Factors Controlling the Distribution and Behaviour of Organic Carbon and Trace Elements in a Heavily Sewage Polluted Coastal Envoironment

MOHAMED A. EL SAYED*

National Institute of Oceanography and Fisheries, Alexandria, Egypt

ABSTRACT. The coastal area south of Jeddah, Saudi Arabia, eastern Red Sea, receives daily more than 100,000 m^3 of domestic sewage. The solid material of the dumped wastes was analyzed for its organic carbon, Al, Fe, Mn, Cu, Zn and Cr contents and their mass emission was calculated. To trace the impact on the coastal area, the same elements were analyzed in sediments and suspended matter in the receiving basin and along a coastal strip extending for about 10 km southward the discharge point.

It was found that the impact of the effluent was limited to the area in the proximity of the effluent discharge point where concentrations in both sediments and suspended matter were several times higher than in the other parts of the area. Away from the effluent, concentrations were comparable to those measured in uncontaminated carbonate sediments. In the dilution basin, the distribution of the elements correlated with the dilution pattern of the effluent water. Normalization to aluminium revealed however, that only Fe, Cu and Zn were enriched in the sediments (EF 1.7, 6.3 and 6.8 respectively), while Mn and Cr were depleted. This behaviour was attributed to the difference in the oxidation-reduction kinetics of the redox sensitive elements (Fe, Mn, Cr) and to interaction with the organic matter and formation of insoluble sulphides (Cu and Zn). In the suspended matter all the elements showed a positive deviation from linearity at intermediate salinity. The excess was accounted for by the resuspension of bottom sediments (Fe, Cu and Zn) and adsorption of mobilized elements (Mn).

KEY WORDS: Organic carbon, trace elements, sediments, geochemistry, Red Sea.

^{*}Present Address: Faculty of Marine Science, KAU, P.O. Box 80207, 21589, Jeddah, Saudi Arabia.

Introduction

The Red Sea has long been considered as a pristine environment. Bordered by relatively weakly industrialized countries it received little flux of hazardous industrial wastes compared to other land locked seas such as the Mediterranean. Since the beginning of the 70's, the entire region has suffered from important industrial, touristic and demographic mutations, which are expected to affect the Red Sea environment, particularly the coastal area. Unless adequate and severe measures are implemented to protect it, coral reefs, mangrove stands and sea grass beds, ecosystems specific to tropical seas and characterized by their biological diversity (Odum and Odum, 1955; Veron, 1986) will be subjected to dramatic and probably irreversible damage.

The city of Jeddah, Saudi Arabia, is one of the most important urban agglomerations on the eastern coast of the Red Sea. At present the population of Jeddah is approximately 2.5 millions, however, it is rapidly increasing and it is expected to reach 6 million by the year 2020. This accelerated demographic expansion along with important industrial development is not accompanied with adequate development of the network of wastewater collection and treatment. Only 10% of the city is attached to the sewage collection and treatment network while the rest is generally using septic tanks. Severe coastal eutrophication, red tides and episodic fish mortality demonstrate the impact of sewage discharge in the coastal area. Some recent studies have shown the impact of sewage discharge on the physical and chemical characteristics of water and sediments (El Rayis, 1998; El Rayis and Moammer, 1998; Basaham, 1998; El Sayed, 2002 a&b) and on the development of mangrove stands (Mandura, 1997).

Al-Khumra is the most important sewage treatment station (STS) of the city. Its nominal treatment capacity is 80,000 m³d⁻¹, however, it receives practically more than 100,000 m³ day⁻¹ (non official figures vary between 150 and 200 × $10^3 \text{ m}^3 \text{d}^{-1}$), most of which is released without any treatment. Recent studies (El Sayed, 2002a&b) have shown that the effluent of the STS discharges considerable quantities of solid material and nitrogen and phosphorus. The dispersion of the effluent was traced using coprostanol and its presence was detected several kilometers away from the discharge point (El Sayed and Niaz, 1999).

This study was undertaken to measure the impact of sewage discharge on the level of organic carbon and the elements Al, Fe, Mn, Cu, Zn, Cr and V in the sediments and suspended particulate matter (SPM) of the coastal area and to investigate the processes that may influence their distribution.

Area of Study

The coastal area under investigation lies between 21°10′ and 21°22′N″, south of Jeddah city and extends for about 10 km (Fig. 1). The area is composed of two zones:





Fig. 1. Study area and sampling locations: a) coastal strip; and b) dilution basin.

1) A narrow coastal strip (CS) extending ~10 km south of the discharge point and lying between the fringing reef and the shoreline. Both width and depth of the area vary considerably but are rarely greater than 500 and 2 m respectively (Fig. 1a).

2) A shallow lagoon type basin in which the effluent is discharged and diluted (DB). Natural and artificial barriers limit water circulation particularly in the south of the lagoon (Fig. 1b).

Detailed description of the area is given in El Sayed (2002a)

Material and Methods

i – Sample Collection and Preparation

To achieve the defined objectives we must recognize the composition of the suspended solids of the effluent itself. Due to the expected temporal variability, 18 effluent water samples were collected hourly; sampling started at 07 am. For the analysis of trace elements, water samples were collected in acid pre-cleaned polyethylene bottles, while glass bottles were used for the recovery of suspended particulate matter (SPM) for the determination of particulate organic carbon (POC). Samples were immediately placed in iceboxes until transported to the home laboratory.

Twenty-seven sampling locations were selected to represent the study area. Nine stations situated at regular intervals were defined in the CS area and 18 stations were chosen in the DB area (Fig. 1a&b). Surface sediments from the CS area were manually collected by scoping. In the DB area, sediments were collected using a grab sampler. Samples were placed in plastic bags and stored in icebox until transported to the laboratory. For the sampling of SPM from the DB, surface water was manually collected in appropriate clean containers on Z-boat and stored in iceboxes.

In the laboratory, suspended matter assigned for the analysis of POC was recovered on pre-weighed Whatman GF/C membranes pre-combusted at 450°C using a Millipore all-glass filtration system. After filtration, filters were oven dried at 70°C and reweighed to determine the weight of the SPM and stored for analysis. SPM used for the analysis of trace elements were obtained by filtering water samples through 0.45 μ m pores size Mellipore cellulose acetate membranes using Sartorius polycarbonate filtration system. Filters and filtration apparatus were acid cleaned according to the conventional methods (Aminot and Chaussepied, 1983). Dried filters were weighed before and after filtration to calculate the weight of the recovered material. Sediments were freeze-dried and representative subsamples were taken for grain size analysis. Subsamples for chemical analysis were sieved to separate particles greater than 2 mm. 1 - Grain size analysis: Dried sediments were subjected to standard wet sieving method for the determination of the three major fractions, gravel, sand and mud.

2 - Carbonate determination: Carbonate content in the sediments was estimated by treating a known weight of the dried powdered sediments with 0.2 M HCl for 16 hours. The weight loss was considered equivalent to the carbonate content.

 $3 - Organic \ carbon$: Organic carbon was measured in the SPM using the wet dichromate-sulfuric acid oxidation method (Le Corre, 1983). The same method was applied on sediments but the volume of the oxidant and the sample weight were adjusted according to the sediment nature.

 $4 - Trace \ elements^*$: The elements Al, Fe, Mn, Cu, Zn, Cr and V were measured in the powdered freeze-dried sediments and SPM after acid digestion using a mixture of HNO₃-HF-HClO₄. Digestion was carried out under reflux in Teflon cups at about 120°C for 12 hours after which the extract was evaporated to near dryness and the residue was taken in 10-15 ml of hot 1 M HCl. Concentrations in the acid extract were measured using Atomic Absorption Spectrophotometer (Varian SpectraAA plus 250) excepting Al, which was measured using ICP (Perkin Elmer 400). The accuracy and precision of the measurements were checked by analyzing ten replicates of the reference material LKSD No. 287 (CNMET, Canada) and the reference marine sediment 356 (IAEA, Monaco). The analytical results and the certified values are in close agreement (Table 1).

| Element | Al ₂ O ₃ | Fe µgg ⁻¹ | $\begin{array}{c} Mn\\ \mu gg^{-1} \end{array}$ | Cu µgg ⁻¹ | $Zn \ \mu gg^{-1}$ | Cr µgg ⁻¹ |
|------------------------|--------------------------------|-------------------------|---|--|--------------------|-------------------------|
| Certified value | 5.9 | 2.8 | 229 | 18.5 | 194 | 33 |
| Analytical value SD | 5.53 ± 0.1 | 2.13 ± 0.05 | 204 ± 11 | $\begin{array}{c} 16.8 \\ \pm \ 0.8 \end{array}$ | 187 ± 6 | 38 ± 2 |

TABLE 1. Comparison between the analytical and certified concentrations in the reference material⁺.

⁺The reference sample BCSS-1 (NRCC) was analyzed for Mn and Cu; for the other elements the reference sample LKSD-4 (CCRMP) was used.

Results

i – Effluent Composition and Fluxes

The composition of the effluent discharge is generally determined by the type of activities connected to the network, type of treatment and the hydraulic flow. The later determines the residence time in the network and the treatment station that will affect interactions and the treatment efficiency.

^{*}Al, Cr and V were only measured in sediments and V was not measured in the coastal strip sediments.

The hourly fluctuations of SPM, OC and trace elements are presented in Table 2. Both SPM and POC showed, with two exceptions, a relatively regular distribution. SPM averaged 91 mgl⁻¹ indicating a weak epuration efficiency. This is confirmed by the concentration of the POC, which averaged 37.4%. If we consider that OC represents approximately 50% of the organic matter, organic matter in the effluent suspended matter will represent about 75%. In typical untreated sewage, organic matter represents about 80% of the total solid load (Aminot *et al.*, 1990).

| Sampling | SPM mg/l | POC | Al ug/g | Fe | Mn ug/g | Cu | Zn | Cr |
|----------|-------------|-------|------------|-------|------------|------|------|------|
| time | IIIg/1 | 70 | μg/g | µg/g | µg/g | µg/g | µg/g | µg/g |
| 07 | 119 | - | 7558 | 9605 | 151 | 93 | 1750 | 442 |
| 08 | 93 | 38.80 | 8201 | 10194 | 161 | 97 | 1655 | 403 |
| 09 | 98 | 37.65 | 6261 | 9357 | 181 | 83 | 1450 | 264 |
| 10 | 95 | 31.53 | 8681 | 10514 | 194 | 111 | 1366 | 292 |
| 11 | 82 | 36.87 | 7837 | 9606 | 185 | 101 | 1845 | 404 |
| 12 | 73 | 31.81 | 7926 | 9607 | 188 | 136 | 1627 | 293 |
| 13 | 109 | 42.18 | 6705 | 9667 | 154 | 115 | 1660 | 333 |
| 14 | 103 | 28.49 | 3762 | 4573 | 107 | 73 | 2159 | 181 |
| 15 | 120 | 40.02 | 6873 | 7409 | 164 | 96 | 1479 | 259 |
| 16 | 70 | 36.41 | 9604 | 10818 | 153 | 156 | 2327 | 331 |
| 17 | 70 | 35.43 | 7299 | 4262 | 146 | 110 | 1307 | 311 |
| 18 | 94 | 36.67 | 7594 | 8906 | 172 | 109 | 1445 | 328 |
| 19 | 74 | 38.76 | 9122 | 9890 | 187 | 108 | 1362 | 358 |
| 20 | 62 | 28.73 | 8743 | 6830 | 158 | 118 | 1193 | 375 |
| 21 | 83 | 38.22 | 11315 | 9654 | 185 | 130 | 1110 | 444 |
| 22 | 76 | 35.50 | 13857 | 7679 | 196 | 125 | 1490 | 536 |
| 23 | 146 | 37.52 | 15161 | 6883 | 161 | 123 | 1590 | 579 |
| 24 | 72 | 38.81 | 14944 | 8876 | 188 | 132 | 1209 | 412 |
| Average | 91.6 | 36.08 | 8970 | 8574 | 168 | 112 | 1557 | 364 |
| RSD | 3.36 | 3.84 | 34 | 22 | 13 | 18 | 20 | 27 |

TABLE 2. Concentration of SPM, POC and particulate trace elements in the effluent.

Al and Fe are by far the dominant elements with concentrations averaging 8970 and 8574 μ gg⁻¹ respectively. Concentrations of Zn and Cr, 1557 and 364 μ gg⁻¹ respectively, are also remarkably high while Cu and Mn are the last in importance but still have elevated concentrations (Table 2). A simple correlation analysis reveals the partition of the elements into two groups. The first is

composed of Cu, Cr and Al while the second is constituted of Fe-Mn association (Fig. 2). No correlation was found between any of the elements and the POC.



FIG. 2. Relationship between Fe and Mn, and Al and Cu and Cr in the SPM of the effluent.

The daily mass emission of SPM, POC and trace elements was calculated using the average effluent composition and supposing an average daily water flow of 100,000 m³. The fluxes given in Table 3 are considered as representing the lower limits because of the use of minimum approximation for the water flow. It appears that the sewage effluent represents an important source of POC and trace elements particularly in the absence of other land-based sources.

| Element | Kg/day | Kg/year |
|---------|--------|----------------------|
| SPM | 9160 | 3.34×10^{6} |
| POC | 3308 | 1.21×10^{6} |
| Al | 82 | 30 000 |
| Fe | 80 | 29 000 |
| Mn | 1.5 | 548 |
| Cu | 1.0 | 365 |
| Zn | 14.3 | 5200 |
| Cr | 3.3 | 1205 |

TABLE 3. Daily and annual mass emission of SPM, POC and particulate trace elements into the coastal area.

ii – Field Results

A – Coastal strip sediments

The area is mainly covered with muddy-sand sediments. The sediment veneer is the result of extensive erosion of reefal limestone marine bar and coastal terraces bordering the coastline (Basaham et al., 1998). Carbonates represent the major component of the sediment matrix averaging 61% (Table 4). This means that about 40% of the sediments are land-derived material transported by wind and episodic runoff (Basaham et al., 1998). Organic carbon (OC) ranged between 0.63 and 1.42% averaging 0.82%. The most organic rich sediments are those collected from the area near to the sewage outfall and the lowest values are generally associated with the highest sand contents. These concentrations are generally higher than the average 0.4% measured in uncontaminated Red Sea sediments (Mohamed, 1949; El Saved and Hosny, 1980; Behairy et al., 1983; Basaham et al., 1998). The OC enrichment is most probably due to the enhanced primary productivity resulting from the discharge of great quantities of nutrients with the wastewater that is added to the organic matter discharged with the effluent (El Sayed, 2002a). Water eutrophication is depicted from the large algal mat coverage that is observed particularly in the northern part of the area near the discharge point.

| Element | OC % | Carbonate % | Al % | Fe % | Mn μg/g | Cu µg/g | Zn μg/g | Cr µg/g |
|---------------------------|---------|----------------|---------|---------|------------|------------|------------|------------|
| Count | 9 | 9 | 9 | 9 | 9 | 9 | 9 | 9 |
| Average | 0.82 | 61 | 0.68 | 0.27 | 49 | 5.3 | 13.1 | 20.9 |
| SD | 0.25 | 16 | 0.51 | 0.19 | 31 | 3.0 | 6.1 | 4.8 |
| Maximum | 1.42 | 84 | 1.48 | 0.60 | 97 | 10.0 | 23 | 28.0 |
| Minimum | 0.63 | 48 | 0.11 | 0.04 | 9 | 1 | 5.0 | 13.9 |
| Arabia* Gulf sediments | _ | > 90 | 0.29 | 0.26 | 71 | 5 | 12 | 19 |
| Al-Kharar [#] | _ | _ | 0.80 | 0.72 | 70 | 4 | 9 | _ |
| Al Kasr** | _ | _ | _ | 0.20 | 20 | 5 | 11 | _ |

TABLE 4. Average composition of the surface sediments of the coastal strip area compared to that of other carbonate rich sediments.

*Sandy sediments, Basaham et al. (1998)

[#]Basaham, (personal communication)

**El-Sayed (1983)

Element concentrations are relatively low and reflect the sediment nature (Table 4). Concentration of Al, Fe and Mn (average 0.68, 0.27% and 49 μ gg⁻¹ respectively), mostly found in detrital material, are very low due to dilution with carbonate sediments. It appears from Table 5 that the concentrations of the ensemble of the measured elements are comparable to those measured in high carbonate Red Sea coastal sediments (El Sayed, 1983; Abu-Shanab, 2000) and the Arabian Gulf sandy sediments (Basaham *et al.*, 1998). It could therefore be concluded that the contaminated solids discharged with the effluent water are mostly retained in the vicinity of the discharge area and that trace metal pollution will be limited to this region.

B – The Dilution Basin (DB)

1- Sediment characteristics

The consequences of sewage dumping are clearly detected due to important modifications of sediment texture and organic carbon. The major sediment characteristics are given in Table 5. Sediments are generally coarse grained; the sand fraction represents more than 60% in more than 80% of the samples. Gravel showed a remarkable increase reaching more than 40% in some locations. This fraction is composed of whole shells of mollusks and gastropods. Carbo-

nate is still the major sediment component, however, with respect to the CS sediments it showed a considerable increase with an average of 93.6%. Local development of calcareous organisms may have largely contributed to this enrichment.

| Sediment component | Gravel % | Sand % | Mud % | Carbonate % |
|--------------------|-------------|-----------|----------|----------------|
| Average | 8.9 | 69.9 | 19.5 | 93.6 |
| Minimum | 0.1 | 20.8 | 2.4 | 78.2 |
| Maximum | 40.8 | 92.3 | 79.1 | 99.0 |

TABLE 5. Average grain size composition and carbonate content in the DB sediments.

Using the hydrochemical parameters, El Sayed (2002a) divided the area into an outer zone I, including stations from 1 to 10 and station 18, slightly influenced by the sewage discharge and an inner zone II, including stations 11 to 17 where the influence is clearly felt. The distribution of the OC appears to follow the same trend (Fig. 3a and Table 6). In the outer zone OC is generally less than 1% averaging 0.45% and is comparable to the concentrations encountered in remote areas free of anthropogenic inputs. In the inner zone OC averages 3.35% and is about eight times higher than it is in the first one. The overall OC average in the entire area is double that in the CS sediments. Stations 11 and 14 are particularly rich in OC while Station 13, the nearest to the effluent discharge, showed lower concentrations (Fig. 3a). Grain size distribution justifies this difference. Station 13 is under the influence of the turbulence caused by the effluent; only coarse and dense particles can settle. At the other stations, the low energy environment enables settlement of fine material; sediments at both sites are entirely muddy.

2- Distribution of trace elements in surface sediments

The distribution of major and trace elements in the sediments of the area is the mirror image of the OC distribution and reflects the role of the sewage effluent as a major source of these elements into the area (Tables 6 and Fig. 3a&b). The distribution satisfies the distinction of two zones, one unaffected by the sewage discharge while the other one is affected to varying degrees depending on the distance from the effluent and the sediment type. This is clearly shown in Table 7 where average concentration for each area is presented separately and the ratio between them is calculated. The ratio varied between 2.7 and 6.9 for the elements Al, Fe, Mn, Cr and V, and is 26 for Cu and 28 for Zn.









| Element | OC % | Al µg/g | Fe µg/g | Mn μg/g | Cu µg/g | Zn µg/g | Cr µg/g | V µg/g |
|-----------------------------|---------|------------|------------|------------|------------|------------|------------|-----------|
| Overall average | 1.56 | 4698 | 1978 | 22 | 24.8 | 80 | 7.6 | 5.8 |
| Average I Sts. 1-10 & 18 | 0.45 | 2158 | 554 | 13.3 | 2.3 | 6.9 | 4.2 | 2.4 |
| Average II Sts. 11-17 | 3.3 | 8933 | 3815 | 36.5 | 60.3 | 195 | 12.9 | 11.0 |
| II/I | 7.5 | 4 | 6.9 | 2.7 | 26 | 28 | 3.1 | 4.6 |

TABLE 6. Average OC and elemental concentration in the sediments of the two zones of the dilution basin.

3- Distribution of POC and trace elements in SPM

The results of the average concentration of SPM, POC, Fe, Mn, Cu and Zn are given in Table 7. POC is generally higher than 3% and its overall average is 5 times its average concentration in the sediments but is largely lower than its concentration in the effluent. Settlement of organic rich particles and mixing with organic poor particles may explain the difference with the effluent. Trace element concentrations are also invariably lower in the SPM of the DB than in the SPM of the effluent. With respect to the concentrations in the sediments, the suspended matter has lower Fe concentration, higher Mn and Zn and comparable Cu.

| Area | SPM mg/l | POC % | Fe µg/g | Mn μg/g | Cu µg/g | Zn µg/g |
|--------------------------------|----------------|----------------|-------------------|-----------------|----------------|----------------|
| The entire basin (range) | 40 (17-125) | 5.06 (3-10) | 1147 (50-4300) | 84 (3.6-160) | 18 (7.8-63) | 113 (8-660) |
| Outer zone I Sts. 1-10 & 18 | 23.2 | 3.7 | 566 | 22.9 | 12.9 | 36.6 |
| Inner zone II Sts. 11-16 | 70.8 | 7.2 | 2020 | 175 | 25.7 | 228 |
| II:I | 3.1 | 1.95 | 3.6 | 7.6 | 2.0 | 6.2 |

TABLE 7. Average concentration of SPM, POC and particulate trace elements in the dilution basin.

The geographic distribution of SPM, POC and particulate elements is similar to the distribution of the hydrochemical parameters (El Sayed, 2002a) and to that of trace elements in the sediments (Figs. 4 & 5). The schematic division of the area into two zones seems also applicable to the particulate trace elements. The average concentration calculated for each zone (Table 7) shows that concentrations in the zone near the effluent are generally highly enhanced particularly for Mn and Zn. The significant negative correlation between salinity and the constituents of the SPM and the positive correlation between the constituents themselves (Table 8) supply additional evidence on the role of the effluent, which act as principal source of SPM and associated elements.



FIG. 4. Distribution of SPM and POC in the dilution basin.





| Element | SPM | POC | Fe | Mn | Cu | Zn |
|----------|--------|--------|--------|--------|--------|--------|
| Salinity | -0.916 | -0.884 | -0.883 | -0.902 | -0.720 | -0.890 |
| SPM | | 0.868 | 0.911 | 0.966 | 0.824 | 0.920 |
| POC | | | 0.852 | 0.803 | 0.562 | 0.734 |
| Fe | | | | 0.949 | 0.830 | 0.924 |
| Mn | | | | | 0.919 | 0.982 |
| Cu | | | | | | 0.939 |

TABLE 8. Correlation matrix for the different components of the SPM in the dilution basin.

Discussion

In arid regions where land runoff is very scarce, land-based sources principally sewage effluents become principal sources of liquid and solid contaminants to the coastal area. Trace elements are remnant contaminants; their ultimate fate is the sediments (Forstner and Wittmann , 1983). The study of the biogeochemistry of trace elements is of great importance in order to define their pathways and consequently their probable impact.

It has been shown that the sewage effluent of Al-Khumrah STS constitutes an important source of OC and trace elements to the coastal area south of Jeddah (Table 3). It has also been shown that, distant from the effluent (CS area), the impact is limited to the enrichment of bottom sediments in organic carbon and no evidence of trace element accumulation was observed.

In the area of discharge, the geographic distribution of OC and trace elements in the sediments revealed that their build-up is taking place near to the discharge point and that close associations exist between them. OC is positively correlated with all the elements (Table 9) and preferentially with Cu and Zn. Association of Cu and Zn with the organic matter in the marine environment is widely reported (Angelidis and Gibbs, 1989; Mat *et al.*, 1994, Basaham and El Sayed, 2002a). Both elements are known to form stable complexes with the organic matter and may adsorb on it. However, the correlation between OC and trace elements including Al and Fe is not very strong. The strong and significant correlation with Al and Fe support the association of trace elements with the mineral phase (Table 9). Al is found in the aluminosilicate minerals while for Fe the situation is more complex due to its redox properties. According to previous studies (El Sayed and Niaz, 1999; El Sayed, 2002a) oxic bottom water overlay surface sediments in the outer basin; Fe is expected to be found as hydrous oxides reputed for their high adsorptive capacity (Laxen, 1984; Fegan *et al.*,

| Element | Fe | Mn | Zn | Cu | Cr | V | OC | Carbonate |
|---------|-------|-------|-------|-------|-------|-------|-------|-----------|
| Al | 0.962 | 0.904 | 0.855 | 0.784 | 0.945 | 0.947 | 0.531 | -0.844 |
| Fe | | 0.946 | 0.924 | 0.873 | 0.962 | 0.956 | 0.500 | -0.849 |
| Mn | | | 0.810 | 0.732 | 0.948 | 0.958 | 0.453 | -0.888 |
| Zn | | | | 0.984 | 0.899 | 0.854 | 0.752 | -0.840 |
| Cu | | | | | 0.821 | 0.778 | 0.826 | -0.811 |
| Cr | | | | | | 0.973 | 0.603 | -0.860 |
| V | | | | | | | 0.613 | -0.865 |
| OC | | | | | | | | -0.572 |

TABLE 9. Correlation matrix for the major and minor constituents of the sediments of the dilusion basin.

1992). In the internal zone, anoxic conditions prevail in the bottom water and sediments. Under these conditions dissolved iron and the solubilized Fe (II) will precipitate as monosulphides or as pyrite (Jackobs *et al.*, 1985; Heurta-Diaz and Morse, 1992). Pyrite was detected in the sediments of the area and considered as one of the important mineral constituents (El Sayed *et al.*, 2002). Trace metals may co-precipitate with iron sulfide or may form their own insoluble sulphides. The kinetics of the oxidation-reduction reaction of the redox sensitive elements differs according to the element in question, which may introduce some modifications in the inter-element relationships. This is clearly illustrated by calculating the enrichment factor (EF), which is represented by the equation:

EF = (element conc./Al conc.)_{polluted area} / (element conc./Al conc.)_{reference}

the reference concentrations are represented by the averages calculated for the outer zone in the DB. The results (Table 10) indicate the relative enrichment of Fe, Cu and Zn and the impoverishment of Mn and Cr while V shows a constant ratio to Al. It is interesting to remark that the simple comparison of the element concentrations in the two zones is misleading since it indicates that the inner zone is invariably contaminated relative to the outer one. The enrichment of iron and the depletion of Mn despite their common redox behavior could be explained by the rapid kinetics of the precipitation of FeS_x in the presence of excess H₂S (Stumm and Morgan, 1981) resulting in the apparent enrichment of Fe. On the contrary reduced Mn (II) continues to diffuse to the water column producing the inverse effect. It seems that Cr, which has two oxidation states Cr (III) and Cr (VI), behaves similar to Mn. Jung *et al.* (1996) interpreted Cu enrichment and Mn depletion in anoxic sediments to precipitation of Cu sulfide and the dissolution of Mn oxide. Cu and Zn are known to form stable insoluble

sulfides and they may form solid solution with iron sulphide or may adsorb on it (Piper, 1971; Raiswell and Plant, 1980; Emerson *et al.*, 1983; Shea and Helz, 1988; Heurta-Diaz and Morse, 1992). Moreover, Cu and Zn tend to be associated with organic matter, which explains the high enrichment factor. Plot of the concentration of the elements against Al illustrates the situation clearly (Fig. 6). Plot of the enriched elements (Fe, Cu and Zn) is best fitted by an exponential model while a linear model best fits Mn, Cr and V. Another support comes from the comparison between the concentrations of sedimentary and particulate trace elements in the inner zone of the dilution basin (Table 11). Fe is 47% lower in the SPM whereas Mn is more than four times higher and Cu is also distinctly lower in the SPM. Zn has almost comparable concentrations.

TABLE 10. Average element/A1 ratios calculated for the sediments of the two zones of the dilution basin and the enrichment factor as defined in the text.

| Element | Fe | Mn | Cu | Zn | Cr | V |
|--------------------------------|------|-------|-------|-------|-------|-------|
| Outer zone I Sts. 1-10 & 18 | 0.26 | 0.006 | 0.001 | 0.003 | 0.002 | 0.001 |
| Inner zone II Sts. 11-17 | 0.43 | 0.004 | 0.007 | 0.022 | 0.001 | 0.001 |
| EF | 1.7 | 0.66 | 6.33 | 6.83 | 0.74 | 1.11 |

Additional evidence may arise from the examination of the behavior of SPM and its constituents during their transit in the dilution basin. Based on the observation that the effluent water is the major supplier and vector of the SPM, the effluent water was attributed zero salinity and the concentrations of the different components equal the average composition of the effluent (Table 2). The scatter diagrams reveal some interesting points (Fig. 7). The behavior of SPM is not only governed by the dilution of the effluent water with seawater. SPM is in excess at intermediate salinities. Resuspension of bottom sediments and enhanced algal development are the most probable causes. It has been shown that 40% of the effluent discharged inorganic nitrogen are consumed in the area resulting in the formation of 9 tons of organic matter (El Saved, 2002a). POCsalinity relationship reveals the presence of excess POC than that should have been found according to a simple dilution process (Fig. 7). Average OC concentration in the sediments of the area of the inner basin is 3.58%* which is largely lower than its corresponding value in the SPM (7.45%). It is therefore expected that any sediment resuspension will result in an appreciable loss of POC. Considering that the concentration of SPM at salinity 39 was 18 mgl⁻¹ (average of the lowest values measured at salinity 39) and the average concentration at the

^{*}Average OC in sediments and SPM was calculated for stations 11-16, station 17 was not included due to lack of SPM data.



Fig. 6. Relationship between Al and Fe, Cu, Zn, Mn, Cr and V in the sediments of the dilution basin.

| Component | POC % | Fe µgg ⁻¹ | Mn µgg ⁻¹ | Cu µgg ⁻¹ | Zn µgg ⁻¹ |
|------------|-------|----------------------|----------------------|----------------------|----------------------|
| SPM* | 7.45 | 2020 | 157 | 25.7 | 228 |
| Sediments* | 3.58 | 3815 | 36.5 | 60.3 | 195 |
| Ratio | 2.1 | 0.53 | 4.3 | 0.43 | 1.17 |

TABLE 11. Comparison between the concentration of OC and trace elements in the SPM and sediments of the inner zone of the DB.

n =sample 17 was not included (see text).

intermediate salinity 36 was 71 mgl⁻¹ (Table 7) and knowing the concentration at zero salinity (concentration in the effluent water = 91.6 mgl⁻¹), it was found that the SPM in the inner basin was constituted of 7.7 l^{-1} mg from the effluent, 16.61 l^{-1} mg from the outer zone and an excess of 47.34 mg l^{-1} which is believed to come from sediment resuspension and primary productivity. Using concentrations OC in the bottom sediments in the inner zone (supposing that all the excess SPM is coming from bottom sediment resuspension), concentrations in the SPM in the outer zone and concentrations in the suspended matter of the effluent, the theoretical concentrations resulting from the mixing of these three end-members in the calculated proportions become available (Table 12). Comparison of the reconstitued POC concentration with that measured in the inner zone of the dilution basin reveals the presence of a surplus of about 0.4 mg l^{-1} organic carbon, which should have resulted from the in situ primary productivity (Table 12). The real contribution of the algal production is certainly more than enough to compensate for the loss due to the resuspension of sediment poor in organic matter.

The plot (Fig. 7) shows that Mn is in excess in the intermediate salinity area with respect to a pure mixing process confirming the hypothesis of release from bottom sediments under reducing conditions and re-oxidation and adsorption on SPM in the surface oxic waters. The observed excess is the result of two antagonistic processes; one is the product of the reduction in the sediments and the refixation on the SPM that results in the augmentation of the concentration on the SPM. The other is the resuspension of depleted bottom sediments, which would produce the inverse effect.

The other elements Fe, Cu and Zn showed also excess at intermediate salinities, which could be attributed to resuspension and mixing with enriched sediment particles. Measured concentrations of the elements which are enriched in the bottom sediments iron, Cu and Zn were found lower than the calculated concentrations. The difference is interpreted as being due to presence of freshly formed organic matter not yet enriched in these elements that act as diluting agent. Iron is the most affected by this process because it is mainly found in the



Fig. 7. Relationship between salinity and SPM, POC, particulate Mn, Fe, Cu and Zn in the dilusion basin.

detrital material and the dilution effect is consequently very high. Meanwhile reconstituted Mn concentration, element impoverished in bottom sediments, is largely inferior to the measured one. This is believed to result from the read-sorption and/or precipitation of the solubilized sedimentary Mn as particulate Mn in the surface water layer due to the prevailing oxidizing conditions.

| Contribution | OC mgl ⁻¹ | Fe mgl ⁻¹ | Mn mgl ⁻¹ | Cu mgl ⁻¹ | Zn mgl ⁻¹ |
|----------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| From the effluent | 2.54 | 61.7 | 1.2 | 0.80 | 11.05 |
| From the outer basin SPM | 0.61 | 9.4 | 0.38 | 0.43 | 0.61 |
| Resuspension from sediment | 1.69 | 180.4 | 1.75 | 2.85 | 9.22 |
| Total reconstituted | 4.84 | 251.1 | 3.33 | 4.08 | 20.88 |
| Measured concentration | 5.22 | 143.0 | 12.43 | 1.83 | 16.20 |

TABLE 12. Comparison between the measured and reconstituted concentrations of OC, Fe, Mn, Cu and Zn in the SPM of the inner basin.

Conclusion

Al-Khumra sewage effluent discharges more than $100,000 \text{ m}^3$ of mixed treated and untreaterd sewage to the coastal area south of Jeddah and represents a major source of POC and trace elements in the area. Flux calculations indicate that the effluent carries daily about 9 tons of solid wastes. 3.5 tons of organic carbon, 80 kg of Al, 80 kg of Fe 1.5 kg of Mn, 1 kg of Cu, 14 kg of Zn and 3 kg of Cr are associated with the solid material. Using the specific flux as a comparison tool, it is concluded that the treatment efficiency of the station is insufficient.

The distribution of OC and trace elements in the area has shown that the effluent is the major source and that its impact is very restricted and is localized in the inner part of the discharge basin near the discharge point where absolute concentrations are several times higher than the outer area.

In the sediments, oxidation-reduction reactions and probably the association with the organic matter controlled the distribution of the elements and enhanced the enrichment of Fe, Cu and Zn and the depletion of Mn and Cr. This mechanism is supported by the results of the distribution of the particulate trace elements.

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محمد عبد الخالق السيد^ا المعهد القومي لعلوم البحار والمصايد ، الإسكندرية – مصر

المستخلص. تستقبل المنطقة الواقعة جنوب مدينة جدة على الساحل الشرقي للبحر الأحمر حوالي مائة ألف متر مكعب من مياه الصرف الصحي يوميًا. تم تحليل المواد الصلبة المحمولة بواسطة مياه الصرف وذللك لقياس محتواها من الكربون العضوي ، الألومينيوم ، الحديد ، المنجنيز ، النحاس ، الزنك و الكروم و حسبت كميات العناصر التي تلقى يوميًا. ولتتبع تأثير مخلفات الصرف على المنطقة الساحلية فقد تم رصد نفس العناصر في الرواسب والمواد العالقة في منطقة حوض الصرف وفي الحزام الساحلي و حتى مسافة عشرة كيلومترات جنوب نقطة الصرف.

وقد وجد أن تأثير المصب على المنطقة لا يتعدى حدود المنطقة الواقعة بالقرب من نقطة الصرف حيث كانت التركيزات المقاسة لجميع العناصر في الرواسب و المواد العالقة أضعاف مثيلاتها في الأجزاء الأخرى من منطقة الدراسة. وقد وجد أن توزيع العناصر المختلفة يتفق و مسار تخفيف مياه الصرف. وعند استخدام الألومنيوم كعنصر مرجعي وجد أن العناصر التي تراكمت في الرواسب كانت الحديد والنحاس والزنك بينما اضمحلت تركيزات المنجنيز و الكروم. وقد عزى هذا السلوك إلى الاختلاف في ديناميكية عملية الأكسدة – إختزال لعناصر العيضو وترسيب والكروم بينما عزى ذلك إلى التفاعل مع المواد العضوية وترسيب

العنوان الحالي : كلية علوم البحار ، جامعة الملك عبد العزيز ، ص.ب. ٨٠٢٠٧ ، جــدة ٢١٥٨٩ ، المملكة العربية السعودية.

الكبريتيدات لعناصر النحاس و الزنك. في المواد العالقة أبدت جميع العناصر حيوداً موجبًا عن الخطية في علاقاتها مع الملوحة وقد عزيت الزيادة إلى إعادة تعليق رواسب القاع في حالة الحديد و النحاس و الزنك و إلى إعادة ادمصاص العناصر التي سبق تحريرها من الرواسب مثل المنجنيز.