

NUTRIENT FLUXES FROM SEDIMENTS OF THE NORTHERN GULF OF AQABA UNDER VARIOUS ANTHROPOGENIC ACTIVITIES

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ABSTRACT

Fluxes of inorganic nutrients and dissolved inorganic carbon (DIC) from the sediments to the water column was investigated in sites with various anthropogenic activities. Lab incubations of sediments collected from four different sites were carried out under controlled conditions. The sites were Marine Science Station (MSS), two industrial, Phosphate Loading Berth (PLB) and Industrial complex (IC) and one tourist site at Hotel Areas (H). Sediments at the MSS site were composed mainly of carbonates while at the other sites, silicate represented the dominant mineral. Fluxes of different solutes were estimated from linear regressions of concentrations over incubation time. Fluxes of ammonium, phosphate and dissolved inorganic carbon (DIC) were higher for MSS sediments compared to fluxes for H, PLB, and IC sediments (4.1, 1.7, 1.7 fold for ammonium, 3.3, 3.6, 1.6 fold for phosphate, and 1.2, 1.4, 1.2 fold for DIC respectively). This was interpreted by the high permeability and the carbonate content of the MSS sediments. Despite the higher organic content in the PLB sediments, lower flux rates were estimated. This was attributed to the refractory type (low degradable) of the organic matter in the PLB sediments compared to a labile (degradable) organic matter in the MSS sediments. These results demonstrated the probable importance of the sediments as a sink for organic material and as a suitable degradation environment for organic deposits.

Keywords: nutrient, sediments, pollution, Gulf of Aqaba

INTRODUCTION

Shelf and coastal areas are considered as the most productive parts of the ocean. It has been reported that 20 to 50% of total primary production occurs in these areas (Romankevich, 1984), which comprise only 8% of the total ocean area (Ott, 1988). About 83% of the total organic matter sedimentation occurs in the shelf sediments (Jorgensen, 1983). Due to this high storage capacity of organic matter, the sediments are expected to have an important

regulatory and buffering function for pollutants in the ocean. Most of the deposited organic materials are degraded, remineralized, and then recycled to the water column.

Degradation and remineralization of organic matter in the sea are important processes for the regeneration of inorganic material including nutrients, which could sustain primary productivity in the marine ecosystem. The role of the sediments in these processes has been considered to be important (e.g. Charpy-Rouband *et al.*, 1990, Ciceri *et al.*, 1999, Stimson and Larned, 2000, Rasheed *et al.*, 2003 a, Rasheed *et al.*, 2003 b). Moreover, mineralization of organic deposits in the sediments can convert organic pollutants to non-harmful inorganic compounds. The accumulation of these inorganic nutrients in the sediments will produce a gradient in nutrient concentrations between pore waters and the overlying water column. These differences cause solutes back to the water column, which means fluxes of these nutrients to the overlying waters. Benthic nutrient fluxes are controlled mainly by the rate of the degradation processes (Rasheed *et al.*, 2003 a), diffusive transport (Charpy-Rouband *et al.*, 1990), advection processes (Huettel *et al.*, 1998), bioirrigation and bioturbation from different burrowing organisms (Aller, 1988; Kristensen, 1988), as well as the physical and chemical properties of the sediments (e.g. Haddad *et al.*, 1992; Capone *et al.*, 1992; Canfield *et al.*, 1993).

The Gulf of Aqaba, one of the two northern branches of the Red Sea and a part of the Syrian African rift system, is about 180 km long, 14-26 km wide and up to 1830m deep (Fig. 1). Aqaba is the main port of Jordan and has a special concern as a special economic zone. The sun, beaches, clarity of the water as well as the sea flora and fauna of the Gulf of Aqaba make this area one of the most important tourist sites in Jordan. Hence, Aqaba hosts several industrial and human activities. Industrial activities by the sea include mainly the Fertilizer Complex and Phosphate Loading Berth, whereas tourism activities include some hotels and coffee shops, which lie directly along the seashore. These activities produce wastewaters discharged into the sea and may influence the quality of seawater.

In this study, sediment cores were collected from different sites along the Jordanian coast of the Gulf of Aqaba. Lab incubation experiments were carried out for these sediments in order to investigate the effect of anthropogenic stresses on the fluxes of inorganic materials to the water column. This study also aimed to assess the ability of sediments to act as a sink for any new artificial materials that may be introduced to the sea by human activities.

MATERIAL AND METHODS

Sampling site

Sediment cores for incubation experiments were collected from four different sites along the Jordanian coast of the Gulf of Aqaba (Fig. 1). The northern station (H) hosts some hotels and other tourism activities. The sediments from this area are mainly composed of silicates (Table 1) and covered by sea grass. The sediments from the Phosphate Loading Berth (PLB) are composed mainly of quartz (silicate) with higher content in total phosphorus (~7.5%, Table 1) compared to the other sites. Marine Science Station (MSS) is located in a marine reserve hosting a substantial coral reef community and other fauna and flora. Therefore, sediments at this site are dominated by carbonate minerals (Table 1) composed of coral

fragments, remains of foraminiferans, calcareous red algae and sea urchins (Rasheed *et al.*, 2003a). At the most southern part of the Jordanian Gulf, Industrial complex (IC) hosts companies producing fertilizers and a thermal power station. The sediments at this site are dominated by quartz (Table 1).

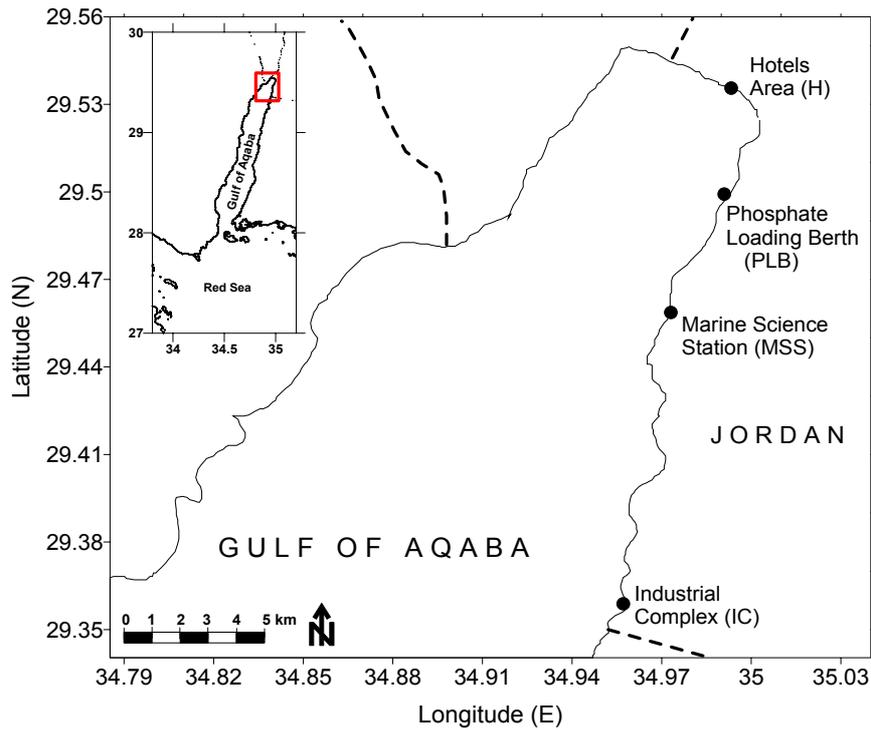


Figure 1. Study area in the northern Gulf of Aqaba and the sites of the collected sediments.

TABLE 1

Some Physical and Chemical Prosperities of the Investigated Sediments

Site	Permeability (m^2)	stdev	OC (g/kg)	stdev	CaCO ₃ (%)	stdev	TP (g/kg)	stdev	TN (g/kg)	stdev	C/N ratio
H	15×10^{-12}	5	0.81	0.01	6.82	0.31	0.71	0.06	0.13	0.02	6.23
PLB	12×10^{-12}	7	3.20	0.02	9.68	0.47	74.79	3.83	0.13	0.03	24.61
MSS	128×10^{-12}	8	2.59	0.03	73.70	0.62	0.34	0.05	0.59	0.04	4.39
IC	55×10^{-12}	5	1.43	0.02	9.68	0.16	0.51	0.06	0.14	0.02	10.21

Sediments sampling and incubation

Sediment cores for incubations were collected by diving, using acrylic cylinders with 9.5 cm inner diameter and 40 cm length. The sediments were collected by inserting the cylinders with sharp edges at the lower end into the sediments with a plastic hammer. The sediments were sent to the lab for incubation after about 1 hr from sampling.

In order to unify the water above the sediments during incubation, the waters overlaying in each collected core were removed and sea waters collected from a selected 1m depth site in front of the MSS were added to each core. The height of the sediments in the cores were about 15 cm and the length of the water columns were about 25 cm. The cores were then covered by gas-tight plastic lids with two sampling port. To homogenize the water above the sediments, rotating disks of 7 cm each were used for stirring and placed 5 cm above the sediments surface. The incubation was performed at ambient temperature of about 25°C which was closed to the in-situ water temperature at sampling time (July, 24-25 °C). Redox potential for the water above the sediments was measured for each cores using a Mettler Toledo Electrode at different time intervals (Fig. 3). For inorganic nutrients (ammonium, nitrate, nitrite and phosphate) and dissolved inorganic carbon (DIC) analysis, 50 ml of the overlaying water was withdrawn using a syringe at different time intervals and replaced by 50 ml of seawater collected from the same selected site mentioned above. About 45 ml of the water was used for nutrient analysis and the remaining 5 ml used for DIC determination was placed in appendorf vials without any air bubbles and kept in the refrigerator until analysis. The incubation was repeated two times for statistical purpose. The duration of the incubation was about 130 hr.

Fluxes of solutes were estimated from linear regressions of solutes concentrations over incubation times. Statistical analysis, Anova (95% significance level), was performed to evaluate the significance of differences in the incubation results from the different study sites.

Analytical procedures

Calcium carbonate content of the sediments was measured by complexometric titration of calcium carbonate with 0.1 N of hydrochloric acid according to Muller (1967). Organic carbon content in the sediments was measured following the method of Gaudette and Flight (1974). In this method, 0.2 g sediment was treated with H₂SO₄ (12 M) and potassium dichromate and then titrated with ferrous ammonium sulphate solution. The samples were treated with 1 N HCl to remove any inorganic carbon in the samples. Kjeldahl digestion was used to determine total nitrogen in the sediments. Organic nitrogen in the sediments was converted to inorganic nitrogen by concentrated H₂SO₄ (12 M), which was measured as ammonium following the standard method of Strickland and Parsons (1972). For total phosphorus determination in sediments, an ignition method was used (Andersen, 1976). Following this method, 0.2g of sediments was combusted in a furnace (450°C) and the ash was boiled in 1N HCl for 15 minutes. The sample was diluted to 100 ml with distilled water and phosphate was then measured spectrophotometrically following the method of Strickland and Parsons (1972). Permeability of the sediments was measured using a constant head permeameter as described by Klute and Dirksen (1986).

Analysis of inorganic nutrients (ammonium, phosphate, nitrate and nitrite) in the water was performed spectrophotometrically following the methods of Strickland and Parson (1972). Dissolved inorganic carbon (DIC) concentrations in the water samples were measured using a flow injection system (Hall and Aller, 1992). Calibration standards were prepared freshly from NaHCO_3 .

RESULTS

Sediment properties

Some physical and chemical properties of the sediments are shown in Table 1. The highest permeability was found in the MSS sediments which may be related to the CaCO_3 content. Sediments of H and PLB have relatively low permeabilities, but were still considered as permeable sediments. According to Rusch and Huettel (2000), sediments with a permeability of $>10^{-12}$ are considered as permeable. PLB and MSS sediments had higher organic carbon content compared to sediments of the other sites. CaCO_3 and TN were higher in MSS sediments and as expected, TP was notably higher in PLB sediments. C/N ratio was the lowest in the MSS sediments and the highest in the PLB sediments as high organic carbon content with low TN were found at this site.

Nutrient fluxes from the sediments

Results of sediment incubations showed growth or reduction of the different measured parameter with time (Figs. 2 & 3). Immediately with the performance of the incubation, ammonium concentrations in all chambers for all incubated sediments started to increase gradually with an average rate of $1.5 \text{ mmol m}^{-2} \text{ d}^{-1}$. Maximum increase rate was found in the chamber with the MSS sediments while the minimum rate was found in the H sediments. The rates of ammonium growths in all chambers were almost stable and have not been affected during the incubation as it was observed in some other parameters (Figs. 2 & 3, see below). The calculated fluxes from this incubation are represented in Fig. 4. Highest flux of $2.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ was recorded in the MSS chamber which constituted 4.1, 1.7, 1.7 fold the fluxes measured at H, PLB and IC sites respectively. Time course of phosphate concentrations in the incubated chambers are shown in Fig. 3. As for ammonium, phosphate concentrations started to increase at once the incubation began. However, rates of phosphate growth in the chambers were not stable. The rates were higher during the first 60 hr of incubation (average of $\sim 0.03 \text{ mmol m}^{-2} \text{ d}^{-1}$) than the rates during the last period of incubation (average of $\sim 0.015 \text{ mmol m}^{-2} \text{ d}^{-1}$). Phosphate grew faster in the MSS chamber and then in the IC chamber and grew slower in the H chamber (differences are shown in table 2). This was reflected on the calculated fluxes, as the value of the MSS chamber was the highest one ($0.040 \text{ mmol m}^{-2} \text{ d}^{-1}$, Fig. 4) compared to 0.012, 0.011, $0.025 \text{ mmol m}^{-2} \text{ d}^{-1}$ for H, PLB, and IC chambers respectively. Similar to ammonium and phosphate, DIC increased gradually in all incubated chambers during the incubation (Fig. 2). The increase of DIC was also higher in the MSS chamber than in the other chambers. However, the difference was not apparent as in the case of ammonium and phosphate (Table 2). Yet, the fluxes of DIC resulted from MSS sediments incubation was 1.2, 1.4, 1.2 fold of the H, PLB, and IC sediments respectively (Fig. 4).

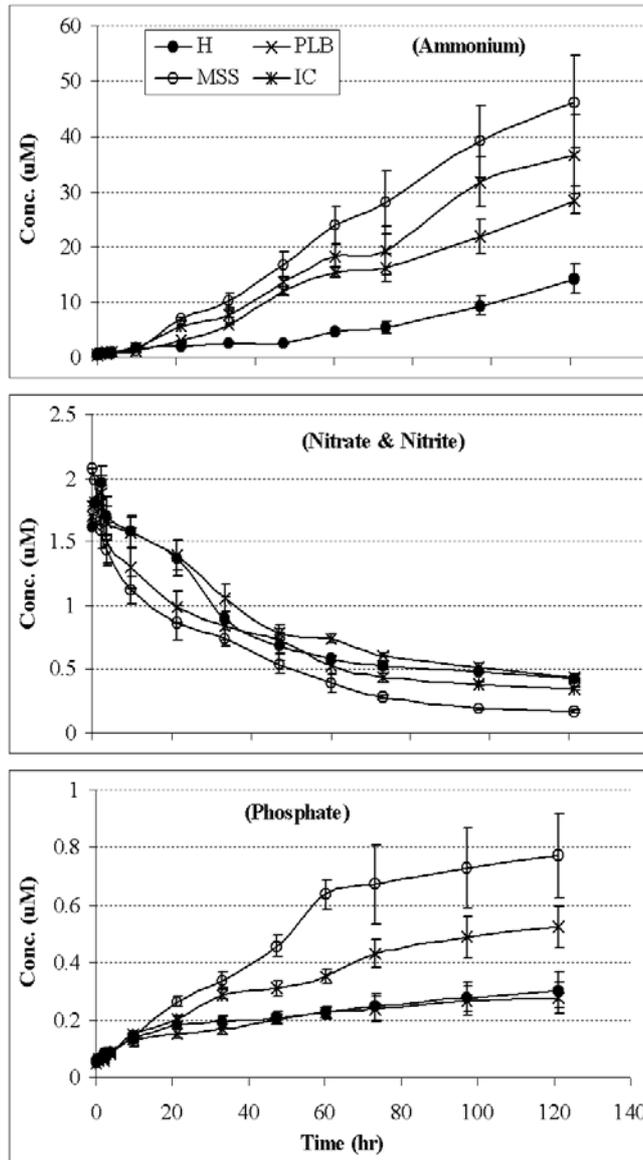


Figure 2. Time course of ammonium, phosphate, nitrate and nitrite concentrations (μM) during the incubation of the sediment collected from the four study site.

Redox potential (RP) was measured as an indication of oxygen concentration in the chamber (Fig. 3). As redox potential decreased oxygen decreases and reduced environment was initiated. At once incubation started, redox potential decreased immediately with an average rate of $1.5 \text{ v m}^{-2} \text{ d}^{-1}$. Higher decline rates at the first 60 hr for all chambers were observed than the rates at the end of incubation (1.7 fold). Here, the reduction rate of the MSS chamber was higher in comparison with the other chambers as indicated from the value differences (Table. 2). Following the pattern of redox potential, nitrate and nitrite concentrations decreased in all incubated chambers, with the highest decrease rate at the MSS chamber (Table 2, Fig. 3). Consequently, flux into the sediments in this chamber was also higher than those of the other chambers (Fig. 4).

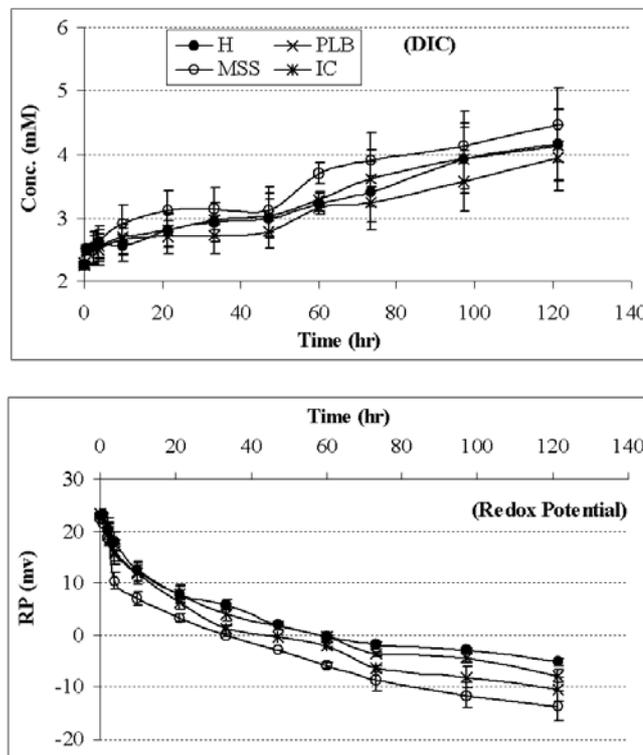


Figure 3. Time course of DIC (mM) and redox potential (mv) during the incubation of the sediments collected from the four study site.

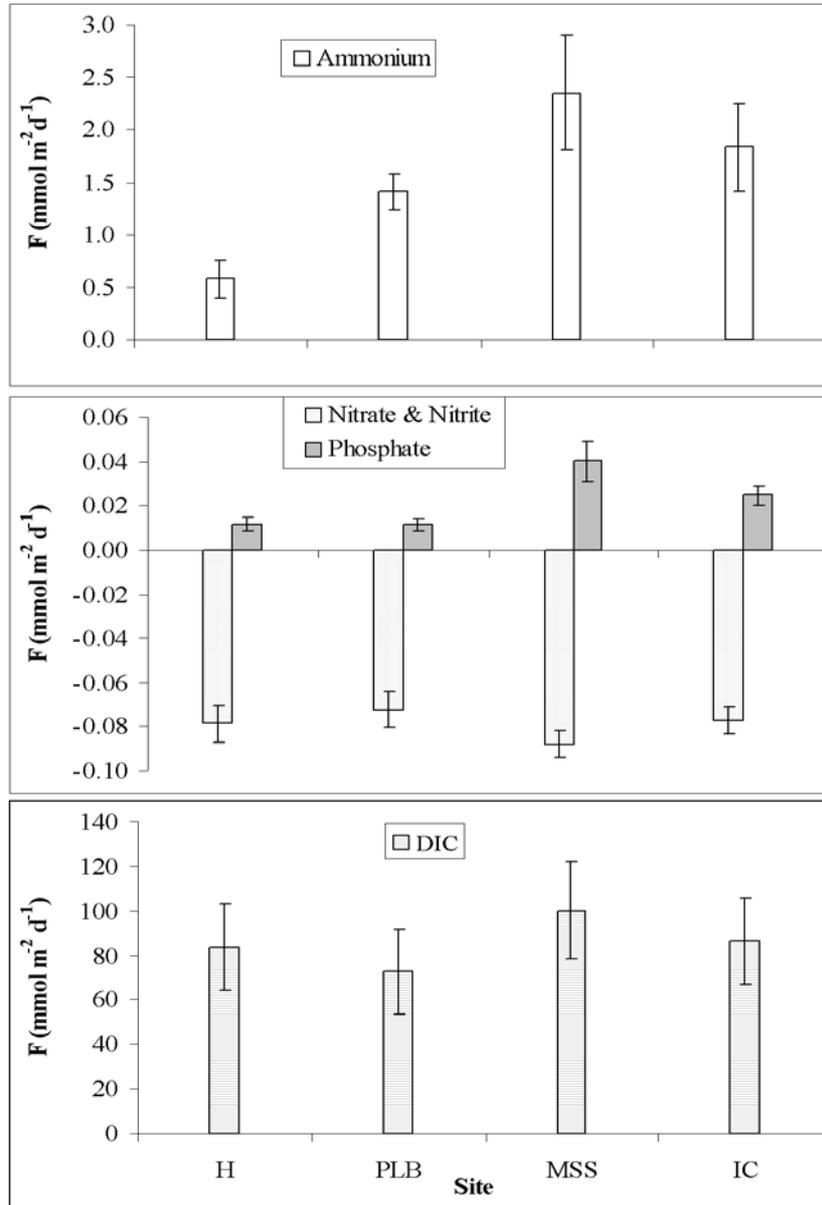


Figure 4. Nutrient and DIC fluxes (mmol m⁻² d⁻¹) from different incubated sediments.

Discussion

These results reveal the flux differences which resulted basically from the degradation of organic compounds in different sediment types from different locations. High fluxes were measured for MSS sediments compared to the other sediments (Fig. 4). Statistical analysis, based on the concentration differences obtained from the incubations (Figs. 2 & 3), showed mostly higher mean differences and lower p values for MSS sediments in comparison to any other sediments (Table 2). Fluxes resulted from IC sediments were also higher than those obtained for PLB and H sediments (Fig. 4).

TABLE 2
Mean Differences (MD) and P Values Obtained from ANOVA Test at a Significance Level of 5% Calculated Based on the Differences between the Measured Concentrations during the Incubations

	<i>Ammonium</i>		<i>Phosphate</i>		<i>DIC</i>		<i>Nitrate & nitrite</i>		<i>Redox potential</i>	
	MD	P	MD	P	MD	P	MD	P	MD	P
MSS & H	11.78	0.0102	0.20	0.0080	0.22	0.0030	0.25	0.0011	5.55	<0.0001
MSS & PLB	6.23	0.0119	0.21	0.0057	0.36	0.0003	0.27	0.0027	4.51	<0.0001
MSS & IC	3.37	0.0140	0.12	0.0090	0.19	0.0010	0.13	0.0043	2.88	<0.0001
IC & H	8.42	0.0098	0.09	0.0097	0.03	0.2354	0.12	0.0124	2.67	0.0007
IC & PLB	2.86	0.0167	0.10	0.0048	0.17	0.0015	0.14	0.0170	1.63	0.0013
PLB & H	5.56	0.0109	0.01	0.0052	0.14	0.0029	0.02	0.5789	1.05	0.0031

Inorganic compound fluxes from the sediments depend mainly on the rate of organic matter degradation which results in mineralization of organic carbon, nitrogen, phosphate and biogenic silicate. The accumulation of these inorganic materials in the sediments produces solute concentration gradients between pore water and the overlying seawater, which drives the solute back to the water column. In aerobic sediments, oxic respiration can supply nitrate and nitrite for the water column (Hammond *et al.*, 1983; Berelson *et al.*, 1998). In anaerobic sediments, ammonium can be supplied from nitrate reduction; phosphate remains soluble under anaerobic conditions (Libes, 1992). The degradation processes depend mainly on temperature (*e.g.* Alperin *et al.*, 1994; Trimmer *et al.*, 2000), chemical and physical prosperities of the sediments such as permeability, mineralogy of the sediments (*e.g.* Haddad *et al.*, 1992; Keil *et al.*, 1994; Mayer, 1994; Henrichs, 1995; Adams and Bustin, 2001), quality and quantity of degraded organic materials (*e.g.* Kristensen *et al.*, 1995; Dauwe *et al.*, 2001). Temperature could not be a factor as temperatures were the same for all sediment incubations.

Effect of permeability

Conspicuously, permeability of the MSS sediments was the highest one among all other sediments (2.3, 10.7, 8.5 fold of IC, PLB and H sediments respectively, Table 1). This might increase the degradation rate of organic material and the concentrations of inorganic degradable compounds in the sediments and subsequently enhance fluxes of these compounds to the water column. Rasheed *et al.* (2003a) found 1.5 fold higher organic matter mineralization rates in sediments with 2 fold higher permeability. In flume and field

experiments comparing degradation of algal material in sediments with different permeabilities, Huettel and Rusch (2000) found 2.7 fold higher degradation rate in sediments with a permeability of $4.6 \times 10^{-10} \text{ m}^2$ than in sediments with a permeability of $2.8 \times 10^{-11} \text{ m}^2$. Increased oxygen consumption and organic matter mineralization rates with increasing sediments permeability were also reported in other studies (e.g. Marinelli *et al.*, 1998; Dauwe *et al.*, 2001). Increasing sediments permeability increases the circulation of water through the pores of the sediments and thus, enhances the mineralization rates of organic materials (Shum and Sundby, 1996; Huettel and Rusch, 2000). Accompanied with high permeability, high oxygen penetration depth was found (Huettel and Rusch 2000), which enhance the aerobic degradation of organic materials (Ziebs *et al.*, 1996; Marinelli *et al.*, 1998). Hence, the high permeability of the MSS sediments might be a reasonable factor which affect the degradation rate of the deposited organic materials and enhanced the fluxes of dissolved materials to the water.

Effect of mineralogical structure

Sediments from MSS site were mainly carbonate (74%, Table 1), while the other sediments consisted mainly of siliceous material with low content of carbonate (10, 10, 7% for IC, PLB, and H sediments respectively, Table 1). Carbonate sands dissolve at a faster rate than silicate (Banfield and Nealson 1998) and may act as a buffer for different remineralization reactions through precipitation and dissolution of carbonate, which produce and or consume CO_2 , HCO_3^- and H^+ . This may enhance organic matter degradation as reported by Rasheed *et al.* (2003 a & b). Carbonate sediments contain many small pores resulting from the skeletal remains of corals and sea urchins, which constitute these sediments (Rasheed *et al.*, 2003a). These pores increase the surface area of the carbonate grains and surface roughness which in turn increase the ability of the sediments to accumulate more organic matter (Mayer, 1994). A conclusion can be made that the high carbonate content in the MSS sediments may be also a realistic reason for the degradation of organic particles and the subsequent fluxes of inorganic materials.

Content and type of organic materials

As a concept in any chemical reaction, quantity of the products in a reaction depends on the quantity of the limiting reactant which is defined as the reactant with the less molar quantity. Degradation processes may occur aerobically and anaerobically. In an aerobic reaction, oxygen is used as an energy source for the oxidation of organic deposits. Anaerobic reaction utilizes nitrate, manganese oxides, iron oxides, sulphate and CO_2 as an energy source (Latimer, 1952; Berner, 1971). In the two reaction types, and if we suppose that we have excess of oxidizing agent in the degradation reaction, then the limiting factor of the reaction will be the molar quantity of the organic matters and the remineralization will be enhanced as organic loading increase. This has been emphasized by several authors (e.g. Sloth *et al.*, 1995; Trimmer *et al.*, 2000; Dawe *et al.*, 2001). Denitrification process (using NO_3^- as an electron acceptor) has been reported to be enhanced with organic content (Nowicki *et al.*, 1997). In this study, organic content was highest for PLB sediments (3.2 g kg^{-1}) then for MSS sediments (2.6 g kg^{-1}). Total phosphate was measured to be very high in the PLB sediments in comparison with the other sediments (>100 fold for all sediments, Table 1). In total, PLB sediments had the higher amount of organic materials. Yet, the flux values were clearly higher in the incubation

in MSS and IC sediments than for PLB sediments especially in the case of ammonium and DIC fluxes (Fig. 4). This deducts a question of how lower fluxes were obtained from the PLB sediments which had a larger organic content compared to the MSS and IC sediments. This question can be logically answered by the type of organic materials. Organic compounds can be divided into degradable ones (labile compounds) and low degradable ones (refractory compounds). The latter may be degradable in the presence of oxygen (Hulthe *et al.*, 1998), but it is known that oxygen is typically depleted in the first 15 mm of the sediments (Revsbech *et al.*, 1980), and most mineralization processes in the sediments occur anaerobically. Hence, refractory compounds are mostly non degradable and can be preserved in the sediments for long time. MSS hosts a marine reserve with a thriving coral community including corals themselves and other living organisms accompanied with corals as it is considered as one of the most diverse and complex biological communities (Sorkin, 1995). Organic material resulted from these communities are supposed to be a degradable as it consider labile and fresh (Hulthe *et al.*, 1998). Furthermore, C/N ratio of 4.39 calculated for MSS sediments (Table 1) may indicate an organic matter of phytoplankton fresh detritus for this site, as a C/N ratio of 5-6 is expected for phytoplankton detritus (Froelich *et al.*, 1979). In coral reef areas, phytoplankton density is relatively high (*e.g.* Yahel *et al.*, 1998) and the decomposition of the detritus derived from phytoplankton is relatively fast (Henrichs and Doyle, 1986). Accordingly, high degradation rate of organic deposits and high fluxes of inorganic materials are expected for the MSS sediments. This explains the higher ammonium, phosphate, and DIC flux rates at the MSS than the rates in the other sediments. However, the higher organic content of MSS sediments compared to IC and H sediments might play a role in the higher rates at these sediments. The sediments at phosphate area (PLB) are composed mainly of very fine phosphate deposits originating from the main raw phosphate loading berth (Abu-Hilal, 1985). The high C/N ratio of these sediments (24.61, Table 1) indicates that these sediments are expected to be refractory materials with low mineralization rates and low flux rates.

CONCLUSION

The study shows that anthropogenic industrial (Industrial complex and Phosphate Loading Berth) and tourist activity (Hotel area) do not effect significantly the concentrations of inorganic material in the water column as indicated from our flux results. In the Marine Science Station as a preserved area, higher flux rates were found compared to the other sites as a result of high sediment permeability and carbonate structure of the sediment grains, high organic matter content as well as type of organic matter deposited at this site. However, the sediment in Phosphate Loading Berth had the highest organic content with low flux rates which might be attributed to the non degradable (refractory) nature of the deposited sediments at this area.

In general, the sediments can be considered as a good sink for organic material. Part of these materials can be remineralized within the sediments and the other part can be preserved for a long time in the deep layer of the sediments.

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