the reduced inorganic mineralization products Mn^{2+}, Fe^{2+}, and H_2S (Canfield *et al.* 1993a, Aller 1994). Thus, for example the Fe reduction indicated at 1 - 2 cm depth at GD9 and -30 (Fig. 6) could both represent dissimilatory reduction by heterotrophic bacteria or a reduction coupled to reoxidation of reduced sulfur species.

The benthic rates of two of the pathways of C oxidation, denitrification and SO_4^{2-} reduction, could be directly determined (Table 2). In view of the relatively high NO_3^- concentrations in the bottom water at GD30 and GD9, the rates of denitrification were low compared to other reports from continental margin sediments (e.g. Devol and Christensen 1993). Also when compared to the other rates in Table 2, denitrification contributed little to carbon mineralization at these sites. Bacterial sulfate reduction, on the other hand, proved to be significant at all stations explaining about 50% of the $\sum CO_2$ accumulation at GD30 and GD9 and all at GD1. This is in good agreement with other coastal sediments with oxic bottom water where SO_4^{2-} reduction typically accounts for 50% of C mineralization (Jørgensen 1982). The complete dominance of SO_4^{2-} reduction at GD1 was expected as O_2 was absent, NO_3 was virtually so, and the Mn and Fe pools only indicated slight Mn and Fe reduction near the surface, leaving SO_4^{2-} as the only available oxidant. At both the anoxic stations, the SO_4^{2-} reduction rate decreased with depth as would be expected as a gradual depletion of the degradable fraction of the organic matter accompanies burial (Fig. 7). At GD1 the higher reactivity of organic matter in the fluff layer was evident as the (volume-based) C_{org} content was actually lower here than in the underlying sediment. Still, the SO_4^{2-} reduction rates stabilized at much higher levels at GD1 than at GD160. This distribution is explained by the implacement of turbidite at GD1, revealed by the x-radiographs (Fig. 3), and the high rates suggest that the latest tur-

bidite is quite young. The final increase in the SO_4^{2-} reduction rate at 17 cm depth at GD1 may represent the previous sediment surface as suggested for the black band observed near this depth. To obtain a quantitative dating of the sediment, analysis of the ^{210}Pb distribution is currently being performed.

At GD9, the increase in SO_4^{2-} reduction rate from the surface to 4 - 5 cm depth (Fig. 7) was not related to obvious changes in C_{org} (Fig. 4), which suggested that SO_4^{2-} reduction near the surface was partially inhibited by competition from other respiratory pathways (cf. Sørensen and Jørgensen 1987). Oxygen, NO_3^-, and Mn oxides were only available for respiration very close to the surface, so the only electron acceptor more favorable than SO_4^{2-} present to 4 - 5 cm depth was poorly crystalline Fe(III) oxides (Fig. 6), and we, thus, suggest that these oxides are important electron acceptors in the this depth interval. Indeed, recent studies have indicated that in many coastal sediments, dissimilatory reduction of Fe and, in some cases, Mn may be as important in C oxidation as is SO_4^{2-} reduction (Aller 1990, Canfield *et al.* 1993a, b). These studies have shown that bioturbation, the mixing of the sediment by the benthos, is essential in transporting the particulate Fe and Mn oxides into the anoxic sediment and maintaining high turn-over rates of these oxidants. The presence of an active infauna at GD30 and GD9 was evident from the worm burrows and the mixed appearance of the sediments (Fig. 3) as well as from the distribution of ΣCO_2 and NH_4^+, the products of the oxidation of organic matter, in the pore-water (Fig. 5). In spite of much higher metabolic rates at these stations than at GD1, a much smaller build-up of the metabolites was seen in the upper 10 cm, but below this depth, as irrigation decreased, concentrations rose.

Although SO_4^{2-} reduction rates were high at all stations, H_2S did not accumulate in the pore waters. This is common for bioturbated sediments, where H_2S can react with Fe oxides that are continuously being mixed in (Thamdrup *et al.* 1994a), but it was surprising that no H_2S accumulated to at least 15 cm depth at GD1. In addition to the rate of SO_4^{2-} reduction, the concentration of H_2S in pore waters is regulated by the availability of reactive Fe (Canfield *et al.* 1992), and the speciation of Fe in the basin sediment is therefore currently under investigation. A particularly high capacity for sulfide retention in the sediments may also be of significance for the suboxic state of the water column.

The anaerobic respirations Mn, Fe, and SO_4^{2-} reduction produce Mn^{2+}, Fe^{2+}, and H_2S. However, the burial of these reduced species, often in precipitated form as, e.g., $MnCO_3$ and FeS_2, is typically much slower than the reduction rates in coastal sediments (Jørgensen 1982, Canfield *et al.* 1993a). Instead they may be transported towards the sediment surface by bioturbation and there be oxidized with O_2 as the final oxidant (Howarth 1984, Thamdrup *et al.* 1994a). Thus, although sediment accumulation rates are not available for Golfo Dulce, it is most likely that most of the oxygen uptake measured in the sediments was not coupled to oxic respiration of organic matter but rather to the reoxidation of reduced inorganic substances. The imbalance between the O_2 uptake and the ΣCO_2 efflux from the sediments implies that the sediments are not at a steady state, and that reduced inorganic compounds are building up in the sediments. If all the reduced species were being reoxidized with O_2 as the final oxidant, the O_2 and ΣCO_2 fluxes should be approximately similar. An imbalance like the one observed is expected when bottom-water oxygen concentrations decrease.

The metabolic rates in the sediments showed a similar variation between the shallow and deep sites as did the benthic fluxes, but at all sites the flux of ΣCO_2 was only about half of the accumulation rate in the upper 10 cm, and the difference was even larger for NH_4^+ (Table 2). In the oxic sediments, oxidation of NH_4^+ to NO_3^- could be a sink at the sediment surface and thus diminish the flux. However, the small NO_3^- fluxes and rates of denitrification exclude nitrification as a significant sink for NH_4^+ (Table 2). There are no indications, that the processing of the sediment involved in the incubations for ΣCO_2 and NH_4^+ accumulation rate determinations affects the rates strongly. Thus, although the SO_4^{2-} reduction rates determined during these incubations varied from the rates from whole-core incubations, the variation was not systematic (Table 2). We therefore attribute the differences to heterogeneity of the sediments. At the shallow stations, where the largest difference was seen, this could include a spatial and temporal patchiness of the irriga-

tion. At present we have no explanation for the extremely high C/N flux ratios from GD30 and GD9.

Decreases in both amount and quality of the organic matter could influence the decrease in metabolic rates from the shallow to the deep sites. The upper 10 cm of sediment contained less than half as much C_{org} at GD1 than at GD9 and -30, and the strong decrease in respiration rates with depth in the water column indicated that only the more refractory organic matter (including the observed macroscopic plant debris) reached the deep basin. For a recent discussion of other factors that may also affect the rates of decomposition (or, conversely, the extent of carbon preservation) in the sediments see Canfield (1994).

The oxic respiration in the water column of 0.7 mol m^{-2} d^{-1} was about 20 times the sediment ΣCO_2 accumulation rates at the shallow sites (Table 2). Since the water column rate is based on linear interpolation of one measurement at 1 m and one at 20 m depth, it should be regarded as a rough estimate. Still, it suggests that carbon cycling in Golfo Dulce is strongly concentrated above the pycnocline.

Comparison of the detection limit for the depth-integrated denitrification rate in the anoxic water column (11 mmol m^{-2} d^{-1}) and the range of benthic carbon mineralization rates measured at the anoxic stations GD1 and GD160 (1.9 - 12 mmol C m^{-2} d^{-1} based on ΣCO_2 flux, ΣCO_2 production, or SO_4^{2-} reduction; Table 2), demonstrates that most carbon oxidation in the anoxic part of the basin probably took place in the sediments. Thus, the benthic exchange may significantly affect the water-column chemistry. Sediment metabolism was dominated by SO_4^{2-} reduction with ΣCO_2, NH_4^+, PO_4^{3-}, and H_2S as the end-products (Eqn. 1). As H_2S was to a large extend trapped in the sediment through reaction with Fe minerals, the main effect of the sediment metabolism on the water column should be the release of ΣCO_2, NH_4^+, and PO_4^{3-}. Of these metabolites, the release of NH_4^+ should be most easily observed, as the concentration in the water entering the bay is very low. Oxidation of NH_4^+ is not expected under anoxic conditions. If we assume that NH_4^+ was not permanently trapped in the sediment but released at a rate equal to its rate of production, then the mean of the different estimates of benthic carbon mineralization rates at GD1 and GD160 (Table 2; mean 6.6 mmol m^{-2} d^{-1}) corresponds to an NH_4^+ efflux of 1 mmol m^{-2} d^{-1} (cf. Eqn. 1). If the NH_4^+ released was distributed over the 100 m of anoxic water column, the accumulation rate there was 0.3 µmol L^{-1} $month^{-1}$. Ammonia concentrations in the anoxic bottom water were generally lower than 1 µM, which implies a turn-over time of less than 3 months. From this rough calculation it is clear that the exchange of bottom water in Golfo Dulce could be quite frequent. Whether such exchange occurs throughout the year or only during winter where upwelling is most intense, as suggested by Richards *et al.* (1971), remains to be determined. Measurements of water-column parameters at monthly intervals should provide a better quantitative understanding of the hydrographical conditions that appear to maintain the basin in an anoxic, non-sulfidic state.

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RESUMEN

Se investigaron las aguas y los sedimentos más superficiales de un fiordo tropical de 200 m de profundidad en relación a la zonación química, a las tasas de procesos respiratorios y a los flujos bénticos. Se encontró oxígeno hasta profundidades de 100 m aproximadamente, si bien solamente la parte superior de la oxiclina se encontraba asociada a la picnoclina, ésta última localizada por encima del umbral. Aguas ricas en nitratos entraban en la bahía a nivel del umbral (60 m) y se esperaba denitrificación en las aguas anóxicas. Solo se detectaron pequeñas cantidades de ácido sulfhídrico en las cercanías del fondo, de manera que los nitratos aparecen como un posible oxidante del

sulfhídrico. Estas observaciones reproducen en gran medida las de un estudio realizado en 1969, lo cual sugiere que el intercambio de agua es lo suficientemente frecuente como para prevenir el desarrollo de condiciones altamente reductoras en las aguas profundas. Las altas tasas de respiración aeróbica son indicativas de un intenso reciclaje del carbono en la zona eufótica. Estas tasas disminuían rápidamente con la profundidad, y asimismo las tasas de denitrificación y de reducción del sulfato eran 100 veces menores que las de la toma de oxígeno en la superficie. La zonación química, así como las radiografías por rayos X, indican que los sedimentos bajo aguas óxicas estaban fuertemente irrigados y bioturbados, mientras que los sedimentos de las zonas anóxicas eran laminados y compuestos de turbiditas. Las tasas de oxidación del carbono eran de 5 a 10 veces mayores en los sedimentos de aguas óxicas que las de los sedimentos de aguas anóxicas del fondo de la bahía. La reducción del sulfato era un proceso dominante que representaba del 50 al 100 % de la oxidación del carbono en los lugares óxicos y anóxicos, respectivamente. Incluso en los lugares anóxicos no se acumulaba ácido sulfhídrico en las aguas intersticiales, por lo que se sugiere una intensa sedimentación de fases de hierro reactivas.

REFERENCES

Aller, R.C. 1990. Bioturbation and manganese cycling in hemipelagic sediments. Phil. Trans. R. Soc. Lond. A 331: 51-58.

Aller, R.C. 1994. The sedimentary Mn cycle in Long Island Sound: Its role as intermediate oxidant and the influence of bioturbation, O_2, and C_{org} flux on diagenetic reaction balances. J. Mar. Res. 52: 259-295.

Anderson, J.J. & A.H. Devol, 1987. Extent and intensity of the anoxic zone in basins and fjords. Deep-Sea Research 5/6: 927-944.

APHA (American Public Health Association). 1992. Standard Methods for the examination of Water and Wastewater. APHA, Washington D.C.

Bender, M., W., Martin, J., Hess, F., Sayles, L. Ball, & C. Lambert, 1987. A whole-core sqeezer for interstitial pore-water sampling. Limnol. Oceanogr. 32: 1214-1225.

Canfield, D.E. 1994. Factors influencing organic carbon preservation in marine sediments. Chem. Geol. 114: 315-329.

Canfield, D.E. & D.J. Des Marais, 1991. Aerobic sulfate reduction in microbial mats. Science 251: 1471-1473.

Canfield, D.E., R. Raiswell, & S. Bottrell, 1992. The reactivity of sedimentary iron minerals towards sulfide. Am. J. Sci. 292: 659-683.

Canfield, D.E., B. Thamdrup, & J.W. Hansen, 1993a. The anaerobic degradation of organic matter in Danish coastal sediments: Iron reduction, manganese reduction, and sulfate reduction. Geochim.Cosmochim. 57: 3867-3883.

Canfield, D.E., B.B., Jørgensen, H., Fossing, R., Glud, J., Gundersen, N.B., Ramsing, B., Thamdrup, J.W., Hansen, L.P. Nielsen, & P.O.J. Hall, 1993b. Pathways of organic carbon oxidation in three continental margin sediments. Mar. Geol. 133: 27-40.

Cline, J.D. 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. Limnol. Oceanogr. 14: 454-458.

Córdoba, R. & J.A. Vargas, 1996. Temperature, salinity, oxygen, and nutrient profiles at a 200 m deep station in Golfo Dulce, Pacific coast of Costa Rica. Rev. Biol. Trop., 44, Suppl. 3:,233-236.

Devol, A.H., & Christensen, J.P. 1993. Benthic fluxes and nitrogen cycling in the sediments of the continental margin of the eastern North Pacific. J. Mar. Res. 51: 345-372.

Fossing, H. & B.B. Jørgensen, 1989. Measurement of bacterial sulfate reduction in sediments: Evaluation of a single-step chromium reduction method. Biogeochemistry 8: 205-222.

Fossing, H. & B.B. Jørgensen, 1990. Oxidation and reduction of radiolabeled inorganic sulfur compounds in an estuarine sediment, Kysing Fjord, Denmark. Geochim. Cosmochim. Acta 54: 2731-2742.

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

Hall, P.O.J. & R.C. Aller, 1992. Rapid, small-volume, flow injection analysis for ΣCO_2 and NH_4^+ in marine and freshwaters. Limnol. Oceanogr. 37: 1113-1119.

Hebbeln, D. 1994. Late quarternary paleoclimate of Costa Rica - Golfo Dulce and adjacent areas, p. 67-75. *In* Wolff, M. & Vargas, J.A. (eds.). RV Victor Hensen Costa Rica Expedition 1993/1994, Cruise Report.

Howarth, R.W. 1984. The ecological significance of sulfur in the energy dynamics of salt marsh and coastal marine sediments. Biogeochem. 1: 5-27.

Ingvorsen, K. & B.B. Jørgensen 1979. Combined mesurement of oxygen and sulfide in water samples. Limnol. Oceanogr. 24: 390-393.

Jones, M.N. 1984. Nitrate reduction by shaking with cadmium. Water Res. 18: 643-646.

Jørgensen, B.B. 1978. A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments. I. Measurement with radiotracer techniques. Geomicrobiology J. 1: 11-27.

Jørgensen, B.B. 1982. Mineralization of organic matter in the sea bed - the role of sulfate reduction. Nature 296: 643-645.

Jørgensen, B.B. & F. Bak, 1991. Pathways and microbiology of thiosulfate transformations and sulfate reduction in a marine sediment (Kattegat, Denmark). Appl. Environ. Microbiol. 57: 847-856.

Jørgensen, B.B., H., Fossing, C.O., Wirsen, & H.W. Jannasch, 1991. Sulfide oxidation in the anoxic Black Sea chemocline. Deep-Sea Res. 38: S1083-S1103.

Kristensen, E. & T.H. Blackburn, 1987. The fate of carbon and nitrogen in experimental marine systems: influence of bioturbation and anoxia. J. Mar. res. 45: 231-257.

Kruse, B. 1993. Measurement of plankton O_2 respiration in gas-tight plastic bags. Mar. Ecol. Progr. Ser. 94: 155-163.

Kuever, J., C., Wawer, & R. Lillebæk, 1996. Microbiological observations in the anoxic basin Golfo Dulce, Costa Rica. Rev. Biol. Trop., 44, Suppl. 3:49-57.

Lewis, B.L. & W.M. Landing, 1991. The biogeochemistry of manganese and iron in the Black Sea. Deep-Sea Res. 38: S773-S803.

Lord, C.J., III. 1980. The chemistry and cycling of iron, manganese, and sulfur in salt marsh sediments. Ph.D. thesis, University of Delaware, Delaware.

Lovley, D.R. & S. Goodwin, 1988. Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reactions in aquatic sediments. Geochim. Cosmochim. Acta 52: 2993-3003.

Mackin, J.E. & R.C. Aller, 1984. Ammonium adsorption in marine sediments. Limnol. Oceanogr. 29: 250-257.

Middelburg, J.J., G.J., de Lange, H.A., van der Sloot, van P.R. Emburg, & S. Sophiah, 1988. Particulate manganese and iron framboids in Kau Bay, Halmahera (Eastern Indonesia). Mar. Chem. 23: 353-364.

Murray, J.M., H.W., Jannasch, S., Honjo, R.F., Anderson, W.S., Reeburgh, Z., Top, G.E., Friederich, Codispoti, L.A. & Izdar, E. 1989. Unexpected changes in the oxic/anoxic interface in the Black Sea. Nature 338: 411-413.

Nichols-Driscoll, J. 1976. Benthic invertebrate communities in Golfo Dulce, Costa Rica, an anoxic basin. Rev. Biol. Trop. 24: 281-297.

Nielsen, L.P. 1992. Denitrification in sediment determined from nitrogen isotope pairing. FEMS Microb. Ecol. 86: 357-362.

Rasmussen, H. & B.B. Jørgensen, 1992. Microelectrode studies of seasonal oxygen uptake in a coastal sediment: role of molecular diffusion. Mar. Ecol. Progr. Ser. 81: 289-303.

Richards, F.A. 1960. Some chemical and hydrographic observations along the North coast of South america. I. Cabo Tres Puntas to Curaçao, including the Cariaco Trench and the Gulf of Cariaco. Deep Sea Res. 7: 163-182

Richards, F.A. 1965. Anoxic basins and fjords, p. 611-645. In Chemical Oceanography. Riley, J.P. & Skirrow, G. (eds). Academic, London.

Richards, F.A. & W.W. Broenkow, 1971. Chemical changes, including nitrate reduction, in Darwin bay, Galapagos Archipelago, over a 2-month period, 1969. Limnol. Oceanogr. 758-765.

Richards, F.A., J.J. Anderson, & J.D. Cline 1971. Chemical and physical observations in Golfo Dulce, an anoxic basin on the Pacific coast of Costa Rica. Limnol.Oceanogr. 16: 43-50.

Rosenfeld, J.K. 1979. Ammonium adsorption in nearshore anoxic sediments. Limnol. Oceanogr. 24: 356-364.

Skei, J.M. 1988. Framvaren, environmental setting. Mar. Chem. 23: 209-218.

Sørensen, J. 1987. Nitrate reduction in marine sediment: Pathways and interactions with iron and sulfur cycling. Geomicrobiol. J. 5: 401-421.

Sørensen J. & B.B. Jørgensen 1987. Early diagenesis in sediments from Danish coastal waters: Microbial activity and Mn-Fe-S geochemistry. Geochim. Cosmochim. Acta 51: 1583-1590.

Stookey, L.L. 1970. Ferrozine - a new spectrophotometric reagent for iron. Anal. Chem. 42: 779-781.

Thamdrup, B., H. Fossing, & B.B. Jørgensen, 1994a. Manganese, iron, and sulfur cycling in a coastal marine sediment, Aarhus Bay, Denmark. Geochim. Cosmochim. Acta 58: 5115-5129.

Thamdrup, B., R.N. Glud, & J.W. Hansen, 1994b. Manganese oxidation and in situ manganese fluxes from a coastal sediment. Geochim. Cosmochim. Acta 58: 2563-2570.

Williams, P.J. LeB. 1984. A review of measurements of respiration rates of marine plankton populations, p. 357-390. *In* Hobbie, J., Williams, P.J. LeB. (eds.) Heterotrophic Activity in the sea. Plenum, New York.