Environmental Assessment, Documentation and Spatial Modeling of Heavy Metal Pollution along the Jordan Gulf of Aqaba Using Coral Reefs as Environmental Indicator

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By

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Umweltbewertung, Dokumentation und räumliche Modellierung der Schwermetallverschmutzung entlang der Küste von Aqaba (Jordanien) unter Verwendung von Korallenriffen als Umweltindikator

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Abstract

To get meaningful data for pollution assessment along the Jordanian coastline, and in order to avoid the ambiguities usually associated with the analysis of seawater and sediments, coral reefs were used as an environmental indicator as their skeletons assimilate records of metals over hundreds of years.

Two phases of reef sampling were carried out. The first included regular samples taken along the coastline of Aqaba (27km long) at depths of 4-15m, and used to determine spatial distribution of pollution. The second phase included three 20cm-deep cores obtained from within the industrial zone. These cores were drilled from pre-dated communities, where the growth rate was determined earlier to be 10mm y^{-1}, therefore the core obtained represented a period of 20 years (i.e. 1980-2000). The cores were used to reconstruct the metal pollution history at the most heavily used site along the coast (industrial zone).All samples were examined with respect to their metal content of Cd, Pb, Cu, Zn, Ni, and Cr.

Almost all of them have shown records above the calculated background values. Mean values of Cd, Pb, Cu, Zn, Ni and Cr recorded along the coast were 1,25; 4,26; 9,76; 11,40; 2,29 and 10,522, µg g^{-1} respectively, and for core samples 1.4; 4.2; 5.7; 6.4; 2.3 and 8.21 µg g^{-1} respectively.

Spatial distribution of metal enrichment in reef samples have shown a general and clear increasing trend towards the south. Same increasing trend was also in core samples where the six metals have shown a prominent increasing trend towards the core surface indicating an increase of coastal activities during the last twenty years.

High and relatively high values were recorded at the oil port, the industrial area and main port, and thus categorized as highly impacted areas. Intermediate metal content were recorded in samples of the north beach, and thus classified as being relatively impacted, where the lowest metal concentrations were observed at the marine reserve, the least impacted site along the coast.

The high enrichment of metal is attributed mainly to anthropogenic impacts. The natural inputs of the six metals studied in the Gulf of Aqaba are generally very low, due to the geographic positions and the absence of wadi discharge and as a result of low rainfall.

Several potential sources of heavy metals were investigated. The industrial-related activities, port operations and phosphate dust were among the main sources currently threatening the marine ecosystem in Aqaba.

Applying the Principle Components Analysis method (PCA) to all samples taken along the coastline has resulted in categorizing three different groups according to their metal enrichment, the first is composed of samples taken from the north beach and the main port with intermediate to high enrichment, the second joined the samples of the marine park and the marine reserve with low and relatively low enrichment, and the last group joined samples of the industrial zone and the oil port with high enrichment.

The Principle Component Scores were also utilized to confirm the spatial distribution and relationships of the examined heavy metals along the coast. Two models (interpolated by SURFER® 7.0 and ArcView® 3.2a) were developed, the first was based on the PC scores of the first component, and shows clearly the positive anomalies in metal concentrations along the coast. The second model was developed by plotting the second factor scores on a landuse map of Aqaba. According to these models, it has shown that the positive anomalies are associated with three different zones; industrial area, the main port and the oil port.

The results have shown that coral reefs can be used as good environmental indicator for assessments and monitoring processes, and they can provide data and information on both the spatial distribution of pollution and their history.

The present work is the first to document the environmental status along the whole coast of Aqaba and the first to use coral reef as a tool/ indicator.

Zusammenfassung

Um aussagekräftige Daten zur Einschätzung der Umweltverschmutzung entlang der jordanischen Küste zu erhalten, und um die normalerweise mit der Analyse des Meereswassers und den Sedimenten entstehenden Amlugintäten zu vermeiden, wurden Korallenriffe als Umweltindikator benutzt, da sich in den Skeletten die Assimilation von Metalle über Jahrhunderte nachweisen lässt.

Die Riff-Probenahmen wurden in zwei Phasen durchgeführt. Die erste Phase umfasste reguläre Proben, die entlang der Küste von Aqaba (27 km lang) in einer Tiefe von 4-15 m entnommen wurden, um die räumliche Verteilung der Verschmutzung zu bestimmen. Die zweite Phase umfasste drei 20 cm tiefe Bohrkerne, die im Bereich der Industriezone entnommen wurden, um die Geschichte der Metallverunreinigung in dem am stärksten betroffenen Bereich entlang der Küste (Industriezone) zu rekonstruieren. Diese Kerne wurden in bereits früher datierten Riff-Kommunen mit einer Wachstumsrate von 10 mm/Jahr gebohrt. Die in einem Kern erfasste Periode beträgt somit etwa 20 Jahre (d.h. 1980-2000). Alle Proben wurden auf den Metallgehalt von Cd, Pb, Cu, Zn, Ni und Cr geprüft.

Fast alle Proben weisen Werte auf, die höher als die berechneten Hintergrundwerte liegen. Die verzeichneten Durchschnittswerte der regulären Proben entlang der Küste betrugen für Cd, Pb, Cu, Zn, Ni und Cr: 1,25; 4,26; 9,76; 11,40; 2,29 bzw. 10,522 µg g^{-1} und für die Kernproben betrugen die Werte: 1,4; 4,2; 5,7; 6,4; 2,3 bzw. 8,21 µg g^{-1}.

Die räumliche Verteilung der Metallanreicherung in den Riffen zeigt einen deutlich zunehmenden Trend in Richtung Süden. Der gleiche Trend findet sich auch in den Kernproben wieder, wobei die sechs Metalle zusätzlich auch einen deutlich zunehmenden Trend von unten nach oben aufweisen, und somitie die zunehmenden anthropogenen Aktivitäten im Küstenbereich während der letzten zwanzig Jahre anzeigen.

Hohe und relativ hohe Werte wurden im Ölhafen, der Industriezone und im Haupthafen verzeichnet und somit als stark betroffene Bereiche eingestuft. Mittelmäßige Metallgehalte wurden in den Proben am Nordstrand ermittelt und somit als relativ betroffen klassifiziert. Die niedrigsten Metallkonzentrationen wurden im Bereich des Marineschutzgebietes beobachtet, das somit das am wenigsten betroffene Areal entlang der Küste darstellt.

Die hohe Anreicherung der Metalle ist hauptsächlich auf anthropogene Einflüsse zurückzuführen. Der natürliche Eintrag in den Golf von Aqaba bei den sechs analysierten

Metallen ist im Allgemeinen recht niedrig, aufgrund der geographischen Position, den kleinen Niederschlagsmengen und folglich auch der geringen Schuttzufuhr aus den Wadis.

Verschiedene potentielle Herkunftsquellen der Schwermetalle wurden untersucht. Die industriebedingten Aktivitäten, Hafenbetrieb und Phosphatstaub konnten hierbei als Hauptverursacher der akuten Bedrohung für das Marine-Ecosystem in Aqaba erkannt werden.

Eine Hauptkomponentenanalyse (PCA) angewendet auf alle entlang der Küste entnommenen Proben ergab, dass sich drei verschiedene Gruppen in Abhängigkeit von der Metallanreicherung herausstellen lassen: die erste Gruppe umfasst Proben vom Nord-Strand und dem Haupthafen mit mittelmässiger und hoher Anreicherung, die Zweite enthält die Proben vom Marine-Park und dem Marineschutzgebiet mit niedriger und relativ niedriger Anreicherung, und die letzte Gruppe besteht aus den Proben der Industriezone und dem Ölhafen mit hoher Anreicherung.

Die Hauptkomponentenwerte (Principle Component Scores; PCS) wurden auch verwendet, um die räumliche Verteilung und die Beziehungen der getesteten Schwermetalle entlang der Küste zu bestätigen. Es wurden zwei Modelle entwickelt (interpoliert mit SURFER ® 7,0 and Arc View ® 3.2a). Das erste Modell basierte auf den PCS der ersten Hauptkomponente und zeigt klare positive Anomalien der Metallkonzentrationen entlang der Küste. Das zweite Modell basiert auf den PCS der zweiten Hauptkomponente und ist in einer Karte im Zusammenhang mit der Landnutzung von Aqaba dargestellt. Danach zeigt sich ein deutlicher Zusammenhang der positiven Anomalien im Zusammenhang mit den drei verschiedenen Landnutzungszonen, nämlich dem industriellen Areal, dem Haupthafen und dem Ölhafen.

Die Ergebnisse zeigen, dass sich Korallenriffe als Indikator für die Bewertung und überwachung von Umwelt prozessen eignet. Sie können Daten und Informationen, sowohl über die räumliche Verteilung von Umweltverschmutzungen, als auch über ihre Geschichte liefern.

Die vorliegende Arbeit ist die erste ihrer Art, die das Korallenriff als Instrument und Indikator verwendet, um den Umweltstatus entlang der gesamten Küste von Aqaba zu dokumentieren.

1 List of Contents

1 Gulf of Aqaba

1.1 Physical and Chemical Features

The Gulf of Aqaba oriented NNE-SSW is the northernmost sea-flooded part of the Syrian-African rift system. The gulf is a semi-closed basin, separated from the Red Sea by the Straits of Tiran, a narrow passage about 250m deep, (Fig.1). The gulf extends over a length of 180 km and a width of 5 to 26 km, and reaches almost 1800m depth.

Sea level in the northern part of the gulf fluctuates during the year by up to one meter. The level is high from December through May and lower during the period July through October. The difference is reportedly due to the influence of monsoon winds in the Indian Ocean (Hulings, 1989).

Tides in the gulf are minimal, with a range on the order of one meter or less. They are semi-diurnal (two high and two low tides every 24 hours).

Currents specifically, and circulation generally appear to be largely wind-driven, with additional influence from tides, density gradients, and evaporation. Prevailing winds are from north, and thus the predominant wave direction is from the north.

The gulf is characterized by a low rate exchange of water with the Red Sea due to the narrow and shallow passage of Straits of Tiran. The gulf also acts like closed lake, with summer stratification and biannual turnover. The lower mass of water is colder and nutrient-rich, and has even less exchange with the Red Sea across the shallow Straits of Tiran, than surface water. This can lead to algal blooms on the reef following winter storms, which cause upwellings. The residence time of water can exceed two years in the upper depths of the Gulf and three years in the lower depths (ISPAN, 1992).

The water of the gulf is exceptionally clear, the high transparency is related in part to the absence of major rivers or streams flowing into the sea.

The relative isolation of this desert-enclosed sea, coupled with exposure to an arid, hot climate and high evaporation, cause temperature and salinity to be unusually high as compared to the average range for oceans. Surface water temperature approaching 28 °C may occur during the summer months and fall to just above 20 °C in the winter. Temperatures within the water mass reflect a degree of stratification versus vertical and lateral mixing by water currents. Vertically, temperature falls within depth in the summer although there appears to be an inversion at certain depths in winter months because the deep water mass has a temperature reportedly above 20 °C.

The lack of regular fresh water input, and the high evaporation rate contribute heavily to the particularly saline conditions within the gulf. The salinity is relatively high and ranges between 40 and 45g/l compared to an ocean's average salinity of 35g/l. Vertical salinity differences are very small between 50-150m. In general, the eastern side of the Gulf is less saline, most likely due to the influx of Red Sea (ICRI, 1995).

Another prominent feature of the gulf is its great depth in proportion to its width. It has an average depth of 800m increasing to about 1,800m as a maximum depth.

The gulf is a host to more than 1000 species of fish, 110 species of hard coral, 120 species of soft coral in addition to sponges, snails, crabs and sea turtles, (Hulings,1989).

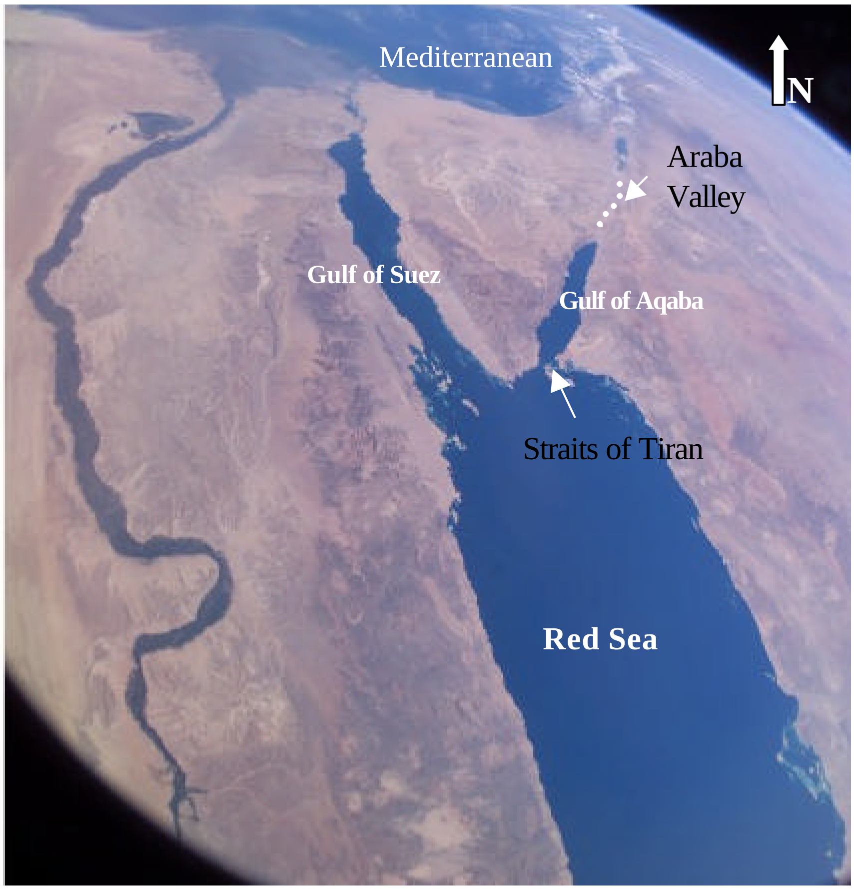


Fig. 1. Space photo showing the Red Sea and both; the Gulf of Aqaba and Gulf of Suez.

Twenty percent of molluscs and echinodermata as well as several species of algae occurring in the gulf may be endemic. Of between 300-350 species of fish which have been recorded in Aqaba, 7 are recognized as endemic, (ICRI, 1995).

These marine creatures live in a complex ecosystem where a very fragile equilibrium maintains all these animals in a necessary co-existence, as part of the chain which creates the coral reefs and their surroundings.

From almost invisible life-forms to huge fish or mammals, all are equally important and contribute to the food chain, thus creating the conditions for the building and the healthy state of the coral reef.

Despite the fact that the Gulf of Aqaba is one marine unit, there are still differences in relation to its currents, temperature, salinity and coral reef communities that make the northern part different from the southern and the western part different from the eastern one. Example of such differences is the presence of five species of sea grasses on the western coast, only three have been recorded in the eastern coast, (Heiss *et al.*, 1999).

In conclusion, all of the above special combinations of conditions makes the gulf especially vulnerable to the effects of pollution low rates of exchange, combined with high rate of evaporation mean that introduced pollutants can affect the gulf for long periods of time.

1.2 Geological Setting

The Gulf of Aqaba occupies the southern part of the segment of the great valley that extends from the Zagros-Taurus mountains in Turkey through the Red Sea and into East Africa.

In its greater depth and narrower width, the Gulf of Aqaba graben differs from the Gulf of Suez graben. The Gulf of Suez has experienced at least since Early or Late Eocene time, and since that time has been filled with sediments. By contrast, the Gulf of Aqaba did not originate until Late Pliocene or Early Pleistocene time and it lacks Neogene sediments. When rifting began, the Gulf of Aqaba was not connected to the Red Sea but extended as an isolated trough from the Araba Valley to the submerged ridge at the Straits of Tiran (Fig.1). The graben could have resulted from either movement in several stages along a left-lateral wrench fault, or from gravitational and tensional effects with dip-slip movements, the last major being of Middle Pleistocene age (Friedman,1985 in Hulings,1989).

The lateral submarine slopes of Gulf of Aqaba are fault planes and are virtual precipices; for the most part the shores are equally precipitous. Alluvial fans extend from the mountains to the shore and into the gulf.

The carbonate deposition and recent sedimentological systems in Aqaba, is very much a result of the unique tectonic history and the present tectonic setting. The gulf is marked by negative Bouguer gravity anomalies and minor magnetic anomalies, which suggest that the graben it occupies is a relatively simple downfaulted basin. The gulf is the southernmost active segment of the Dead Sea Rift. It is assumed that this is a transform plate-boundary. The left-lateral slip along the rift has since Miocene increased to an amount of 105 km. It separates the Sinai sub-plate in the west from the Arabian plate in the east. Boarding areas of the rift are elevated nearly 4 km. This elevation decreases northwards. The volcanic activities are all the same very minor. The rift connects the area of seafloor spreading beneath the Red Sea with the area of Zagros-Taurus of continental collision.

The long subparallel faults of the gulf encloses three big, deep and enlarged enechelon sediment basins. These are so called pull apart basins, fault bound depressions. The sediments infill are as much as 5 km thick, (Heiss *et al.*,1999).

Bathymetry.

The Gulf is about 16 to 26 km wide. At its northernmost tip its width decreases to about 5 km. Considering its narrow width the gulf is very deep . The 400m-fathom contour defines two basins, a northern and a southern, separated by swells. The Gulf of Aqaba is separated from the Red Sea by a sill which has been reported to be 340 m deep. The walls of the Gulf of Aqaba are very steep. The normal gradient ranges from 60 to 70 percent, (ISPAN,1992).

It is practically non continental shelves boarding the gulf. The coastal plains are missing or particular tight. The continental slopes are among the steepest in the world, (Hulings,1989). The gulf profile is asymmetrical because the eastern slope can get as steep as 25 to 30° contrary to the western only getting as steep as 16°.

The deficit in water budget of the gulf resulting from high evaporation is balanced by the inflow of water from the Red Sea. However, the inflowing current from the Red Sea is a less saline surface flow, therefore the more saline (denser) water resulting from the large evaporation-precipitation ratio, sink and form a counter flow to the south, (Loya,1988).

Reefs

The reefs in the gulf are all north of the 27° N latitude, they are some of the northernmost reefs in the Indian Ocean. Corals belong under the phylum Cnidaria in the kingdom Animalia. The phylum include hydras, jellyfishes, sea anemones and coral animals (IUCN/UNEP 1988). Details on the coral reef ecosystem of the gulf are in Chapter four.

1.3 The Jordanian Coastline: General Features

The 26.5 kilometer-long Jordanian shoreline of the Gulf of Aqaba provides the only access to the sea for Jordan for ship transport, fishing, and industrial development that requires large amount of cooling water.

The coast has been divided generally into zones for development purposes, the city of Aqaba, the port area, the south tourist area including the marine park and the public beach and the industrial zone area.

The fringing reefs along the Jordanian coast is of extreme environmental importance. It is part of the northern most reef in the northern Hemisphere. This reef system is considered the most diverse within the Northern Hemisphere with many endemic species (IUCN,1993).

The north beach of Aqaba consists primarily of sand and gravel beaches. In the nearshore, seabed is sandy with few corals. The slope of the nearshore seabed increases southward, leading to very deep water relatively close to shore.

Further south along the coast, more coral reef areas are evident. These reefs are found scattered nearshore, where that of offshore is extending in a more continuous way, although such continuity is interrupted by several bays.

Morphologically, the reef of Aqaba fringe the shoreline, with the area offshore of the reef zone dropping abruptly into deeper water. In most areas, a shallow lagoon separates the shoreline from a shallow, fringing reef flat.

On rare occasions, usually separated by one or more years, extremely low tides occur in the upper gulf during which the reef flat and part of the shallow lagoon may be uncovered for up to 20 minutes each low tide over a period of up to 2 days.

Several studies have reported the effects of such extreme low tides, (*e.g.*, Fishelson,1973b, Rawber,1974 both in Loya,1988). It has been shown that most of the colonies are able to regenerate after exposure if parts of the living tissue remain intact on the skeleton. It is clearly here that the worst time for any major source of pollution in this area would be during one of these extreme low tides when corals on the reef flat could be exposed directly to such impact.

The Jordanian coast displays a belt of discontinuous fringing reefs that are developed preferentially on small capes and are separated by wide embayment. The position of these bays correspond to wadi mouths and they are characterized by a sandy sea bed colonized by scattered coral heads and sea grass beds. The fringing reef lining the coast vary in their distribution. In exposed zones, an extensive 2 to 10 m wide reef flat is formed, while in less exposed areas, patch reefs may coalesce to constitute an irregular reef flat (Hulings,1989).

The beaches of the Gulf of Aqaba are narrow and the sand is immature. These beaches are of low relief with a gentle foreshore slope (5-15º), (Abu Jaber,1991).

1.4 Shoreline Classification

The Jordanian shoreline is highly variable. The coast can be classified on the basis of its morphology into three distinct zones which differ considerably in their morphology, sand budget and their surrounding topography. The zones were classified according to several authors(*e.g.,* Abu Jaber,1991) as: the northern sandy coast, the northern eastern cliffed coast, and the southern crenulated coast, (Fig. 2; Fig. 3).

1.4.1 The Northern Shoreline

The northern shoreline has a cusped/bayed morphology and is lined offshore by an arcuate bar system, where the offshore bar and the cusped/bayed shoreline are out of phase. The longshore currents along the northern coast is an oscillatory motion in which the wave set up erodes an embayment on the coast and accretes an offshore cusp and the wave set down accretes a cusp on the shore. The beach material is composed entirely of fine sand.

1.4.2 The Northeastern Shoreline

Unlike the northern beach, this stretch of shoreline is utilized for port facilities . It is narrow and built by angular, coarse, immature rock fragments ranging in size from pebbles to boulders and by the finer fraction which is derived from adjacent mountains. The shoreline is paralleled by a system of discontinuous reefs that can either act to buffer the high wave energy resulting in an accretionary beach, or else the channels between reef patches can funnel the wave energy in the form of strong directed rip currents and deplete the beaches of their sediment. The lack of sand along these four kilometers may be attributed to many factors including the absence of alluvial fans, the funnel injection of waves in between natural channels of the reefs, and the various man-made development structures.

1.4.3 The Southern Shoreline

The southern beaches are barren and comprise the largest portion of the Jordanian coastline. It extends 14 km, from the Marine Science station in the north to the Saudi border at the far south.

The southern beaches are lined offshore by a buffer of live coral reefs, alternating between patchy corals and fringing corals. The sandy stretches along the southern coast are patchy, the major sources of sand for these beaches are; the sediments carried from adjacent beaches by long shore currents, the sediments produced as a result of the scouring of waves at the base of the alluvial fans, and the sediments carried by flash floods during the rainy season. The southern shoreline is made up of a series of capes and embayment. The wide bays are generally located at the mouth of a wadi outlet separated by narrow capes

Similar to the northern coast, the offshore corals serve along this shoreline as a protection to the beaches by acting as a buffer to the incoming wave energy. The resultant waves approaching the beach are weak and incapable of moving sediments into their system. Sandy beaches are commonly protected offshore by a wide reef flat while beaches lined offshore by patch reefs are made up of pebble to cobble size lag sediments.

However, the combination of large fetch and narrow continental shelf along the southern beach produces an exposed and eroding coast.

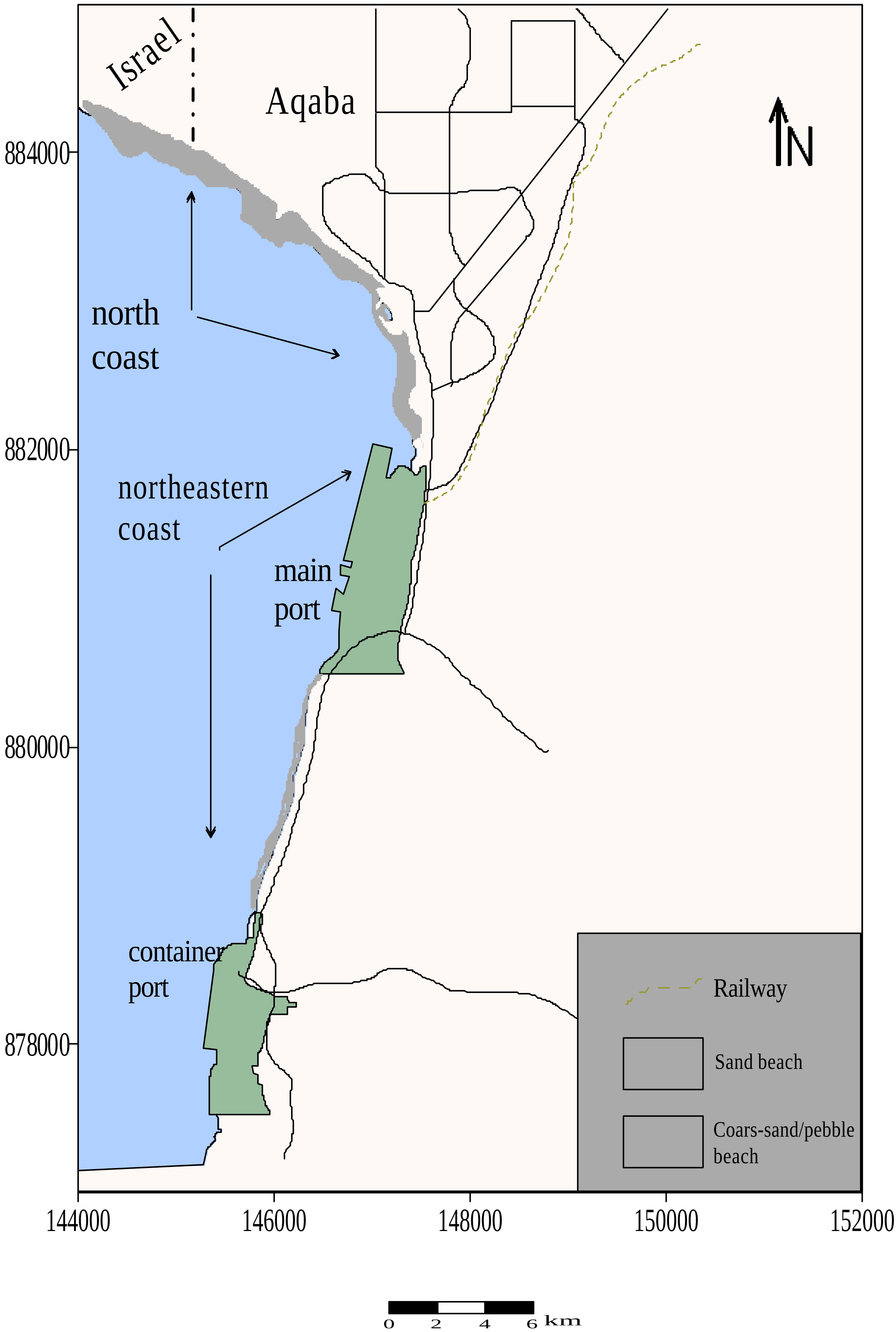


Fig.2. The north and northeastern shorelines of Aqaba.

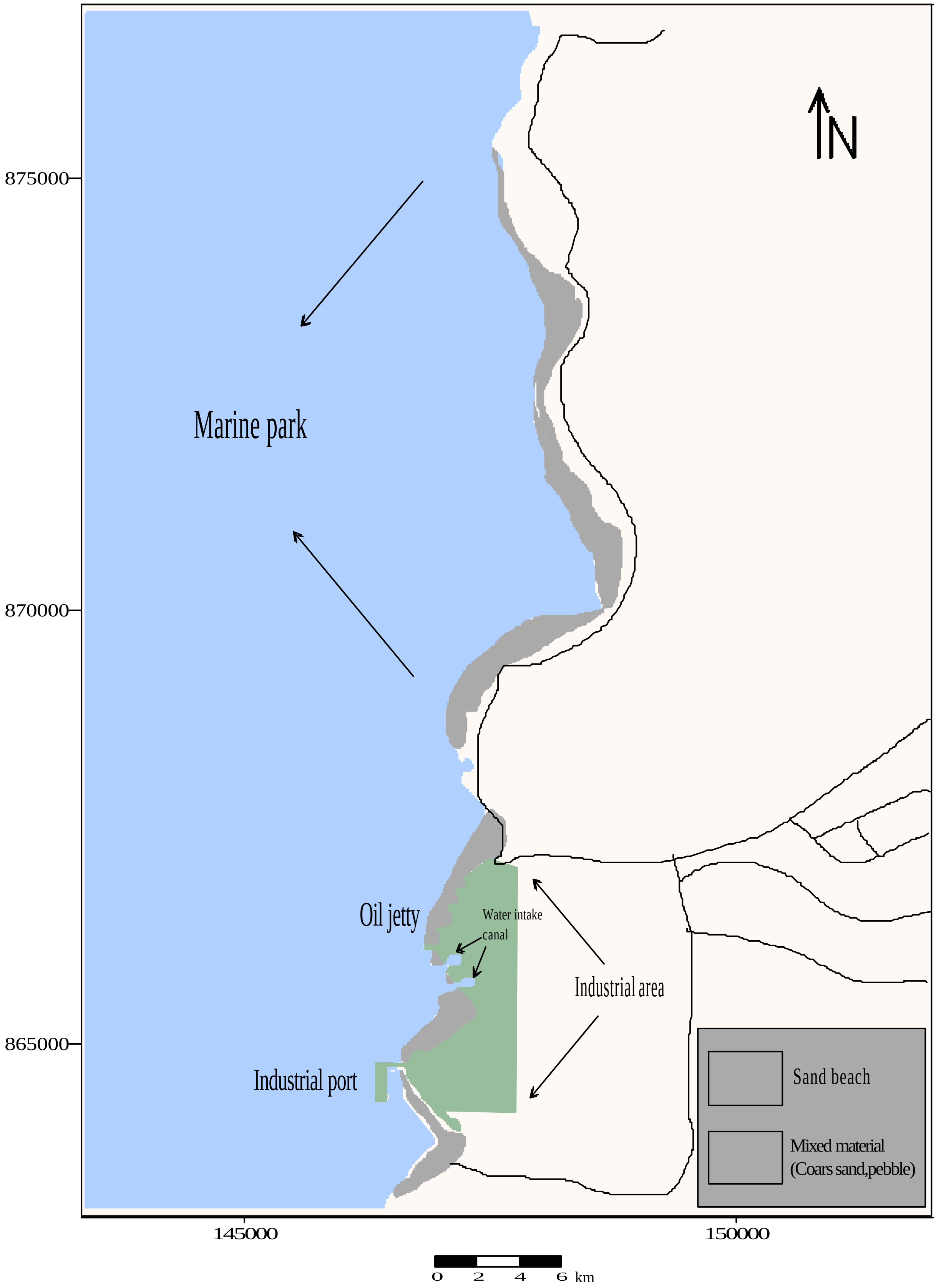


Fig.3. The south shoreline of Aqaba.

1.5 General Review on the Quality of the Seawater and Bottom Sediments of the Jordanian Gulf of Aqaba

The present section describes the seawater and bottom sediments environmental quality along the Jordanian coast. The information stated below were obtained mainly from the monitoring program of the Marine Science Station in 1999. Noteworthy is that heavy metal concentrations in seawater and bottom sediments will be discussed in some details in Chapter Seven.

1.5.1 Seawater

Major and minor constituents of seawater are summarized in Table1.

Ammonia (NH3):

Mahasneh (1984) has reported relatively high values of ammonia in the surface water along the Jordanian coast. The annual mean ammonia concentration over the entire coastal Jordanian section of the gulf presented by the author was 0.068 mg l^{-1}. According to Mahasneh, a sewage outfall in the northern section of the gulf contributed significantly to this high mean.

Badran (1996;1998) and Rashid (1998) found higher ammonia concentrations in winter and spring than in summer. The annual concentration range in the Jordanian coastal water according to both authors was from 0 to 0.01 mg l^{-1}.

Nitrate and nitrite (NO_3 ,NO_2)

Badran (1996) and Rashed (1998) reported outstandingly clear seasonality of both nitrate and nitrite concentrations in both coastal and offshore waters. Maximum nitrate concentrations were recorded in deep waters, below 150m during summer. Nitrite had a summer maximum at about 100m. In the open coastal water nitrate concentration was minimum at 0.001 mg l^{1} in summer and reached a maximum of 0.072 mg l^{1} in winter. Nitrite had a similar pattern, but with about half the concentrations.

Phosphate (P_2O_5)

According to Badran, (1996) and Rashed, (1998), phosphate concentration in offshore waters had homogeneous values throughout the water column in winter and spring. Minimum values were recorded in the upper 50m waters during summer. In coastal waters the concentration range was between 0.001 to 0.002 mg l^{-1}.

No reports have mentioned a clear seasonality of the phosphate concentrations in the upper water (0-400m) of the Gulf of Aqaba. Hulings and Abu-Hilal (1983) identified some short term seasonality patterns which were irregular and unpredictable with respect to the main hydrographic seasons of the gulf.

Dissolved Oxygen(DO)

Dissolved oxygen concentration in the Jordanian coastal waters of the Gulf of Aqaba ranges between 6.0 and 7.5 mgl^{-1}. According to Klinker *et al.*,(1976), there is a strong relationship between oxygen concentration and both salinity and temperature in the upper 200m of water of the gulf. No details on such relationship has been explained by the author except concluding that the oxygen saturation, in general is a function of both water temperature and salinity, (Hulings,1989).

Table (1): Chemical characteristics of waters of the Jordan Coast, (MSS,1999)

Parameter	**Mean value**
Alkalinity	2.4-2.7 meq-HCl kg^{-1}
Ammonia	0.004-0.015 mg l^{-1}
Bicarbonate (HCO^{-3})	167 mg l^{-1}
Bromine	85.0 mg l^{-1}
Cadmium	0.024 mg l^{-1}
Calcium	0.425 g kg^{-1}
Calcium/Chloride	0.019
Chlorinity	21.49 $^{o}/_{oo}$
Cobalt	1.06 µg kg^{-1}
Copper	3.11µg kg^{-1}
Flourine	1.4 mg kg^{-1}
Iron	4.07µg kg^{-1}
Magnesium	1.390 g kg^{-1}
Magnesium /Chloride	0.0647
Manganese	0.026 g l^{-1}
Nickel	6.95 µg kg^{-1}
pH	8.3-8.4
Potassium	455 mg l^{-1}
Sodium	1.29 g l^{-1}
Sulfate	3.00 g l^{-1}

1.5.2 Sediments

Bottom sediments of the Gulf of Aqaba in general are typically loose unconsolidated reef sediments. They generate mainly from reef rock, calcareous algae, fragmented solid biogenic material, calcium carbonate skeletal remains such as foraminifaran tests and molluscan shells, beach rock fragments, fecal material produced by sediment ingesting organisms and terrigenous material driven from the surrounding desert by wind or runoff, (Hulings,1989).

A detailed investigation was carried out by Alrosan,(1998) on the composition of the bottom sediments of the Jordanian coast. He reported an annual average of calcium carbonate concentration of 74%, organic carbon of 0.35%, total nitrogen 0.05%, and total phosphorous of 0.07%.

Total phosphorous concentration in bottom sediments range between 87 to 460mg kg^{-1} (MSS records). In general, carbonate sediments are known for adsorbing soluble phosphorous from the seawater, this explains the high concentration might be recorded at some locations. However, concentrations higher than 500 mg kg^{-1} are attributed to anthropogenic activities, (Jickells,1995).

Average concentration of organic nitrogen in bottom sediment 210 mg kg^{-1}. No seasonal property in the concentration was found. Organic carbon concentrations range between 0.9 to 2.9 g kg^{-1}, with no regular or seasonal pattern as well. All recorded values of both organics carbon and organic nitrogen were relatively and compare fairly well those sediments from other parts of the gulf.

Monitoring programs along the coast show that the upper 5cm section of the bottom surface sediments is fairly well oxygenated (MSS,1999).

Chapter Two
General Background

2 General Background

2.1 Justification and Importance of the Study

More than a quarter of the world's reefs are at high risk, and just under a third of these habitats are at moderate risk from human disturbance. Of the broad categories of potential threat to coral reefs evaluated, overexploitation of marine resources, including destructive fishing practices, and coastal development present the greatest threat. Globally, 58% of the world's reefs are at risk, (WRI,1998).

The Gulf of Aqaba represents a natural resource of major economic importance to the four riparian countries; Jordan, Egypt, Israel and Saudi Arabia, in terms of development of tourism and other industries and access to sea transportation. The 27 km of the Jordanian coastline is of particular significance to the national economy. This coastal strip is considered one of the main focal points of the Jordan's economic activity; it has the fastest growing employment opportunities, it is the recreational area for hundreds of thousands of the country's population during autumn, winter and spring seasons, and it is a major attraction in an expanding tourist industry.

The Gulf of Aqaba has several features that make it unique compared with any other ecosystem (See Chapter1); it is biologically extremely diverse and contain rare and endemic species, the reefs at the northern end of the gulf have the distinction that they are the most northern reef in the world, they support a higher marine biodiversity than that found at similar latitudes elsewhere, (Hulings,1989).It is also reported that the reef of the gulf to have a higher number of species per unit area than other reef area in the world (Loya,1988).

Development in the whole northern portion of the gulf has been a rapid phenomenon. During the last two decades the whole Jordanian coastline has been modified- and still- from its natural state by a variety of development associated with economic growth. These include the construction of housing projects, buildings, roads, hotels, power stations, ports, storage facilities, potash and fertilizer production industries.

An essential requirement for natural resources management and sustainable development is an improved understanding of these resources and the natural and anthropogenic processes affecting them. This must be founded on sound data and information gathered routinely. This is actually the main objective of the present work to establish a baseline for the metal concentration and the pollution status along the coastline as a contribution towards an integrated system of pollution-related database which in turn will contribute to sound management of our unique natural resources.

In Jordan, it is important to conserve the coral reefs because they can provide Jordan increasing economic benefits which, if successfully managed, could be sustainable. Significant tourism development opportunities are available because of the fringing nature of the reef. Corals are also a good source of food and medicine, they also provide a natural protection to the coastline. The sea would otherwise reclaim these coastlines.

Industries on the other hand, also provide Jordan with increasing benefits. These industries are the largest revenues generator in the Aqaba Governorate with annual revenues of about $ 400 million mainly from fertilizer and mineral processing (MoP,2003). Industries in Aqaba are primarily associated with port operations, some also need large amounts of cooling water, hence their locations next to the sea is advantageous.

Tourism is a key factor in the growing economy of Jordan and the Aqaba region (attraction is made possible due to the existence of healthy and beautiful coral reef). In this region tourism generated estimated revenue of around $85 million (NIC, 2003).

Much worth to mention that the Government of Jordan has transformed the city of Aqaba into a Special Economic Zone by the end of the year 2001. The zone is envisaged as a duty free area that will attract investment to Aqaba and contribute to national economic growth.

It is clear here that the two sectors, tourism and industry depend on the same resources, the marine environment, therefore a careful planning should be done to achieve effective separation between them and to be sure that none of them will bring any significant negative impact on the other, especially with the substantial future growth of both in Aqaba. Such planning should always consider the environmental issues as part of the any sound sustainable development.

Therefore, the integration of environmental issues within the development plans must be based on clear and accurate as much as possible on up to date data. In some cases, future planning rely much on trends recorded in the past, this is exactly what the present work has tried to do and contribute to the existing efforts in documenting the environmental conditions in Aqaba in order to be integrated and considered in any future development towards maintaining the balance while using our natural resources.

Additionally, the present work comes along with the already submitted Strategic Environmental Assessment Plan submitted in 2001, (ASEZA,2001), which aims to identify significant environmental issues, physical areas and constraints and assist in integrating environmental resources into Aqaba vision.

Against the above, observations have shown that the status of some parts of the marine ecosystem of Aqaba have been affected by the release of leachable metals, (Abu-Hilal,1993), nitrate, (Hulings *et al.*,1983) and phosphate, (Abu-Hilal,1985). The coral reef in particular has suffered damage from human activities such as swimming, snorkeling, scuba diving, souvenir and coral hunters and fishing. All these activities can leave a negative impact on the corals.

Finally, as the city of Aqaba is a major resort area in Jordan, the study of the pollution history of this area would provide a lesson, and the information obtained would be useful to the city planners taking steps to prevent further deterioration of the environment, to the environmental professional who works on environmental impact assessment, and to the decision makers who set the priority for applying remedial actions.

2.2 Reasons Beyond Using Coral Reef

To get meaningful data for pollution assessment by analysis of seawater is difficult because sea water is a dynamic fluid medium and a ten fold difference in concentrations in samples collected at one location is commonly observed (Philips,1987).

In addition, the concentration of certain metals in seawater is so low that different methods of analysis lead to different results. On the other hand, the record from sediments data could be altered by human activities such as dredging and processes like remineralization and recrysatlization. In a study of heavy metals in seawater, marine sediments and corals, Esslemont *et al.* (2000) noted that in some measurements, metal availability as represented by metal in coral, may have been inadequately represented by sediment data, and therefore corals are deemed to be very useful indicators of pollution level because their skeletons assimilate records of certain metals over hundreds of years.

Moreover, since corals remain in the same place throughout their lifetime, they are ideal organisms for recording environmental changes as they precipitate their $CaCO_3$ (aragonite) skeletons directly from seawater. Therefore changes in seawater chemical composition may be recorded as a chemical record preserved within the internal growth bands of the coral skeleton and as trapped samples of suspended particulate matter, (Lesley *et al.* 2003).

Over the past two decade, the coastal water of Aqaba has been extensively used by the community and industries for the disposal of domestic and various industrial wastes, therefore increasing the level of pollutants in coastal water. All previous work have focused mainly on seawater and sediments to detect pollution.

The present work is the first to use coral reef as a tool or indicator to document pollution in the study area.

The study is envisaged also be considered as a new contribution for the documentation of pollution, along with other similar observations, in which such scientific researches could support sound decision making for planning and management of our natural resources. In addition, all of such studies and observations are important also for the EIA processing either for conducting or reviewing, since they introduce invaluable data and documentation for the existing condition of the ecosystem.

The present research comes also along with other efforts carried out (and being) to conserve the marine environment in Aqaba (*e.g.* MSS monitoring programs; Al Farajat,2002).

2.3 Relevant Literature Review

Detailed observations and measurements of coral reefs began only about 20 years ago. The review during the present work has been made through a wide range of relevant journals *inter alia.,* Journal of Aquatic Ecosystems; Ecosystem, Health and Management; Environmental Pollution; Marine Pollution Bulletin; Journal of Experimental Marine Biology and Ecology; Coral Reef; Environmental Monitoring and Assessment; and Bulletin of Environmental Contamination and Toxicology, in addition of course to the several visits conducted by the author to the concerned and relevant institutions in the region for consultations, discussions and advice when necessary.

The references list at the end of the thesis brings to the readers the main literatures that were of great help to the author in conducting the present work. It will be noticed that most of the literature are very recent (post 1990) due to increasing interest and understanding of using coral reef as environmental recorders.

Research on trace elements and other pollutants distributions and background in biota, water and sediments of the Gulf of Aqaba are very limited (Abu-Hilal,1987).

No previous similar work has been done on documentation of the pollution history along the Jordan coastline, however there were some works including some monitoring programs and environmental impact studies that have been done mainly in places where problems have arisen, for example around the phosphate loading facilities.

Some other scientific papers have described the pollution status at specific spots along the coast; the following summarizes the most relevant ones:

- Wahbeh (1990) and (1995):

The author has studied example on the use of bioindicators to document pollution in the aquatic ecosystems, in particular the toxicity and accumulation of selected heavy metals (Cd, Cu, Zn *inter alia.*) in bivalve species from the Jordanian coastline of the Gulf of Aqaba. He has reported high metal concentrations in some species at the phosphate-loading berth as well as near the old sewage plant.

- Badran and Foster (1998):

The authors have studied the environmental quality of the Jordanian coastal waters. Based on records of long term (14 months) fine temporal resolution (weekly), monitoring of the ambient water temperature, DO, the inorganic nutrients ammonia, nitrate, nitrite, phosphate and silicate and chlorophyll *a* was carried out. Modification in the coastal water quality were assessed as the difference between the magnitude of a specific parameter recorded at a coastal station and the concurrently recorded value of the parameter at the reference offshore station, relative to the annual mean value at the reference offshore station. The port of Aqaba was found to be acutely modified with respect to all measured parameters. The industrial area has consistently positive modification in phosphate concentration. In addition, ammonia and silicate concentrations were positively modified at all coastal stations.

- The MSS Monitoring Program:

The Marine Science Station has started conducting an environmental monitoring program in 1998 along the Jordanian coastline in response to the Gulf of Aqaba Environmental Action Plan; a project financed by the Global Environment Facility (GEF). The aim of this program was to assess the current conditions of the marine environment along the Jordanian coast and to develop and implement priority measures to halt currently existing and prevents further pollution. The program was concerned with determining the quality of seawater and sea sediments in addition to conducting biological surveys. Seawater was tested for temperature, salinity, transparency, pH, alkalinity, dissolved oxygen, ammonia, nitrate, nitrite, phosphate, silicate and chlorophyll *a*. The sediments were tested for color, odor, sulphide, total nitrogen, total phosphate, ignition loss, particle size distribution, organic substances, Cu, Zn, Cr, Cd and Pb, (MSS, 1998).

In the semiannual reports of this monitoring report, it was recorded that there was relatively high nutrient and chlorophyll *a* concentrations, especially in the northernmost stations of the coast. It was attributed at that time to both natural factors such as the geographic setting and wind regime and to anthropogenic factors such as incidental uncontrolled discharges from Aqaba and sewage discharge as well as fish farming in Eilat. As for the quality of sediments, and in particular in terms of trace metals tested in the monitoring program, it was mentioned that in general, the concentrations are in the normal range, but as one of these reports has mentioned 13 out of 36 cases have recorded to be generally high. Concentrations of lead and zinc relative to the other metals were high.

- Abu-Hilal and Badran (1990):

Abu-Hilal and Badran (1990) have studied the concentration of Cd, Co, Cu, Fe, Mn, Pb and Zn in sediment cores taken from different sites along the Jordanian coast. They have described the main sources of metal pollution as local ones, mainly around the phosphate loading berth and sewage outlet in the northern stations and near the cooling water outlet from the industrial complex in the southern coast. The average range values reported were, 0.8-3.0, 8.0-28.0, 3.0-12.3, 6720-13110, 44-189, 9.3-27.7, 15-83, and16-135 ppm for Cd, Co, Cu, Fe, Mn, Pb and Zn respectively. The authors have shown also that the values reported in their work (at that time) exceed the values reported 20 years ago (*of* Friedman 1970) for the similar sediments from the very near northwestern portion of the gulf, near the town of Eilat, and compared with those values they indicated that the total concentrations of the measured metals have increased many times within the 20 year (1970-1990).

2.4 Objectives of the Study

- The main objective was to identify potential environmental indicators for heavy metal contamination and pollution hot spots around the coastline of Aqaba.
- To document the metal content in the coral reef along the coast of Aqaba.
- Obtaining information about the extent and spreading of these anthropogenics.
- Researching the chronological pollution. (reconstruct the history of pollution for the Jordanian coastline) and studying the present additions of pollutants; metals in particular, into the marine ecosystem as well as determining the enrichment factor during the period of 20 years in terms of metal content in selected reef cores.

The ultimate objectives:

- It gives an alarm –once a pollution is confirmed- towards more efforts to preserve this ecosystem.
- To sustain the reef system in order to serve the tourist sector in Jordan i.e. the economic considerations.

2.5 The Study Area

In chapter one, the general features of the Jordanian coastline which represent the study area has been discussed (Fig.4). Six sampling sites have been identified according to the potential pollution sources. The sites are (from north to south) the North beach area (NB), the Main Port (MP), the Marine Science station (MSS), the Marine Park (MPK), the Oil Port (OP) and the Industrial Area (IZ).The sampling sites are shown in (Fig. 5). Chapter six contains detailed description on the sites and the activities used to take place there.

2.5.1 Climate Prevailing the Study Area

In general, the climate of the study area is dry and hot. June, July and August are the hottest months of the year. During these months the average monthly temperatures range between 30.6 and 32.1 °C. December, January and February are the months of winter. Mean temperatures are ranging between 14.9 and 17.6 °C. The proximity to the Gulf of Aqaba and the changes in the topography play a noticed role in the variation of the temperature in the different locations of the city of Aqaba. The most moderate months of the year with regards to the temperature are March-May and September- November. The total annual precipitation does not exceed 40-50 mm.

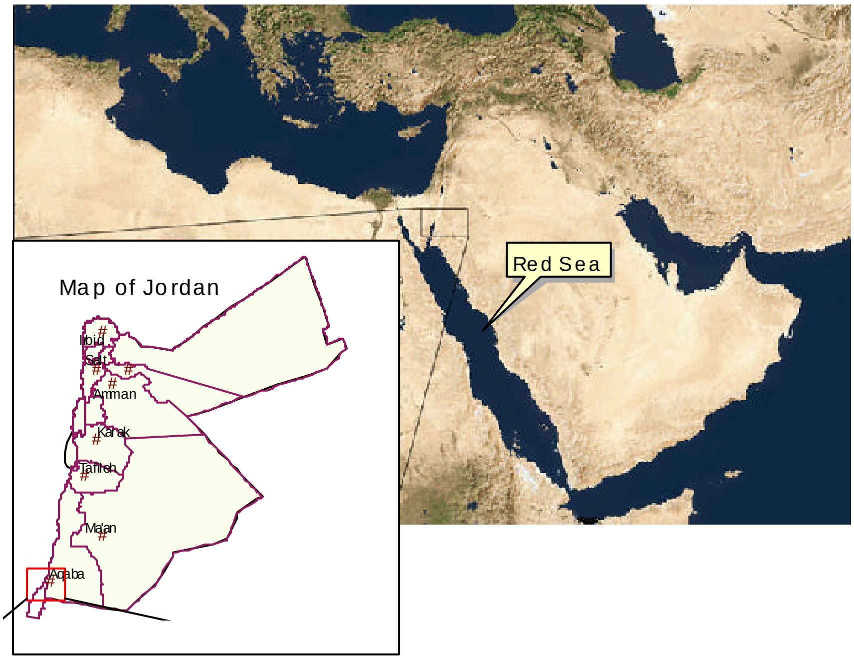


Fig. 4. Location of the Study Area

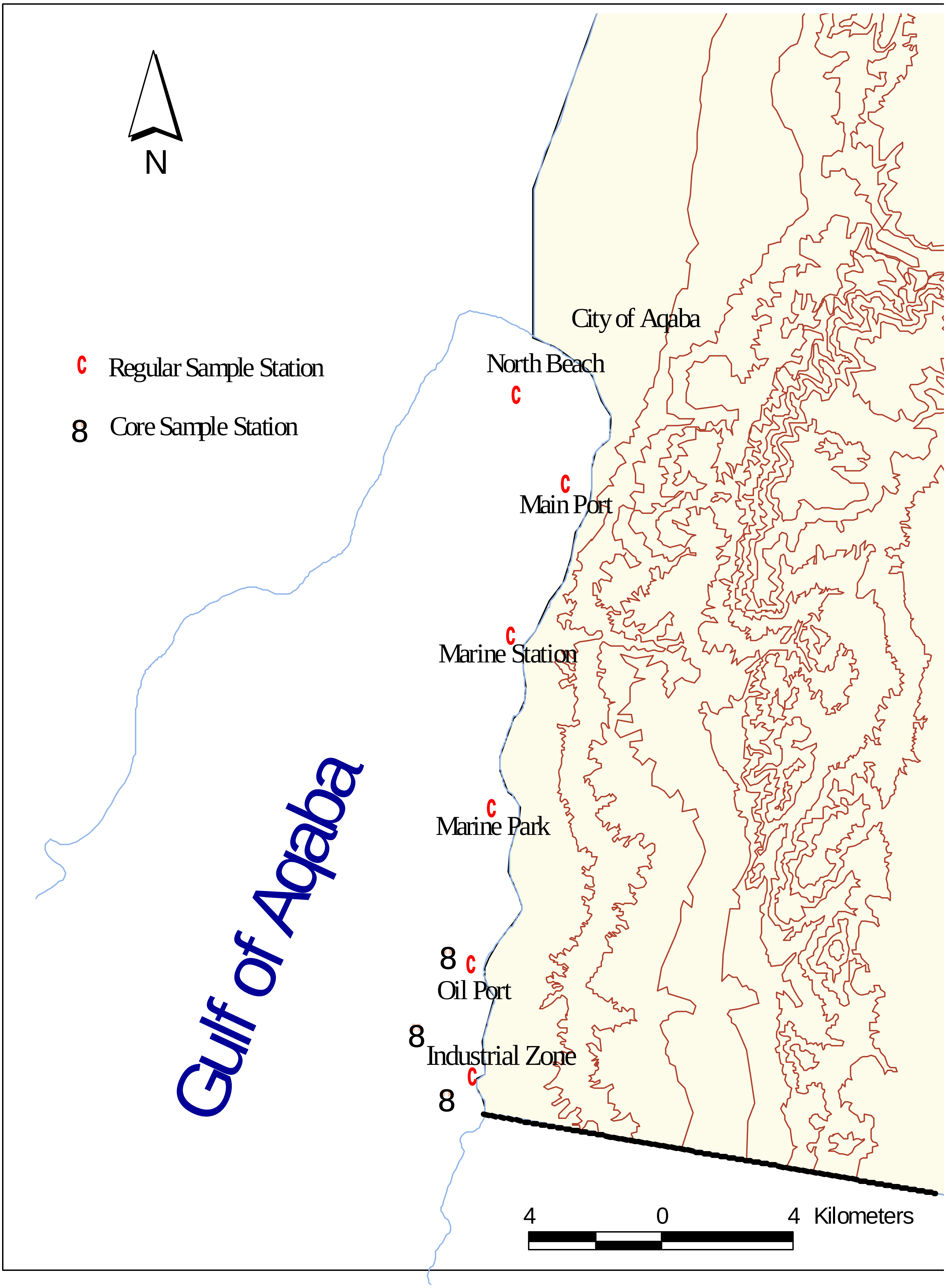


Fig.5. The sampling sites.

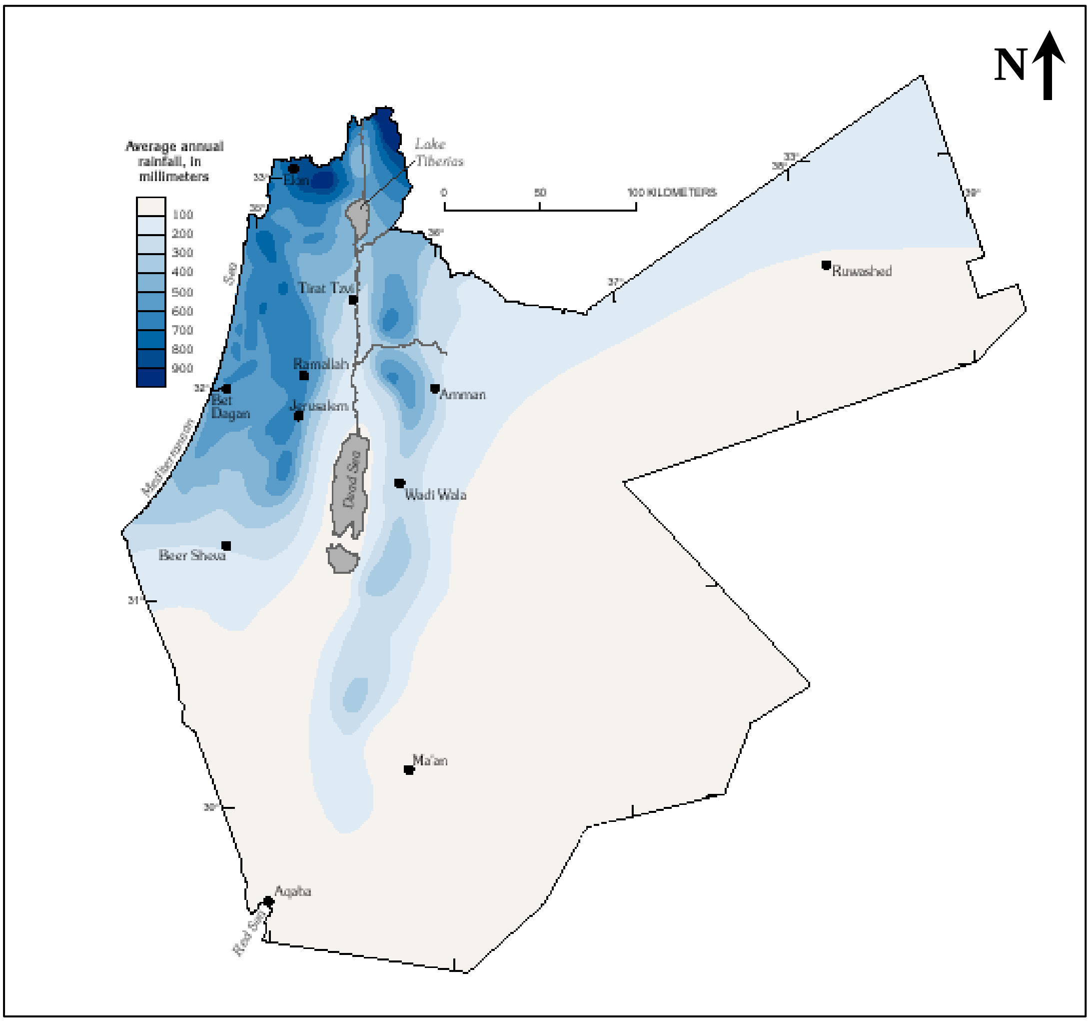


Fig. 6. The general annual rainfall distribution pattern in Jordan, showing as well that of the study area (DoM,1999).

Fig. 6. shows the rainfall pattern in the study area as part of the general distribution in the whole country.

2.5.2 Local Geology of the Study Area

The following describes in brief the main rock units present in and surrounding the study area as has been described in the mapping survey of NRA, (1988).

Generally, the area is dominated by rocks ranging in age from Pre-Cambrian to Recent. The igneous rocks of Precambrian are represented in the area by the so called Aqaba Granite (Basement) Complex. This group of rocks range in composition from the older highly weathered Grey Granite – Granodiorite to the younger less-weathered red Granite. The basement complex is dominated by many intrusives, both acidic and basic. Stratified rocks are represented in some areas by Paleozoic and Cenozoic (Quaternary) Sandstone.

Paleozoic Sandstone are found in small areas in the surroundings unconformably overlying faulted blocks of granite. They are composed of medium to coarse grained sandstone of variable colours of reds and browns with some thickness of 40m.

In the southern part of the study area these are unconsolidated, bedded, nearly flat lying quaternary sediments. They are composed of gravel, sands and silts which were derived from the igneous rocks and Paleozoic sandstones.

The southern part of the study area, nearby the industrial complex, outcrops of alluvial terraces are found. Thicknesses are ranging from 5 to 50 meters.

They consist mainly of granite, granodiorite, quartz diorite and sandstone debris. The grain size of the younger terrace sediments is usually finer than that of the older terrace sediments. The older terrace sediments are bedded and their grain size ranges from very fine to boulder. The Pliocene Pleistocene is suggested as the age of these sediments (NRA,1988).

Fossil coral reefs occur mainly well preserved, in four localities along the shore; east of Marine Science Station; opposite to the national camp site; opposite to the northern end of the marine park and opposite to the Royal Diving Center. Three major cycles of fossil coral reef development have been recognized in these localities. There were attributed to the eustatic sea level changes as a correspond to glacial and interglacial episodes of the late Pleistocene,(NRA,1988).

2.6 Methodology

2.6.1 Reasons Beyond Selection *Porites* Species for Sampling

The use of Scleractinian corals (Plate.1) as proxy tool to record the environmental changes has increased over the last ten years, including parameters such as metals, isotopes, particulate organic matter, hydrocarbons and climate, (Bastidas, *et al.*,1999).

Porites are very useful indicator for environmental monitoring, because their skeletons assimilate records of certain metals over hundreds of years. Their annual growth bands allow for the reconstruction of accurate chronologies. At the same time the thickness of these bands themselves can serve as an environmental proxy, (Heiss, *et al.*,1999).

2.6.2 Sampling

During the present work, two phases of sampling were carried out. The first; regular samples, were taken for two purposes; to study the spatial distribution of studied metals along the coast and to detect if there is significant enrichment in their concentrations, where the second phase included the core sampling and carried out to study the temporal variation in the concentration of these metals during the last 20 years.

The selection of the sampling sites was made on the basis of possible pollutant sources in case of the regular ones, and to determine –in core samples-as possible the historical pollution at the industrial area which the most area along the coast that is heavily used.

The sampling stations for both the cores and the regular samples are those indicated in Fig.2.

2.6.2.1 Core Samples

The sampling technique followed during this research has been suggested by many authors (Heiss, *et al.*,1993; Kumarsingh *et al*.,1998).

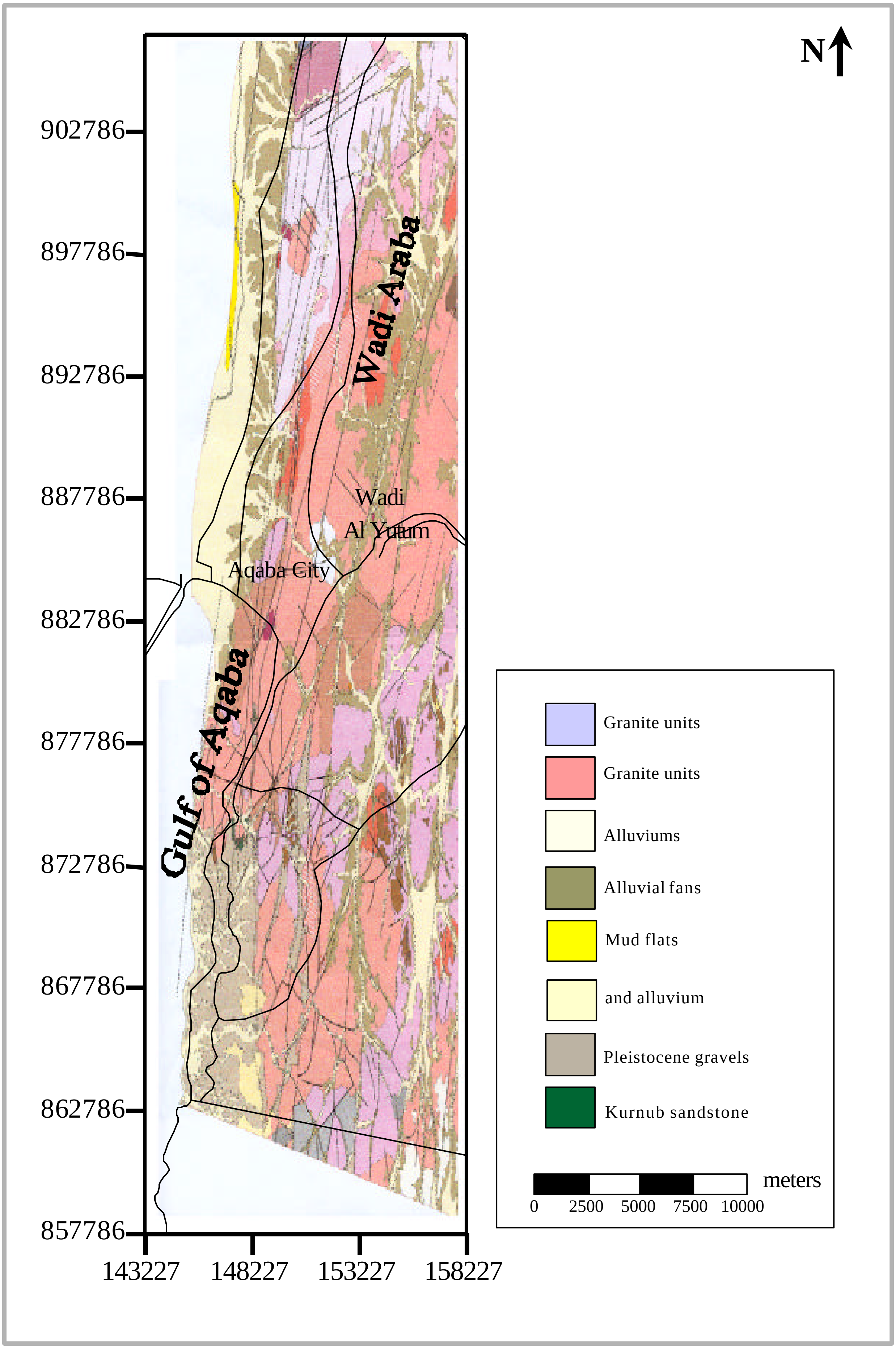


Fig.7 The main geological units dominating the study area of the Aqaba's coast (NRA, 1988).

The cores have been obtained by using a diamond-tipped rock corer which is usually attached to a pneumatic drill fed from SCUBA diving tanks, (the air is usually supplied through the first stage regulator). The volume of such tanks is 15*l*, and the air inside is pressurized to 200 bar, and can provide an air capacity of 3000*l* . The core cutter has a length of 20cm and an outside diameter of 45mm.

The initial millimetres were drilled by turning the core barrel by hand several times on the coral surface. Drilling was done parallel to the growth axis, and a guide-plate constructed from a 15cm*15cm*3cm marine ply-board through which a circular hole was cut to accommodate the corer, was used to prevent the corer tip from skidding over the coral surface at the beginning of the core drilling.

Three 20 cm cores of *porites sp.* were used for conducting the second part of this research to study the historical enrichment of metals over the last 20 years. Two of these cores were drilled at the reef edge and the fore reef (5 m water depth: core A), (8m water depth: core B) respectively. The third core (C) was provided gratefully by Peter Zolda from the University of Vienna which was drilled only two weeks before, consequently further drilling and may be some damage and disturbance to the reef community was avoided.

However the resulting cavities of the two cores were filled with coral rubble and capped with cement to prevent invasion and destruction of the colony by boring organisms.

2.6.2.2 Regular Samples

Regular reef samples were collected at different depths from the top 10 cm of the reef colonies, in which these samples are containing at least the last 7 to 10 years of skeleton growth based on an average growth rate of 8-11mm yr^{-1} (Dullo,1991). Sampling this part of the colony of the same species is necessary so all samples can be correlated. All regular samples were collected in the period May 17^{th} to July 1^{st}, 2001. These samples have been collected to study the general distribution of the heavy metals along the coast.

2.6.2.3 Laboratory Work

For both, the core and the regular samples, live tissues were later removed by soaking the cores in fresh water for approximately 1hour. After soaking, any remaining tissue were removed with a light jet of water. The cores were then air-dried and kept in pre-cleaned plastic labelled-bags for further processing.

Core specimens were cut with a water lubricated circular geological saw along the coral's maximum growth axis to obtain slices of 1cm thickness representing the average growth rate of the sampled communities . The upper topmost slice was roughly assigned to the year 2000 for the three cores; the core sampling was conducted on 25-28 March, 2001.

One gram dry weight from each sample (the sample here refers to one homogenised sample for each regular sample and one specimen section of 1cm thick for core samples) of skeletal material was taken for metal analysis. The standard procedure for soil and biota from EPA (# 3050) was performed for the analysis; briefly 10ml of HNO_3-H_2O 1:1, 5ml of HNO_3 conc., 4ml of H_2O_2 36% and 5ml of HCl conc., added and heated to 90°C. Then each sample was filtered and distilled water was added until a final volume of 50ml, (Bastidas *et* al.,1999). Metal content determinations were performed with a Perkin-Elmer 2380 atomic absorption spectrophotometer using standard reference material (EM Science, lot 80-36). All analysis were done in duplicate.

All values were within ±5% as determined from analysis of five replicates from the same core (one) fraction. Recoveries from spiked samples and blanks were within 97 to 103%.

2.6.3 Growth Rate and Dating of the Core Samples

The growth rate of the same sampled colonies was determined shortly prior starting the present research by Zolda, (2001). The researcher has measured the growth rate as part of biological research on the carbonate production of the Aqaba's reef. The methodology he has followed is the same routine procedure described and used-according to him- by many researchers (*e.g.,* Le Tissier, *et al.,* 1994; Dodge, 2000). Briefly, the procedure is as follows;

A slab approximately 0.5cm thick is cut along the axis of the reef core using a circular geological saw. The reef slab is then x-rayed on Agfa struturix D4 X-ray film, with a MPCH x-ray machine set at 40kVp for a period of 10sec., at a distance of 0.9m (determined according to the slab thickness). The x-radiograph is subsequently used to obtain a positive black and white print, which later is scanned and processed by the software CoralXDS - Coral X-radiograph Densitometry System.

The average growth rate of the reef colonies calculated by the researcher was 10mm y^{-1}, with almost no significant variation in the growth rate of the studied colonies over the last 20 years.

Noteworthy to mention that in contrast a *Porite*-core taken from a colony growing in the vicinity of the phosphate loading berth demonstrated a drastic decrease in growth rate over the same time range, where it was determined to be 6-8mm y^{-1}, (Dullo,1991). Such decrease was attributed to the excess of nutrients at the that area corresponded by phosphate.

2.6.4 Background Values

One of the problems raised during the present work is the absence of specific, defined and well documented reference (*Background*) values for the heavy metals in reef. Therefore it was necessary to investigate several sources and possibilities for reference values.

Some authors have used literature values to compare their data, this is might not support the exact status of the conclusions since the values recorded in literature don not necessarily reflect the low values, this is because each area and each ecosystem has its own characteristics. Offshore samples have been also used in several researches, but they might not be also the right choice. This is simply due to the high possibility that even the remote areas could be affected by coastal activities and shore pollution, specially in closed and semi-closed systems such as the Gulf of Aqaba. The third option to use as a reference point is referring to values recorded in bottom layers of core samples. This option generally might look as the most appropriate, specially where coral reefs provide an accurate chronology, but however the question is still ; does the bottommost layer of any core contain less pollutants?. This is not always true, as any core bottom might be underlaid by older layer (not being sampled) which might be enriched by heavy metals from old natural or anthropogenic sources.

Plate.1 One of the sampled Porite reef communities.

However, to avoid such problematic issue in the present work, and in order to get reasonable assessment, the three references were considered but in one average value, (Table 2).

Moreover, researching and investigating more than one source for reference value gives a wide vision on the extent of metal enrichment in the Aqaba reefs. For examples studying the literature values assists in comparing the present work with other similar ecosystem, and provides also an idea on the extent of the metal pollution in other parts of the world. Offshore or deep water values for example might describe the extent of metal transportation from sources.

For the calculations of Enrichment factor (EF) in core samples during the period of 1982-2001, the concentration of the core bottom horizons was used as a background value, as has been suggested by several authors (*inter alia*., Ruiz-Fernandez, *et al.*, 2001; Ramos *et al.*, 2003, Beiras *et al.*, 2003). however, the following describes the process of selecting reference values:

Three samples were also taken from offshore, assuming that due to the low currents in the Gulf this area has not been affected heavily by coastal activities. Literature values were taken from researches on tropical areas which encompass some similar physical and chemical characteristics. In addition of course to the consideration of metal concentrations recorded in core bottoms.

In Fig. 6, it is clear that the content of all six metal in offshore samples was the lowest among the other two sets of samples. Cadmium values from literature was extremely high (4.2µgg^{-1}), where lead in the core bottom layers was high (3.09µgg^{-1}), compared with 0.77 and 0.13µgg^{-1}) for the literature and offshore values respectively. Copper content was relatively high for both the core bottoms and the literature samples (3.57 and 4.6µgg^{-1} respectively). The core bottoms have shown also significant content of Cr (4.57µgg^{-1}).

However, as there was some significant differences for some metals among the three proposed background values, this justifies to get their average value in order to have more meaningful and reliable conclusions.

Table 2. Background values ($\mu g g^{-1}$) of four different sources.

Core bottom Values		Cd	Pb	Cu	Zn	Ni	Cr
	Core A	1,24	3,27	4,43	0,67	0,34	3,92
	Core B	0,32	3,2	3,2	3,9	1,8	5,1
	Core C	0,27	2,8	3,1	4,3	1,9	4,7
	Mean	0,61	3,09	3,57	2,95	1,34	4,57
Literature values (tropical areas)							
Bastidas *et al.*,1999		4,2	1,03	3,3	0,82	0,21	0,79
David, C.,2003		3,2	0,5	7,1	1,2	1,1	1,85
Crylon, *et al.*,1998		5,2	0,8	3,4	2,8	0,8	3,85
Mean		4,2	0,77	4,6	1,6	0,7	2,16
Offshore values							
Coordinates							
X	Y						
146100	870500	0,14	0,11	0,32	0,92	0,42	0,92
146400	870430	0,16	0,11	0,41	0,83	0,88	0,65
146300	870520	0,21	0,18	0,43	1,1	0,78	0,32
Mean		0,17	0,13	0,38	0,95	0,69	0,63
Overall mean							
Core bottom		0,61	3,09	3,57	2,95	1,34	4,57
Literature value		4,2	0,77	4,6	1,6	0,7	2,16
Offshore samples		0,17	0,13	0,38	0,95	0,69	0,63
Mean		1,66	1,33	2,85	1,83	0,91	2,45

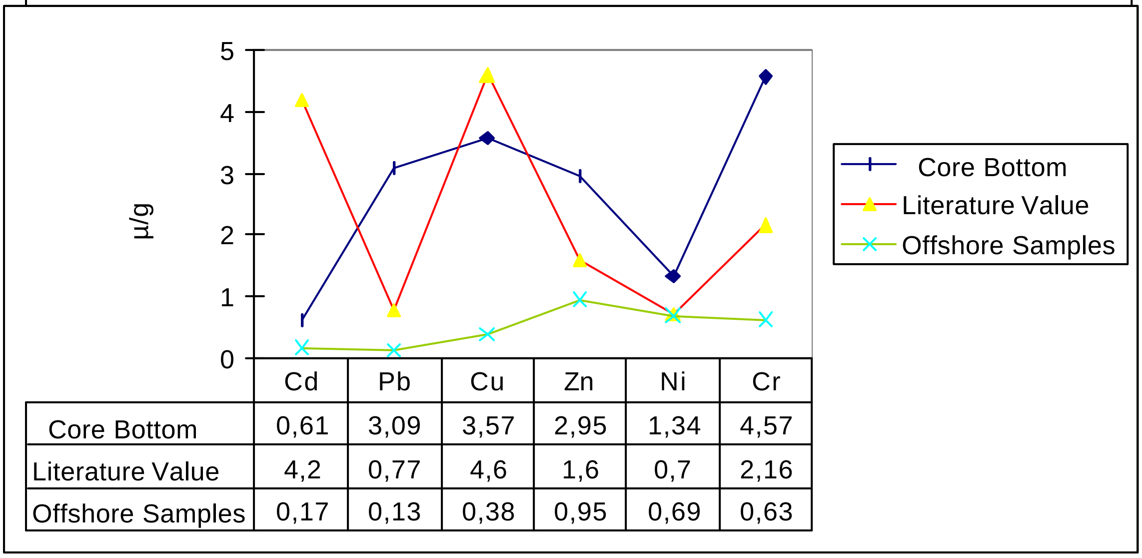


Fig.8. Comparison of the investigated background average values.

Chapter Three

Aquatic Ecosystems

3 Aquatic Ecosystems

3.1 Introduction

Aquatic ecosystems are responsible for a large proportion of the planet's biotic productivity. For example, about 30 % of the world's primary productivity comes from plants living in the ocean (Apobka,2000;WHO,2000). Aquatic systems do not exist only completely under water. However, they are also found at the interface of land and water. These ecosystems include wetlands located at lake shores, river banks, the ocean shoreline, and any habitat where the soil or vegetation is submerged for some duration. Thus, an aquatic ecosystem is generally defined as any system where the lifeforms are at least partially submerged for a part of the day or year (Adey and Loveland,1998).

When compared to terrestrial communities, aquatic communities are limited abiotically in several different ways. Firstly, organisms in aquatic systems must be able to survive partial to total submergence. Water submergence has an effect on the availability of atmospheric oxygen, which is required for respiration, and solar radiation, which is needed in photosynthesis.

Secondly, some organisms in aquatic systems have to deal with dissolved salts in their immediate environment. This condition has caused these forms of life to develop physiological adaptations to deal with this problem. Thirdly, aquatic ecosystems are nutritionally limited by phosphorus and iron, rather than nitrogen. Lastly, aquatic ecosystems are generally cooler than terrestrial systems. This condition limits metabolic activity, which is generally controlled by temperature (Apobka,2000).

3.2 Aquatic Ecosystem Types and Characteristics

3.2.1 Lakes and Reservoirs

Lakes are natural features formed from the accumulation of fresh water in depressions. Sources for the water include precipitation, runoff, streamflow, and groundwater flow. Reservoirs are bodies of fresh water that are artificially created by humans (Adey and Loveland, 1998).

Lakes are often categorized by scientists according to their nutrient status. Lakes rich in nutrients, like nitrogen and phosphorus, are commonly called eutrophic. These aquatic ecosystems are usually cloudy because of large populations of plankton and zooplankton, have diverse populations of fish, and are often depleted of dissolved oxygen during periods of warm temperatures.

Oligotrophic lakes are bodies of water that are nutrient poor. These lakes are often crystal clear and have low biotic productivity. Humans have altered the nutrient status of many lakes through the addition of nitrates, urea, and phosphates. This process, which results in physical, chemical and biological changes in the lake, is called eutrophication (Cole,1994).

3.2.2 Rivers and Streams

The accumulation of runoff and groundwater water into low lying channels creates streams and rivers. These important components of the hydrologic system move water from areas where precipitation exceeds evapotranspiration to lakes and oceans. Humans use rivers for recreation, bathing, water consumption, transportation, and as a method of diluting sewage and industrial waste into the environment (NRC,1992).

3.2.3 Fresh Water Wetlands

Wetlands are terrestrial habitats that are partially submerged by fresh water. These habitats support many different species of fish, birds, and animals. Their high productivity make them valuable sources of food for herbivores and carnivores. In the prairies, potholes are the home to millions of migrating birds like waterfowl, and they support many species of unique amphibians and reptiles. When associated with rivers and lakes, wetlands can act filters removing nutrients, sediment and some pollutants from flowing water. Wetlands are, however, under attack by development. In the prairies, wetlands are being filled-in to increase the amount of land available for farming. In other areas, wetlands are being converted into urban development, (OUC,2003).

3.2.4 Coastal Zone and Marine Ecosystems

The coastal zone is the area of the ocean where water depth is less than 200 meters. Within the coastal zone are several unique habitats, including estuaries, tidal wetlands, and coral reefs. Estuaries are coastal areas where the saline waters of the ocean meet with fresh water from streams and rivers. These habitats are usually very productive because of the accumulation of nutrients from fresh water runoff. In estuaries and along coastlines, tidal movements of waters can create tidal wetlands like marshes or mangroves. Tidal marshes are common in temperate areas, and are dominated by sedges and grasses. Mangroves develop in tropical areas and have trees as the dominant vegetation type. Warm shallow tropical water can often support coral reefs. Coral reefs match tropical forests in numbers of individuals, species diversity, and types of lifeforms (Alongi,1997).

Marine ecosystems are a part of the largest aquatic system on the planet, covering over 70% of the Earth's surface. The habitats that make up this vast system range from the productive nearshore regions to the barren ocean floor. Important marine ecosystems are oceans (including open sea which occupies about 90 % of the total surface area of the ocean, but contains only 10 % of all marine plant and animal species), estuaries and salt marshes, lagoons, tropical communities (mangrove forests and coral reefs), rocky subtidal (kelp beds and seagrass beds), and intertidal (rocky, sandy, and muddy shores) areas (WRI,2003).

Marine ecosystems are home to a host of different species ranging from tiny planktonic organisms that comprise the base of the marine food web (i.e., phytoplankton and zooplankton) to large marine mammals like the whales, manatees, and seals. In addition, many fish species reside in marine ecosystems including flounder, scup, sea bass, monkfish, squid, mackerel, butterfish, and spiny dogfish. Birds are also plentiful including shorebirds, gulls, wading birds, and terns. Some marine animals are also endangered including whales, turtles, and many others. In summary, many animal species rely on marine ecosystems for both food and shelter from predators (IUCN,1992).

Marine ecosystems contain several unique qualities that set them apart from other aquatic ecosystems, the key factor being the presence of dissolved compounds in seawater, particularly salts. In general 85% of the dissolved substances are Sodium (Na) and Chlorine (Cl) in seawater. On average seawater has a salinity of 35 grams per thousand grams (ppt) of water. These dissolved compounds give seawater its distinctive "salty" taste, affect species composition of particular marine habitats, and prevent oceans from freezing during the winter. Daily changes in factors such as weather, currents, and seasons as well as variations in climate and location will cause salinity levels to vary among different marine ecosystems (Schulz,2000).

Like other aquatic ecosystems, marine ecosystems require nutrients and light to produce food and energy. However, both nutrients and light are limiting factors in marine ecosystem productivity. Like many other aquatic plants, photosynthetic marine organisms (i.e., phytoplankton) rely upon sunlight and chlorophyll *a* to absorb visible light from the sun as well as nitrogen (N), phosphorus (P), and silicon (Si) to generate food and promote growth and reproduction.

However, the amount of light penetrating the ocean surface tends to decrease with increasing water depth, therefore photosynthesis can only take place within a small band near the surface of the water (the photic zone). In addition, nutrient availability often varies significantly from place to place. For example, in the open ocean, nutrient levels are often very poor causing primary production to be very low. In contrast, nearshore waters such as estuaries and marshes are often rich in nutrients, allowing primary production to be very high (Porcella, *et al.,* 1995).

In some instances, nearshore ecosystems have an excess of nutrients due to runoff and other terrestrial sources. Excess nutrients can cause an over-stimulation of primary production, depleting oxygen levels and causing eutrophic conditions to occur in coastal habitats.

Marine ecosystems are very important to the overall health of both marine and terrestrial environments. According to the World Resources Center (2003), coastal habitats alone account for approximately 1/3 of all marine biological productivity, and estuarine ecosystems (i.e., salt marshes, sea grasses, mangrove forests) are among the most productive regions on the planet. In addition, other marine ecosystems such as coral reefs, provide food and shelter to the highest levels of marine diversity in the world.

The diversity and productivity of marine ecosystems are also important to human survival and well-being. These habitats provide us with a rich source of food and income, and support species that serve as animal feed, fertilizers for crops, additives in foods (i.e., ice-cream) and cosmetics, i.e., creams and lotions (McIntyre,1995). Areas such as mangroves, reefs, and seagrass beds also provide protection to coastlines by reducing wave action, and helping to prevent erosion, while areas such as salt marshes and estuaries have acted as sediment sinks, filtering runoff from the land.

Despite the importance of marine ecosystems, increased human activities such as overfishing, coastal development, pollution, and the introduction of exotic species have caused significant damage and pose a serious threat to marine biodiversity, (Praagman,1999).

3.3 Marine Life

The oceans that cover 71 percent of the earth's surface provide a haven for a multitude of biologically diverse life forms, ranging in size and complexity from the smallest known, the virus, to the very largest, the blue whale.

Although the basic building blocks of life are the same, the conditions under which marine organisms live and propagate have influenced their evolution, in the process endowing them with biochemical, biophysiological and genetic characteristics that are quite different from those exhibited by terrestrial life. Information about these characteristics, and the organisms that exhibit them, is mostly lacking (IUCN/UNEP,1988). For example, scientists estimate that less than 20 percent of terrestrial organism have been closely investigated; the figure for marine organisms is considerably less than 5 percent (WRI,2003).

The marine environment is critical to the natural and cultural heritage of the world. Not only do many marine areas support a great diversity of plants, animals, and natural habitats, but the oceans play an essential role in climatic cycles and other global processes. Marine ecosystems and resources are fundamental to the sustainable development of coastal countries/ regions, providing food, minerals, pharmaceuticals, construction materials, and vast range of other products. The often support growing tourism and recreation industries and play a vital role in transport and in the culture and lifestyle of coastal people.

However, marine ecosystems throughout the world face increasingly serious threats from pollution, overexploitation, conflicting uses of resources, damage and destruction of habitat, and other harmful consequences of human development. Biodiversity is especially at risk. Conserving marine biodiversity is therefore a priority.

3.4 Change and Variation in the Coastal Zone

Coastal regions are some of the most sensitive and yet severely impacted environments in both industrial and developing nations. Extensive efforts to monitor reef ecosystems are underway in regions that have been subjected to rapid physical and chemical changes affecting the land-sea margin.

Studies in recent years have examined trace metal concentrations in corals, usually being able to link this to a local (or even global) anthropogenic source of contaminants (Shen and Boyle,1987; Scott,1990; Linn *et al.*,1990; Guzman and Jimenez,1992; Esslemont,1999; Bastidas and Garcia,1999; Fallon *et al.*,2002).

The porite coral species is commonly used in these studies because it flourishes in the Great Barrier Reef, the Caribbean, as well as in tropical Asia-Pacific regions. Metal concentrations observed in Porites show a large range: Cu (n.d.—37 ppm), Fe (n.d.—210 ppm), Mn (n.d.—15 ppm), and Zn (0.8–122.1 ppm) (Howard and Brown,1987a; Bastidas and Garcia,1999). This is indicative of the extent of pollution to which reefs and coastal regions in general are subjected in many parts of the world.

Coral reefs have been used by humans as recreation areas and as a source of food and other products for thousands of years. The effects of humans on coral reefs are not well understood, especially on a regional or global scale.

Important transformations in the coastal environments due to anthropogenic action have occurred during the last 150–200 yr (Palanques et al,.1988).

3.5 Natural Variability

Coastal marine ecosystems are not in steady state, but exhibit continuous changes in production and species composition of different trophic levels (Hodgson,1999). Our awareness and scientific understanding of this variability has increased during the last decades.

Coral reefs are complex ecosystems based around physical structures built by coral and algae that are themselves dependent on light. Globally, coral reefs are undergoing change with widespread impacts from human use and "natural" influences of global climate dynamics (McIntyre,1995).

Human impacts have been often described, both direct (e.g. over fishing and poison/dynamite fishing, limestone mining, land reclamation, pollution) and indirect (e.g. tourism, coastal and catchment developments). Most human impacts and changes can be managed to ensure sustainable and economic benefits.

Reef ecosystems have adapted and survived major global changes in climate through geological time. For example, 16,000 to 22,000 years ago, sea level was some 100 m lower than today. The sea level rose so fast about 14,000 years ago that corals were unable to follow the sea level. This created a strong unconformity in the reef structure all over the world ocean(Hodgson,1999).

Science is just starting to gain an understanding of these changes and the process and limits involved. Apparently natural phenomena such as widespread crown-of-thorns starfish outbreaks and coral bleaching events are under active evaluation; human impacts can exacerbate the effects but the degree of human causal influence remains uncertain. The fundamental structure of reefs depends on corals and algae using carbon dioxide and accumulating calcium carbonate (calcification). Recent findings (e.g. Dullo *et al.*,1996, Hodgson,1999) show that changes in the global carbon dioxide are having significant effects on reef calcification by influencing the calcium carbonate Saturation State. From pre-industrial time (1800 AD) it is estimated that calcification has decreased by around 10% and could decrease a further 20% by 2100 AD if atmospheric CO2 concentration doubles (the current scenario).

The Red Sea, west central Pacific, the Caribbean and high latitude reefs such as Bermuda are likely to experience the greatest changes. The ramifications of a 30% decrease in reef calcification over this 300 years of industrialization need urgent attention and understanding, both at a whole reef system scale and at the level of organism physiology and reproduction (IUCN,1993).

Degradation of water quality and pollution reaching from point and non-point sources seriously affects the quality of coastal marine waters, particularly in enclosed and semi-enclosed seas, most lakes, rivers, estuaries and groundwater systems. Toxic chemicals, nutrients, pathogens, oxygen demanding wastes, sediments (silt), petroleum hydrocarbons and litter are among the most relevant pollutants. Degradation of water quality due to pollution is one of the main cause for degradation of water-related ecosystems. Polluted waters represent also considerable threat to public health, for example by exposure during recreational activities, by ingestion of contaminated water or eating contaminated seafood (WHO,2000).

Damage to ecosystems and loss of habitats are quite common and widespread in all segments of coastal and marine environment exposed to pollution. The most affected systems are those in marine waters adjacent to the coast.

However, pollution is not the only culprit. Physical alteration and destruction of natural coastlines (e.g., by land reclamation, deforestation, coastal constructions), seabed mining, destructive fishing practices, artificially changed water courses and hydrological regimes (e.g., by large scale irrigation schemes, erection of dams and creation of reservoirs, changed land-use practices) often lead to serious physical degradation of coastal and marine habitats with concomitant changes in their ecosystems. Mangroves and seagrass beds, and coral reefs are particularly vulnerable. The increasing incidence of eutrophication of coastal waters with toxic alga blooms frequently associated with eutrophication, are telling signs of spreading ecosystem degradation (Grousseta *et al.*,1995).

3.6 Categorization of the Polluting Compounds in the Aquatic Ecosystem:

In general, environmental pollutants can be categorized as follows (GTZ,1991;2000):

- Primary polluting compounds are those emitted and discharged into the environment where they could be (a) degraded into harmless end products, such as water, carbon dioxide, etc., (b) transformed into resistant compounds, or (c) persistent during the physical, chemical and biological weathering processes.

- Secondary polluting compounds are those breakdown/conversion products, which are produced during the environmental weathering of the primary polluting compounds; they might be more toxic than their parents, such as some photo-oxidation products, or at least temporarily resistant to further degradation and they can affect the fate of other pollutants, and

Tertiary polluting compounds are those primary and secondar pollutants which are buried, accumulated in the ecosystem in inactive, non-bioavailable form but become active, bioavailable as a result of the presence of primary and secondary polluting compounds or extreme change in environmental conditions. Tertiary polluting compounds could be heavy metals in the sediment mobilized by complexing agents produced during photo-oxidation of petroleum compounds, or by slow dissolution, (Literathy,1993).

Chapter Four

Coral Reef Ecosystem

4 Coral and Coral Reef Ecosystems

4.1 Introduction

Appearing as solitary forms in the fossil record more than 400 million years ago, corals are extremely ancient animals that evolved into modern reef-building forms over the last 25 million years. Coral reefs are unique (e.g., the largest structures on earth of biological origin) and complex systems. Rivaling old growth forests in longevity of their ecological communities, well-developed reefs reflect thousands of years of history (Kühlmann,1988).

Coral is a soft living organism, called a polyp, which secretes a skeleton of calcium carbonate. Some corals are solitary (only one polyp), but most species form colonies composed of hundreds or thousands of polyps covering a stony skeleton of calcium carbonate and called hard corals, or a soft skeleton composed of a protein/calcium carbonate material and called soft corals (Plate 2). This living tissue forms a very thin sheet of cells over the skeleton and measures less than 2mm in thickness, (Sorokin,1993).

4.1.1 Classification, Growth Requirements and Distribution

Corals are anthozoans, the largest class of organisms within the phylum Cnidaria. Comprising over 6,000 known species, anthozoans also include sea fans, sea pansies and anemones. Stony corals (scleractinians) make up the largest order of anthozoans, and are the group primarily responsible for laying the foundations of, and building up reef structures. For the most part, scleractinians are colonial organisms composed of hundreds to hundreds of thousands of individuals, called polyps (Lalli and Parsons, 1995).

Reef-building corals are restricted in their geographic distribution. This is because the algal-cnidarian symbiotic machinery needs a narrow and consistent band of environmental conditions to produce the copious quantities of limestone necessary for reef formation. The formation of highly consolidated reefs only occur where the temperature does not fall below 18°C for extended periods of time. This specific temperature restriction -18°C- does not, however, apply to the corals themselves. In Japan, where this has been studied in detail, approximately half of all coral species occur where the sea temperature regularly falls to 14°C an approximately 25% occur where it falls to 11°C (Roessler,1986). Many grow optimally in water temperatures between 23° and 29°C, but some can tolerate temperatures as high as 40°C for limited periods of time. Most require very salty (saline) water ranging from 32 to 45 parts per thousand. The water must also be clear to permit high light penetration. The corals requirement for high light also explains why most reef-building species are restricted to the euphotic (light penetration) zone, approximately 80 m (Lalli and Parsons,1995).

The number of species of corals on a reef declines rapidly in deeper water, while high levels of suspended sediments can smother coral colonies, clogging their mouths which can impair feeding. Suspended sediments can also serve to decrease the depth to which light can penetrate. In colder regions, murkier waters, or at depths below 70 m, corals may still exist on hard substrates, but their capacity to secrete limestone is greatly reduced (Roessler,1986).

In light of such stringent environmental restrictions, reefs generally are confined to tropical and semitropical waters. The diversity of reef corals, i.e., the number of species, decreases in higher latitudes up to about 30° north and south, beyond which reef corals are usually not found. Bermuda, at 32° north latitude, is an exception to this rule because it lies directly in the path of the gulf stream’s warming waters (Barnes,1987 in Lalli and Parsons,1995).

Another factor that seems to affect the diversity of reef-building corals is the ocean in which they are located. At least 500 reef-building species are known to exist in the waters of the Indo-Pacific region. In comparison, the Atlantic Ocean contains approximately 62 known species. The fossil record shows that many species once found across the Atlantic, Pacific and Indian Oceans gradually went extinct in the Atlantic, where the affects of ice ages had strong impacts on the Caribbean area wherein most of the Atlantic reefs reside. Following the closure of the seaway between the Caribbean and the Pacific, several species of corals became restricted to the Caribbean (Roessler,1986).

The average annual growth rate of skeleton 0.3-1.9 cm per year. This rate depends of course on many factors (Sumich,1996), some are already listed above, but however this is beyond the scope of the present work.

4.1.2 The Symbiotic Algae; Zooxanthellae

Microscopic algae which lives in large numbers inside the coral tissue and represents one of the most interesting aspects of coral biology. They live, divide and conduct photosynthesis within cells of polyp and may represent up to 50% of polyp's body weight.

This is an example of a perfect symbiotic relationship; the association between two different organisms in which there is a mutual benefit from the relationship, the following section contain more on the symbiotic relationship with corals.

4.2 Reef Formation and Types of Reefs

4.2.1 Reef Formation and Composition

Most corals, like other cnidarians, contain a symbiotic algae called zooxanthellae, within their gastro dermal cells. Reef building depends on the mutualistic relationship between the coral and this type of algae, where both benefit.

The coral provides the algae with a protected environment and the compounds necessary for photosynthesis. These include carbon dioxide, produced by coral respiration, and inorganic nutrients such as nitrates, and phosphates, which are metabolic waste products of the coral. In return, through photosynthesis, zooxanthellae convert carbon dioxide and water into oxygen and carbohydrates and help also the coral to remove wastes. The coral polyp uses carbohydrates as a nutrient. The polyp also uses oxygen for respiration and in turns, returns carbon dioxide to the zooxanthellae. Through this exchange, coral saves energy that would otherwise be used to eliminate the carbon dioxide.

Most importantly, they supply the coral with organic products of photosynthesis. These compounds, including glucose, glycerol, and amino acids, are utilized by the coral as building blocks in the manufacture of proteins, fats, and carbohydrates, as well as the synthesis of calcium carbonate ($CaCO_3$). The mutual exchange of algal photosynthates and cnidarian metabolites is the key to the prodigious biological productivity and limestone-secreting capacity of reef building corals (Lalli and Parsons,1995; Sumich,1996; Barnes and Hughes,1999).

Zooxanthellae also promote polyp calcification by removing carbon dioxide during photosynthesis. Under optimum conditions, this enhanced calcification builds the reef faster than it can be eroded by physical or biological factors.

Zooxanthellae often are critical elements in the continuing health of reef-building corals. As much as 90% of the organic material they manufacture photosynthetically is transferred to the host coral tissue (Sumich,1996). If these algal cells are expelled by the polyps, which can occur if the colony undergoes prolonged physiological stress, the host may die shortly afterwards. The symbiotic zooxanthellae also confers its colour to the polyp. If the zooxanthellae are expelled, the colony takes on a stark white appearance, which is commonly described as "coral bleaching" (Lalli and Parsons,1995; Barnes and Hughes,1999). Massive reef structures are formed when each stony coral polyp secretes a skeleton of $CaCO_3$.

Most stony corals have very small polyps, averaging 1 to 3 mm in diameter, but entire colonies can grow very large and weigh several tons. Although all corals secrete CaCO3, not all are reef builders. Some corals, such as Fungia sp., are solitary and have single polyps that can grow as large as 25 cm in diameter. Other coral species are incapable of producing sufficient quantities of CaCO3 to form reefs. Many of these corals do not rely on the algal metabolites produced by zooxanthellae, and live in deeper and/or colder waters beyond the geographic range of most reef systems (Sumich,1996).

The skeletons of stony corals are secreted by the lower portion of the polyp. This process produces a cup, called the calyx, in which the polyp sits. The walls surrounding the cup are called the theca, and the floor is called the basal plate. Thin, calcareous septa (sclerosepta), which provide structural integrity, protection, and an increased surface area for the polyp's soft tissues, extend upward from the basal plate and radiate outward from its centre. Periodically, a polyp will lift off its base and secrete a new floor to its cup, forming a new basal plate above the old one. This creates a minute chamber in the skeleton. While the colony is alive, CaCO3 is deposited, adding partitions and elevating the coral, (Sorokin,1993).

When polyps are physically stressed, they contract into the calyx so that virtually no part is exposed above the skeletal platform. This protects the organism from predators and the elements (Sumich,1996). At other times, the polyp extends out of the calyx. The timing and extent to which a polyp extends from its protective skeleton often depends on the time of the day, as well as the species of coral. Most polyps extend themselves furthest when they feed on plankton at night.

In addition to a substantial horizontal component, the polyps of colonial corals are connected laterally to their neighbours by a thin horizontal sheet of tissue called the coenosarc, which covers the limestone between the calyxes. Together, polyps and coenosarc constitute a thin layer of living tissue over the block of limestone they have secreted. Thus, the living colony lies entirely above the skeleton (Barnes and Hughes,1999).

4.2.2 Types of Reefs

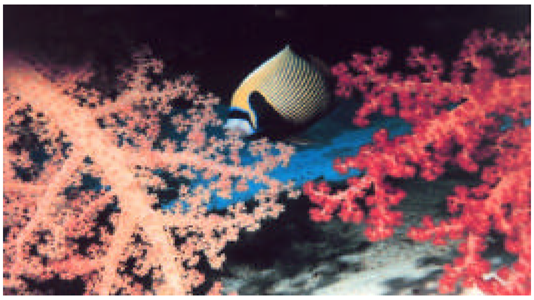
At one time it was mistakenly thought that coral grew at the bottom of deep tropical seas and succeeding generations grew on top of the dead calcium carbonate skeletons. This idea was dispelled by dredging operations that indicated that reef corals were able to grow only in shallow water, (Sorokin,1993).

Three types of reefs are recognized (Kühlmann,1988): the fringing reef, the barrier reef, and the atoll (Fig.9).

a. The first type is a fringing reef. Fringing reefs border shorelines of continents and islands in tropical seas. Fringing reefs are commonly found in the South Pacific Hawaiian Islands, and parts of the Caribbean.

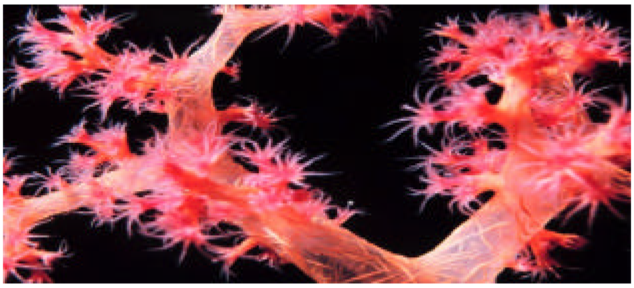
b. The next type is the barrier reef, which occurs farther offshore. Barrier reefs form when land masses sink, and fringing reefs become separated from shorelines by wide channels. Land masses sink as a result of erosion and shifting crustal plates of the earth. (Crustal plates lift or sink the seafloor and adjacent land masses.) Barrier reefs are common in the Caribbean and Indo-Pacific. The Great Barrier Reef off northern Australia in the Indo-Pacific is the largest barrier reef in the world. This reef stretches more than 2,000 km.

c. If the land mass is a small island, it may eventually disappear below the ocean surface, and the reef becomes an atoll. Atolls are reefs that surround a central lagoon. The result is several low coral islands around a lagoon. Atolls commonly occur in the Indo- Pacific. The largest atoll, named Kwajalein, surrounds a lagoon over 60 miles (97 km) long.



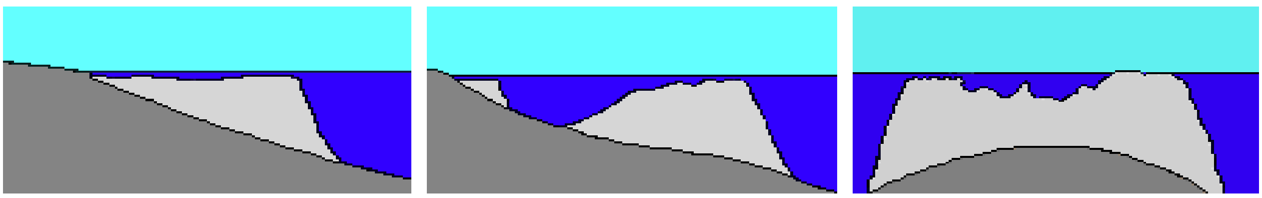
a

b



c

Plate 2. Type of corals; a: Soft corals, b: hard corals and c: close up of a , (photos by Red Sea Dive Center, Aqaba)



Fringing reef Barrier reef Atoll reef

Fig. 9. Types of Reefs, (Kühlmann,1988).

4.3 Importance of Corals and Coral Reefs

Coral reefs are important for many different reasons:

1. Corals remove and recycle carbon dioxide. Excessive amounts of this gas contribute to global warming, (Sorokin,1993 ;Roessler,1986).
2. Reefs shelter land from harsh ocean storms and floods, (Roessler,1986; Salvat,1987).
3. Reefs provide resources for fisheries. Food items include fishes, crustaceans, and mollusks, (Wells,1988; Sorokin,1993).
4. Coral reefs attract millions of tourists every year, (IUCN,1993).
5. The coral reef is an intricate ecosystem and contains a diverse collection of organisms. Without the reef, these organisms would die, (Sorokin,1993; Roessler,1986).
6. Some evidence suggests that the coral reef could potentially provide **important medicines**, including **anti-cancer drugs** and a compound that blocks ultraviolet rays, (Sumich,1996).
7. Coral skeletons are being used as bone substitutes in **reconstructive bone surgery**. The pores and channels in certain corals **resemble those found in human bone**. Bone tissue and blood vessels gradually spread into the coral graft. Eventually, bone replaces most of the coral implant, (Sumich,1996).
8. The coral reef provides a living laboratory. Both students and scientists can study the interrelationships of organisms and their environment, (Sorokin,1993).

4.4 Status of Coral Reefs Classified by Potential Threat from Human Activities

Coral reef ecosystems are under increasing pressure, primarily from human interaction. Of the approximate 600,000 km2 of coral reefs worldwide, it is estimated that about ten percent have already been degraded beyond recovery and another thirty percent are likely to decline significantly within the next twenty years (ICRI,1995). Unless more effective coral reef management is implemented, more than two thirds of the world's coral reefs may become seriously depleted within two generations. The increase in population growth and migration to the coastal areas where coral reef ecosystems thrive exacerbate the problem. Coastal congestion leads to increased competition for limited resources, to increased coastal pollution, and to problems related to coastal construction .

Coral reefs are the most complex and probably the most sensitive to pollution out of all marine habitats primarily due to their self-supporting characteristics. Factors that reduce light penetration, such as a continuous thick film of oil, interrupts the photosynthetic cycle of specific coral reefs, leading to secondary effects. Corals need sunlight because they depend for their survival on tiny algae that live in their tissues. As noted earlier, the lack of sunlight also upsets the relationship between the polyps and their algae. When there is an ample supply of nutrients in the water, the algae no longer depend on their host for these materials. Although the algae proliferate in the host cells, they begin to withhold the products of photosynthesis from the polyp, which starves. Eventually the algae either leave or are expelled by the host (Wells,1988).

According to the recently published report Reefs at Risk (WRI,1998) by the World Resource Institute, land-based pollution from coastal development, inland pollution, and erosion are among the greatest threats to reefs worldwide. Globally, 36% of all reefs were classified as threatened by overexploitation, 30% by coastal development, 22 %by inland pollution and erosion, and 12 percent by marine pollution. When these threats are combined, 58 % of the world's reefs are at risk ,defined as medium and high risk (Fig. 10). In the Caribbean and

Atlantic Ocean, the analysis reports indicate that almost two-thirds of the reefs are at risk, with four of the five major threats from land-based sources of pollution.

The importance of addressing land-based sources of marine pollution was established by the International Coral Reef Initiative (ICRI,1995), which noted that one of the three most significant threats to reefs is "inadequate planning and management of coastal land use, including upland activities." ICRI further emphasized the importance of integrated coastal management approaches for addressing land-based sources of pollution.

The latest classification on the status of the world's reef, was made by the World Resources Institute (WRI,1998). Reefs were classified according to the Reefs at Risk Indicator. This indicator flags problem areas around the world where, in the absence of good management, coral reef degradation might be expected, or predicted to occur shortly, given ongoing levels of human activity. Such degradation includes major changes in the species composition, relative species abundance, and/or the productivity of coral reef communities, attributable to human disturbance.

This indicator categories the threats as; low, medium and high, based on a composite of four separate risk factors, (Fig.11):

- Coastal development
- Marine-based pollution
- Overexploitation, and
- Inland pollution and erosion

In the Red Sea, although in the past most of the region's reefs have been reported to be in good condition, about 60 percent of these habitats were assessed recently as at risk primarily due to coastal development, overfishing, and the potential threat of oil spills in the heavily trafficked Arabian Gulf and southern end of the Red Sea. According to the WRI, (1998), almost two-thirds of the Arabian Gulf's reefs are at risk, largely because over 30% of the world's oil tankers move through this area each year. Industrial pollution and coastal development are threats in some areas as well.

Corals in many parts of the Gulf of Aqaba have been degraded through indistralization, tourism impact and related development.

Reefs in the northern Red Sea and the Arabian Gulf are especially vulnerable to degradation due to limited water circulation and temperature extremes. About 8% of the world's mapped reefs are found in the Middle East,(IUCN/UNEP,1988).

Within the Gulf of Aqaba, reefs were estimated to be approximately 70 percent under low threat and 30 percent under high threat (Fig. 11.), largely from coastal development. This is regarded as a potential underestimate due to the threats posed by tourism and shipping (WRI,1998).

However, once degraded, reefs can take decades or even centuries to recover. Scientists believe that without additional measures, global coral reef cover **will be substantially reduced by the middle of the next century.**

Studies show that **10%** of the world's reefs have already degraded beyond recovery, and that 20-30% will be seriously threatened in the next two decades, (ICRI,1995).

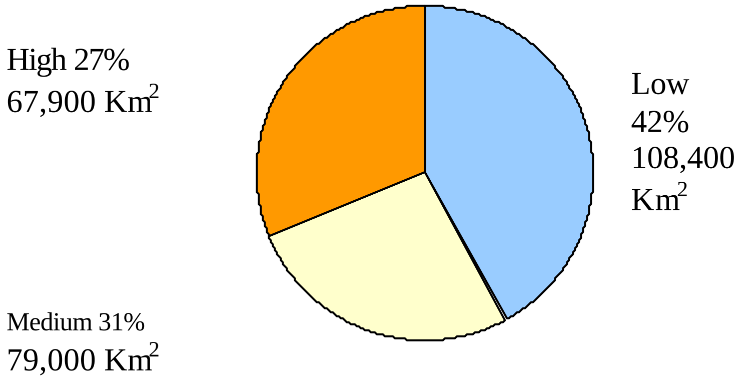


Fig. 10. Classification of threats facing the world's coral reef,(WRI,1998).

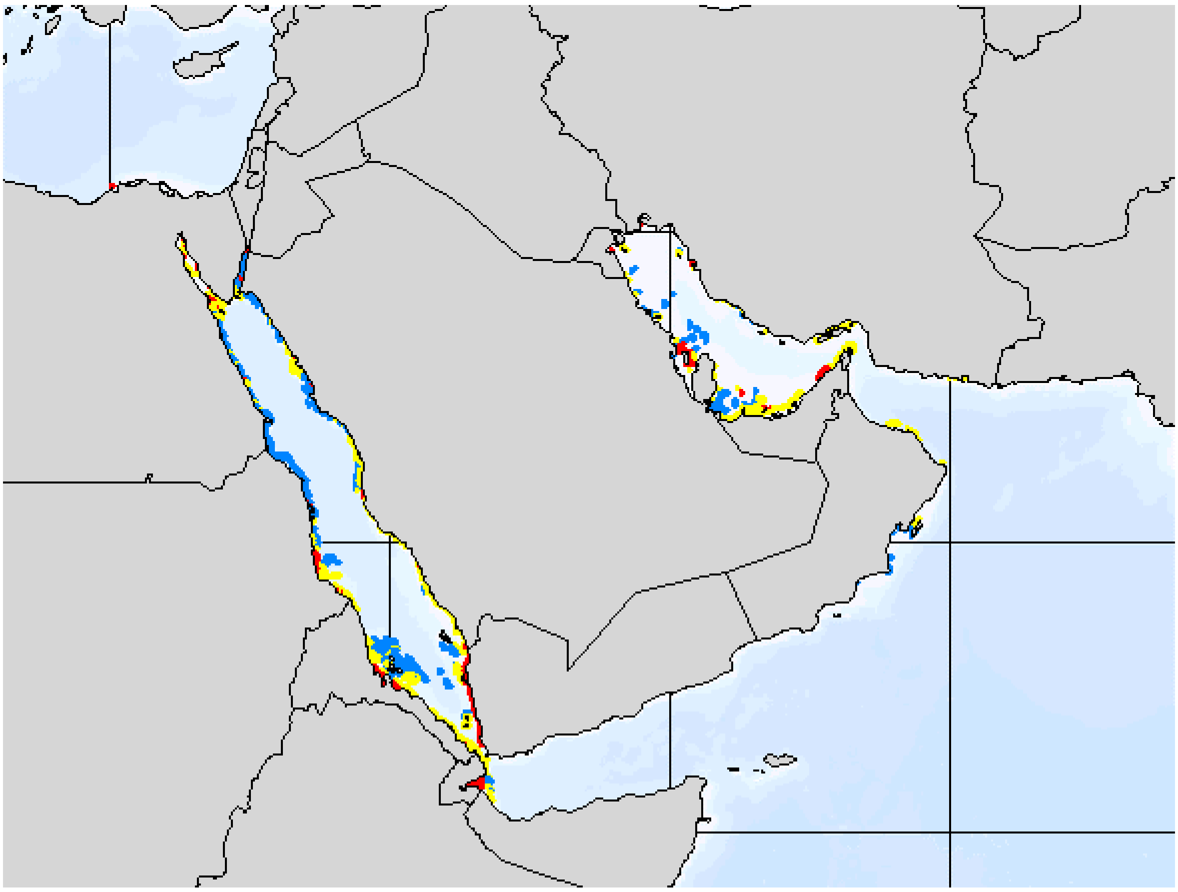


Fig.11. Estimated threat to coral reefs: low medium high, (WRI, 1998).

4.5 The Aqaba's Coral Reef Ecosystem

Occurring at close to coral's northerly latitudinal limit, Gulf of Aqaba reefs have taken advantage of clear, oxygen-rich water and calm conditions necessary for their growth.

However, their distribution and development is limited by the severe marine terrain. Reefs most commonly occur in depths above 50 meters, but few flat areas exist in the gulf with sufficient light and other appropriate conditions. Along the Jordanian coast there are narrow fringing reefs, which are atypical of reefs in general because they lack prominent lagoons. In the northern Jordanian coast, near the town of Aqaba, there are relatively few coral communities and the near shore bottom is primarily sandy and rocky. Coral reefs occur on the points or capes along the southern section of the Jordanian coast, in the area of the marine park, and are interrupted by perpendicular grooves where alluvial fans have delivered sediments (Fig.12).

The reefs here extend approximately 30 meters offshore, at which point the sea bottom drops off rather abruptly, yielding water deep enough for large ocean-going ships to navigate without hitting bottom.

A shallow inner reef flat lies beneath less than one meter of water and reaches the shore in some areas. The Gulf of Aqaba reefs are home to a remarkable diversity of species. This results from the relative oceanographic isolation of the Red Sea, which provides a protected and stable environment for many species not found in other parts of the world (Hulings,1989).

In the gulf, scientists have identified 48 genera, including more than 120 different species of hard corals and 110 species of soft corals. In a 10-meter stretch of reef it is possible to encounter as many as 30 different species of coral, more than one would find in most other areas of the world. There are numerous other invertebrates, including anemones, hydroids, bryozoa, crustacea, echinoderms, sponges, mollusks (80 species), worms, sea squirts, and a plethora of uncatalogued microorganisms, (ISPAN,1992).

The Jordanian reefs are home to a large variety of fishes. These include small reef-associated species such as butterfly fish, triggerfish, blennies, cardinal fish, stonefish, trumpet fish, putter fish, and various pelagic fish such as mullets and mackerel. Blacktip and hammerhead sharks also inhabit the region, as well as the plankton eater and world's largest fish - the whale shark. From February to April, schools of larger pelagic skipjack tuna and bonito pass through the area. Hawksbill turtles have also been seen in the Gulf. In the entire Red Sea marine region, 10% of the species are endemic, a higher proportion than in many other locales, (ISPAN,1992; ICRI,1995).

4.6 Threats to Jordanian Coral Reefs

The oceanographic conditions in the Gulf of Aqaba - partial enclosure, low levels of wave action and little mixing with the open ocean - leave Jordan's coral reefs particularly vulnerable to human encroachment, as pollutants do not get flushed out. The main environmental problems along the Aqaba coast, and actually along the whole Gulf of Aqaba are those induced by industries and port-based activities. Other problems include solid waste, tourism and wastewater. The major threats are reviewed shortly below, noteworthy is that all of these threats have been analyzed and dealt with in more details in chapter nine as part of this present work. This is because these threats are considered also as potential sources for metal inputs into the gulf's water:

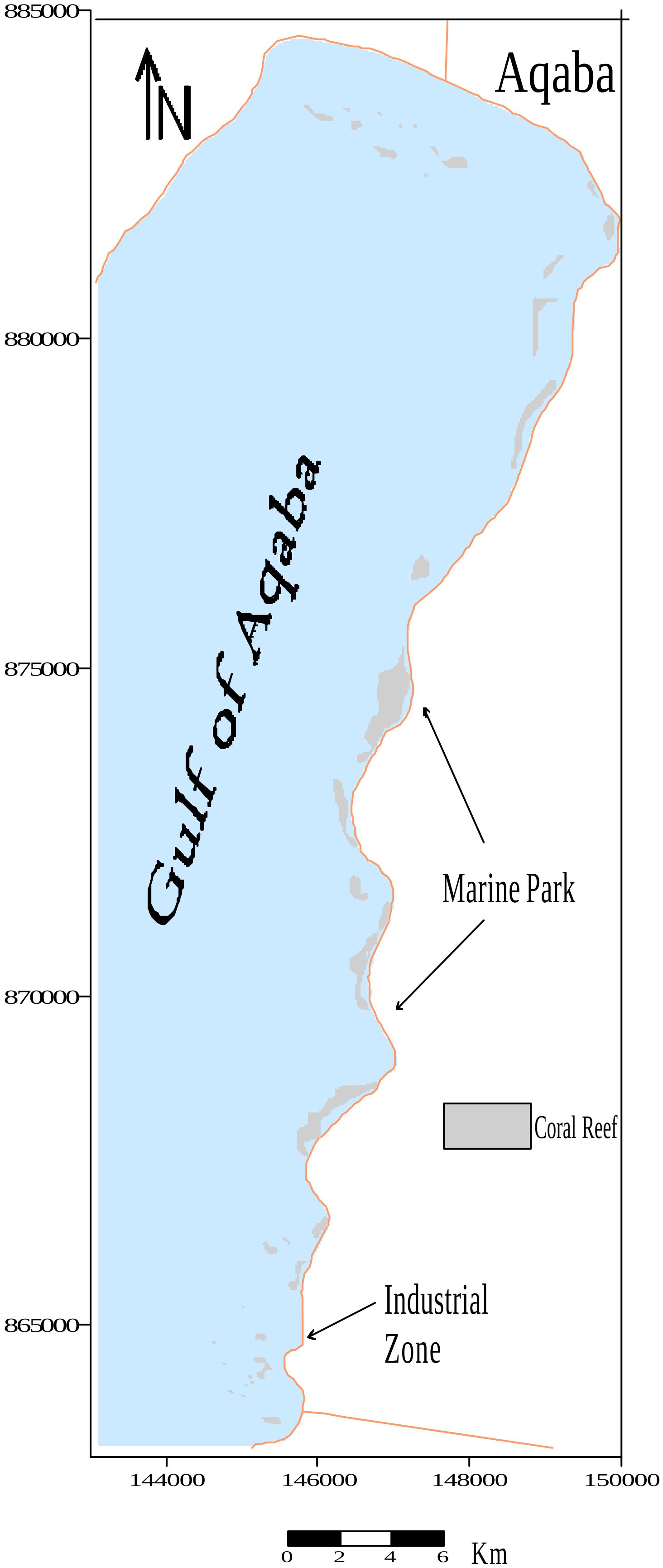


Fig.12 General distribution of coral reef communities along the coast of Aqaba.

4.6.1 Nutrients and Pollution from Coastal Industries

Jordan's south coast industrial zone, adjacent to the Saudi Arabian border, contains the primary industries along the Gulf of Aqaba coastline. The principal industries located within this Zone are a large fertilizer manufacturing facilities, a storage area and loading terminal for potash, the Solvochem tank farm for chemicals oils and solvents, and a 260 MW thermal power station.

The related threats include both chemical and thermal pollution, specifically within this zone. Heated chlorinated cooling water discharges from the present and planned power stations may have an impact on nearby corals and marine life. At the present facilities, over 45,000 cubic meters of cooling water per hour is discharged into the Gulf of Aqaba from three outlets around 200 meters from shore and some 20 meters below the surface.

The loading of fertilizer products onto ships and the unloading of some raw material including sulphur and ammonia at the industrial port poses a serious risk to the marine environment in case of accidental spills.

The other threat is the addition of nutrients into the gulf. According to official reports, 4.0 to 7.0 million tons of raw phosphate is exported through the Gulf of Aqaba, (PERSGA,2001). During transportation and loading a small proportion of this enters the waters of the gulf. The early estimated of the loss was 0.05 of the amount handled, (JPMC,1999). Phosphate dust has been considered a major source of nutrients loading to the Gulf, (Abu-Hilal,1985).

The environmental effects of the dust include reduction of water clarity, and rate of light penetration. It includes also siltation on the coral reef and depression of coral growth rates. Other possible effects are increasing the levels of dissolved phosphate nutrients, and other toxic heavy metals such Cd and Zn, (Abu-Hilal,1985).

4.6.2 Shipping and the Port Facilities

The Gulf of Aqaba is a vital shipping lane for Jordan. Large port facilities exist in the city of Aqaba and support heavy ocean-going traffic.

The main port facilities near the town of Aqaba have harmed reefs through chronic low level release of toxic substances, collisions between ship hulls and propellers and the substrate, and the agitation of bottom silt.

The other port facilities along the coast are distributed along the southeastern shoreline where the container port, cement loading berth and passenger terminal are located, and at the southernmost, nearby the Saudi border, where both the industrial and oil port are located. This segmentation in the distribution port facilities along the coast has brought the damage to more than one site. This is in part due to the fact that some of these facilities have been constructed prior the bilateral land exchange agreement between Jordan and Saudi Arabia in late 1960's, in which Jordan has got an extra 12 km of shoreline on the Gulf of Aqaba, so since then the total length of the Jordanian coastline become 27km.

4.6.3 Oil Pollution from Ships

Ship traffic in the Gulf of Aqaba poses a major, sustained risk of damage to coral reefs and related marine life from oil pollution. More than 2300 ships use the port of Aqaba each year. The oil spill occurs mainly through, small spills that caused by the accidental or intentional release of oil-contaminated bilge or ballast water or medium spills caused by the release of oil as a result of defective equipment or procedures at an oil terminal or pipeline facility. Major spills caused by the rupture of a bunker oil tank in a bulk/cargo vessel collision (500 metric tons), shipwreck of a bulk/cargo vessel (1,500 metric tons), or a tanker collision causing the rupture of a single oil tank (7,500 metric tons).

Small to minor oil spills have occurred frequently in the Gulf of Aqaba, Disastrous spills caused by the wreckage of a fully loaded oil tanker (100,000-150,000 metric tons) were not recorded (APC,2001).

4.6.4 Sedimentation from Construction, Coastal Erosion

Aqaba's reefs are also vulnerable to the effects of poor planning in the construction of ports, highways, marinas, and tourist facilities on the shore which destroy the natural sea bottom by covering it with sediment.

Even construction set back from the water can uproot land and increase the delivery of harmful sediments into coastal waters. These sediments bury corals, inhibit their reproduction, and cloud the water, thereby reducing photosynthesis.

4.6.5 Tourist Development

The Aqaba reef system is a major tourist attraction. Unregulated tourism, however, can harm reefs. Corals are very sensitive to physical contact, as even the slightest disturbance can kill a large number of individual coral polyps.

Studies in the Red Sea area reveal discernible differences in coral densities and fauna abundance between reefs that experience low and high visitor frequency rates (IUCN,1993). Careless tourists break off pieces of living coral, kill corals by stepping on them or scar them by anchoring their boats recklessly. Jordanian reefs have already witnessed a substantial increase in residential debris, fish traps, and litter, all of which could increase with tourism. Even well-regulated tourism can harm coral reefs if it exceeds their carrying capacity.

4.7 Environmental Indicators

Environmental indicators are being increasingly used to emphasize the relevance of monitoring. However, indicators must also be effective. In particular, they must be able to answer management questions, be accessible to the target audience and be sufficiently precise

There is a popular move towards constructing environmental indicators to reflect different aspects of the environment or environmental policy. Areas of interest include environmental quality, the effectiveness of management strategies, and environmental commitment (i.e. the resources made available for managing the environment). The term indicator is used in several ways. It can imply a conceptual framework (DETR,1999; EPA,1999), a measurement or index, or an assessment statistic (EPA,1997). These are recognizable components of any monitoring programme, but rephrasing them as indicators sharpens the focus of environmental monitoring, ensuring that it is relevant.

4.8 Review of Corals as Geochemical Proxies

Corals have become potentially viable proxy monitors of the environment following recognition that coral skeletons record heavy metals in response to varying climate, and pollution (Shen *et al*., 1987). Several publications that describe environmental heavy-metal records in coral skeletons now exist (*e.g,* Dodge and Brass,1984; Bastidas,1999; Fischer and Wefer,1999).

Massive reef-building corals grow on the order of 1 cm yr^{-1} with most species producing annual density bands over a life span of several centuries (Fig.13); because of this, density bands record growth over a long sequence of time. Corals generally accrete one high- and low-density skeletal band annually (Knutson *et al.*,1972 in David,2003).

Density bands result from variations in coral growth, which reflect changing environmental conditions. The chronological reliability of density bands along with the chemical composition of the calcium carbonate (CaCO3) skeleton provide valuable records for reconstructing past environmental and climatic conditions (Barnes and Lough 1989; Lin *et al.,* 1990; Helmle *et al.,* 2000).

The skeleton formed in winter has a different density than that formed in summer because of variations in growth rates related to temperature and cloud cover conditions.

During growth, corals incorporate trace elements and stable isotopes from the surrounding seawater into their skeletons, which can be used for paleoenvironmental studies.

Skeletal density has previously been shown to correlate with light (Knutson *et al.,*1972, Buddemeier, 1974; Wellington and Glynn, 1983 in David, 2003), temperature (Highsmith,1979; Lough *et al*. 1999 in Fischer and Wefer,1999), cloud cover, and rainfall (Barnes and Lough,1989) on annual and seasonal timeframes. Skeletal records also reflect growth responses to anthropogenic perturbations such as sedimentation (Dodge and Brass,1984; Barnes and Lough,1999), oil dispersants (Helmle *et al.*,2000), and lead pollution (Dodge and Gilbert,1984).

Corals are widely used as environmental indicators because of their apparent sensitivity to physical and chemical changes in the marine environment (Shen,1986). These changes are reflected in the health and physiology of coral polyps, (Howard and Brown,1987) as well as in the physio-chemical characteristics of the aragonite exoskeleton (Lough and Barnes,1990; Fallon *et al.*,2002). Moreover, the skeletal growth bands that massive scleractinian corals accumulate have been recognized to be useful in timeseries studies for tracing variations in seawater properties, nutrient levels, and even pollutants entering the marine environment . A valuable attribute of using corals as proxy indicators of these parameters lies in its capacity for sub-annual dating resolution. Dating is accomplished by interpreting skeletal density banding (Barnes and Lough,1999), cyclicity in its isotopic and geochemical composition (David,2003), and/or by investigating other tracers defining particular historical events e.g. fluorescent banding for terrestrial runoff, (David,2003).

Corals provide a continuous time-series record of the marine environment and have been used to monitor past sea surface temperatures (SST) through chemical (Sr/Ca, U/Ca, Mg/Ca, B/Ca) and isotopic (δ18O) records preserved in their aragonite skeletal lattice (*e.g.,* Fallon *et al.,*2002). Similarly, rainfall, runoff, and upwelling events have been identified through the use of (δ18O), Ba/Ca, Cd/Ca, and Mn/Ca (Shen *et al.,*1987; Fallon *et al.,*2002). Less well developed is the use of corals as marine biomonitors of environmental pollution based on abundances of trace metals, such as Hg, Cu, Zn, Pb, Mn, Fe, V, Cd, and others (*e.g.,* Howard and Brown,1986; Shen and Boyle,1987; Hanna and Muir,1990; Bastidas and Garcia,1999).

However, corals have been chosen as environmental indicators as they meet the following (Hanna *et al.,*1990; Allison,1996; Lough and Barnes, 1990):

1. Corals accumulate the pollutant without being killed by the relatively high levels; encountered in the marine environment;
2. Corals are sedentary, and therefore representative of the study area;
3. Corals are a common and widespread group of marine carbonate forming organisms and have an important contribution to sedimentary and paleoenvironmental studies;
4. Corals are sufficiently long lived;
5. Corals are of reasonable size, giving a adequate skeleton and tissue for analysis;

6. Corals has been shown to exist between the coral pollutant make-up and pollutant concentrations in the surrounding water;
7. Corals have skeletal chronological bands which preserve a record of their environmental history.

Coral skeletons are large storehouses of information and they have the potential to provide a wide range of proxy environmental records. Skeletons have been considered as diaries in which corals daily record information about themselves and their environment (Barnes, 1972 in Taylor *et al*.,1995).

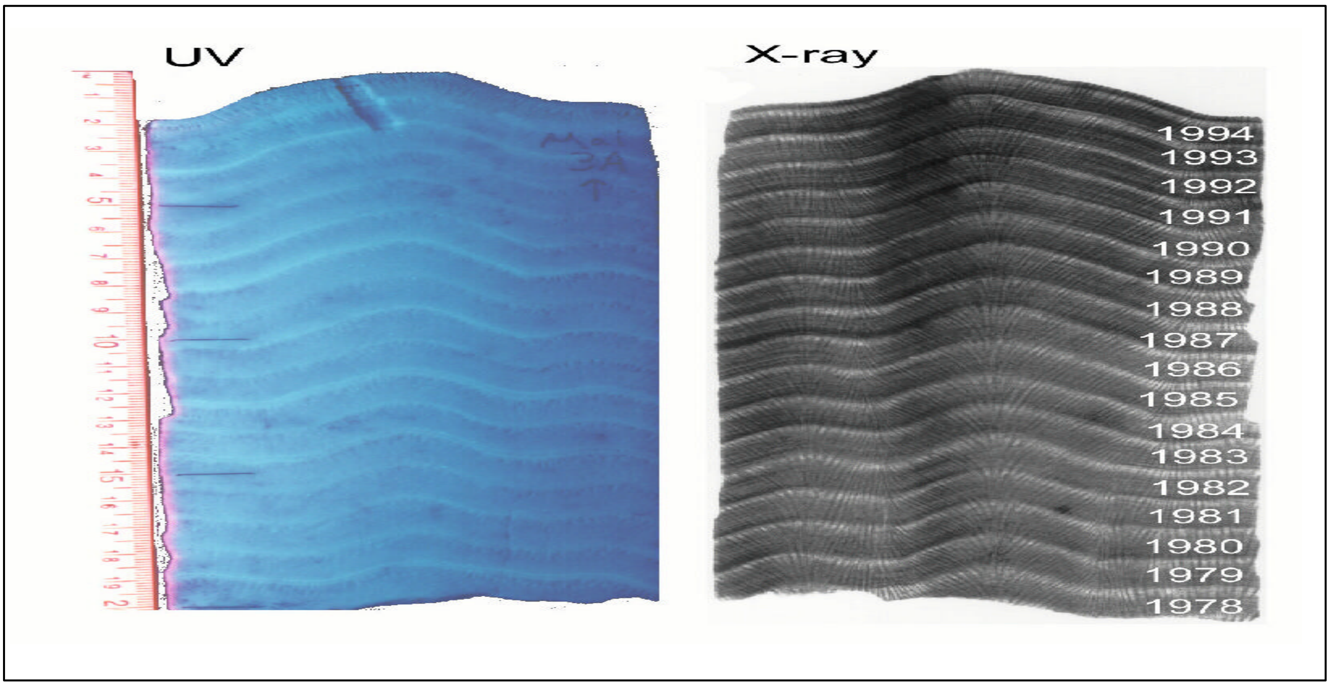


Fig. 13. X-radiograph showing the growth bands of porite coral reef from Aqaba, (Zolda, 2001).

Chapter Five

Heavy Metals; An Overview

5 Heavy Metals; An Overview

5.1 General Background

Heavy metals are natural constituents of rocks and soils and enter the environment as a consequence of weathering and erosion. They occur in very limited amounts of the earth's crust, with an average concentrations of 50 mg kg^{-1} for copper (Cu^{2+}), 0.2 mg kg^{-1} for Cadmium (Cd^{2+}) 15 mg kg^{-1} for lead (Pb^{2+}), 75 mg kg^{-1} for nickel (Ni^{2+}) and 70 mg kg^{-1} for zinc (Zn^{2+}) (Whitney,1990).

Many metals are biologically essential i.e. have a role as activators and constituents of many enzymes, (Bowen 1966 in Wahbeh,1990), but all have the potential to be toxic to biota above certain threshold concentrations. Following industrialization, *unnatural* quantities of metals such as arsenic, cadmium, copper , mercury , lead , nickel and zinc have been released, and continue to be released into the aquatic environment through storm water and wastewater discharges.

As, Cd, Cu, Hg and Zn are the five metals with most potential impact that enter the environment in elevated concentrations as a consequence of agricultural activity. Zinc and Cu are used in small amounts as fertilizers in some soils deficient in these elements, and As, Cd and Hg are constituents of some fungicides. Cu is also used as an algaecide, and Cd and Zn occur as contaminants of phosphatic fertilizers (Organotin compounds), which have no natural counterparts and are generally introduced into the marine environment through biocide applications, principally as constituents of antifouling paints (Whitney,1990).

The major routes of environmental entry of heavy metals include atmospheric transport of dust and through sediment movement in overland flows and in waterways (Bryan,1971). Additional quantities of metals are also added to the environment via the discharge of effluent and urban stormwater. Particulate metals in suspension and in bottom sediments are not generally directly available to aquatic organisms. The exception to this are sediment bound metals which can be accumulated following solubilization in the acidic juices of a sediment-feeder's gut (Ellen,1997).

The rates at which metals are solubilized from particulates is dependent on environmental factors including dissolved oxygen concentrations, pH, salinity and temperature. Once dissolved in the water column, metals may be accumulated by marine invertebrates from solution via passive uptake across permeable surfaces such as gills and the digestive tract. Cellular metal toxicity is primarily due to the chemical inactivation of cellular enzymes responsible for normal organism survival and function, and organism growth, reproduction and behavior are potentially effected by elevated environmental metal concentrations (Ellen, 1997).

In aquatic systems, heavy metals can be found in different forms, whereby influencing their toxicity for fish and other bio-organisms, including free ions, organic and inorganic complexes, precipitates, mineral particles and metals present in biota. In addition, the toxicity of individual heavy metal captions in water bodies depends on the presence of other metals or poisons as well as on water characteristics such as temperature, PH value, dissolved oxygen and salinity (Rainbow,1995). Furthermore, it depends on the water living organisms like stage of life and their behavioral response (Fialkowski *et al.*,1998).

Potential impacts from heavy metals are generally restricted to locations adjacent to major cities or industrialized areas on the coastal fringe and to site draining areas of intensive agriculture. Once introduced into the marine environment, heavy metals have the potential to affect sediment nutrient cycling, cell growth and regeneration, as well as reproductive cycles and photosynthetic potential of marine organisms. Example on this, is the results of Australian studies of marine environmental metal contamination, they indicate that surficial sediments adjacent to most urbanized and industrialized estuaries are contaminated with metals, particularly Pb and Zn, (Koop *et al.*,2001).

Heavy metals and some hazardous pollutants, which are discharged to the sea, are generally adhered to fine-grained particles and settles with sediments on the seabed. Some of these contaminants can remain in the environment for a long time (such as DDT, PCB) and many of them cannot be degraded (heavy metals). They are ultimately accumulated in the sediments or in organisms. Heavy metals and persistent lipophilic organic compounds are absorbed and accumulated in organisms. This process is known as bioaccumulation (Suess and Erlenkeueser,1975; Taylor *et al.*,1995).

Bioaccumulated substances may be passed up the food chain to predator species. This process, which is known as biomagnification, is one of the ways that contaminants may become hazardous to people, (Beiras,2003).

The following is a brief summary on the metals profiles studied in this work and their entry to the marine environment:

5.1.1 Cadmium (Cd)

Cadmium is widely distributed in the Earth's crust at an average concentration of about 0.2 mg kg^{-1} and is commonly found in association with zinc. Higher levels are present in sedimentary rocks: marine phosphates often contain about 15 mg kg^{-1}. Weathering and erosion result in the transport by rivers of large quantities of cadmium to the world's oceans and this represents a major flux of the global cadmium cycle; an annual gross input of 15,000 tonnes has been estimated, (Bryan,1971). Volcanic activity is also a major natural source of atmospheric cadmium release. The global annual flux from this source has been estimated to be 100-500 tones (Wilson,1988).

Cadmium is non essential element for living organisms, but considered the most toxic element to human life and is more toxic than Cu^{2+}, Pb^{2+}, Ni^{2+}, $Zn^{2+,}$ (WHO,1991 and1995).Cadmium shows very high toxicity to both aquatic and terrestrial organisms even at low concentrations. For dissolved cadmium, acute LC_{50} values as low as 3.5 µg l^{1} have been demonstrated for planktonic organisms (Muniz, *et al*.,2004).

The principal applications of cadmium fall into five categories:

- protective plating on steel;
- stabilizers for PVC;
- pigments in plastics and glass;
- electrode material in nickel-cadmium batteries; and
- as a component of various alloys.

The relative importance of the major applications has changed considerably over the last 25 years. The use of cadmium for electroplating has decreased, with its share in 1985 less than 25% (Wilson,1988). In contrast, the use of cadmium in batteries has grown considerably in recent years from only 8% of the total market in 1970 to 37% by 1985.

Non-ferrous metal mines represent a major source of cadmium to the aquatic environment. Contamination can arise from mine drainage water, waste water from the processing of ores, overflow from the tailings pond, and rainwater run-off from the general mine area. The release of these effluents to local watercourses can lead to extensive contamination downstream of the mining operation. Disused mines can also be a source of water contamination (Johnson and Eaton, 1980 in Morley,1997).

At the global level, the smelting of non-ferrous metal ores has been estimated to be the largest human source of cadmium release to the aquatic environment . Discharges to fresh and coastal waters arise from liquid effluents produced by air pollution control (gas scrubbing), together with the site drainage waters.

The manufacture of phosphate fertilizer results in a redistribution of the cadmium present in the rock phosphates between the phosphoric acid product and gypsum waste. In many cases, the gypsum is disposed of by dumping in coastal waters, which leads to considerable cadmium inputs. The atmospheric fall-out of cadmium to fresh and marine waters also represents a major input of cadmium at the global level.

The average cadmium content of sea water has been given as about 0.1 $\mu g\ l^{-1}$ or less (Yim, 1981 in Owen 2000). WHO, (1995) reported that current measurements of dissolved cadmium in surface waters of the open oceans gave values of < 5 ng l^{-1}. The vertical distribution of dissolved cadmium in ocean waters is characterized by a surface depletion and deep water enrichment, which corresponds to the pattern of nutrient concentrations in these areas (Shen and Boyle,1987). This distribution is considered to result from the absorption of cadmium by phytoplankton in surface waters and its transport to the depths, incorporation to biological debris, and subsequent release. In contrast, cadmium is enriched in the surface waters of areas of upwelling and this also leads to elevated levels in plankton unconnected with human activity . Oceanic sediments underlying these areas of high productivity can contain markedly elevated cadmium levels as a result of inputs associated with biological debris (Simpson,1981)

5.1.2 Lead (Pb)

Lead is a bluish or silvery-gray soft metal. With the exception of the nitrate, chlorate, and, to a much lesser degree, chloride, the salts of lead are poorly soluble in water. Lead also forms stable organic compounds. Tetraethyllead and tetramethyllead are used extensively as fuel additives. Both are volatile and poorly soluble in water. Trialkyllead compounds are formed in the environment by the breakdown of tetraalkylleads. These trialkyl compounds are less volatile and more readily soluble in water. Lead is mined, most usually as the sulfide, "galena". Lead is a non essential element for living organisms and is an accumulative poison.

Hence, entry into the aquatic environment occurs through releases (directly or through atmospheric deposition) from the smelting and refining of lead, the burning of petroleum fuels containing lead additives and, to a lesser extent, the smelting of other metals and the burning of coal and oil. Metallic lead deriving from shotgun cartridges or used as fishing weights is lost in the environment and often remains available to organisms (WHO,1995;Schulz,2000).

5.1.3 Copper (Cu)

Uses of copper include electrical wiring and electroplating, the production of alloys, copper piping, photography, antifouling paints and pesticide formulations. Major industrial sources include mining, smelting, refining and coal-burning industries. Certain of these anthropogenic sources may led to significant concentrations entering the aquatic environment (either directly via sewage or industrial discharges or through atmospheric deposition) but copper will also enter the aquatic environment through natural sources, e.g. from the weathering of or the solution of copper minerals (CCREM,1987).

5.1.4 Zinc (Zn)

Zinc is one of the most ubiquitous and mobile of the heavy metals and is transported in natural waters in both dissolved forms and associated with suspended particles (Mance and Yates,1984) In river water, zinc is predominantly present in the dissolved form. In estuaries, where concentrations of suspended particles are greater, a greater proportion of the zinc is adsorbed to suspended particles (CCREM,1987). In low salinity areas of estuaries, zinc can be mobilized from particles by microbial degradation of organic matter and displacement by calcium and magnesium. In the turbidity maximum, zinc associated with suspended sediment will be deposited with flocculated particles where it can accumulate particularly in anaerobic sediments (Schulz,2000). In seawater, much of the zinc is found is dissolved form as inorganic and organic complexes. However, zinc (and nickel) are less toxic metals. Zinc is the most abundant trace element in human body. It functions as a cofactor where many enzymes depends upon it as well as body cells.

Zinc is used in coating to protect iron and steel, in alloys for die casting, in brass, in strips for dry batteries, in roofing and in some print processes. It may enter the aquatic environment through natural or anthropogenic sources, including sewage and industrial discharges

Zinc is an essential element for many marine organisms and, as such, is readily bioaccumulated. Several species of crustacean are able to regulate the uptake of zinc but, at higher concentrations, this process appears to breakdown leading to an influx of zinc(Schulz, 2000).

5.1.5 Nickel (Ni)

Entry into the marine environment

Nickel is a ubiquitous trace metal and occurs in soil, water, air, and in the biosphere. The average content in the Earth's crust is about 0.008%. Levels in natural waters have been found to range from 2 to 10 µg l^{-1} (fresh water) and from 0.2 to 0.7 µg l-1 (marine). The prevalent ionic form is nickel (II) (WHO,1991).

Most nickel is used for the production of stainless steel and other nickel alloys with high corrosion and temperature resistance. Nickel alloys and nickel platings are used in vehicles, processing machinery, armaments, tools, electrical equipment, household appliances, and coinage. Nickel compounds are also used as catalysts, pigments, and in batteries. The primary sources of nickel emissions into the ambient air are the combustion of coal and oil for heat or power generation, the incineration of waste and sewage sludge, nickel mining and primary production, steel manufacture, electroplating, and miscellaneous sources, such as cement manufacturing. Nickel from various industrial processes and other sources finally reaches waste water. Residues from waste-water treatment are disposed of by deep well injection, ocean dumping, land treatment, and incineration (WHO, 1991).

Entry into the aquatic environment is by removal from the atmosphere, by surface run-off, by discharge of industrial and municipal waste, and also following natural erosion of soils and rocks. In rivers, nickel is mainly transported in the form of a precipitated coating on particles and in association with organic matter(Schulz, 2000).

5.1.6 Chromium (Cr)

Chromium occurs ubiquitously in nature with natural levels in uncontaminated waters ranging from fractions of 1 µg to a few µg l^{-1}. Sea water contains less than 1µg l^{-1} chromium (US NAS,1974), but the exact chemical forms in which chromium is present in the ocean, and surface water is unclear. Theoretically, chromium can persist in the hexavalent state (Cr IV) in water with a low organic matter content. In the trivalent form (Cr III), chromium will form insoluble compounds at the natural pH of water, unless protected by complex formation. The exact distribution between the trivalent and hexavalent state is unknown, (Wilson,1988).

Almost all the hexavalent chromium in the environment arises from human activities. Chromium compounds are used in ferrochrome production, electroplating, pigment production, and tanning. These industries, the burning of fossil fuels, and waste incineration are sources of chromium in air and water, (Owen and Sandhu,2000). In the hexavalent oxidation state, chromium is relatively stable in air and pure water, but is reduced to the trivalent state when it comes into contact with organic matter in biota, soil, and water. There is an environmental cycle for chromium, from rocks and soils to water, biota, air, and back to the soil. However, a substantial amount (estimated at 6.7 x 10^6 kg per year) is diverted from this cycle by discharge into streams, and by run-off and dumping into the sea (Schulz,2000).

Cr has been considered a metal with low biogeochemical mobility which should reduce its toxicity potential(Muniz *et al.*,2004)

5.2 Heavy Metal Content in Coastal Areas

Heavy metal contamination of the coastal area is a serious problem in many parts of the world, a selected list showing the heavy metal content in estuary and coastal sediments is given in Table 3 to illustrate the extent of the problem in selected developed and developing countries.

5.3 Mechanism of Taking Up Heavy Metals by Corals

During the formation of $CaCO_3$, metal ions are taken up by the aragonite lattice, according to an ion-exchange reaction, i.e. $CaCO_3$+Me^{2+} ¼$MeCO_3$+Ca^{2+}. The metal-to-calcium (Me/Ca) ratio of coral aragonite is mainly controlled by three factors: (1) the distribution coefficient of the metal ion between aragonite and seawater, (2) the Me^{2+} /Ca^{2+} ratio of the surface oceanic water, and (3) biological (Howard and Brown,1984; Brown,1987; Schulz,2000).

Some researchers usually refer to the Me/Ca^{2+} ratios in corals to evaluate aquatic environmental conditions in which the corals grew. Pb/Ca ratios in corals, for example, has been used as a chemical tracer to evaluate the availability of lead. Shen and Boyle (1987) showed that Pb/ Ca in coral skeleton increased in the 1940s due to the use of leaded fuels for motor vehicles. Bastidas and Garcia, (1999) have also confirmed that Pb/Ca ratio can be applied as a recorder of marine pollution from anthropogenic activities. In order to assess lead contamination due to rapid development near a coastal area, Medina- Elizalde *et al*.,(2002) measured lead chronology in the coastal environment using Pb/Ca ratio in scleractinian coral. Similarly, other Me/Ca ratios in corals may be used to extend the pollution assessment to other metals present in the ambient seawater.

On the other hand, however, most of the researchers prefer to use the content apart from the Me^{2+} /Ca^{2+} since the metal concentration eventually is the same and will show the same results and tendencies (Druffel,1997;Ramos *et al.*,2004).

However, soluble metals in seawater probably represent the most obvious and direct route of metal uptake available to corals although this pathway may not be the primary contributing factor to their metal status.

In summary, trace metals can be incorporated into corals by a variety of mechanisms: substitution of dissolved metal species into the crystal lattice (e.g., substitution for Ca), trapping of particulate (detritus) matter within skeletal cavities, uptake of organic matter from coral tissue, or coral feeding (Barnard *et al.*,1974). Regardless of the incorporation mechanism, corals have been shown to be good tracers of pollutants in the marine environment (Howard *et al.*,1987; Shen and Boyle, 1987; Bastidas, *et al.*,1999). Fig.14 shows the possible direct and indirect pathways of metal incorporation into corals.

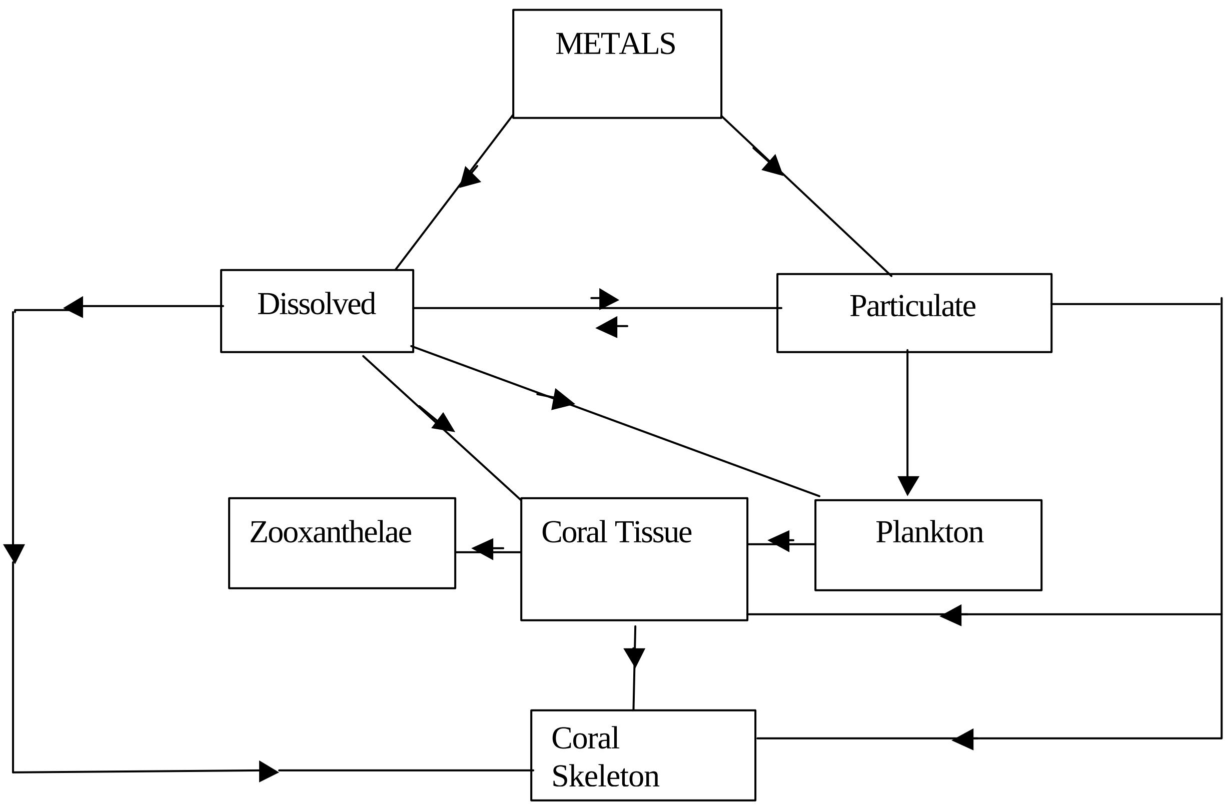


Fig. 14. Direct and indirect pathways of metal incorporation into *sclertinian* corals. (Howard *et al.*, 1987)

Table 3. Heavy metal content (mg kg^{-1}) in selected estuary and coastal sediments (Fung and Lo, 1997).

Description		Cd	Cr	Cu	Ni	Pb	Zn
Surficial sediment							
From reviews: (Fowler,1990; Snodgrass,1980; Young *et al.*,1980;Hungspreugs and Yuangthong,1983)	L	0.01 - 5	-	-	2 - 34	2-98	5 - 135
	U	0.21 –9.9	-	-	10.3 - 63	12.5 -280	75 -2800
	M						
Australia (south), Spencer Gulf, (Dossis and Warren,1980)	R	1.5 - 24	_	_	_	50 - 967	_
	BG	0.15			_	15	_
Brazil, Patos Lagoon Estuary, (Baisch *et al.* 1988)		0.1 -20	8 - 337	0.8 - 20	_	8 - 267	20 - 214
Hong Kong,Victoria Harbor, (HKEPD,1988)		0.8	100	401 -800	_	100	251 - 300
Australia, Fly River Delta, (Dossis and Warren,1980)		_	_	28	_	13	91
Australia,Torres Strait, (Baker and Harris 1991)		_	_	8.2	_	2.8	23
Ireland,Cork Harbor, (Berrow,1991)		< 0.1	6- 11	9- 13	LL- 13	14-23	59 - 75
Spain, Pasajes Harbor, (Legorburu and Canton,1991)		2.9 - 6.4	61 - 165	112-372	43 - 99	159 -346	650 -1390
Malaysia Estuary, (Mat *et al.*,1994)		2.4 - 2.7	_	32.2 - 50.1	16.4-20.4	42.3 -45.9	228 - 310
Core sediment							
Thailand:Upper Gulf (Hungspreugs and Yuangthong,1983)	T	1.25	21	8	-	17.5	20
	B	0.15	16	6.25	-	8	14
	EF	8.3	1.3	1.2	-	2.2	1.4
Italy: Tyrrhenian Sea (Leoni and Sartori,1991)	T	-	194	46	161	85	170
	B	-	190	36	166	36	113
	EF	-	1.0	1.3	0.97	2.4	1.5
California:Newport Bay (Legorburu and Canton,1991)	T	-	NR	NR	-	45	129
	B	-	NR	NR	-	7	41

	EF	-	2	ABOVE 2	-	6.4	3.1
Washington: Sinclair Inlet (Schell,1982)	T	-	50	60	50	80	110
	B	-	43	15	28	9	58
	EF	-	1.2	4.0	1.8	8.9	1.9
Great Barrier Reef (Brady *et al.*1994)	T	-	-	16	-	-	50
	B	-	-	2	-	-	40
	EF	-	-	8	-	-	1.25
England and Wales (Rowlatt and Lovell,1994)	T	-	18-100	-	-	3.1-110	15-153
	B	-	45	-	-	12	22
	EF	-	0-2.2	-	-	0-9.2	0-7.0
Continental Crust (Wedepohl,1991)		0.10	88	35	45	15	69
Shales, (Wedepohl ,991)		0.13	90	45	68	22	95
Granitic Rocks, (Wedepohl,1991)		0.09	12	13	7	32	50

Table 3 Cont.

U: Upper concentration ranges

L: Lower concentration ranges

M: Mean

T: Topmost layer

B: Bottommost layer

EF: Enrichment factor calculated by T/B

NR: Not reported

IP: Irregular profile

BG: Background

R: Range

Chapter Six

Environmental Overview of the Existing Activities along the Coast of Aqaba

6 Environmental Overview of the Existing Activities along the Coast of Aqaba

6.1 Spatial Distribution of Coastal Activities and Pollution Sources

The coast of the Gulf of Aqaba is subjected to several sources of pollution due to several activities occurring at the coastal area. The activities vary between industrial, tourist and other development aspects. The main sources of environmental concerns on the coastal are the following (Fig.15).

6.1.1 The North Beach

Adjacent to the borders of Israel, the north beach is subjected to intermittent sources of pollution coming from the town of Eilat, especially the sewage network which leaks frequently causing negative hygienic effects on the health of swimmers. The latest of these 'outbreaks' occurred in October 1998, (ASEZA,2003). However, the area of north beach is used mainly for recreational activities, where different hotels and other services facilities are located

The public beaches on the north produce solid waste which are dumped into the water by tourists and locals using the beach, specially in weekends and official holidays.

6.1.2 The Main Port

The main port area has one major pollution element which is the "phosphate dust". The problem was a big concern in the past, but after the installation of secondary choke feeders in 1994 the amount of dust was reduced significantly, (APC,2002).

However, the problem remains in moderate magnitudes where phosphate dust is always present when loading and unloading activities are performed. The past has its toll on the present though, the coral communities in the area are in a damaged state due to phosphate sedimentation with no adequate regrowth occurring.

A stretch of about 1.2 km between the main port and the rice and cement loading facility maintains an intact and healthy coral community. This is an area of special concern which requires the maintenance of this community. The other ports area comprise the cement port, the rice port, the passenger terminal and the Aqaba Central Power Plant which was discharging cooling water directly to the sea before stopping operation lately in 1997.

6.1.3 South Coast (the tourist area and the marine park)

This area comprises the Marine Park and the Royal Diving Center, which are subjected to varied tourist activities including diving, swimming and snorkeling. Known for the rich and healthy corals found along the shoreline, as well as for the presence of large sea grass beds, the Aqaba Marine Park was established in 1996 as a multi-use park to preserve the nearshore marine environment of the south coast while allowing for certain uses at sustainable levels.

The park extends approximately 7 km from the northern boundary of the Marine Science Station to the Royal Diving Center in the south. On the terrestrial side, the park extends 50m east of the mean high water mark, and on the marine side, it extends to either 70m bathymetric contour line or to the 350m westward from the mean high water mark., whichever is greatest (see also Fig.3).

6.1.4 The Industrial Area

This is the most heavily polluted segment of the coast due to various input of industrial activities to the seawater. Loading/unloading operations play a major role in the input of pollutants to the marine environment. Cooling water outlets are other significant sources as well as construction activities. The area contains an oil terminal, a potash storage facility, a mixed fertilizer manufacturing facility and a new chemical related facility .

6.2 Overview of the Existing Industrial Activities in Aqaba

Being Jordan's only outlet to the sea, the Gulf of Aqaba has a major role to perform in the heart of Jordanian economic development. Consecutive growth and expansion of the Jordanian industries has led to an increase in the exploitation of Aqaba as a heavy-medium industrial center.

Jordan's three gigantic industries (Phosphate, Potash and Cement) all export their products from Aqaba and have port terminals and storage facilities. In addition to that, the Jordan Phosphate Mines Company has established a fertilizer complex in 1980 that produces and exports large amounts of fertilizers to several world markets. A heavy oil-based thermal power station with a capacity of 520 MW is functional in Aqaba.

Recently, by the year 2001 three other heavy industries have been established, two of them; Jordan Bromine Company and Jordan Magnesia company have only storage and export facilities along the coast (at the oil port and the industrial port), where the third one; Kemira Arab Potash Company (KEMAPCO) has its own industrial complex where it is used for the production of several fertilizers as well as storage and export activities. This new established industry is also - in addition the power plant and the phosphate industrial complex –using seawater for cooling To add to this collection of heavy industries, about ten other medium industrial facilities are present ranging from the production of fertilizers to the storage of solvent chemicals. The following gives detailed overview on some of these major industrial activities;

6.2.1 The Phosphate Industrial Complex

The complex is divided into five operation units: the phosphoric acid unit, Aluminum fluoride unit, DAP-fertilizer unit, sulfuric acid unit and the utilities unit. The complex was designed to produce fertilizers and other intermediary industrial chemicals. Table 4 provides an overall inventory of waste types generated in the five main units of the complex. The wastes are divided into air and gaseous emissions, liquid wastes and solid wastes (JPMC,1999).

6.2.2 The Industrial Port

The industrial port is the last port terminal in the Jordanian coastal stretch. It lies on the southern border of Jordan and is used for bulk cargo handling (loading-unloading) and export of fertilizers, phosphoric acid, salt and potash. On the reverse route, several chemicals are imported through the industrial port (sulfur, aluminum hydroxide and ammonia).

The major environmental concerns in the industrial port are the dust emission of imported and exported chemicals (sulfur, potash) despite the installation of dedusting equipments on each junction point of the conveyor belt system. Sulfur dusts are produced due to the continuous failure of the chain bucket and the conveyor system which is not spill proof.

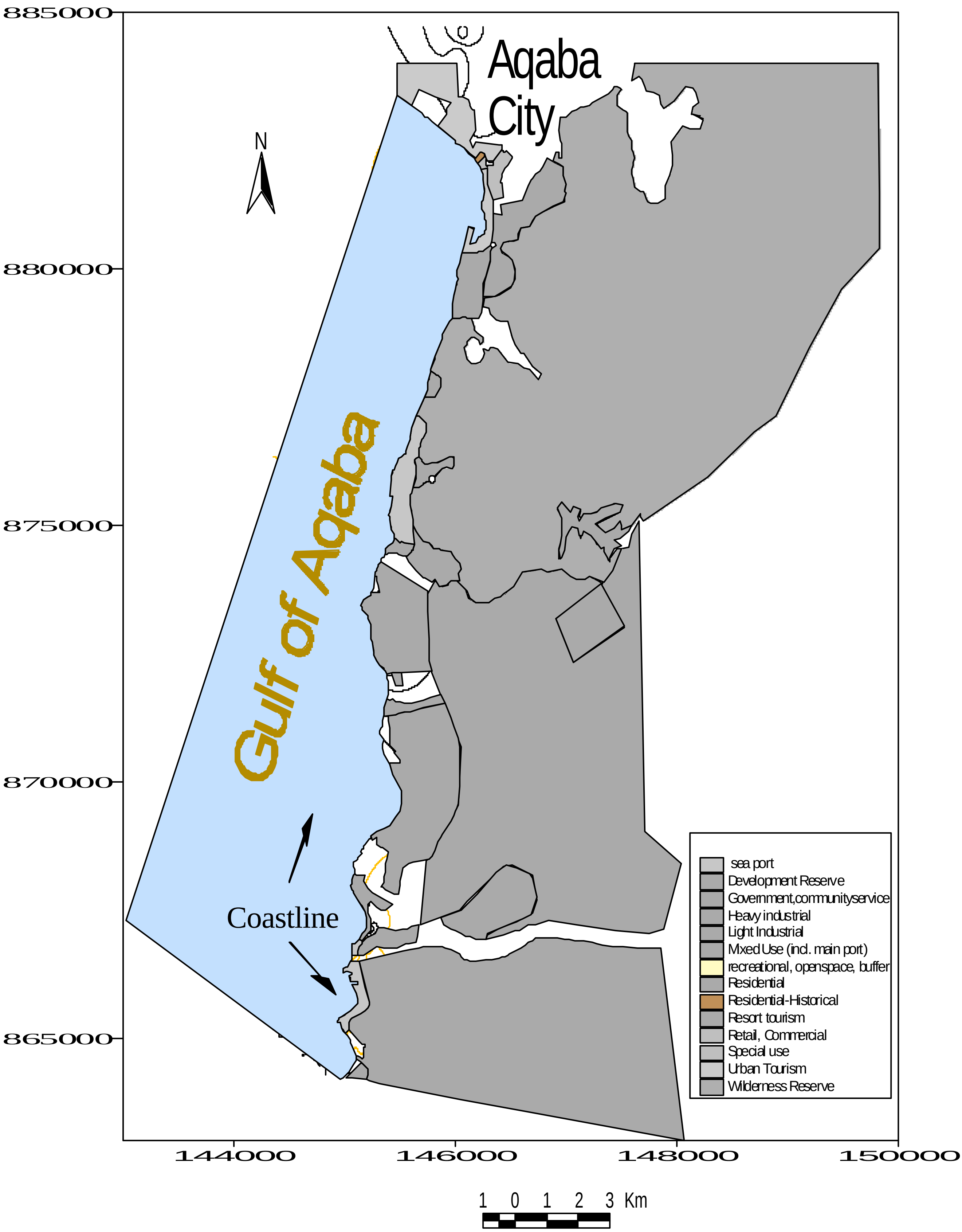


Fig.15. Land use map showing the main activity zones along the coast of Aqaba, (ASEZA, 2002)

Table 4. An inventory of wastes generated from the Fertilizer Industrial Complex. (JPMC,1999)

Unit	Air Emissions	Liquid Wastes	Solid Wastes
Phosphoric Acid	Vent gases containing particulate dust and fluoride	Washwater of gaseous emissions scrubbers, recycled within the facility or disposed to evaporation lagoon	1- Gypsum transported by conveyor belts to Gypsum dump(12 million ton/yr). 2- Dust particulates due to loading and unloading of phosphate rock.
Sulfuric Acid	1. SO_2+SO_3 and acid mist 2. Particulate air emission may contain heavy metlas from elemental sulfur 3. Minor H_2S	1- Hot Seawater 2- Steam condensate (having H_2S and SO_2 dissolved recycled in utilities)	a. Elemental sulfur (belt, loading and unloading) b. Impurities produced at the filter unit of melted sulfur (7tons/day) disposed at gypsum dump.
Aluminum Fluoride	CO,CO_2,NOxand SOx	Excess water from crystallization unit disposed to evaporation pond or recycled.	Silica produced at a rate of 30-40 tons/day disposed at gypsum dump
DAP (Di-Amino Phosphate)	1. Gaseous ammonia and fluoride from reactor. 2. Fluoride and phosphate penfoxide	Washing water from scrubbers mixed with diluted phosphoric acid at a rate of 200m^3/day recycled to scrubbers.	---------
Utilities	CO, CO_2, NOx and SOx	---------	Domestic sludge from WWTP (6-7 ton/yr) disposed at gypsum dump.

Yellow sulfur dust is always present in the industrial port and the roads and around conveyor belt. Consequently high amount of this sulfur reaches the sea floor and covers corals.

In addition, some incidents were reported – but not well documented- where water becomes saturated with white powders thought to be spilled fertilizers. One particular incident occurred in July 1998 where surface sea water (close to the beach) had a white coloration that lasted for five days,(ARA,2001).

6.2.3 The Phosphate Berth at the Main Port

The phosphate company operates at the main port storage houses and two berths for loading phosphate rock on exporting ships. This is used to be environmental focal point in Aqaba where huge amounts of phosphate dust used to escape this operation and pollute the ambient air reaching to the town of Aqaba. Maximum amount of deposition was estimated by JICA in 1996 to be 21.6g/m^2 in hourly values. Maximum dust dispersion on the sea site was predicted to be 2.13kg/m^2 while that on the ground site was estimated to be 0.42kg/m^2, (JICA,1996).

6.2.4 Aqaba Thermal Power Plant

This station is located 20km south of the main port of Aqaba (in the industrial zone). The plant operates on a conversional steam-producing thermal power plant system, where electricity is generated through a series of energy conversing stages: fuel is burned in boilers to convert the cooling water to high-pressure steam which is used to drive a turbine to generate electricity. The fuel used is heavy and high-sulfur fuel. It is transported to the station via tanker fleet of around 100-120 tankers day^{-1}. The water required for cooling is seawater abstracted from the sea, used once and returned back, chemically unchanged. Only 0.15-0.20 ppm of residual chlorine is present in the water to disinfect it and remove bacteria and algae. The return cooling water is still discharged directly in an open tunnel into the sea, (plate 3).

Another source of environmental concern regarding the operation of the plants is the oil pollution coming from the tanker fleet energizing the plant with heavy oil. The tanker drivers usually empty the excess oil from the tanks on the land adjacent to the facility and on the right and left side of the coastal road (some are actually very close to the beach).

6.2.5 Jordan Cement Factories (Aqaba Facility)

The facility is used for storage and export via the cement terminal. Cement is transported from the main factories (outside Aqaba) by tankers to Aqaba site and pumped by closed pipes to the storage domes. The cement is transported through a fabric filter to the conveyor belts leading to the port. The main environmental concern in this site is the dust generated when loading and unloading the cement to the domes and in the terminal.

6.2.6 The Arab Potash Company

The Aqaba facility of this company is a storage site for potassium chloride prior to exporting via the industrial port. The potash is transported from the main factory, 200km north of Aqaba via trucks. It is unloaded into hoppers and transported by a closed conveyor belt system into the warehouses for storages. It is exported through the industrial port after being transported to the berth through a conveyer system.

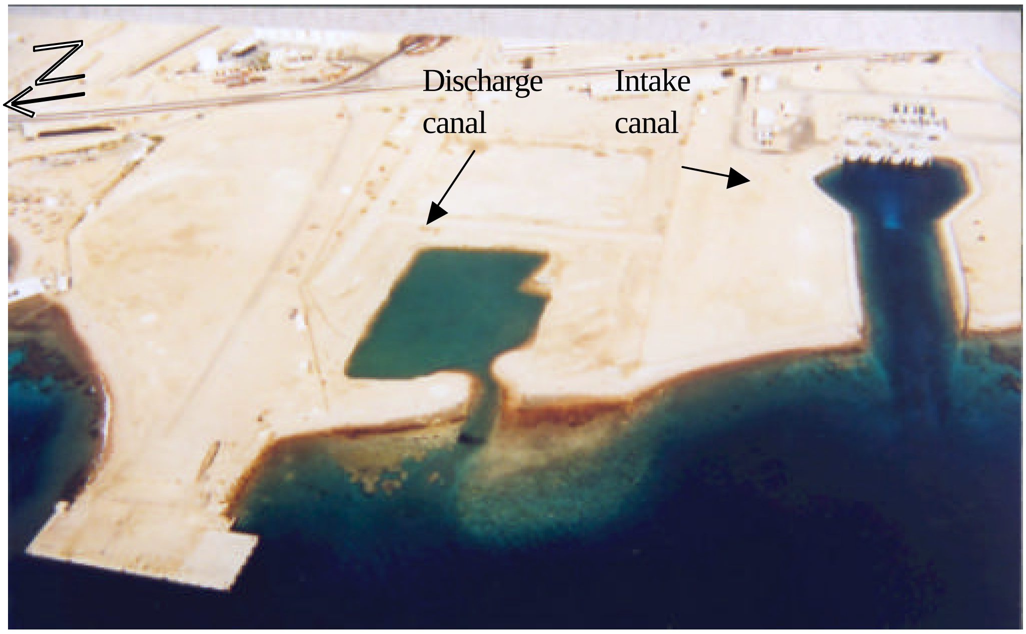


Plate.3 Arial photograph to show one of the intake and discharge canals for seawater used in cooling process at the Aqaba Thermal Power Plant.

The main environmental concern at the site is the domestic wastewater pipe which opens to the sea directly discharging the effluent of the partially treated (preliminary separation) domestic wastewater coming from the facility. Monitoring of seawater quality in the area of this pipe by the concerned authorities in Aqaba show a clear sign of pollution coming from the sewage pipe (MSS,1999).

The extremely high values of ammonia (20.23 mg l^{1}.: pipe outlet, 0.306 mg l^{1}.and 0.026 mg l^{1}. 10m and 50 m south of the pipe respectively, reference sea value is 0.004 mg l^{-1}) are indicative of the discharge of untreated sewage waste into the sea. The values of ammonia decrease in a statistically significant, but environmentally unsatisfactory rate, which shows the dilution with sea water does not improve the conditions to the extent required,(ARA,1998). Coral formations near the shore have been markedly affected by pollution, and the non-seasonal growth of attached algae indicates a state of “cultural eutrophication” caused by anthropogenic factors (personal observation,1998).

One other environmental concern at the potash site is the potash dust emitted during loading and unloading. Potash trucks are exposed for accidental and/or deliberate dumping and discharge of some potash during loading or transport.

6.2.7 Aqaba Central Power Plant

This plant has stopped systematic operation and production of electricity since 1997. The plant works now as an emergency back up for the Aqaba Thermal Plant. For maintenance and fitness reasons, the plant operates once a month. Since the plant stopped operation, the stream of returning cooling sea water stopped discharging into the sea. Other liquid wastes (used oil and sludge, boiler wash water and drainage water) have also been halted. In addition to that, the sanitary wastewater septic tank has not been emptied yet since the plant started in 1977 (ARA,1998). Danger of contamination of sea water by sewage seepage still exists.

6.2.8 Solvochem

Located adjacent to the oil jetty (see Fig.3), the facility serves as a storage unit for imported chemicals, oils and solvents. no processing occurs at the facility. the stored chemicals include Xylene, Toluene, Ethanol, Isobutanol, Acetone, Methanol and Hexane. The chemicals are stored in tanks unlined with cement basins which increase the potential of contamination .

Other minor industries include the Indo-Jordan Chemical Company (storage facilities),the National Ammoniax Company, Jordan Kuwait Company for Agriculture and Food Products.

Chapter Seven

Heavy Metals Content and Spatial Distribution along the Coastline: Assessment and Documentation of the Current Trend

7 Heavy Metals Content and Spatial Distribution along the Coastline: Assessment and Documentation of the Current Trend

7.1 Heavy Metals in the Gulf of Aqaba

7.1.1 Introduction

The increase in the levels of trace metals in the marine environment is a worldwide problem and the discharge of trace metal wastes has many obvious impacts on the marine environment such as the increase in residue levels in water, sediments and biota, decreased productivity, and increase in exposure of humans to harmful substances. In the Red Sea region which is one of the most arid regions of the world, typical sources of metal contamination are represented by oil industry, offshore oil platforms, oil terminals, and ships in addition to stainless steel, power stations and cement industries. Although scientific interest on the Red Sea and its adjoining marine environments, i.e. the Gulf of Suez and the Gulf of Aqaba began long ago, very little is known about the levels and distributions of trace metals in this region. Therefore, the determination of trace metals is important and will fill a gap in the present knowledge of this area.

The heavy metals in seawater, sediments and biota of the Gulf of Aqaba (the Jordanian portion) is beyond the scope and objectives of this work, but in order to give a comprehensive and deep insight to the environmental condition prevailing the coastline as well as for comparison purposes and of course supporting the documentation presented in this work, the following sections include a brief review of most of the work conducted on metal pollution in Aqaba .

7.1.2. Heavy Metals in Seawater

Metal concentrations in coastal waters are generally higher than at intermediate and offshore sites. This is interpreted as being a direct consequence of their proximity to inputs either the natural or anthropogenic.

The early reviewing of literature and reports available on the concentrations of trace metals in the Gulf of Aqaba (in particular the Jordanian' waters) has shown that most of these metals have concentration significantly higher by a factor up to 3 in surface compared to deeper layers (Table 5).

Among the very little data available on the concentration of trace metals in the Aqaba's seawater, the data obtained by the Environmental Monitoring Program of the Marine Science Station, (1999) represent the most recent investigations (Table 6). The results were based on samples taken from three selected stations along the Aqaba coastline. However, the range of the mean concentrations of Cd, Cu, Pb, Ni and Zn was 0.07-0.13; 0.74-2.28; 0.73-1.43; 6.92-11.09 and 5.71-11.55 $\mu g l^{-1}$ respectively. No further data were available.

However, investigations of the correlation between trace elements recorded in seawater revealed the presence of strong and significant relationships between several pairs of trace elements in the gulf. Most of the significant relationships between metals were positive indicating that the appearance of local high concentration for one metal by possible contamination correlates with high values for other metals.

Table 5. Concentrations of trace metals (μg L^{-1}) in the northern Red Sea and the Gulf of Aqaba compared to other values in different regions (Modified after Shriadah *et al.,* 2004).

Location	**Metals**				
	Zn	**Ni**	**Cu**	**Cd**	**Pb**
Red Sea (Off shore waters, Egypt)	0.13–1.17	0.05–0.52	0.07–0.29	0.02–0.78	0.02–0.68
Red Sea (Coast, Egypt)	-	-	5.1	-	-
Red Sea (Jeddah, KSA)	6–14	-	3.5–4.0	0.3	1.1–27
Eastern harbor and El-Mex Bey, Egypt	-	-	4.9	1.88	0.5
Eastern harbor and El-Mex Bey, Egypt	112.8	0.44	-	-	-
Oporto coast,NW Portugal	-	-	0.52–4.2	0.4–3.5	0.48–4.1
Santa Cruz de Tenerife, Canary Islands	0.50–110.90	0.50–13.67	0.50–40.10	0.08–0.31	0.20–116.88
Bahrain (Arabian Gulf)	0.03–11.25	0.13–0.53	0.03–0.38	0.03–0.38	0.03–0.23
South Aegean, Greece	0.13–29.12	0.55–15.98	0.16–15.21	0.018–1.6	0.227–9.218

It might also reflect similar sources and/or similar biogeochemical behaviours (Saad and Kandeel,1988). Comparing the concentrations found here with those reported in the literature (Table 6), it is concluded, on the whole, that the concentrations of heavy metals observed in the Gulf of Aqaba of Jordan are relatively higher than those compiled by most workers in the Mediterranean Sea and are relatively higher than the typical open ocean water (Hamza and Amierh,1992; Shriadah and Emara,1991; Emara and Shriadah,1991; Leal *et al.*,1997).

Table 6. Mean concentration of heavy metals ($\mu g l^{-1}$) in waters at three different sites along the Aqaba coastline; measured on August, 1998 and in reference Ocean Waters. (MSS,1999).

Parameter	Station	Mean
Cadmium	1	0.11
	2	0.07
	3	0.13
	Ocean Waters	**0.11**
Copper	1	2.28
	2	1.13
	3	0.74
	Ocean Waters	**2.00**
Lead	1	1.09
	2	1.43
	3	0.73
	Ocean Waters	**0.03**
Nickel	1	8.65
	2	11.09
	3	6.92
	Ocean Waters	**2.00**
Zinc	1	5.71
	2	11.55
	3	11.32
	Ocean Waters	**2.00**

Results from a recent regional survey on the trace metals in the water column of the Red Sea and Gulf of Aqaba (Shriadah *et al.*,2004) revealed a small range of variation and regional irregularities. It indicated significant higher concentrations for Fe, Cd and Pb compared to other metals. Compared to the northern Red Sea, significant higher concentrations for Ni and Cd are measured in the Gulf of Aqaba.

7.1.3. Heavy Metals in Sediments

Similar to seawater, researches on trace elements and other pollutant distributions and background levels in sediments of the Gulf of Aqaba are very limited (Abu-Hilal, 1985,1987, 1993; Whabeh,1987; Abu-Hilal and Badran,1990).

Sediments can act as a major pollutant reservoir because metals and other contaminants can bind to the sediments and become bioavailable to the rest of the food chain. Several organisms such as filter feeders take in low levels of heavy metals which then bioaccumulate through the food chain. Bioaccumulation is the accumulation of food contaminant by oral uptake and digestion. Heavy metals, in particular, have a high affinity for fine sediment particles.

Sediment is a matrix of materials which is comprised of detrital, inorganic, or organic particles, and is relatively heterogeneous in terms of its physical, chemical, and biological characteristics. It is often stated that sediments have a marked ability for converting inputs of metals from various sources into sparingly soluble forms, either through precipitation as oxides or carbonates, or through formation of solid solutions with other minerals, (Li *et al.*,2000).

Thus, aquatic sediments constitute the most important reservoir or sink of metals and other pollutants. However, due to various diagenetic processes, the sediment-bound metals and other pollutants may remobilize and be released back to overlying waters, and in turn impose adverse effects on aquatic organisms.

In sediments, heavy metals can be present in various chemical forms, and generally exhibit different physical and chemical behavior in terms of chemical interactions, mobility, biological availability and potential toxicity.

It is necessary to identify and quantify the forms in which a metal is present in sediments to gain a more precise understanding of the potential and actual impacts of elevated levels of metals in sediments, and to evaluate processes of transport, deposition and release under changing environmental conditions.

Numerous extraction schemes have been described in the literature; *Inter alia.,* Tessier *et al.*,1979; to evaluate the possible chemical associations of metals in sediments and soils (Li *et al.*,2000).

In Aqaba, the heavy metal concentrations in sediment cores as reported by Abu-Hilal and Badran (1990) at different depths of five coastal stations along the Aqaba coastline, (Table7) show that these sediments contain high Cd, Co, Cu, Fe, Mn, Pb and Zn concentrations originated from metal pollutants discharged into the water of the gulf from permanent sources of pollution.

The heavily polluted sites were the port area and near the sewage outlets (the old one). At these two sites, the surface and vertical distribution of trace metals are similar to the distribution of organic carbon, total phosphate-phosphorous and fluoride which were derived over the past years from local release from deposited phosphate rock particle, raw sewage and boat and ship activities in addition to the industrial activities.

Table 8 shows also the concentrations of some selected metals in bottom sediments investigated as part of a monitoring program in 1998.

7.1.4. Heavy Metals in Organisms

Toxic metals released into the marine environments tend to accumulate in sediments and subsequently are taken up by filter-feeding organisms. Some Marine animals have adapted to live with raised levels of heavy metals. They do this either by removing the metals from their bodies, or by storing them in a non-poisonous form. By storing; metal compounds can be bound to special proteins called metallothioniens. This makes the metals less toxic and allows the animals to tolerate a certain level of pollution.

By removal: metallic compounds can be secreted (put into) the shell, scales, fur or feathers, gills or eggs of marine animals. In this way they are removed from the body via natural processes of excretion and renewal, (Kumar,1988).

These animals have adapted to live in an environment that contains low levels of heavy metals. However adapting to live under these conditions takes energy and the animals will often be slow to reproduce, grow and develop. They may have reduced lifespan. It is important to remember that the level of pollutants present makes a big difference. In extreme cases some organisms (such as oysters) can undergo a sex change, with the entire population becoming single sex and dying out within a generation, (Kumar,1988).

Example on such organisms is bivalves. Marked variations in the bivalves heavy metal concentrations demonstrated that bivalves such as oysters and mussels are valuable biomonitoring tools for assessing the chemical pollution of the coastal environments

Oysters and other bivalves accumulate metals such as copper and zinc and can tolerate very high metal concentrations without apparent signs of any detrimental effect,(Lauenstein *et al.*,1990; Presley *et al.*,1990 and Goldberg *et al.*,1983 in Wahbeh *et al.*,1995).

However, it is true that marine organisms do need very small quantities of heavy metals. For instance copper forms part of haemocyanin, the respiratory pigment of Crustacea (crabs, prawns etc.). Large quantities of copper, however, as well as of other heavy metals, will inhibit their vital functions, in other words, will severely impair or kill them. In general, the effects –worthy to mention-of heavy metals toxicity can be classified into three main categories :

- the blocking of essential function groups of the biomolecules (e.g. proteins, enzymes)
- the displacement of a metal ion from a biomolecule
- the modification of the structure of the biomolecules in space which is very important for their function, (Shen,1986).

Table 7. Concentration of some heavy metals (ppm dry wt) in sediment cores from the Jordanian coastline of the Gulf of Aqaba, (1) acid leachable (2) total conc., U=upper cores section (0-5cm), M=middle cores section (5-10cm), L=lower cores section(10-15cm). Abu-Hilal and Badran (1990).

Station	Depth	Core sec.	Cd		Cu		Ni		Pb		Zn	
			(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
3	5	U	1.2	2.0	4.0	8.0	12.0	19.0	23.0	85.0	24.0	33.0
		M	0.6	2.0	3.0	8.5	8.0	19.0	14.0	90.0	12.0	32.0
		L	0.7	2.0	3.0	9.0	8.0	19.0	13.0	78.0	12.0	21.0
		Mean	0.8	2.0	3.3	8.5	9.3	19.0	16.7	84.0	16.0	32.0
	10	U	1.7	3.0	4.0	10.0	16.0	26.0	28.0	105.0	24.0	41.0
		M	1.4	2.5	4.0	9.0	14.0	25.0	24.0	95.0	23.0	40.0
		L	1.4	2.5	5.0	10.0	14.0	29.0	25.0	95.0	23.0	40.0
		Mean	1.5	2.7	4.7	9.7	14.7	26.7	25.7	98.0	23.3	4.03
	20	U	2.0	2.5	4.0	9.0	17.0	28.0	33.0	113.0	22.0	40.0
		M	1.5	3.0	3.0	8.5	13.0	23.0	24.0	90.0	16.0	36.0
		L	0.8	2.5	2.0	6.5	7.0	19.0	14.0	73.0	12.0	30.0
		Mean	1.4	2.7	3.0	8.0	12.3	23.3	23.7	92.0	16.7	35.3
	30	U	1.4	2.5	4.0	8.5	14.0	22.0	23.0	75.0	22.0	41.0
		M	1.3	3.0	4.0	9.5	14.0	22.0	23.0	85.0	22.0	42.0
		L	1.2	2.5	4.0	8.0	13.0	22.0	23.0	88.0	20.0	37.0
		Mean	1.3	2.7	4.0	8.5	13.7	22.0	23.0	83.0	21.3	40.0
4	5	U	1.4	4.0	5.0	8.0	14.0	29.0	20.0	88.0	23.0	39.0
		M	1.4	4.0	5.0	8.0	13.0	30.0	20.0	93.0	24.0	43.0
		L	1.4	4.0	5.0	8.0	15.0	31.0	20.0	95.0	26.0	48.0
		Mean	1.4	4.0	5.0	8.0	14.0	30.0	20.0	92.0	24.3	43.3
		U	2.6	4.0	4.0	8.5	13.0	30.0	20.0	98.0	23.0	42.0

	10	M	1.5	4.0	6.0	8.5	15.0	31.0	20.0	95.0	27.0	50.0
		L	1.6	4.0	6.0	9.0	16.0	47.0	22.0	105.0	28.0	48.0
		Mean	1.6	4.0	5.3	8.7	14.7	39.3	20.7	99.0	26.0	46.7
	20	U	2.3	5.5	7.0	10.0	22.0	64.0	36.0	118.0	31.0	60.0
		M	3.0	6.0	6.0	10.0	25.0	63.0	47.0	138.0	25.0	54.0
		L	3.6	7.0	5.0	9.0	27.0	74.0	53.0	163.0	24.0	47.0
		Mean	3.0	6.2	6.0	9.7	24.7	67.0	45.3	140.0	26.7	53.7
	30	U	2.2	4.5	6.0	9.5	18.0	71.0	31.0	115.0	26.0	54.0
		M	1.9	4.5	6.0	9.0	16.0	66.0	28.0	115.0	26.0	54.0
		L	1.6	4.5	5.0	9.0	17.0	76.0	29.0	100.0	28.0	53.0
		Mean	1.9	4.5	5.7	9.2	17.0	71.0	29.3	110.0	26.7	53.7
5	5	U	1.8	4.0	4.0	6.5	14.0	48.0	21.0	118.0	27.0	43.0
		M	2.0	4.0	5.0	8.0	18.0	73.0	23.0	115.0	31.0	56.0
		L	1.8	4.0	5.0	8.0	18.0	85.0	22.0	110.0	32.0	57.0
		Mean	1.9	4.0	4.7	7.5	16.7	69.0	22.0	114.0	30.0	52.0
	10	U	2.0	4.5	5.0	8.0	22.0	82.0	28.0	120.0	32.0	56.0
		M	2.0	4.5	5.0	8.0	21.0	84.0	26.0	113.0	32.0	56.0
		L	2.2	5.0	7.0	9.0	23.0	94.0	28.0	120.0	41.0	63.0
		Mean	2.1	4.7	5.7	8.3	22.0	87.0	27.3	118.0	35.0	58.0
	20	U	3.0	5.5	7.0	10.0	24.0	98.0	30.0	130.0	40.0	66.0
		M	2.0	4.5	6.0	9.0	22.0	87.0	24.0	115.0	38.0	61.0
		L	1.6	4.0	5.0	8.0	21.0	84.0	19.0	115.0	30.0	56.0
		Mean	2.2	4.7	6.0	9.0	23.0	90.0	24.3	120.0	36.0	61.0
	30	U	2.2	4.0	5.0	8.0	16.0	75.0	21.0	105.0	28.0	46.0
		M	1.3	4.0	4.0	7.0	12.0	68.0	14.0	96.0	21.0	40.0
		L	0.9	3.5	4.0	5.5	7.0	50.0	10.0	75.0	20.0	29.0
		Mean	1.5	3.8	4.7	6.8	9.3	64.0	15.0	91.0	23.0	38.0

Table 8. Concentration ((µg g^{-1}) of selected heavy metals in bottom sediments at 40 m at two station at the industrial area.(MSS, 1999).

Parameter	**Station1**		**Station 2**	
	September	*October*	*September*	*October*
Cadmium	1.00	2.00	5.00	5.00
Chromium	3.00	2.00	6.00	6.00
Copper	3.00	3.00	7.00	8.00
Nickel	2.00	3.00	16.00	13.00
Zinc	11.00	10.00	10.00	21.00

Table 9. Mean concentration (µg g^{-1} dry wt) of three trace metals in soft whole tissue of several types of mollusks (Wahbeh,1990).

Species	**Zn**	**Cu**	**Cd**
Acanthopleura hadoni	199.6	26.2	6.1
Cellana radiata	93.3	26.8	5.5
Nerita forskalii	88.4	BDL	11.3
Nerita polita	116.5	BDL	10.0
Mesdesma glabrum	537.5	82.3	5.3

*BDL : below detection limit.

Literature on using certain organisms as indicators for metal pollution in the Gulf of Aqaba are scarce, in particular in the Jordanian portion of the Gulf. Wahbeh, (1990) has researched the level of Zn, Mn, Cu,Cd, Fe and Mg in soft tissue of some intertidal mollusks from Aqaba. He concluded that there is significant concentration differences between different species, and similar significant differences were also found between concentrations of different metals in each species. The author has concluded also that bivalve (*M. Glabrum*) appears to be possible candidate indicator of metals pollution. It has high metal concentration factor, a sedentary burrowing existence and abundant occurrence in Aqaba.

However, although the author has not related the high content of metals found in the mollusks to pollution sources, he mentioned that the data obtained in his work was relatively above what is considered usually as normal rates in those organisms.

It would be good eventually if such work is updated and integrated in other similar surveys so each can support the outputs of the others. Table 9 shows the results of Wahbeh, (1990).

7.2 Assessment of Heavy Metal Content in the Coral Reef along the Coastline

The assessment of metal pollution in Aqaba was carried out through two parallel rounds of sampling and analysis. The first was based upon regular samples collected from six well-surveyed sites, in which the aim was to study the geographical distribution of metal pollution along the whole coast of Aqaba. The second was through obtaining three core samples from what could be considered the most polluted sites; the oil port and the industrial zone. It was meant by studying the vertical distribution of metal content in these core is an attempt to construct the history of metal input and trend during the last twenty years. This period of time represents the beginning of real and extensive development in Aqaba.

However, the following will describe the obtained results, while some detailed interpretation will be discussed in the next chapters.

7.2.1 Spatial Distribution of Anthropogenic Pollutants along the Aqaba Coast

As part of the early stages of this research, which was launched by 2001, sixty five (65) reef samples were collected at six different locations covering the whole coast of Aqaba starting from the northern end with the Israeli borders to the southern border with Saudi Arabia. As mentioned above, the aim at that stage was to research the spatial distribution of-if existing-anthropogenic pollutants. The six sites have been selected according to the different activities used to be carried out within their boundaries.

The six locations are: the north beach, the main port, the Marine Science Station (MSS), the marine park, oil port and the industrial area. These locations were described earlier in chapter 1 and 2 and depicted in Fig. 5.

It is worthy here to mention again that the MSS site is completely protected and it is described as No-activity zone; the area is only designated for scientific research purposes. On the other hand, the marine park is another protected area but with activitiy-controlled zones; some areas are only designated for example for swimming and not for boating, other zones designated for skiing and so on, therefore sampling these sites with its different zones gives an idea might assist in explaining the sources of pollution.

The measured concentrations of heavy metals in reef samples obtained along the coast are depicted in Fig. 1 6.

The following description of the metal distribution along the coast is based on the same grouping of the six sampling sites, therefore discussing the results will describe the general trend of each metal and then details are made for the sites individually when necessary. Figure 17 shows the details of the distribution of the six metals together along the coast, so it is possible to compare the content of certain metal with another at the same site.

Cadmium (Cd)

The Cd content showed very high values in samples taken from the industrial area, where the highest value was 5.1µg g^{-1}, this is 3 to 5 fold higher than the other sampling sites. A very clear decreasing trend in concentrations is observed when moving northward and offshore (Fig. 16 and17).

Except of three samples where Cd was not detected, the lowest concentrations (Ave. 0.15µg g^{-1}) are observed mainly opposite to the Marine reserve of the Marine Science Station and the deeper samples of the north beach.

Compared to the other metals, the Cd is the only metal that shows high distinctive increasing trend (enrichment) southward.

The concentration of cadmium in the north beach was in the range N.D-0.27µg g^{-1}, with an average of 0.15$\pm$ 0.09µg g^{-1}. The samples of this site show the lowest concentration (except MSS samples) with respect to Cd among all of the collected samples. Figure 16 shows also that the site has approximately a concentration close to that recorded at the MSS site, *revealing* -when compared to this well conserved site- that some sound environmental conditions with respect to Cd are prevailing the area.

The cadmium content in the main port area showed wide range of 0.11 to 0.98 µg g^{-1}, with an overall mean of 0.39$\pm$ 0.28µg g^{-1}. This wide range is due to low concentrations observed in offshore samples (deeper) of the main port facilities compared with the high content in samples taken close to the main jetties. In addition many different activities and operations are usually taking place at this main facility, to which such variation in Cd concentrations might be attributed.

The lowest concentrations of Cd, which were recorded at the marine resrve of MSS have, a mean value of 0.13$\pm$ 0.13µg g^{-1}, where the range was N.D-0.31µg g^{-1}. Such a low concentration is expected as the site is well protected, but it is still believed that the relative high (unexpected for such site) values found in few samples were attributed to the current activities of the nearby passenger terminal where there are vessels operated by the Arab Bridge Maritime Company.

The Marine Park, unexpectedly showed also some relative high concentrations of Cd with an overall average of 0.67$\pm$0.15µg g^{-1}, this was (in some samples)even higher than that of the oil port (0.56 $\pm$ 0.16 µg g^{-1}), however regardless the fact that the high mean value of the marine park samples is due to sample MPk4 (0.9µg g^{-1}) and the low mean value of the oil port values is due to low concentration of sample OP1 (0.26µg g^{-1}), the samples of the Marine Park are still considered to have high values compared to what could be expected for such protected areas with least human activities.

The highest value of Cd was recorded at the industrial area; with a maximum of 5.1µg g^{-1}, and a mean concentration of 2.35$\pm$0.8µg g^{-1}. This mean value represents something like

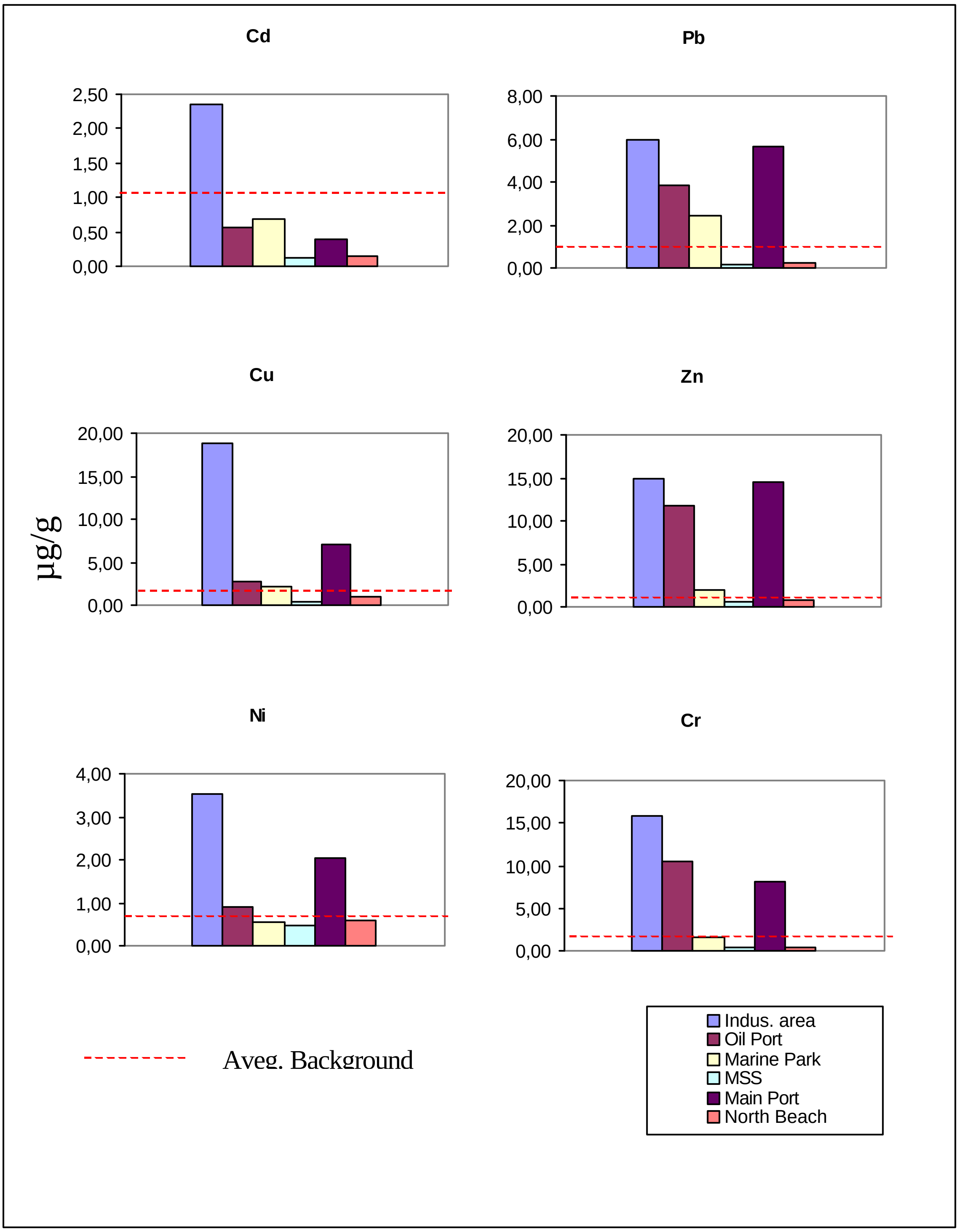


Fig. 16. Mean concentrations of heavy metals along Aqaba coast

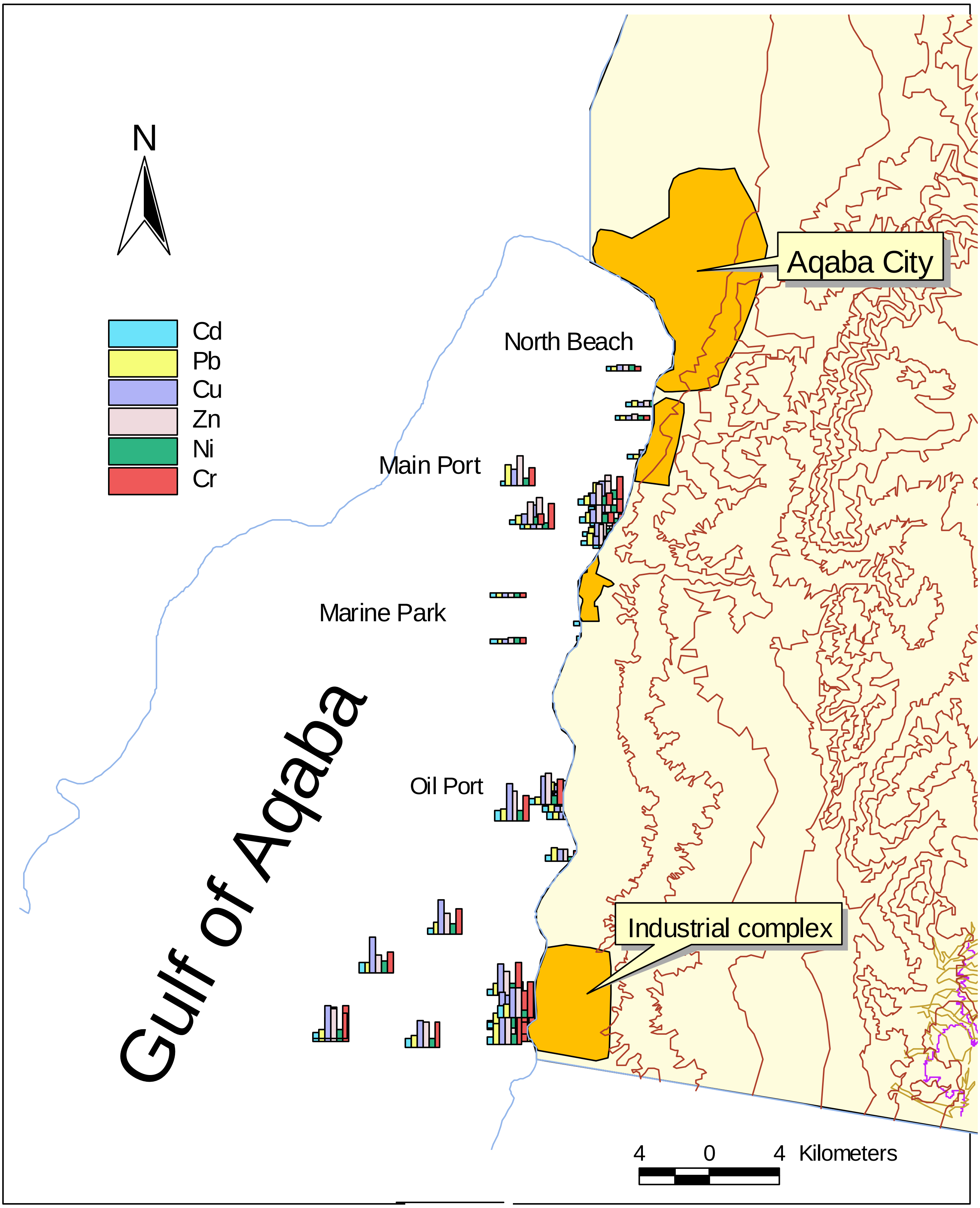


Fig. 17. Distribution of metals along each sampling site.

five fold that of the MSS site which has the lowest concentration of Cd, revealing how the site is being impacted. This site has shown higher variations in Cd concentrations compared with the other sites indicated by the relatively high standard deviation, however several samples in this site have been taken from deep water (offshore) which might explain some low values.

Chapter nine includes more interpretation on the enrichment of Cd and the other metals .

Lead (Pb)

With the exception of a few samples at the north beach and Marine Science Station- which showed non-detected to very low concentrations of lead- all of the other locations along the coast showed some significant values with an overall mean of 4.26$\pm$2.9 µg g^{-1}.

Fig. 16 and 17 show clearly, the high concentration along the coast and how big is the difference compared with the MSS site (Aveg. 0.18 $\pm$0.2µg g^{-1}) and the north beach site (Aveg. 0.21 $\pm$0.2µg g^{-1}).

Maximum values were dominating two sites; the main port and the industrial area with an individual mean of 5.6$\pm$3.25µg $g^{-1}$and 5.99$\pm$1.92 µg g^{-1}respectively. The two sites have also a common feature in terms of Pb concentrations, both have a wide range (1.1-11.2 and 2.3-11.1 µg g^{-1}respectively). The samples have been taken from different depths at these two sites ; the thing that might explain such large variations in concentrations, however comparing the values recorded with the geographical locations of the samples showed that deeper samples generally have relatively lower concentrations.

The oil port site was the third in terms of Pb content after the main port and the industrial area with an average of 3.81 $\pm$ 2.1µg $g^{-1}$and wide range of 0.3-6.6µg g^{-1}. The samples taken from nearby the main jetty have the highest values among all samples.

Wide range of lead concentrations were also observed at marine park location (N.D-6.2 µg g^{-1}) with an overall average of 2.43$\pm$2.4 µg g^{-1}, this is due mainly to the different zones established for various activities (i.e. boating, swimming, skiing, camping, .etc.), the thing which leads to a difference in the type and extent of impact. However, prior to the current park's regulations which include preventing car accessing very close to the sea-land interface (50m setback), people used to drive within this narrow and sensitive zone, which in turns bring an impact specially where almost all vehicles use leaded gasoline in Aqaba.

Copper (Cu)

The Cu profile along the coast shows two major peaks; at the industrial area and at the main Port, (18.27$\pm$5.4 and 7.08$\pm$3.09µg g^{-1}respectively). Not much variations have been noticed along the other sites where the mean concentration at the north beach and MSS were the lowest (0.97$\pm$1.19, 0.45$\pm$ 0.38µg g^{-1}) and Marine Park and oil port (2.21$\pm$2.1, 2.68 $\pm$0.64µg g^{-1}) respectively.

The mean concentration of Cu along the north beach would be much lower when excluding the only sample with relative high value;3.0µg g^{-1}, where the range becomes 0.06-0.9 µg g^{-1}.

Zinc (Zn)

Zinc profile along the coast showed great similarities with, that of lead, however a very wide range of concentration can be seen clearly (0.25-22µg g^{-1}), high content of zinc were observed mainly in the main port, industrial area and oil port. Samples taken from the MSS location were the lowest in their content of Zn (Aveg. 0.53$\pm$0.04µg g^{-1}).

Nickel (Ni)

Compared with the other metals, Nickel showed some homogeneity but with two different groups of values; the first represent concentrations of Ni from the north beach to the oil port where the average is 1.09+0.84 µg $g^{-1}$and the second group of values represent the area starting from the oil port south to the Saudi borders; an area which encompass the industrial zone. The average value in this strip is 3.87±1.02 µg g^{-1}.

Chromium (Cr)

Chromium concentrations along the coast ranged between N.D to 28.2µg g^{-1}. It follows, in general, like the other metals the same trend of increase towards south. Some notices can be pointed out on the Cr concentrations when dealing with the sites individually. It was noticed that the highest value was observed at the oil port (28.2µg g^{-1}), but in terms of individual mean concentrations at each site, the industrial area has the highest mean of 18.04µg g^{1}. This is much higher (> 10 fold) of individual mean concentrations recorded at the marine park, north beach and marine reserve (1.6; 0,14; 0.36 µg g^{-1}), and even that of the oil port area (10.56µg g^{-}).However, more conclusions on the spatial distribution of the Cd, Cr, Pb, Cu, Ni and Zn along the coast can be made by referring to Fig.18 which shows gradually the fluctuations in metal concentrations between the sampling sites.

The correlation (Table. 10) among all of the studied six metals has shown an interesting positive correlation (almost >0.5). Such statistical output confirms the results just discussed above, in which the overall conclusion was on the significant general increasing trend southward of all of the metal group, excluding of course the site of the marine reserve where the lowest metal content was recorded.

This positive and significant correlation has also another meaning. It implies that all of these metals have been introduced into the ecosystem by almost similar sources. The slight differences in the correlation among the whole group indicate also that there is a variety of activities being carried out along the coast (Ramos *et al.,* 2004; Bastidas and Garcia,1999 Kumarsingh, *et al.*,1998). In chapter eight, this statistical relationship is discussed in more details.

7.2.2 Heavy Metals Content and Trends in Reef Cores

The accumulation of selected heavy metals (Cd, Cu, Zn, Pb, Cr and Ni) was studied in reef cores collected from three different sites within the industrial zone (see Fig. 5).

The chronology of the reef growth along the Jordanian coast has been previously estimated by several authors (Dullo *et al.*,1993 and Dullo *et al.,*1996) to be in 6-11mm/yr in average. However the studied cores were collected from colonies (3 colonies) that have been studied shortly before sampling process by Zolda (2001). He has determined the growth rate for these cores to be 10mm/y. This rate was then used to slice the core samples where the surface most layer was roughly assigned to the year 2000 and the bottom most of the core (20cm depth) corresponds to the year 1980.

The three studied cores have been collected from the same zone; the industrial zone which includes both the industrial area and the oil port. The selection of the cores sites was based on the results we have obtained from the regular samples in which it was clear that this zone is more enriched by heavy metals, and therefore it has been decided to get the cores from within it as for further and pronounceable historical documentation of pollution.

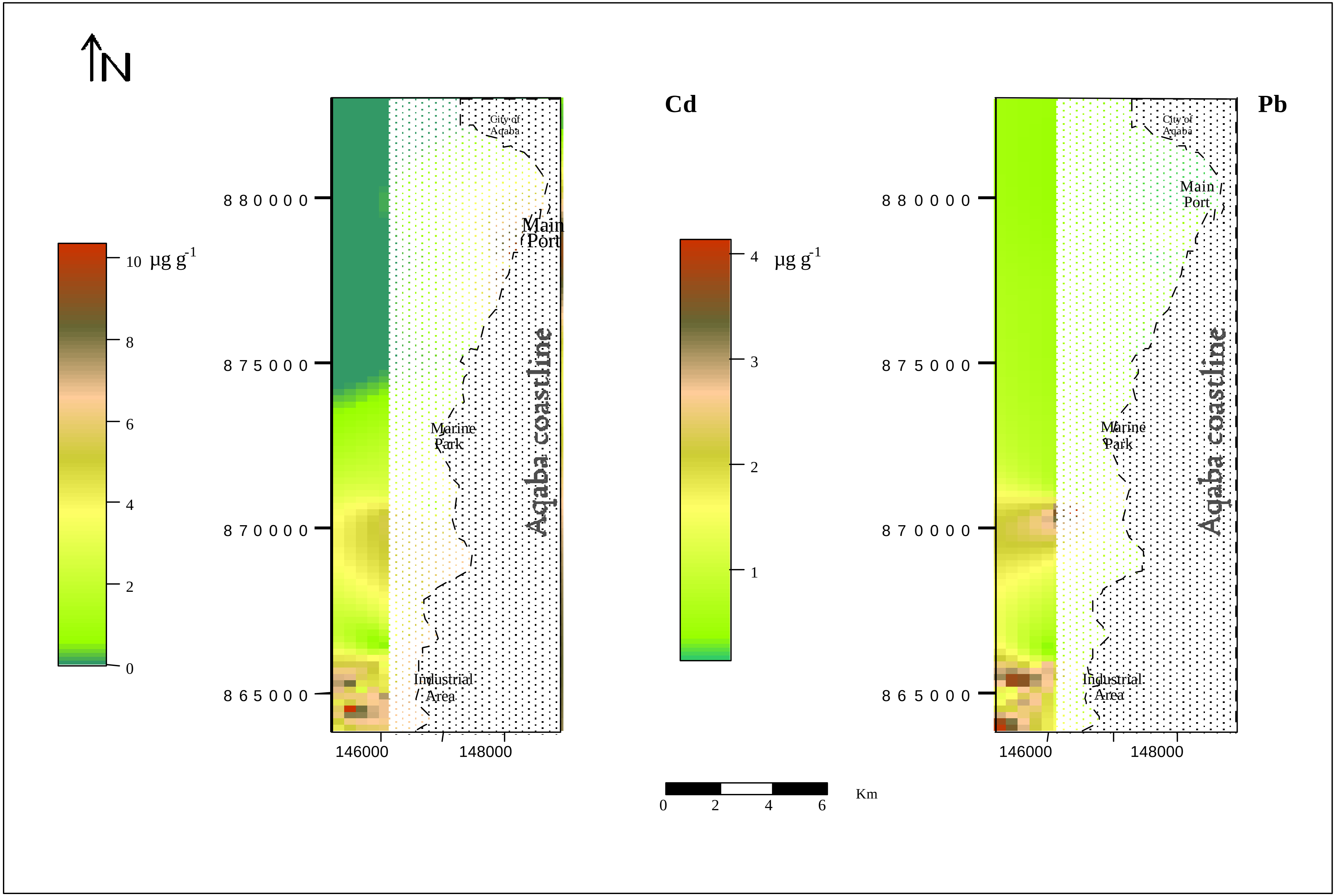


Fig. 18a. Spatial distribution of Cd and Pb along the coast of Aqaba.

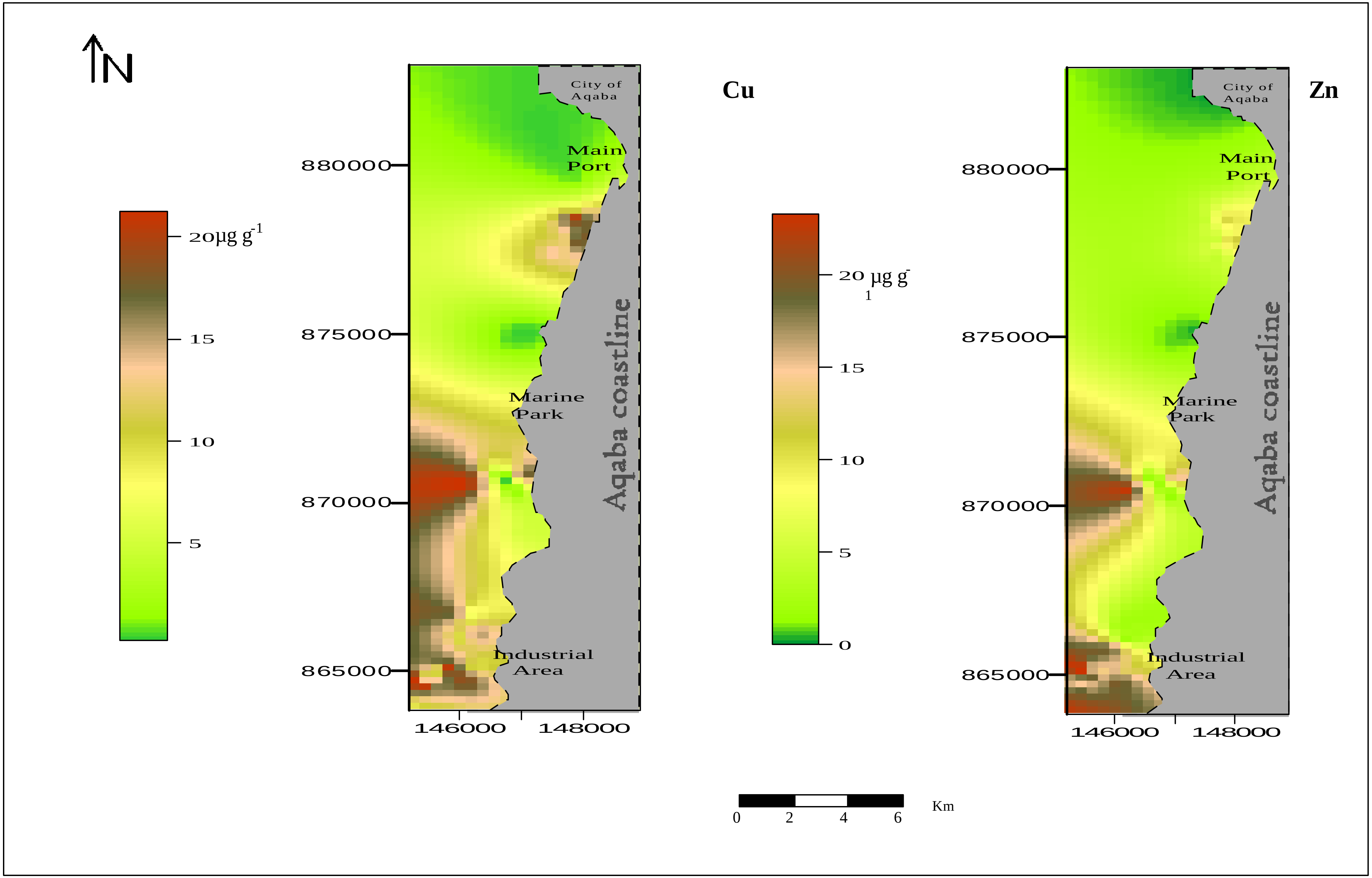


Fig.18b. Spatial distribution of Cu and Zn along the coast of Aqaba.

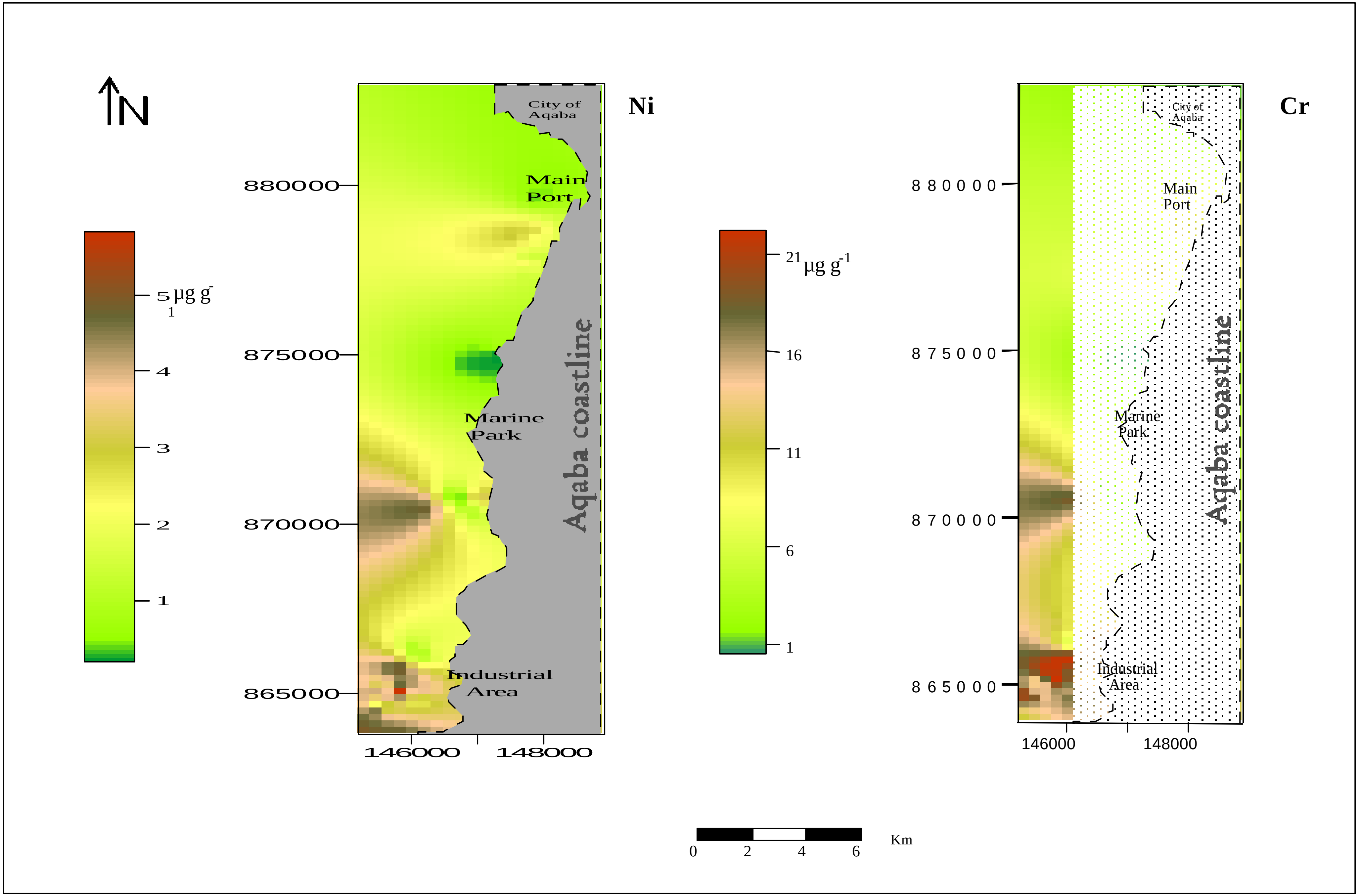


Fig.18c. Spatial distribution of Ni and Cr along the coast of Aqaba.

Table 10. Correlation among the six metals along the Aqaba coast

	Cd	*Pb*	*Cu*	*Zn*	*Ni*	*Cr*
Cd	1					
Pb	0,3672	1				
Cu	0,7644	0,5293	1			
Zn	0,4626	0,6445	0,6478	1		
Ni	0,6532	0,5493	0,8284	0,6226	1	
Cr	0,6597	0,5315	0,7142	0,7656	0,7438	1

Generally, high variability in metal distribution and content between core A and cores B and C was observed. Except for Cr all metals recorded in core A of the oil port were higher than those of B and C (3 to 4 folds). The following describes these concentrations and trends in details.

7.2.2.1 Core A

Core A has been sampled directly opposite to the industrial port (plate 4). The metal concentrations in this core are listed in Table 11 and their profiles are presented in Fig. 19.

All of the selected metals have showed fluctuating concentrations with general increasing trends where the lowest concentrations found at the bottom of the core (the period of 1980-1985) and the topmost having peak values.

Nickel and Cr showed highest concentrations at the surface of the core (1998-2001); 4.22 and 18.37µg g^{-1} respectively, implying that the fluxes of these metals have been progressively augmented with time. Mean values for both were 2.07$\pm$1.2 and 10.9$\pm$5.07 µg g^{-1} respectively.

All profiles generally exhibited increasing tendency during the last 20 year, the exception (steady state) is that for Zn and Cu but only during the period of 1992-1995 and 1988-1993 respectively.

Cadmium in this core shows a relative high concentration (1.92$\pm$0.96µg g^{-1}).Cadmium and lead have shown high and positive correlation (r=0.73). Same significant correlation also exists between Cr and Cu, Zn and Ni (r= 0.78, 0.72 and 0.77 respectively).

The records obtained from this core indicate that anthropogenic input has began simultaneously for all the metals around 1986, in other words the significant increase in heavy metal concentrations has begun as the figure indicates, around the year 1986 as a consequence of the expansion in industries and the associated operations.

It should be noticed that these concentrations have increased most importantly between 1990-2000. A detailed explanation and interpretation for such excess are in the next sections.

The concentrations of Cd, Cu, Pb, Ni, Cr and Zn found in this core (Table 11)are comparable to that found in several cores from different regions (e.g.: Bastidas *et al.*, 1999, Ramos *et al.*, 2003) that are influenced by industrial pollution.

Plate.4 The northern boundary of the industrial port. In the background also, algal growth covering the beach area and several types of solid wastes exist just meters from the shoreline.

7.2.2.2 Core B

Table12 shows the metal concentrations of core B which was sampled directly opposite to the discharge canal of the Power Plant (used to discharge the return cooling water). The concentration of Cd and Pb have shown identical profile and trend along the core depth, (Fig. 20). The chart shows also that the concentrations of both have been at least doubled along the lower part of the core starting from the bottommost up to 5cm. The next upper layers show high variation where the concentration for both metals goes successively high and low. The surface layer of the cores which represent the last five years show relative increase in the concentration but they are not the highest with respect to the Cd and Pb. The mean concentration of Cd calculated along the core depth was 0.79±0.36µg g^{-1} and the range was 0.19-1.62µg g^{-1}, and for the Pb was 3.49±1.57µg g^{-1} and the range was 0.9-6.6µg g^{-1}.

Ni and Cr both have prominent increase towards the top layers of the core. The topmost layer (surface) is marked by the highest concentration of Ni and Cr. Nickel mean concentration along the core axis was 2.7±1.01µg g^{-1} with a range of 1.3-5.2µg g^{-1}, where Cr has a mean value of 8.17± 3.7µg g^{-1} and a wide range 2.9-17.3µg g^{-1}. With these figures it is clear that both metals have high variation and significant enrichment towards the top surface of the core.

Except for one layer (at 10cm depth), Cu concentrations show no significant variation along the core axis, (Fig. 17). The mean concentration of Cu was 3.41±1.32µg g^{-1} and a range (excluding the mentioned layer)1.9-4.2µg g^{-1}.

The mean concentration of Zn in this core is 8.2±3.6µg g^{-1} with a range of 2.2-12.5µg g^{-1}. There is a general increasing trend towards the top layers, but the most prominent enrichment is at depth 4-11cm.

7.2.2.3 Core C

Fig. 21 shows the metal profiles in core C which was taken from an area close to the oil port. Compared with profiles we have obtained from Core A, the metals in this core showed more fluctuations in concentration, but if we consider –for correlation purposes- the records obtained from the bottom of the core; early 1980's layers as a background values, we can see that there is a general relative increasing trend in concentration towards the top layers, observed clearly in Zn, Cr and Ni in the layers of 1990 and onward.

The Cd and Ni average values are (0.81± 0.47) and (2.30±0.84)µg g^{-1} respectively. A distinct peak is observed in the Pb, Cu, Zn, and Cr profiles which represent the layers of 1984-1989, this enrichment is much probably attributed to the heavy use of the port during the first Gulf War where it has been used intensively for the export of Iraqi oil, more details will be discussed in the following sections.

The fluctuations in the concentrations (the decrease in particular) and the relatively low concentrations of these metals present in this core (Table 13) compared with Core A (industrial area) can be explained on the basis that the port area is relatively sheltered zone*;* not affected by other nearby polluting sources in addition to the existing of northward-prevailing winds force any pollutants to move southward.

Another factor might explain the drop in the concentration of the metal concentrations which is the non-operational periods;(APC,2002) the port has stopped operation several times during the last 15 years and also been used for other purposes than oil, like the botanical oil.

7.2.3 The Results Against Background Values

7.2.3.1 Along the Coast

As has been discussed earlier in this chapter, all metals recorded along the coast have shown a general increasing trend towards the south. Except Cd, all metals measured in samples at the main port, oil port and the industrial area were all above the averaged background value (Fig. 16). The difference was determined to be 3-4 fold higher than the averaged background, and actually up to 6 fold higher than the individual value for some offshore samples (Appendix 1). However, the reason beyond having values for Cd lower than that of the background in all sites (except the industrial area) was due to the high values reported in literature (Aveg.=4.2µgg^{-1}) which was used among the other suggested reference values (i.e. offshore samples and core bottom). Excluding such high value from the background average value will definitely show that the recorded concentration of Cd at all sites are much higher.

Among all profiles, the industrial area has shown the highest enrichment with respect to the six metals. Lead, Zinc and Chromium at the main port and the oil port have shown very close values to that recorded at the industrial area. The samples of the MSS and the north beach were the closest to the background values regarding their content of metals. The marine park samples have significant enrichment of Cd and Pb when compared with the average and individual background values.

Comparing the concentrations of the six metals at both; the main port and the oil port shows that they are almost very close, despite the operations at the main port is much higher than that of the oil port.

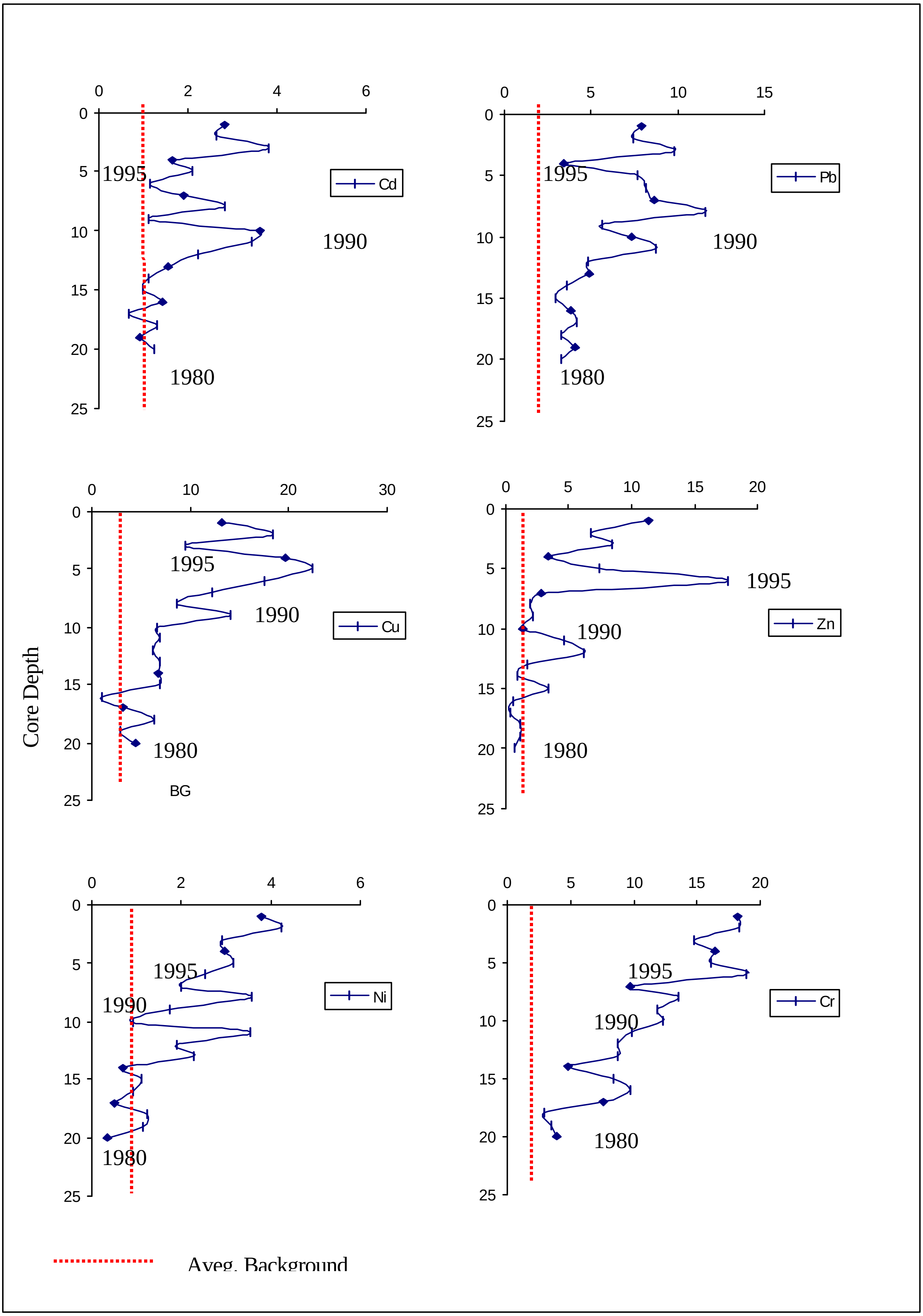


Fig.19. Concentration of heavy metals (µgg^{-1}) in reef core A (Industrial area) from 1980-2000. Zero (0m) depth corresponds to the year 2000.

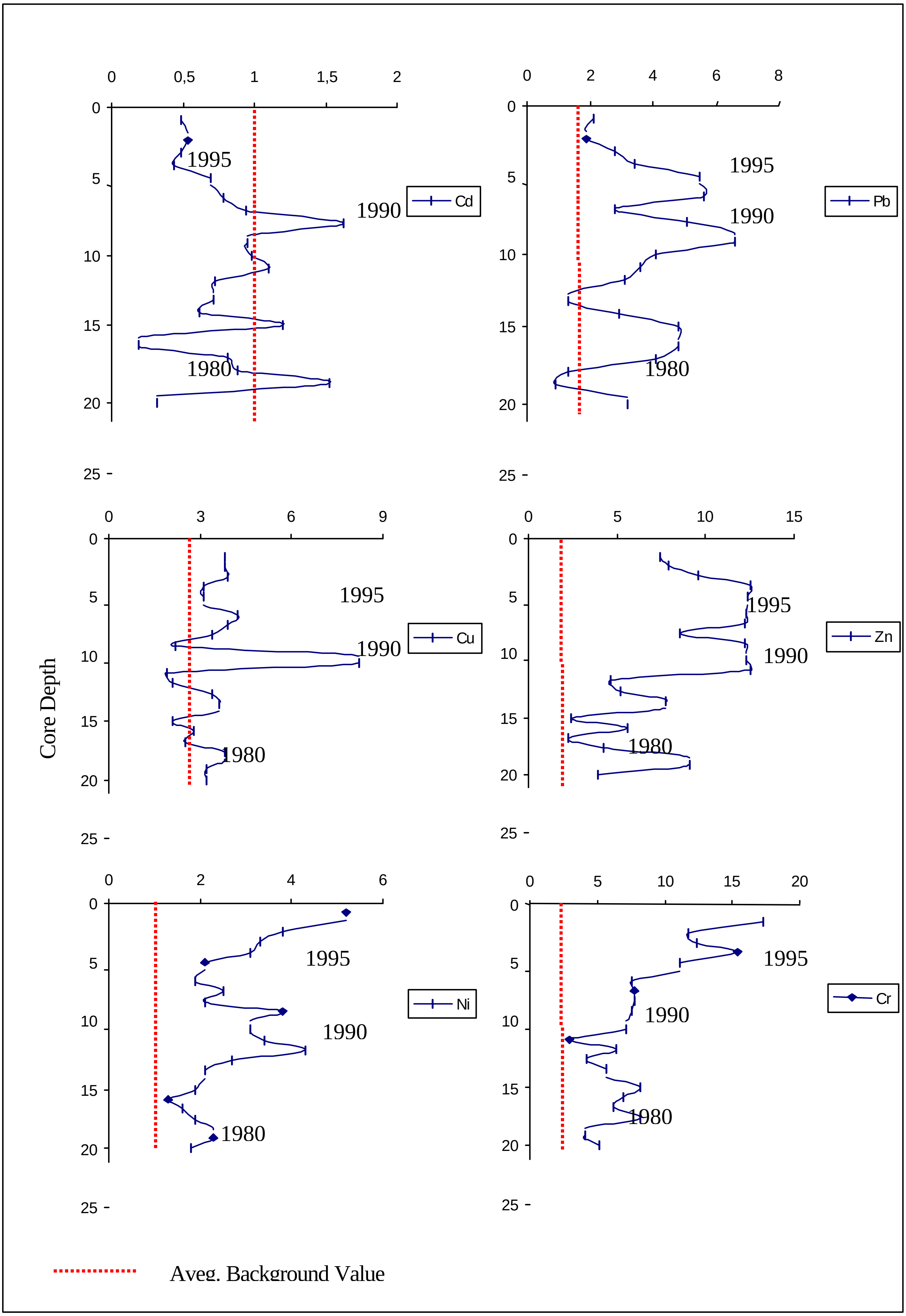


Fig.20. Concentration of heavy metals (μgg^{-1}) in reef core B (Power plant) from 1980-2000. Zero (0m) depth corresponds to the year 2000.

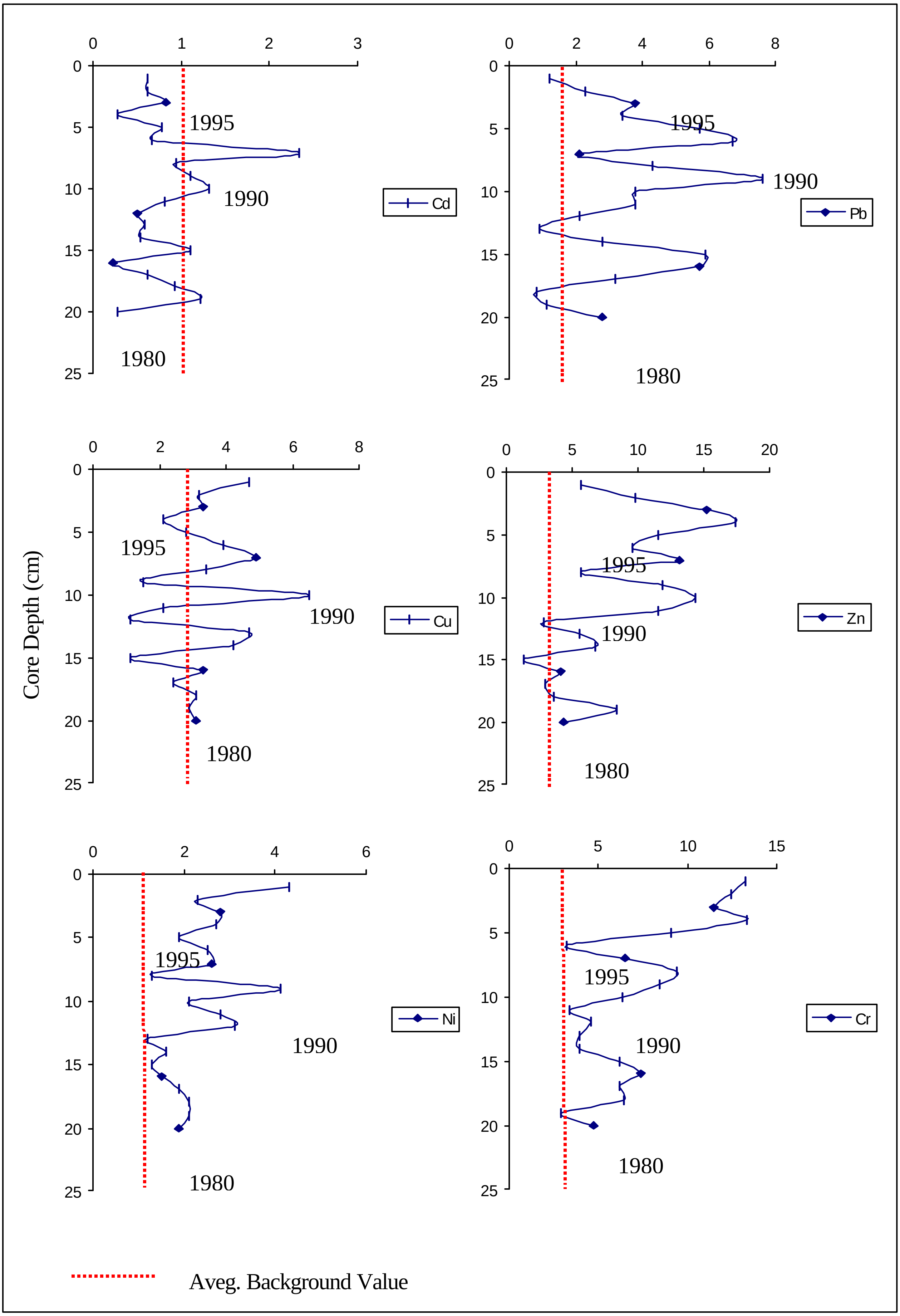


Fig.21. Concentration of heavy metals (μgg^{-1}) in reef core C (Oil port) from 1980-2000. Zero (0m) depth corresponds to the year 2000.

Table 11.Metal concentration (μgg^{-1}) in reef core A.

Depth/cm	Year	Cd	Pb	Cu	Zn	Ni	Cr
1	2000	2,84	7,94	13,22	11,4	3,8	18,2
2	1999	2,63	7,45	18,41	6,83	4,22	18,37
3	1998	3,81	9,82	9,45	8,45	2,9	14,7
4	1997	1,65	3,44	19,66	3,4	2,96	16,46
5	1996	2,11	7,66	22,45	7,45	3,17	16,1
6	1995	1,14	8,12	17,5	17,6	2,54	18,9
7	1994	1,92	8,67	12,2	2,78	1,98	9,73
8	1993	2,82	11,61	8,62	1,95	3,56	13,5
9	1992	1,1	5,6	14,12	2,17	1,74	11,84
10	1991	3,62	7,33	6,56	1,36	0,92	12,3
11	1990	3,42	8,71	6,84	4,67	3,54	9,8
12	1989	2,21	4,81	6,24	6,23	1,88	8,68
13	1988	1,56	4,88	6,92	1,64	2,27	8,7
14	1987	1,1	3,6	6,74	0,94	0,68	4,84
15	1986	0,98	2,94	6,91	3,41	1,12	8,4
16	1985	1,42	3,84	0,98	0,61	0,93	9,74
17	1984	0,68	4,12	3,21	0,39	0,52	7,55
18	1983	1,31	3,23	6,25	1,14	1,24	2,94
19	1982	0,92	4,1	2,84	1,1	1,14	3,5
20	1981	1,24	3,27	4,43	0,67	0,34	3,92

Table 12. Metal concentration (μgg^{-1}) in reef core B

Depth/cm	Year	Cd	Pb	Cu	Zn	Ni	Cr
1	2000	0,49	2,1	3,8	7,4	5,2	17,3
2	1999	0,53	1,9	3,8	7,9	3,8	11,7
3	1998	0,49	2,8	3,9	9,6	3,3	12,4
4	1997	0,44	3,4	3,1	12,5	3,1	15,4
5	1996	0,69	5,5	3,1	12,4	2,1	11,1
6	1995	0,78	5,6	4,2	12,3	1,9	7,5
7	1994	0,94	2,8	3,9	12,2	2,5	7,7
8	1993	1,62	5,1	3,4	8,5	2,1	7,8
9	1992	0,95	6,6	2,2	12,2	3,8	7,5
10	1991	0,98	4,1	8,2	12,3	3,1	7,1
11	1990	1,1	3,6	1,9	12,5	3,4	2,9
12	1989	0,72	3,1	2,1	4,6	4,3	6,4
13	1988	0,71	1,3	3,4	5,2	2,7	4,2
14	1987	0,61	2,9	3,6	7,7	2,1	5,7
15	1986	1,2	4,8	2,1	2,4	1,9	8,2
16	1985	0,19	4,8	2,8	5,6	1,3	6,9
17	1984	0,81	4,1	2,5	2,2	1,6	6,2
18	1983	0,88	1,3	3,8	4,2	1,9	8,2
19	1982	1,52	0,9	3,2	9,1	2,3	4,1
20	1981	0,32	3,2	3,2	3,9	1,8	5,1

Table13. Metal concentration (µgg^{-1}) in reef core C

Depth/cm	Year	Cd	Pb	Cu	Zn	Ni	Cr
1	2000	0,62	1,21	4,7	5,6	4,3	13,21
2	1999	0,62	2,3	3,2	9,8	2,3	12,4
3	1998	0,82	3,8	3,3	15,2	2,8	11,5
4	1997	0,28	3,4	2,1	17,4	2,7	13,3
5	1996	0,78	5,7	2,8	11,5	1,9	9,1
6	1995	0,66	6,7	3,9	9,6	2,5	3,2
7	1994	2,34	2,1	4,9	13,2	2,6	6,5
8	1993	0,94	4,3	3,4	5,6	1,3	9,4
9	1992	1,1	7,6	1,5	11,8	4,1	8,4
10	1991	1,31	3,8	6,5	14,3	2,1	6,3
11	1990	0,81	3,8	2,1	11,5	2,8	3,4
12	1989	0,51	2,1	1,1	2,8	3,1	4,6
13	1988	0,58	0,92	4,7	5,5	1,2	3,9
14	1987	0,54	2,8	4,2	6,7	1,6	3,9
15	1986	1,1	5,9	1,1	1,3	1,3	6,2
16	1985	0,23	5,7	3,3	4,1	1,5	7,4
17	1984	0,61	3,2	2,4	2,9	1,9	6,2
18	1983	0,92	0,8	3,1	3,6	2,1	6,4
19	1982	1,21	1,1	2,9	8,4	2,1	2,9
20	1981	0,27	2,8	3,1	4,3	1,9	4,7

7.2.3.2 In Cores

In core C of the oil port, Zn, Ni and Cr concentrations were almost above the background values, where Cd, Pb and Cu concentrations were above the background values only in the upper parts of the core indicating recent enrichment.

Core B has the same trend against the background values for, Ni, Zn and Cr (except one layer in the middle) where they all have concentrations through the core profile higher than the calculated background.

Core A was observed to have the higher enrichment against the background compared with the other two cores. Except for the Zn, all examined layers along the core show values above that of the background, and actually much higher (3-4 fold) in top layers, (Fig. 19).

Lead in core A was clearly double of that recorded in core B and C, the high concentration was not only marked in the upper layers, but rather along the whole profile. Mean values was 6.05$\pm$2.5 µg g^{-1}.

Cadmium in core A has also distinctive concentrations and trend similar to that of lead. It has a mean value of 1.92$\pm$ 0.92µg g^{-1}, compared with 0.79$\pm$0.36 and 0.81$\pm$ 0.47µg g^{-1} for core B and core C respectively. The high correlation (r=0.736) between Cd and Pb in this core confirms this trend, (Table 14). Cr on the other hand is highly positively correlated with Cu, Zn and Ni (r= 0,781; 0,728 and 0,771 respectively).

Copper concentration in Core B and C (Fig. 20, 21) has the same profile; variations (increasing and decreasing against the background value) along the core layers, and very close mean value for both cores ; 3.41$\pm$ 1.32 and 3.21$\pm$1.35µg g^{-1} respectively. The maximum value recorded for Cu in both cores were recorded at the same layer (10cm depth), an interesting notice that reveals a significant metal influx into the ecosystem at the time reflected in this layer.

Copper concentration in core A on the other hand shows a difference to that recorded in core B and C since almost the content of the metal in whole core profile was above the background value with prominent increasing trend towards the surface where concentrations are 3-4 fold higher than lower layers.

However, it can be easily noticed that all metals observed in Core A share one clear increasing trend towards the surface (i.e. significant enrichment during the period of 1980-2000, more markedly in the last 5-7 years) supported by highly (and relatively high) positive correlations (Table 14).

7.2.4 Enrichment Factors (EF)

The enrichment factor (EF) was calculated for the metal content in the three reef cores (Table15,16,17). It is defined as the ratio between the metal concentrations found at a given horizon and the concentration found at the bottom of the core (Ruiz-Fernandez *et al.*, 2001). When EF >1 for a particular metal, it means that an enrichment (contamination) exists; otherwise, if EF $\leq$ 1, there is no metal enrichment of natural or anthropogenic origin, (Soares *et al.*,1999). For classification purposes, the EF was divided into three categories of pollution: low from EF >1 up to 2; intermediate from 2 to 3; and high for EF larger than 3, taking into consideration of course the highly elevated concentrations at the middle and top layers. However Table 15,16,17 show the EF for the three cores, A,B,C respectively. Each table describes the metal enrichment at each horizon -in the site where the core has been taken- so it gives detailed idea on the history of metal input to the system.

In order to describe the metal enrichment in the whole area of the industrial zone, the enrichment factor was calculated as the ratio of the mean surficial concentration of the three cores and mean concentration of the bottom three cores, (Table18).

The calculated EF for Cd, , Cu and Zn is >2, suggest that the area has an intermediate status of pollution with respect to these metals. The EF of Ni and Cr were >3 indicating high enrichment and therefore pollution by these two metals. This conclusion is made clear in Fig. 22; where Pb is the less enriched (EF=1.21), Cr is the highest enriched.

The reasons for such high content of metal can be easily interpreted as the area is occupied by several industries, and continuously subjected to development, in addition it is heavily navigated, however more elaboration is discussed in the next chapters.

Table 14. Correlation among six heavy metals in the reef cores; A,B, and C (1982- 2001), all correlation is significant $P<0.05$.

Core A

	Cd	*Pb*	*Cu*	*Zn*	*Ni*	*Cr*
Cd	1					
Pb	0,736484	1				
Cu	0,165686	0,36509	1			
Zn	0,2635	0,469353	0,59458	1		
Ni	0,597222	0,699316	0,668064	0,577728	1	
Cr	0,472635	0,610283	0,781497	0,7283	0,771678	1

Core B

	Cd	*Pb*	*Cu*	*Zn*	*Ni*	*Cr*
Cd	1					
Pb	0,07667	1				
Cu	-0,00764	-0,11839	1			
Zn	0,135468	0,288117	0,320223	1		
Ni	-0,11304	-0,21138	0,047776	0,26259	1	
Cr	-0,38385	-0,01443	0,13612	0,194442	0,465869	1

Core C

	Cd	*Pb*	*Cu*	*Zn*	*Ni*	*Cr*
Cd	1					
Pb	-0,04073	1				
Cu	0,28236	-0,3058	1			
Zn	0,292498	0,179724	0,245587	1		
Ni	0,094576	0,03159	-0,12035	0,350576	1	
Cr	-0,12908	0,041997	-0,00735	0,36176	0,37233	1

Fig. 22. Comparison of Enrichment factors (EF) for the six metals.

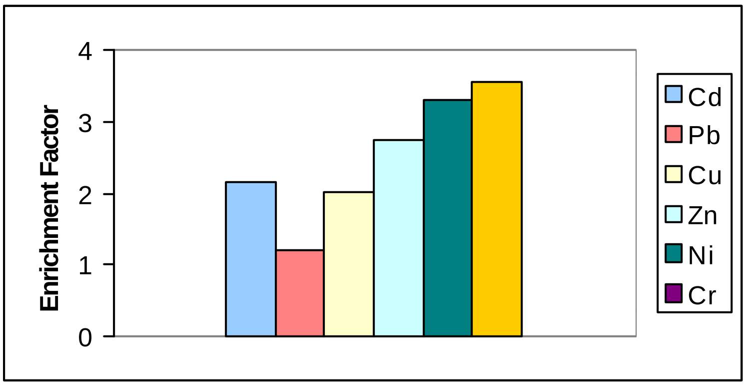


Table 15. Enrichment Factor (EF) in Reef Core A.

Depth/cm	**Year**	Cd	Pb	Cu	Zn	Ni	Cr
1	2000	2,29	2,43	2,98	17,01	11,18	4,64
2	1999	2,12	2,28	4,16	10,19	12,41	4,69
3	1998	3,07	3,00	2,13	12,61	8,53	3,75
4	1997	1,33	1,05	4,44	5,07	8,71	4,20
5	1996	1,70	2,34	5,07	11,12	9,32	4,11
6	1995	0,92	2,48	3,95	26,27	7,47	4,82
7	1994	1,55	2,65	2,75	4,15	5,82	2,48
8	1993	2,27	3,55	1,95	2,91	10,47	3,44
9	1992	0,89	1,71	3,19	3,24	5,12	3,02
10	1991	2,92	2,24	1,48	2,03	2,71	3,14
11	1990	2,76	2,66	1,54	6,97	10,41	2,50
12	1989	1,78	1,47	1,41	9,30	5,53	2,21
13	1988	1,26	1,49	1,56	2,45	6,68	2,22
14	1987	0,89	1,10	1,52	1,40	2,00	1,23
15	1986	0,79	0,90	1,56	5,09	3,29	2,14
16	1985	1,15	1,17	0,22	0,91	2,74	2,48
17	1984	0,55	1,26	0,72	0,58	1,53	1,93
18	1983	1,06	0,99	1,41	1,70	3,65	0,75
19	1982	0,74	1,25	0,64	1,64	3,35	0,89
20	1981	1,00	1,00	1,00	1,00	1,00	1,00

Table 16. Enrichment Factor (EF) in Reef Core B.

Depth/cm	**Year**	Cd	Pb	Cu	Zn	Ni	Cr
1	2000	1,53	0,66	1,19	1,90	2,89	3,39
2	1999	1,66	0,59	1,19	2,03	2,11	2,29
3	1998	1,53	0,88	1,22	2,46	1,83	2,43
4	1997	1,38	1,06	0,97	3,21	1,72	3,02
5	1996	2,16	1,72	0,97	3,18	1,17	2,18
6	1995	2,44	1,75	1,31	3,15	1,06	1,47
7	1994	2,94	0,88	1,22	3,13	1,39	1,51
8	1993	5,06	1,59	1,06	2,18	1,17	1,53
9	1992	2,97	2,06	0,69	3,13	2,11	1,47
10	1991	3,06	1,28	2,56	3,15	1,72	1,39
11	1990	3,44	1,13	0,59	3,21	1,89	0,57
12	1989	2,25	0,97	0,66	1,18	2,39	1,25
13	1988	2,22	0,41	1,06	1,33	1,50	0,82
14	1987	1,91	0,91	1,13	1,97	1,17	1,12
15	1986	3,75	1,50	0,66	0,62	1,06	1,61
16	1985	0,59	1,50	0,88	1,44	0,72	1,35
17	1984	2,53	1,28	0,78	0,56	0,89	1,22
18	1983	2,75	0,41	1,19	1,08	1,06	1,61
19	1982	4,75	0,28	1,00	2,33	1,28	0,80
20	1981	1,00	1,00	1,00	1,00	1,00	1,00

Table 17. Enrichment Factor (EF) in Reef core C.

Depth/cm	**Year**	Cd	Pb	Cu	Zn	Ni	Cr
1	2000	2,30	0,43	1,52	1,30	2,26	2,81
2	1999	2,30	0,82	1,03	2,28	1,21	2,64
3	1998	3,04	1,36	1,06	3,53	1,47	2,45
4	1997	1,04	1,21	0,68	4,05	1,42	2,83
5	1996	2,89	2,04	0,90	2,67	1,00	1,94
6	1995	2,44	2,39	1,26	2,23	1,32	0,68
7	1994	8,67	0,75	1,58	3,07	1,37	1,38
8	1993	3,48	1,54	1,10	1,30	0,68	2,00
9	1992	4,07	2,71	0,48	2,74	2,16	1,79
10	1991	4,85	1,36	2,10	3,33	1,11	1,34
11	1990	3,00	1,36	0,68	2,67	1,47	0,72
12	1989	1,89	0,75	0,35	0,65	1,63	0,98
13	1988	2,15	0,33	1,52	1,28	0,63	0,83
14	1987	2,00	1,00	1,35	1,56	0,84	0,83
15	1986	4,07	2,11	0,35	0,30	0,68	1,32
16	1985	0,85	2,04	1,06	0,95	0,79	1,57
17	1984	2,26	1,14	0,77	0,67	1,00	1,32
18	1983	3,41	0,29	1,00	0,84	1,11	1,36
19	1982	4,48	0,39	0,94	1,95	1,11	0,62
20	1981	1,00	1,00	1,00	1,00	1,00	1,00

Table 18. Enrichment Factor Calculated for the Industrial area

	Suficial layer					
	Cd	**Pb**	**Cu**	**Zn**	**Ni**	**Cr**
Core A	2,84	7,94	13,22	11,4	3,8	18,2
Core B	0,49	2,1	3,8	7,4	5,2	17,3
Core C	0,62	1,21	4,7	5,6	4,3	13,21
Mean	**1,32**	**3,75**	**7,24**	**8,13**	**4,43**	**16,24**
	Bottom layer					
Core A	1,24	3,27	4,43	0,67	0,34	3,92
Core B	0,32	3,2	3,2	3,9	1,8	5,1
Core C	0,27	2,8	3,1	4,3	1,9	4,7
Mean	**0,61**	**3,09**	**3,58**	**2,96**	**1,35**	**4,57**
	Enrichment Factor (EF)					
EF	**2,16**	**1,21**	**2,02**	**2,75**	**3,29**	**3,55**
	Maximum and Minimum Values					
Core A						
Minimum	0,68	2,94	0,98	0,39	0,34	2,94
Maximum	3,81	11,61	22,45	17,6	4,22	18,9
Core B						
Minimum	0,19	0,9	1,9	2,2	1,3	2,9
Maximum	1,62	6,6	8,2	12,5	5,2	17,3
Core C						
Minimum	0,23	0,8	1,1	1,3	1,2	2,9
Maximum	2,34	7,6	6,5	17,4	4,3	13,3

Chapter Eight

Multivariate Statistical and GIS-Based Approach to Identify the Heavy Metal Sources and Distribution

8. Multivariate Statistics; Principle Component Analysis

8.1 Introduction

Metal associations and factor controlling their variability have been assessed using the Principal Component Analysis (PCA). The main aim of PCA is to reduce the number of variables that need to be considered into a smaller number of indices (principal components, PCs) that can be more easily interpreted (Einax *et al.*,1997).

A large number of researchers (*inter alia.,* Julshamn *et al.*,1996; Rubio *et al.,* 2000; Spencer, 2002; Banerjee, 2003; Muniz *et al.,* 2004) have used PCA in the evaluation of environmental data, obtaining interesting conclusions that are not immediately obvious.

The PCA was applied on the entire data by using STATISTICA 6.1, StatSoft Inc. USA. In addition a fully-functional demo-version of XL Miner, QuantLink Inc.; was also used along for demonstrations purposes.

In the present work, Principal Components Analysis was performed in order to characterize spatial regions within the study area and utilizing the outputs of the PCs to support the early conclusions.

8.2 Principal Component Analysis

8.2.1 Overview of PCA

Principal component analysis (PCA) involves a mathematical procedure that transforms a number of (possibly) correlated variables into a (smaller) number of uncorrelated variables called *principal components*. Each principle component is a linear combination of the original variables. All the principle components are orthogonal to each other so there is no redundant information. The principal components as a whole form an orthogonal basis for the space of data. The first principle component analysis is a single axis in space, when projecting each observation on this axis, the resulting values form a new variable. The second principle component is another axis in space perpendicular to the first (Einax *et al.*,1997).

The full set of principle components is as large as the original set of variable. But it is commonplace for the sum of the variances of the first few principle components to exceed 80% of the total variance of the original data (Liu *et al.*, 2003).

The first principal component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible.

Algebraically, the PCA is obtained by finding the so called eigenvalues and eigenvectors. The eigenvalue indicates the amount of variance in the original variables accounted for by each component.

PCA is applied for two main objectives; to discover or to reduce the dimensionality of the data set and to identify new meaningful underlying variables (Einax, *et al.*,1997).

8.2.2 Standardization of Dataset

Standardization refers to the transformation of data by subtracting each value from some reference value, typically a sample mean and dividing it by the standard deviation, typically a sample SD (Einax *et al.,*1997).

This important transformation has been applied to bring all values (regardless of their distributions and original units of measurement) to compatible units from a distribution with a mean of 0 and a standard deviation of 1. This transformation has a wide variety of applications because it makes the distributions of values easy to compare across variables and/or subsets. If applied to the input data, *standardization* also makes the results of a variety of statistical techniques entirely independent of the ranges of values or the units of measurements.

To get more confidence in the outputs of PCA for the present work's data, the PCA was calculated for the raw data and their standardized set in order to notice any difference. However, as been expected since all the of variables are in the same units; no much pronounceable difference was recorded. The output of the computation of the standardized dataset is depicted in (Appendix 5) and included in this chapter for comparison purposes , and also because some columns have shown some relative substantial variance.

8.2.3 PCA Output

Table 19 shows PC loadings and the eigenvalues of all factors computed for our dataset, ranked from the highest to the lowest and are related to the amount of variation explained by the axis, and as shown, the sum of the eigenvalues is 6, which is also the number of variables.

Components 1 and 2 explain "*extract*" a variance of 4.187 and 0.7585 which is 69.786 and 12.643 of the total variance of the six variables respectively .

About 82.42 of the total variance in the variables set is attributed to these two components. The remaining 4 components together account only for 17.571 of the total variance.

8.2.4 Number of Components to Retain

Several criteria are usually used in practice for selecting the appropriate number of components for interpretation; the simplest is to use as many factors as the number of eigenvalues that are greater than 1. The other common method is that of Cattell, (Einax *et al.,* 1997).

According to Cattel's method, the number of components to retain is determined by constructing the so-called Scree plot (Fig. 23). Scree is a geological term referring to the debris that collects on the lower part of a rocky slope. In this method, the magnitude of the eigenvalues (vertical axis) are plotted against their ordinal numbers, and the successive eigenvalues will be shown in a simple line plot.

First the place/point where the smooth decrease of eigenvalues appears to level off to the right of the plot must be defined. To the right of this point, presumably, one finds only "factorial scree.". Thus, no more than the number of factors to the left of this point should be extracted i.e. in the present case two factors are found left of the level-off point, (Fig. 23); eigenvalue 1 and 2 (corresponding variance 69.786 and 12.643).

In the present work and according to the first method, there is only the first eigenvalue which is greater than 1, (Table 19), accounting for approximately 69.7 of total variation, where the screeplot reveals that the second eigenvalue which account for approximately 12.6 could be also considered. However, several workers on environmental assessment usually prefer the Cattel's method as it might include more elaboration on the interpretation (Spencer, 2002; Liu *et al.*, 2003; Banerjee, 2003), therefore the first two components will be considered throughout the following discussion and interpretation.

Table 19. Eigenvalues of the correlation matrix (data set) and related statistics.

Value Number *(Component)*	Eigenvalue	% Total Variance	Cumulative Eigenvalue	Cumulative %
1	4,187202	69,78670	4,187202	69,7867
2	0,758583	12,64305	4,945785	82,4297
3	0,416341	6,93902	5,362126	89,3688
4	0,308244	5,13741	5,670370	94,5062
5	0,213602	3,56003	5,883973	98,0662
6	0,116027	1,93379	6,000000	100,0000

Principal Component Loadings

Variable	PC1	PC2	PC3	PC4	PC5	PC6
Cd	0,382876	0,558506	0,196267	0,625215	0,016037	-0,334373
Pb	0,346061	-0,652482	0,606813	0,215671	0,184902	0,074727
Cu	0,441182	0,259295	0,193614	-0,224033	-0,530361	0,607589
Zn	0,404031	-0,415748	-0,518673	0,110993	-0,507862	-0,353054
Ni	0,432980	0,149178	0,144822	-0,700146	0,246315	-0,467361
Cr	0,433928	0,002184	-0,515534	0,099391	0,604711	0,412762

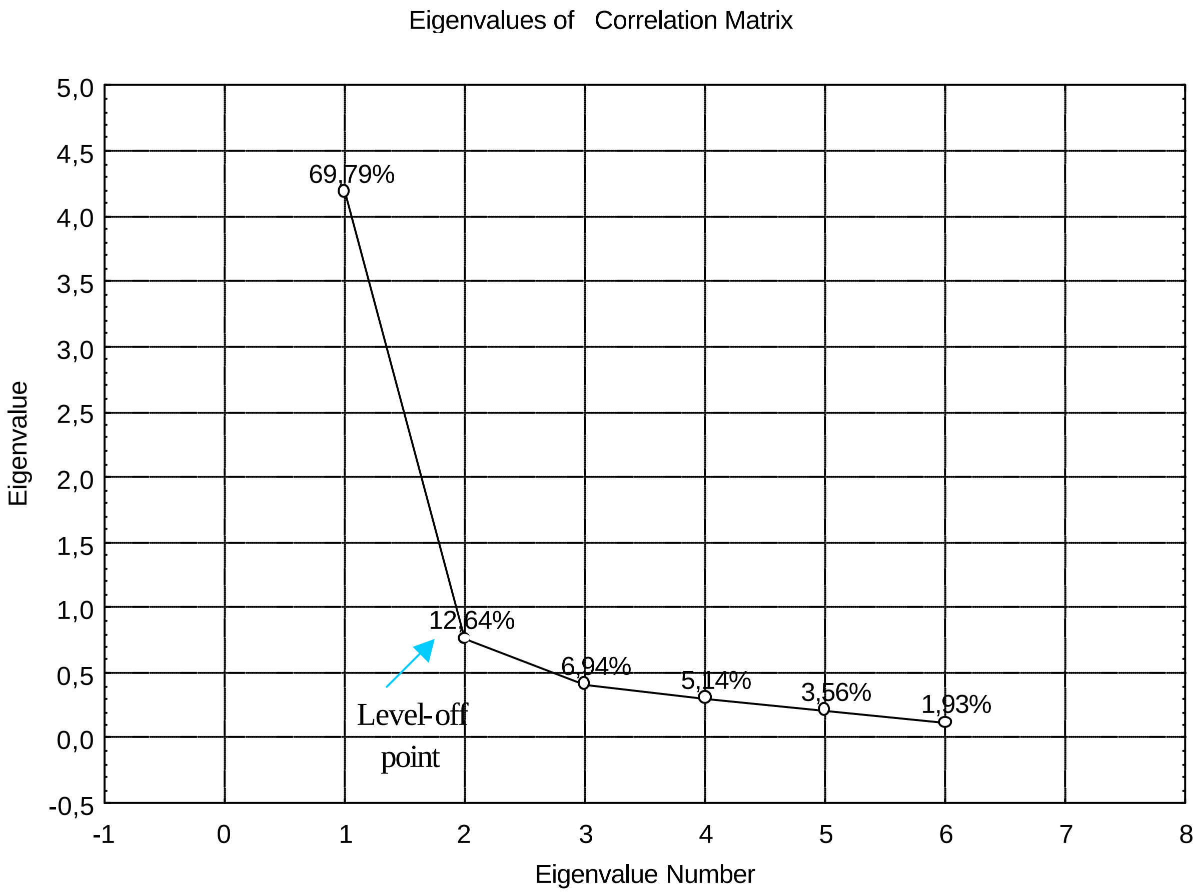


Fig. 23. Scree Plot of the obtained eigenvalues.

8.2.5 Results

The first two factors (PC1 and PC2) identified using the above mentioned method, are explaining almost 83% of the data variance along the coast; the first factor spanning the greater amount of variance (69.79%). The significant correlation determined earlier (see Table 10) between metal concentrations, being in agreement with the PC analysis results, indicates that all metals might have some common sources. This is reflected in the first principle component PC1 (Table 19), where all of the six variable have positive loadings.

PC2 shows however some very slight different trend than the rest of metals explained by the negative loadings of Pb and Zn (-0.652 and -0.415 respectively). This could be considered as a secondary trend in the overall distribution of the metals in the study area where Pb, and Zn have been introduced together to the marine ecosystem by other common sources. Projection of the variables on the PC plot (Fig.24) confirms this conclusion where Pb and Zn are grouped on opposite position to that of the rest of metals.

Moreover, the importance of the trace elements (variables) for the distribution of the samples can be assessed from their position on the projection plane, (Fig. 24). The influence of the elements is given by their position in the plot, where both distance and direction from the origin are important (Julshamn and Grahl-Nielsen, 1996; Soto-Jimenez, *et al.*, 2003; Muniz *et al.*,2004).

The projection plane shows that all metals have relatively the same distance from the origin, suggesting that all these metals vary in a similar amount among samples, and consequently have the same importance for the PCs. The projection shows also the relationship among the metals as described above, where Cd, Cu, Ni and Cr are highly correlated and clustered at one side on the positive plane as shown in the plot, and the Pb and Zn show another high correlation to each other by clustering together on the opposite side of the plane.

The natural inputs of metals into the Gulf of Aqaba is very rare due to the absence of major streams and also to the very low rainfall in the area. Consequently, the enrichment by natural sources is excluded. The first component spanning the greater amount of variance (69.79%) includes the six metals with very close positive loadings (which are related to their abundance in the samples) definitely represent anthropogenic input.

8.2.6 The Component Scores

Table (20) shows the data in the new coordinate system defined by the principal components where the output is the same size as the input data matrix.

In order to get more details and interpretation of the metal distribution, the PC scores of the first two components for all samples collected along the coast were depicted in (Fig.25).

The plot shows that the PC scores are clustered into three main groups. These groups represent actually the collected samples, therefore and since the samples are georeferenced, it was easy to identify each group and its geographical location by referring to the samples it includes. The first group was found to join samples taken from the marine park and Marine Science Station (marine reserve). The second group was formed of samples from both the north beach area and main port, and the third included all samples taken from and around the industrial area and the oil port.

According to the metal concentrations discussed in Chapter 7, the three groups were categorized by the metal content of the entire samples, and hence these three groups reflect the different environmental quality of the study sites. Fig.26 shows a conceptual model describing the geographical distribution of the three clustered groups.

Considering this new categorization of PCA, and the overall conclusions of the former chapters the coast of Aqaba can be divided (after georeferncing) into three main zones with respect to its environmental quality in a descending order: Zone A corresponds to group B; the area is relatively not polluted. The Zone included the area of marine park and Marine Science Station. Zone B, corresponds to group A, the area is intermediate to heavily polluted. The zone includes the area of north beach and the main port. Zone C, the most heavily polluted, corresponding to group C. The zone includes the industrial area and the oil port.

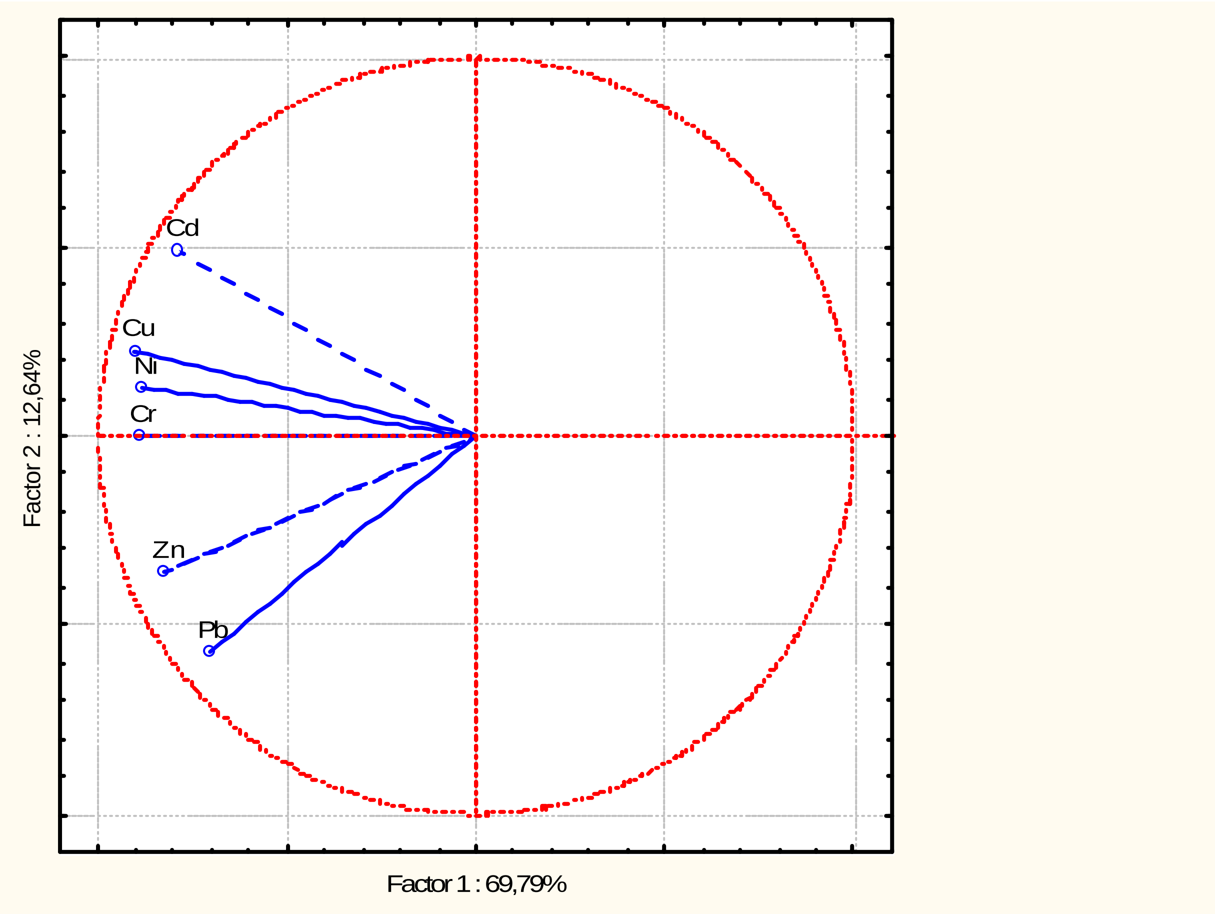


Fig. 24. Projection of the variables on the factor plane (PC1XPC2)

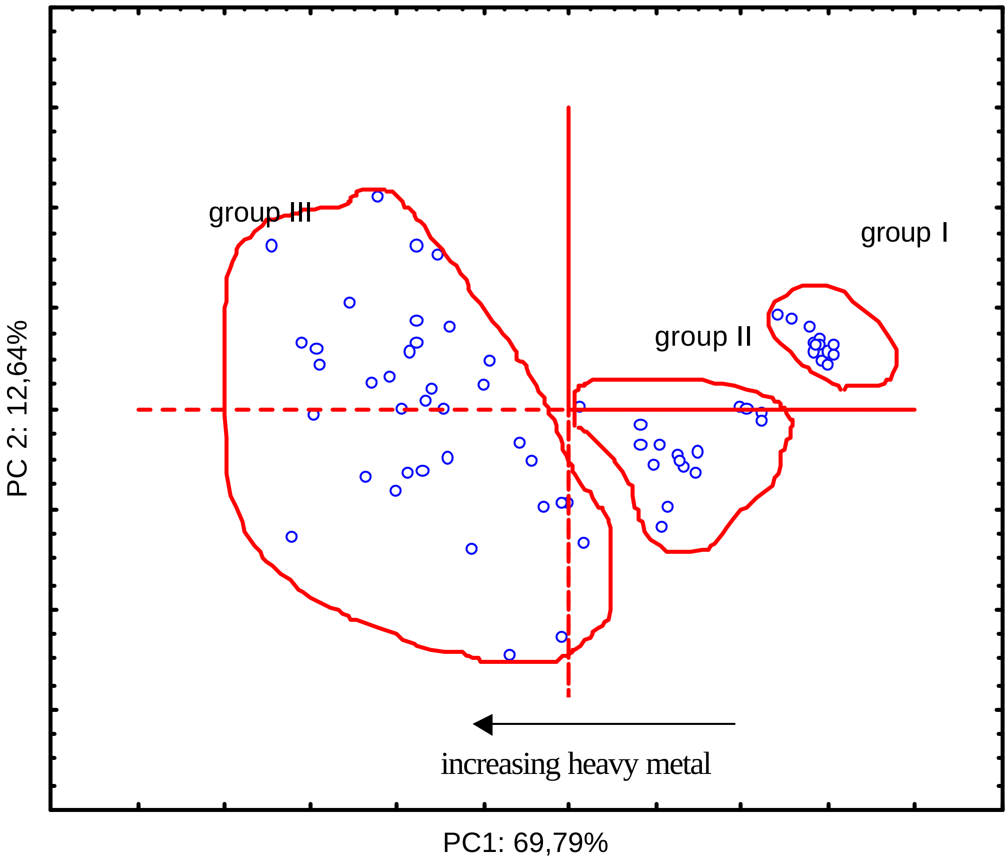


Fig. 25. Projection of the scores of the first two components

Table 20. Principle components Analysis - Scores

Sample No	PC1	PC2	PC3	PC4	PC5	PC6
NB1	-3,00500	0,56587	0,02365	-0,06981	-0,00296	-0,066774
NB2	-2,83901	0,55145	0,11236	-0,10446	0,15616	-0,075179
NB3	-2,81802	0,64787	0,13385	-0,42214	0,07860	-0,160789
NB4	-2,89141	0,67010	0,08887	-0,17830	-0,18332	0,185081
NB5	-2,94096	0,46019	0,04019	-0,18216	0,09156	0,117908
MP1	-0,13113	0,01488	-1,46157	-0,07494	-0,81486	0,512674
MP2	0,66418	-2,44573	0,83860	0,11847	-0,03814	-0,115301
MP3	0,02515	-0,94378	-0,60829	0,26232	0,20148	0,004558
MP4	0,06352	-2,26966	0,95309	0,09620	-0,42227	-0,235827
MP5	1,11931	-1,41169	-0,31778	0,29631	-0,43737	-0,070413
MP6	0,29981	-0,97249	0,82864	-0,21886	0,64105	0,235902
MP7	-1,31905	-0,57637	-0,21503	-0,23526	-0,40553	-0,319437
MP8	-0,83682	-0,37572	-0,21884	-0,52550	-0,29178	-0,213440
MP9	-1,13356	-0,98470	0,24566	0,05383	-0,04741	-0,251169
MP10	-0,98807	-0,55526	-0,05510	-0,51920	-0,37479	-0,413309
MP11	-0,81529	-0,16596	-0,08812	-0,81470	-0,04457	-0,677549
MSS1	-2,88756	0,61215	0,05988	-0,30237	0,15903	-0,139887
MSS2	-2,87912	0,60960	0,11675	-0,08243	0,12342	-0,078508
MSS3	-3,08599	0,60810	0,04145	-0,01575	-0,01578	0,046131
MSS4	-3,07005	0,54176	-0,01359	-0,13866	0,00160	0,151787
MSS5	-2,98850	0,44842	0,13639	-0,20390	0,01984	0,056184
MPK1	-2,78746	0,79083	-0,02913	0,20003	0,04210	0,066409
MPK2	-2,39872	0,90924	0,19950	0,02385	-0,03349	0,220261
MPK3	-2,23618	-0,03880	0,53354	0,18980	0,03732	-0,232058
MPK4	-2,56913	0,88381	0,33000	0,09877	0,15339	-0,227045
MPK5	-2,23823	-0,12456	0,93644	0,17126	0,40004	-0,110054
MPK6	-1,45599	-0,64294	0,86887	0,81608	0,01189	0,438406
OP1	-1,99206	0,00245	-1,09475	0,32996	-0,34065	0,081753
OP2	-1,03600	-0,37655	-1,78713	0,71264	-0,50089	-0,025772
OP3	0,09068	-0,95809	-0,42954	0,40354	1,06568	0,103324
OP4	0,43535	-0,52330	-1,82981	0,18465	1,54494	0,451344
OP5	-0,16935	-1,33079	-0,27838	0,53608	0,29787	-0,299553
OP1a	-1,49665	-0,45030	-0,17038	0,52620	-0,30453	0,151030
OP2a	-2,05713	-0,01445	-0,01648	0,54779	-0,08039	0,161041
OP3a	-1,26394	-0,45701	-0,17811	0,16400	0,31482	-0,052302

OP4a	-1,07156	-1,20410	0,38881	0,34291	-0,23519	-0,366421
OP5a	-1,28572	-0,52031	0,15575	0,27841	0,19959	-0,093023
IC1	2,96469	-0,07790	-0,49845	-0,83502	0,66538	-0,848593
IC2	2,92034	0,57594	-0,66525	0,05563	0,65884	-0,658648
IC3	2,28810	0,26694	0,10697	-1,12535	0,52412	0,209466
IC4	1,93177	-0,01426	-1,23357	-0,38799	-0,07263	0,136837
IC5	1,67592	-0,62064	-0,50293	-0,40048	-0,28712	-0,290025
IC6	1,51360	1,53442	-0,39192	0,12303	0,37425	-0,153821
IC7	0,99900	0,23375	-0,91423	-0,95168	-0,54787	0,044783
IC8	1,57422	0,21085	-0,47337	-0,81690	-0,63099	0,204595
IC9	1,43607	-0,01769	0,91237	-0,78357	0,20208	0,822180
IC10	1,84200	0,54480	0,65086	-0,87216	0,07685	0,208422
IC11	3,18319	-1,28424	0,61023	-0,16626	0,20167	-0,008839
IC12	1,76006	0,65514	0,27896	0,65750	0,04009	-0,205012
IC13	2,53254	1,05521	-0,13294	1,89876	-0,00563	0,038826
IC14	3,44409	1,61988	0,63993	0,81298	-0,47422	-0,782492
IZ1	1,77056	0,86085	-0,46163	0,22653	-0,01003	-0,124931
IZ2	2,36100	-0,66919	-0,05169	-0,03824	1,00663	-0,033518
IZ3	1,74472	1,62335	-0,39750	0,22478	0,63892	0,459037
IZ4	1,87185	-0,65413	-0,45480	-0,08846	-0,24490	0,733934
IZ5	1,42531	-0,48918	0,19795	0,33380	-1,06778	0,663950
IZ6	0,55912	-0,34335	0,76900	-0,89510	0,50561	0,060079
IZ7	1,64304	0,08330	0,03261	-0,08832	-0,89182	-0,459504
IZ8	2,06745	0,32401	-0,01916	-0,76382	-0,93441	0,342291
IZ9	1,38555	0,80355	1,28495	-0,75805	0,15992	0,707497
IZ10	2,20584	2,08442	1,10497	0,02472	-0,19032	-0,435111
IZ11	2,00455	-0,83188	0,74440	0,60633	-0,15592	0,177774
IZ12	0,91728	0,45732	0,13217	0,78218	-0,05956	0,334676
IZ13	3,08060	0,64441	0,78931	1,35460	-0,01274	0,229283
IZ14	2,88720	0,45018	-0,29746	-0,39414	-0,43486	-0,133124

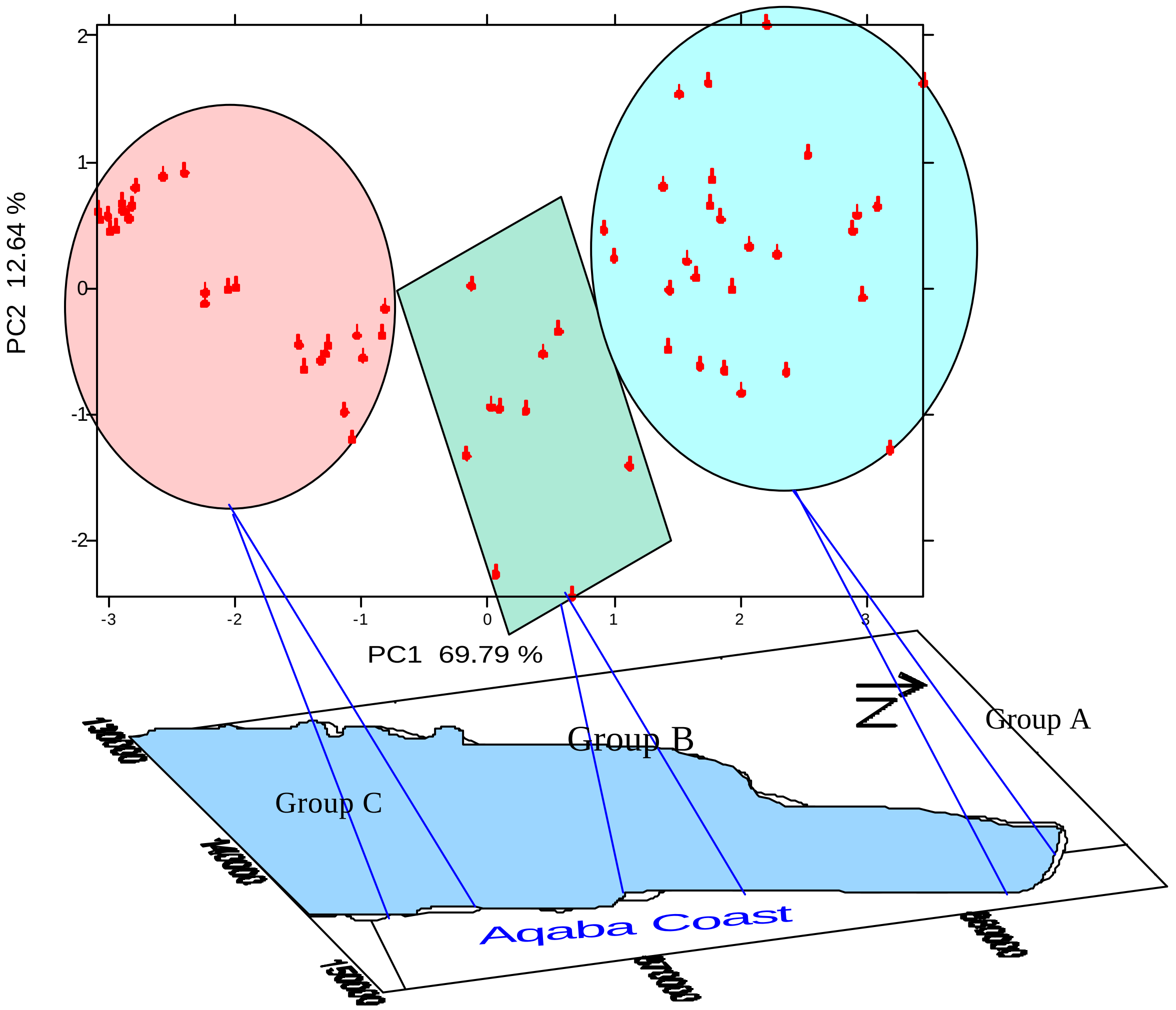


Fig. 26. A model showing clustering the measured samples into three groups, using the results of PC1 and PC2.

8.3 Modeling the Results and Evidencing Spatial Relationship:

One of the purposes of the present work was to study the spatial distribution of this kind of metal pollution along the coast of Aqaba. The data obtained and discussed in the former chapter have shown that there is undoubtedly a status of pollution described as high and medium in some places and low in others. Another ultimate goal also to motivate the concerned parties by presenting a well-defied and clear results. Therefore it was useful to utilize the data obtained throughout this work, more specifically from the PCA to establish models that describe and summarize briefly these results.

According to PCA, PC1 was determined to be representing and reflecting major anthropogenic sources, based on the positive and highly correlated values for the six metals. In other words, PC1 represent the six metals that have been introduced into the ecosystem via common sources.

As shown and discussed in chapter six several activities along the coast are known to contain and include Cd, Pb, Cu, Ni, Cr, Zn-contained material in their processes and operations, for examples, the oil spills, the port operation particularly at the oil berth, the discharge cooling water and the vessels coatings and painting in addition of course to dredging.

On the other hand PC2, by clustering Pb and Zn together suggests another secondary source where these two elements are being discharged together, most probably shipping and boating through their exhaust emissions and the discharge of ballast water and the on-board sewage.

By utilizing the PC1 and PC2, two models were suggested. The development of these models was based mainly on the geostatistic approach, where both the raw data and factor scores (Table 20) were interpolated by kriging method using SURFER ® 7.0 for Windows and ArcView® 3.2a for Windows.

The first model F1 scores were plotted on a map evidencing the coast of Aqaba (Fig. 27). The results of a PCA performed on six heavy metals, identified three areas with positive anomalies. The spatial relationship between these anomalies and the type of coastal activities showed that the areas include: the main port area, the oil port and the industrial zone.This is exactly the same thing concluded earlier in chapter seven.

To confirm such distribution, the second model was developed by using this time the score of PC2 which were composed over georeferenced land use map of the study area (Fig.28). Almost the same distribution was obtained, three main areas with positive anomalies represent the same identified in Fig. 27. The only minor difference noticed here is that the marine park area and the surroundings were dominated by PC2 contours with low values (<0.5) more than the PC1 low-value contours. This is in agreement of what has been mentioned above that Pb and Zn have shown significant correlation over the other elements in PC2, which was attributed to secondary common source that has impacted this area in particular. However, the landuse map included in this mode provides a detail on the nature of the existing activities along the study area.

Concluding on the above, it is now very clear that there are some areas suffer increasingly impacted by uncontrolled activities, which in turn affect the nearby fragile coral reef system, therefore these area should be tackled as priority in any given development and management plans, in addition, of course of the need, to some urgent actions for monitoring and mitigations.

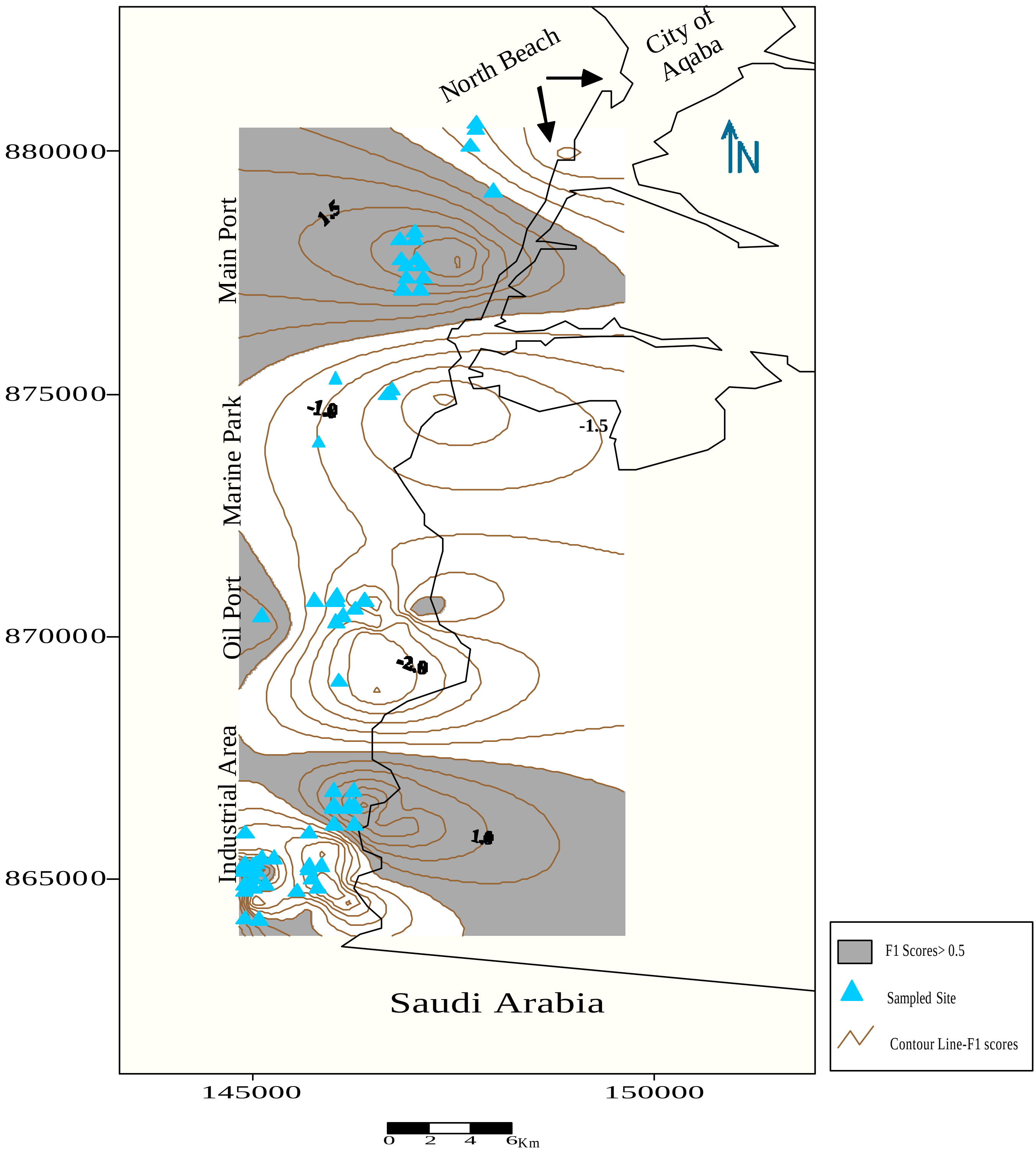


Fig.27. The first spatial model developed by utilizing the scores of PC1 of all examined samples. (Inland contours were self-created by the software, contour interval=0.5)

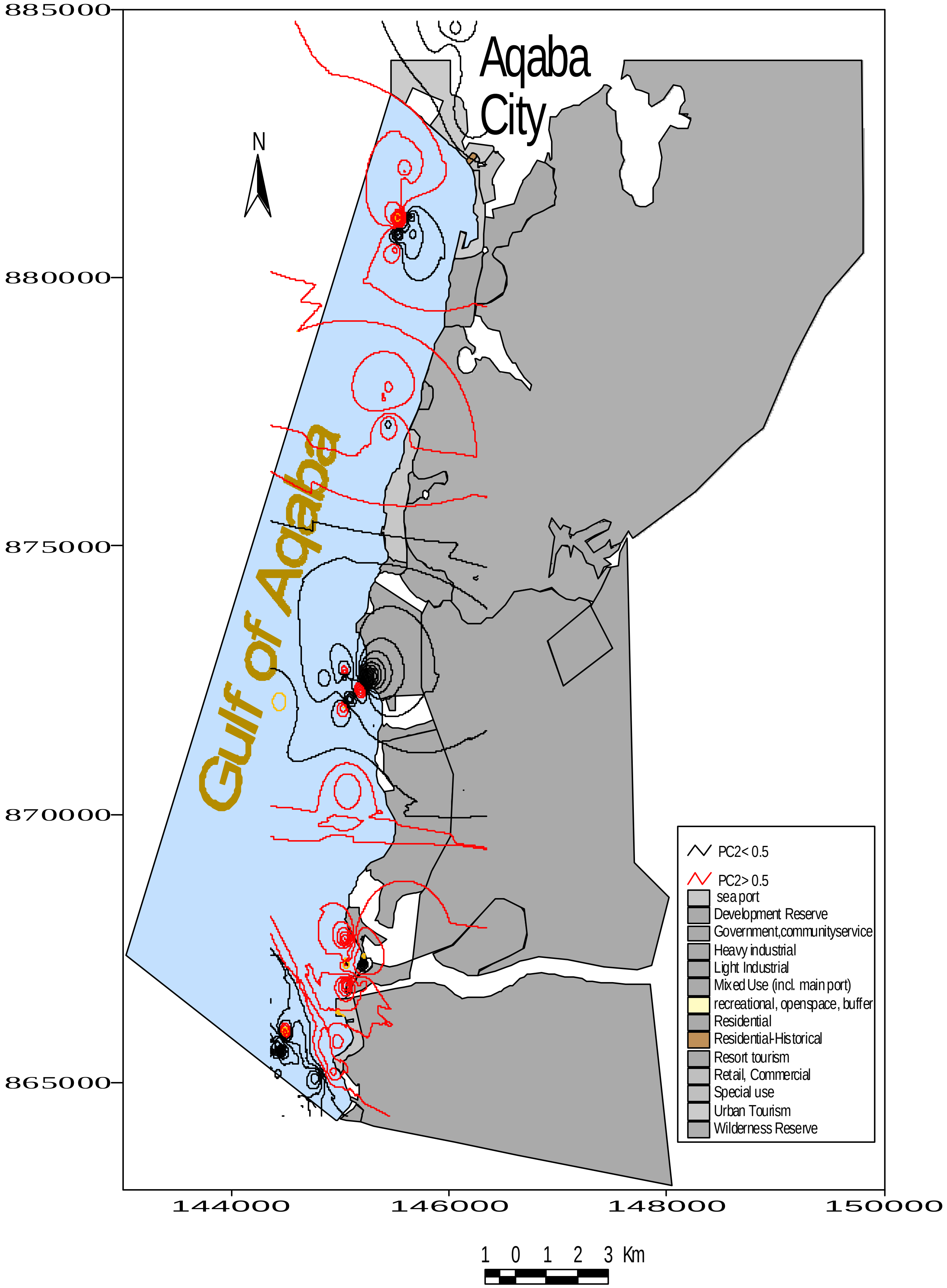


Fig.28. The second spatial model developed by utilizing the scores of PC2 of all examined samples. (Inland contours were self-created by the software, contour interval=0.5).

Chapter Nine

Identification and Assessment of Main Potential Sources of Heavy Metal Pollution in Aqaba

9 Identification and Assessment of Main Potential Sources

9.1 Introduction

It is estimated that approximately 6.1 million metric tons of petroleum products are released to global oceans annually, the majority of which is derived from anthropogenic sources and which pass through the coastal zone before being carried out to sea (Capone and Bauer,1992). Worldwide, major inputs of petroleum into the marine environment occur via industrial discharge and urban runoff (36%), vessel operations (33%), tanker accidents (12%), atmospheric deposition (9%), natural resources (8%) and exploration production (2%) (Queensland Transport,1997).

The fate of petroleum hydrocarbons once they enter the marine environment is similar to that of many organic pollutants. The bulk of the petroleum initially introduced into the water column rapidly becomes associated with hydrophobic organic matter and suspended particulates, the volatile compounds then evaporate and the non-volatiles are deposited into the sediment (Capone and Bauer,1992). The component of petroleum left, the emulsion or `mousse', is not likely to dissolve, adsorb, evaporate or be rapidly biologically degraded and will eventually sink to the bottom and settle in the sediment. While the lighter fractions are suspended in the water column, the most damaging impacts are on larvae and low motility organisms that cannot escape the oil.

The effects are most notable in changes in feeding or reproductive cycles that ultimately affect population size and fecundity. Once the PAHs have settled in the sediment, filter feeders and benthic organisms are affected with the bioaccumulation of toxic compounds in their tissues, genetic mutations and cell atrophy often occurring (Peters *et al.*,1997).

Metals are also strongly associated with particulates and enter the marine environment in a similar fashion to organochlorine compounds. The major routes of environmental entry include atmospheric transport of dust and through sediment movement in overland flows and in waterways. Additional quantities of metals are also added to the environment via the discharge of effluent and urban stormwater. Particulate metals in suspension and in bottom sediments are not generally directly available to aquatic organisms, the exception to this are sediment bound metals which can be accumulated following solubilization in the acidic juices of a sediment-feeder's gut (Waldichuk,1985).

The rates at which metals are solubilized from particulates is dependent on environmental factors including dissolved oxygen concentrations, pH, salinity and temperature (Waldichuk,1985). Once dissolved in the water column, metals may be accumulated by marine invertebrates from solution via passive uptake across permeable surfaces such as gills and the digestive tract . Cellular metal toxicity is primarily due to the chemical inactivation of cellular enzymes responsible for normal organism survival and function (Förstner,1989), organism growth, reproduction and behavior are potentially effected by elevated environmental metal concentrations (Langston,1990).

It is known that rivers and wadis are the most important sources of heavy metals in the aquatic systems and they carry much larger quantities of the elements as particulates than they do as solutes, (Guzman. and Jimenez,1992).

The absence of major rivers or streams flowing into the Gulf of Aqaba, departing the conclusion that any reported metal enrichment is attributed to such source, therefore there is a need to identify the anthropogenic sources that contribute to this enrichment, so as to halt any further degradation of the ecosystem through basically conservative measures and actions.

In Aqaba, although it was impossible to determine the metal input into the coast water from each source, due to many existing sources contributing to the continuous discharge of these metals into the sea, the present work at least tried to investigate and identify their sources by reviewing the obtained results and surveying all potential sources and activities along the coastline that might contribute to the metal budget reaching the ecosystem.

However, in general, the input of heavy metals into aquatic systems originated principally from two main sources, namely naturally or non-point sources and point sources by human's activities. The former includes mainly geological weathering of the earth's crust or their ore deposits, while point sources is usually considered the one which is responsible mainly for water pollution with heavy metals. Such point sources include for example domestic- and industrial wastewater effluents.

The analysis of all types of activities along the coast have shown the following as contributing to the metal enrichment in the system considering of course at first that of natural ones:

9 .2 Natural non-Point Sources

9.2.1 Atmospheric Inputs of Metals to the Coastal Waters:

There have been few number of studies of the atmospheric input to coastal waters, and almost all of what has been done was particularly in North America and Europe, where in most other regions of the world it has largely been ignored, (Jickells,1995). Traditionally, budgets and residence time estimated for trace metals in the ocean have ignored atmospheric inputs. However, for most major and minor components of seawater the atmosphere has generally been assumed to be a secondary source. The continuous attempts to estimate such input are hampered by uncertainties.

In the present work the atmospheric input was ignored for the same purpose mentioned above and also for the fact that any atmospheric input by all mean will not make an enrichment as much as what has been recorded here. In addition, this issue requires the interaction of a wide range of disciplines including meteorologists, geologists, chemists, biologists and modelers in order to be studied in details.

9.2.2 Surface Water Inputs

The average total amount of rainfall during the rainy months of the year in Aqaba do not exceed 50mm. Due to this low precipitation amounts and the high infiltration rates in the study area, runoff does not exist often, but only when an intensive rainfall event sweeps the area (ISPAN,1992).

Rare frequent thunder storms sweep the area carrying casual intense precipitation in rainy months resulting in high annual rainfall. However, when there is heavy rainfall, chances of runoff are being enhanced by the existence of the impermeable rocks and steep slopes of the highlands (Plate5) which provide good conditions for runoff (Al-Farajat,2002).

Plate5. the picture shows part of the north coast and the surrounding granite mountains, in which they-in heavy rainfall seasons - contribute to the metal inputs to the gulf.

The rainfall data are available for the last 20 years. Daily basis-data (Fig.29), show clearly that there is a pattern where 4-5 years of dryness are followed by a wet period. The figure shows also that some peaks have been recorded, and the highest daily value was in the year 1980. This conclusion along with that of considering the runoff as a source of metals both help in interpreting some enrichment found in bottom cores (1980-1985).

According to Al Farajat, (2002), one of the potential pollutant sources, heavy metals in particular is the granite mountains overlooking the main port. These mountains retard wind transportation, and hence causing dust particles to settle on surface. The accumulated deposits, once raining, will be flushed downward into seawater of the main port.

9.2.3 Groundwater Inputs into the Gulf of Aqaba

Al-Farajat (2002) has estimated the annual subsurface discharge of groundwater into the Gulf of Aqaba from the northern region (where the northern portion of the coast is part of) is 7.1 $*10^{6}$ m^{3}/y , along a shoreline of 7.5km with an average flow velocity of $3*10^{-6}$ (m/s), while lesser amount from the southern region (including the southern coast) of 3.26 $*10^{6}$ m^{3}/y along a shoreline of 11 km long with an average flow velocity of $9.4*10^{-7}$ (m/s).

However, the main concern of this conclusion is that any contamination of ground-water would ultimately affect the marine ecosystem through this subsurface discharge, in which different chemical constituents including heavy metals will be introduced to seawater.

Moreover, The southern region according to the researcher possesses relatively deeper groundwater levels compared to the northern region, therefore expected to be less impacted by any pollution sources. where the northern portion of the coast is part of.

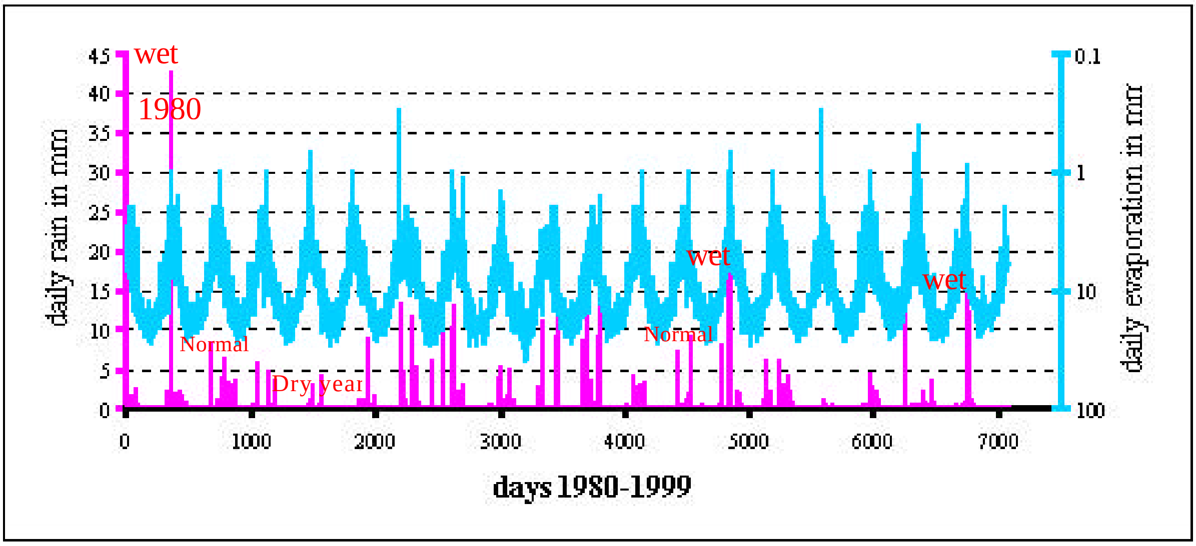


Fig.29. Daily rainfall and evaporation distribution in Aqaba 1980-1999, (diagram modified by Al-Farajat, 2002 based on data obtained from Dept. of Meteorology-Jordan in 1999)

Table 21. Concentrations(mgl^{-1}) of heavy metals in groundwater; measured in wells in northern and southern areas of Aqaba (Al Farajat, 2002)

Well Location	**X**	**Y**	**Zn**	**Ni**	**Cu**	**Cr**	**Cd**	*PB*
	157637	886429	0.014	0.0002	0.0008	0.0043	0.00	0.002
Winds Hedges P.	150644	887976	0.014	0.0016	0.0013	0.0141	0.00	0.002
S.O.S	150454	884411	0.171	0.001	0.0012	0.0056	0.00	0.0016
Islamic Hospital	150109	883639	0.015	0.0008	0.001	0.009	0.00014	0.0041
Horse club 2 (Racing club)	148387	884423	6.595	0.002	0.003	0.0028	0.00001	0.0072
Children School	150074	884518	0.141	0.0013	0.0012	0.0103	0.00003	0.0017
Palm P. N. Well	149088	886289	0.014	0.001	0.001	0.0083	0.00004	0.0013
King H. Mosque	150026	882023	0.026	0.0003	0.0014	0.0042	0.00001	0.0013
J. Dahdal Plantation	149099	883900	0.047	0.0004	0.0011	0.0068	0.00002	0.0011
M. Yaseen	150193	884043	0.013	0.0003	0.0012	0.0078	0.0001	0.0011
T. Kholi Farm	149171	884471	0.014	0.001	0.0013	0.0108	0.00004	0.0017
Al Kasar Hotel	149812	882843	0.048	0.0005	0.0023	0.0057	0.00018	0.0012
S. Aqaba Gas Station	150098	880692	0.018	0.0011	0.0038	0.0095	0.00038	0.0028
H.Bin Ali Mosque	149872	882237	0.238	0.0005	0.0026	0.0043	0.00017	0.0025
Hafira Well 1	149872	881405	0.041	0.00	0.0016	0.0051	0.00014	0.0026
Southern coast								
Industrial complex well	147571	864241	0,0590	0,0020	0,0014	0,0044	0,00006	0,0148

Table 21 shows the measured concentration of heavy metals in groundwater. However, these concentrations reflect the normal content of the six measured metals in groundwater, which usually show very low content, but in case of intrusion of any contaminants rich in heavy metal, this amount will be definitely several fold higher than this normal concentration.

Therefore, the calculated values of the annual amount of metal reaching the gulf via the natural subsurface flow of groundwater is just to show the contribution of such source.

Based on the results of Al-Farajat (2002), (Table 21) and the estimated subsurface discharge towards the gulf, the annual amount of metal discharged into the sea was calculated (Table 22) where, theoretically it is the average concentration of certain metal at certain site (well) multiplied by the annual input of the groundwater into the gulf at that site. It is mentioned here that nor the chemical or the physical process which might affect the transportation (or the rout) of heavy metals via the groundwater subsurface flow have been considered in these calculation, hence such calculation is for demonstration purpose only. Further investigations are therefore highly demanded.

Table 22. Annual amounts of heavy metals (kg y^{-1}) discharged into the sea by subsurface flow of groundwater in the northern coast area. Annual groundwater input into the Gulf $=7.1*10^6$ m^3 y^{-1} for the northern region and $3.26*10^6$ m^3 /y for the southern region, Al- Farjat,(2002)

X	Y	Zn	Ni	Cu	Cr	Cd	Pb
Northwen Region							
157637	886429	99,4	1,42	5,68	30,53	0.00	14,2
150644	887976	99,4	11,36	9,23	100,11	0.00	14,2
150454	884411	1214,1	7,1	8,52	39,76	0.00	11,36
150109	883639	106,5	5,68	7,1	63,9	0,994	29,11
148387	884423	426	14,2	21,3	19,88	0,071	51,12
150074	884518	1001,1	9,23	8,52	73,13	0,213	12,07
149088	886289	99,4	7,1	7,1	58,93	0,284	9,23
150026	882023	184,6	2,13	9,94	29,82	0,071	9,23
149099	883900	333,7	2,84	7,1	48,28	0,142	7,81
150193	884043	92,3	2,13	8,52	55,38	0,71	7,81
149171	884471	99,4	7,1	9,23	76,68	0,284	12,07
149812	882843	340,8	3,55	16,33	40,47	1,278	8,52
150098	880692	127,8	7,81	26,98	67,45	2,698	19,88
149872	882237	1689,8	3,55	18,46	30,53	1,207	17,75
149872	881405	291,1	0.00	11,36	36,21	0,994	18,46
Southern Region							
147571	864241	192,34	6,52	4,564	14,344	0,1956	48,248

As Table 22 shows, the amount of metals discharged into the sea by groundwater is negligible for most of the metals presented here, so it is confirmed here again that we should consider in future that such seepage of groundwater as a potential source of pollutants carried out into the sea once the groundwater itself have got polluted.

However, the natural inputs of heavy metals into the ecosystem –once occur- are very low, and lower than the concentrations already presented in this work and that values reported in the available literature (Bastidas and Garcia,1999; Facchinelli *et al.*,2001; Ramos *et al.*,2004). Consequently, attributing the existing enrichment in reef samples to natural sources is excluded.

9.2.4 Siltation

Siltation of the coral reefs occurs from resuspension of inorganic and organic sediments in the nearshore region by currents. Coral species have varying abilities to shed particles of different size and mineralogy. There appears to be no studies on the relative amounts of organic and inorganic material contributing to the reduced water clarity in the gulf.

It was widely reported that water clarity decreases dramatically during windy periods, yet it is not known whether the resuspended material in the nearshore regions by coral reefs is primarily organic; that is detritus from excessive nutrient loading, or whether the resuspended material is actually fine sediments, perhaps from winnowing of the beach material and other construction materials. If the resuspended material is organic, then the concern is the nutrient input, if however the resuspended material is primarily fine inorganic sediments, and therefore contains heavy metals either from the original beach material or any associated material, for examples vehicle waste oil then this source to be considered.

9.3 Anthropogenic Sources

9.3.1 Point Sources

9.3.1.1 Phosphate Dusts from Port Activities

According to official reports, 4.0 to 7.0 million tons of raw phosphate is exported through the Gulf of Aqaba via the phosphate berth at the main port. Phosphate dust generated during ship loading is considered as important environmental problem in Aqaba because high percentage of this dust is lost and settled on the Gulf's water. The environmental effects of the dust include reduction of water clarity, and rate of light penetration. It includes also siltation of the coral reef and depression of coral growth rates. Other possible effects are increasing the levels of dissolved phosphate nutrients, and other toxic heavy metals such Cd and Zn (Praagman,1999).

The earlier estimates of the phosphate dust lost during transportation and loading by the Jordan Phosphate Mines Company (JPMC) was 0.05 of the amount handled, (Abu-Hilal, 1985). Recent communications with JPMC assured that this figure has been minimized significantly after installing new efficient filter systems by 1996, and the continuous and strict monitoring by the company itself, however, it is well known now that the company is not allowed to load the phosphate into ships while there is strong winds (JPMC,2003).

Abu-Hilal, (1985) has studied the phosphate pollution in the Gulf of Aqaba of Jordan. He reported that the phosphate pollution is located mainly near the phosphate loading berth and the sewage outfall. The conclusions was made based on the determination of the distribution of total phosphorous, fluoride, calcium and calcium carbonate and their association with each other in seven sampling stations along the coast. The total phosphorus in the sediment core collected from a station nearby the berth was 6-13 times higher than any of the samples from other stations along the coast, (Table 23). This abnormal high values decrease with increasing distance from the berth. He concluded also that phosphate pollution is mainly localized in the vicinity of the loading berth although its influence may be detected in other areas along the coast. The abnormally high concentrations of fluoride and total calcium specifically at station 3 of the main port (Table 23) supports this conclusion as well.

The strong correlation (r=0.99) between sedimentary phosphorous and both fluoride and calcium at station 3 indicate that phosphate particles are the main source for sedimentary phosphorous at this station (Phosphate berth). In addition, results of the other stations have shown also that the pollution seems to reach other areas along the coast, but it was clear that the closer sites to the phosphate berth at the main port were more affected. Other reports have shown also that the phosphate with this high level were enough to affect the corals in main port area adversely and many species of stony corals have been killed, leaving predominantly one species (*Stylophora pistillata*) which itself is suffering a mortality rate 4-5 times higher than that in a controlled area to the south (MSS, 2002).

Although that one of the significant environmental and competitive aspects of Jordanian phosphate rock is its relatively low concentration of heavy metals such as cadmium, lead, mercury, arsenic and zinc (Cd,10-18, Cr,50-125, Cu,19-59, Zn,190-510 and Ni >20ppm; *inter alia.*, Okur, 1993, Abu-Hilal, 1993) all of which are considered to be environmentally hazardous, its heavy metal content is still threatening the Gulf considering the millions of tons exported annually via the main port of Aqaba, having in mind the estimated 5% (or even an order less) dust loss released during loading in which it will eventually be accumulated with time and would increase the metal budget in the ecosystem.

However, considering both the results of Abu-Hilal (1985) and the evaluation of the this problem supports and confirms the conclusion that phosphate at least at the main port (indicated from the high concentration of Ca) is one of the point sources that contribute to the metal enrichment through its content of heavy metals which reach the seawater via the blew dust.

Table 23. Ranges and means of elemental concentration (percent, dry weight) in sediment cores from the Jordan Gulf of Aqaba (Abu-Hilal, 1985)

Station*	**Depth (m)**	**%P as P_2O_5**		**% F**		**% Ca**		**% $CaCO_3$**	
		Range	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**
3	5	16.7-19.7	18.62	2.40-2.88	2.65	29.76-30.40	29.93	16.66-20.9	19.04
	10	0.71-5.99	3.05	0.19-0.70	0.48	3.22-8.78	5.54	5.71-8.09	7.26
	20	0.85-4.26	2.47	0.13-0.75	0.38	3.49-11.45	6.42	6.6-12.85	9.03
	30	0.69-3.33	1.47	0.08-0.75	0.32	4.04-11.56	6.33	8.57-15.23	10.71
4	5	0.07-0.11	0.096	0.010-0.013	0.012	2.51-6.20	5.08	5.32-8.22	7.13
	10	0.07-0.10	0.080	0.011-0.015	0.013	4.30-7.50	5.73	7.25-10.15	8.41
	20	0.06-0.09	0.076	0.009-0.011	0.010	3.80-4.50	4.08	4.83-7.14	6.11
	30	0.07-0.09	0.080	0.010-0.012	0.011	3.10-5.10	4.20	4.76-8.57	6.43

*Seven stations have been sampled in this survey, the only presented here are the results of station 3 (the phosphate berth) and station 4 (6km south of station 3) for correlation purpose.

9.3.1.2 Dredging

It is well documented in literature (Brown,1987; Salvat,1987; McIntyre,1995 Cheevaporn et al.,1995; Alongi,1997) that dredging at harbors and marinas is associated with releasing and remobilization and then re-entering of trace metals into the aquatic systems.

Dredging was a frequent activity at the harbor basins in Aqaba, in particular the main port. There are no studies that indicate whether or not the deposited harbor sediments have re-entered the harbor basins the gulf. However during the last 20 years, three major normal expansions have taken place at the main harbor (APC,2002) and one major dredging was within the area of the marine park for the Taba-Aqaba underwater high-voltage cable; (a joint electricity project between Jordan and Egypt). This high-voltage cable is installed between the two regions across the Gulf down to depth of 850m. The project was launched by the end of 1995 and was completed in April 1999. No studies have been conducted to assess the impact resulted by this project, but however, unpublished and non-available Environmental Impact Assessment study (EIA) was conducted by an international firm for this project.

The samples obtained from the nearby colonies at the marine park have shown unexpectedly a relative increase of their metal content. The uncontrolled dredging at that site was probably one of the metal sources. The conclusion is made based on the period represented in the reef samples obtained at that site and the year of a major failure in huge reef block as a consequence of dredging in 1998.

9.3.1.3 Harbor Areas and Marina

Generally, all marina and harbor areas receive inputs from vessel activities. There is a variety of activities associated with vessels that could contribute trace metals including antifouling paint hull coatings, motor exhaust, and hazardous material spills.

Of all the vessel related activities, antifouling bottom paints are amongst the largest source of trace metals, in particular copper at harbors and marinas (Schiff *et al.*, 2004).

At the harbors, it was not possible to track what kind of such products or ingredients are being used, as the bottom painting is carried out mainly by the crew of visiting vessel (using the paints they already have) and not by a local contractors.

At the Royal Yacht Club the only existing marina in Aqaba used for small leisure boats and yachts, current day hull coatings are impregnated with copper and sometimes co-biocides whose goal is to retard the growth of algae and other encrusting organisms, there is no specific paint type is being used and no control over the use of such material by the authorities (Qusous,2003).

However, no samples have been taken from this area as there was not any reef community around, but even if there is any pollution recorded at the basin, it would not extend outside its boundaries. This is due to two reasons, the first; the marina is inherently protected which restricts circulation therefore inhibit the movement of pollutants outside, and second all of examined samples taken from the nearby sites did not show unexpectedly values for metals, specially for copper. Noteworthy is that this matter does not depart the possibility of the nearby areas to be impacted by the routine activities of the boats that use the yacht club.

One more thing of concern is the existing submarine structures at the main harbor which are more than 30 years old. Such structures may contribute to the heavy metal content in the seawater as they suffer chronic corrosion and leaks or even rupture.

9.3.1.4Oil Port

The area opposite to the oil port has shown significant fluctuation in the concentration of all metals. These fluctuation ranged from extremely high to relatively low. The interpretation beyond such variations (although the port is considered as a point source of metals) is that the operations were halted for several times during the last twenty years. However, two major peaks of metal concentrations were observed for samples taken from the oil port area. They could be attributed to the increase in using the terminal during the first Gulf war 1980-1988 as a main route for the export of Iraqi oil. Similar intensive use was also prevailing during the second Gulf war.

Noteworthy is that during periods of no-operation the port was being used for importing the botanical oil. Therefore even if high potential of pollution was absent during that time, there is still a potential but lesser for pollution from routine operations at the port.

9.3.1.5Cooling Water

Currently, there are three large facilities that use seawater for cooling. The intake is operated through an open canal, while the discharge is through pipes extending some 200m from the beach at depth of ~10m (Plate 6). Although the existing operating cooling systems in Aqaba are based on the common known non-contact system, there is still an impact associated with the discharged. Open recirculating cooling water systems are subject to metal corrosion, scale formation, and biological fouling, which has a direct effect on the ecosystem .

Commonly there are several chemical products usually used for treatment purposes. Among these products are the additives which contain copper, zinc, hexavalent chromium, tributyltin and other organometallic compounds contribute to environmental pollution, (Fialkowsk and Newman,1998).

Several metals including copper, zinc, chrome, and tributyltin can be found in the discharge from cooling water systems. Copper and zinc are common materials found in cooling water system components and piping; both are susceptible to corrosion. They are the most common metals used as cooling water treatment chemicals (GTZ,1991). Analyses of samples collected from industrial cooling systems have shown that relatively high levels of these metals are often found, (the author).

9.3.1.6The Byproduct Gypsum

Another point source but might be indirect one is the gypsum ($CaSO_4.2H_2O$). Gypsum is produced at the industrial complex of Jordan Phosphate Company as byproduct of Phosphoric acid. The environmental concern beyond the presence of this gypsum in huge quantities which is usually collected nearby the factory where the dumping area is being known as the

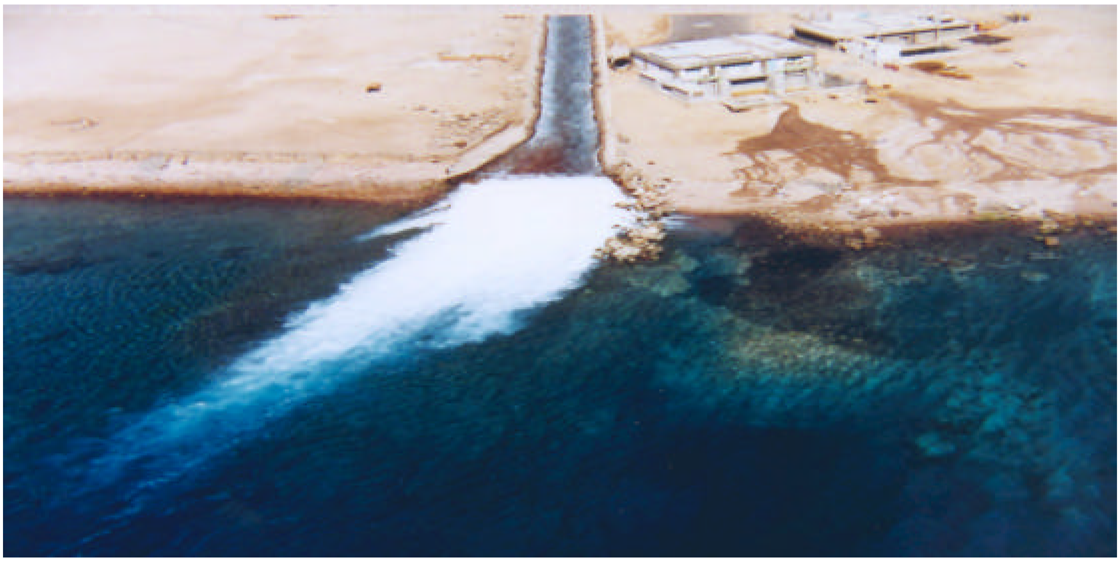


Plate 6. One of the discharge points of cooling water on the southern coast.

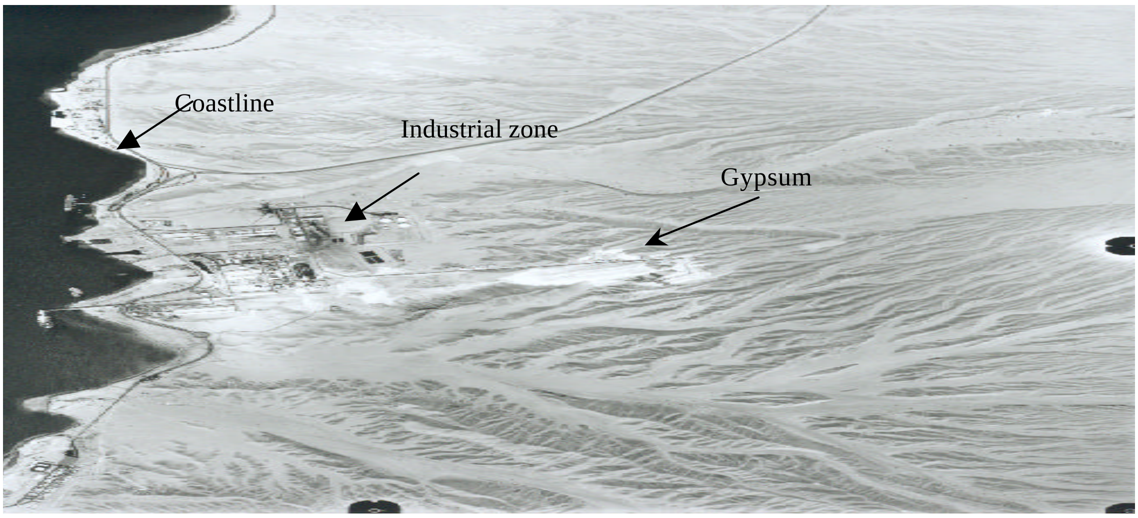


Plate7. The Gypsum Dumping Site, nearby the industrial complex.

mountain of Gypsum, (Plate7) is that gypsum posses high solubility in water, thus lowering pH in the soil, leading to increase the mobility of any available heavy metals which in turn will be transported eventually into the sea once there is considerable rainfall, either directly by washing floods or via traveling with groundwater downwards to the shoreline.

9.3.1.7 Coastal construction

In general coastal construction bring much damage to the marine ecosystem. This is either through dredging, blowing of dust and/or solid wastes accumulated close to the coast (Plate8). During the last 20 years coastal constructions included road construction and expansion, at both the north and the south coasts. Several expansion have taken place at the already existing

Plate8. Coastal construction and the associated material, dust and wastes.

coastal facilities; hotels, harbors, camp sites, oil and industrial ports. In addition to improving the infrastructure along the north coast. There was always no control on the disposal of both solid and liquid wastes generated from such constructions. Construction material such as sand, clinker, paints and others if not disposed properly will eventually reach the seawater adding an extra load of pollutants in general and metals in particular to the ecosystem, specially when such material are installed very close to the beach.

9.3.1.8 Jordan Cement Storage Facility

The facility is used for storage and export via the cement terminal. The cement is transported through a fabric filter to the conveyor belts leading to the port.

The investigations carried out at the site did not show any impact to be considered. The cement is normally transported by tankers from the main factories located outside Aqaba and pumped by closed pipes to the storage domes. Therefore, the facility could be considered as potential source when only the well-controlled conveying system has become damaged or dilapidated.

However, there might be still some little concern in this site during loading and unloading the cement to the domes and the terminal as the dust is usually generated during this operation.

9.3.1.9 Sewage Input

Sewage is no longer routinely discharged into the gulf by the city of Aqaba or the city of Eilat (Israel). The input of sewage from Aqaba is based on leakage through groundwater (ISPAN,1992) and the input from Eilat are from sewage overflows (MoI,2001). However, what should be considered here is that prior constructing the new waste water treatment plant in Aqaba in1987, the waste water of Aqaba was disposed through non-sealed ground septic holes, resulting in infiltration of large quantities down to the groundwater.

The sewage produced at residential areas, at that time and collected in such holes were usually brought by trucks to the old treatment plant south of the main port. Moreover, during the same period of time, partially treated sewage was being discharged from this old plant into the gulf (Wahbeh,1990; ISPAN,1992). Now, this old plant is no longer used. Even sewage produced at the port is now brought by trucks to the new treatment plant as well.

Based on that sewage is considered therefore as a source that had contributed to the metal budget reaching the sea. This was through two routes; the first via the direct discharge of the partially treated waste water from the old plant and the second (which is classifieds as non-point source, but discussed here generally) is transported by the subsurface groundwater flowing towards the gulf.

9.3.2 Non -Point Sources

9.3.2.1 Oil Spills

Ship traffic in the Gulf of Aqaba like elsewhere poses a risk of oil pollution from the following sources (IUCN,1993; Marine SAC, 2003; WRI,2003):

1. Small spills caused by the accidental or intentional release of oil-contaminated bilge or ballast water from freighters (0-2 metric tons).
2. Minor spills caused by the release of oily ballast water from an oil tanker or the release of bunker oil during terminal operations (2-20 metric tons).
3. Medium spills caused by the release of oil as a result of defective equipment or procedures at an oil terminal or pipeline facility (100 metric tons).
4. Major spills caused by the rupture of a bunker oil tank in a bulk/cargo vessel collision (500 metric tons), shipwreck of a bulk/cargo vessel (1,500 metric tons), or a tanker collision causing the rupture of a single oil tank (7,500 metric tons).
5. Disastrous spills caused by the wreck- age of a fully loaded oil tanker (100,000-150,000 metric tons).

Over 2,300 ships pass through the Port of Aqaba annually, but the port has no reception facility for oil- contaminated bilge or ballast water.

Small to minor oil spills have occurred frequently in the Gulf of Aqaba. In 1990, some twenty-two small to minor spills were reported in Israeli waters alone (MoI,2001). In Aqaba, forty-nine small to minor spills were reported in the period 1993-1996, sixteen spills in 1993, eleven spills in 1994, seventeen spills in 1995, and five spills in 1996, in addition to one medium spill in 1995 in which about 54 metric tons of fuel oil spilled into the sea and was most devastating spill in Aqaba (PERSGA,2001).

Noteworthy that there is no official detailed record for oil spills occurred in the Jordanian Gulf of Aqaba, prior to 1996, the date of establishing Prince Hamzeh Centre for Oil Pollution Combat.

9.3.2.2 Land Traffic

During the last twenty years there has been non-gradual increase in car traffic around the Gulf which certainly contributes to an increasing output of gases and particulates. However, there are no estimates available to us on the dimension of air pollution.

Truck traffic, in particular in the Aqaba region also generates air and noise pollution. Although levels of exhaust gases have not been monitored, visual levels indicate high pollution concentrations and noise levels in urban areas adjacent to truck routes. The concern in Aqaba is that the most proportion of the coastal road that links the city of Aqaba with the port and industrial areas is located very close to the shoreline, which increases the possibility of reaching the generated gases and particulates the nearby seawater (Plate 9).

The problem of waste oil disposal is particularly acute in the Aqaba region because of the high volume of bulk/cargo transportation via truck to and from the Aqaba Port and the industrial facilities on the south coast. An estimated 1,200 haulage vehicles enter or leave the Port of Aqaba each day, and several hundreds additional trucks make deliveries or pickups from the industrial zone, resulting in over 400,000 truck trips each year along local roads (PERSGA,2001).

Inadequate provision for waste oil collection and recovery pose a hazard to both the marine an terrestrial environments. Despite an official prohibition barring trucks from entering beach areas, truck drivers commonly drive heavy haulage vehicles to off-road areas within a few meters of the waters edge. Waste oil has been discharged from trucks in sensitive tidal areas, posing a direct hazard to near-shore coral and related marine life. At few points along the coastal truck route, prominent signage prohibiting trucks from entering unpaved beachfront areas can be seen, but this ban remains to be enforced.

In samples obtained from the marine park site, Pb was recorded to have a relatively high concentrations compared with the nearby marine reserve. The area used to be designated only for recreational activities, therefore lead is thought to be introduced to the ecosystem by such non-point sources.

In Jordan, in general and Aqaba in particular most of the motor vehicles, if not all are using the leaded gasoline, (more available and much cheaper than the unleaded gasoline). Before establishing the marine park on 1997 and adopting the management plan, all beach comers used to drive their vehicles jus very close to the coast; only four to five meters from the high water mark, resulting in exhausting gases that would contribute to the metal content of the system.

9.3.2.3 Agricultural Activities

Although the study area is not known to contain any real agricultural activities, small-scale framing along the northern portion of the coast (locally known as Al Hafyaer area) should be considered as a possible source of contaminants.

The area usually planted is situated directly on the beach, less than 20m from the water mark, the potential contamination might take place when farmers use pesticides which might contain heavy metals in this area, which however will be reaching groundwater and eventually transported along into the sea. No data or any related information are available on this issue.

9.4 Unpredictable and Unforeseen Sources

In the former section, it was attempted to investigate the most probable sources of metal input to the ecosystem. Although it was difficult to determine such sources quantitatively due to many factors including the variation in the type of activities along the coast, so the sources mentioned earlier were identified based upon the investigation of all type of activities in Aqaba. The literature collected on similar topics were very useful in identifying such sources.

However, since heavy metals are constituents of many products and material, it was necessary also to consider some sources which might seem to be not so important in terms of the quantities of metals that they might introduce to the ecosystem. Such sources, would be significant when their little impact be considered on the long run, as they accumulate with time.

Among such unforeseen sources is the bioeroding of older reef sections. The results of the present work, has shown that there is significant enrichment of metals in the coral reef of Aqaba. Therefore, these reefs have become in turn a source of metals through the chronological accumulation over time. Bioeroding is a common ecological process, and the reefs are subjected to such process, therefore once takeing place, it would release metals into the ecosystem again and contribute to the metal budget.

Another source is the sewage being discharged by vessels. An undetermined proportion of cargo vessels using the ports of Aqaba have on-board sewage treatment systems, but none of the Gulf-bordering states employ measures to ensure the effective operation of these systems while ships are in port. On the other hand, vessels with no such systems are discharging their sewage into the gulf's water. This is again a monitoring-related issue by the concerned authorities to ensure zero discharge of vessels sewage into the gulf.

Example on this are the three vessels operated by the Arab Bridge Maritime Company, which is servicing the Aqaba-Nuweiba (in Egypt) ferry route. They have no on-board sewage treatment systems and, hence, untreated sewage generated from the 1.2 million passengers who travel this route annually is dumped directly into the gulf (ABMC, 2001).

The location of the Jordanian coastline to the south of Wadi Araba, makes the area exposed to the desert dust carried by the prevailing northerly winds. This dust might bring copper mineral, which could be considered as a source of metal input. However, it can not be decided weather such source is a major secondary one unless the amount of dust and the its content of copper is determined.

Plate 9. Shows the closeness of the highway to the adjacent coral reef.

Chapter Ten
Future Trend, Discussion and Conclusions

10 Future Trend, Discussion and Conclusions

10.1 Future Trend and the Basis of Prediction

Jordan has made progress over the last decade in creating and enhancing mechanisms for environmental protection in Aqaba region. Several new laws, standards and institutions, both governmental and non-governmental have been established. The present challenge is to assure that they are enforced so as to have the maximum positive effect. On the national level, this challenge is clearly addressed in the 1995's Law of Environmental Protection, (later of the Environmental Law of ASEZA (2002) which explicitly calls for removing administrative overlap and ambiguity in enforcement authority. In addition, cooperation with neighbouring countries in the Gulf of Aqaba in the areas of oil spill response and coral reef protection are critical to Jordan's ability to address these two environmental protection priorities.

The basis of predicting the future trend depends on reviewing and analysing the past and the current situation (development), but however this should be done while considering some of the following features which have significant effect on determining such trend:

- The physiographic features of the Gulf of Aqaba create a unique and diverse ecosystem, but one particularly susceptible to damage from pollution. The major pollutants and pollution threats in the region discussed earlier in the former chapters are marine oil spills and discharges, industrial pollutants, uncontained disposal of used motor oil, municipal and ship based sewage, and solid waste from marine and land based sources. Tourism development activities on the other hand may intensify existing sewage and solid waste pollution concerns and may also heighten the risk of direct physical damage to coral reefs.
- The slow, circular currents of the gulf provide abundant nourishment without endangering coral polyps, and the high dissolved oxygen in the warm waters allow luxuriant coral growth. In the absence of high levels of human activity in the region, it could be safely said that the gulf would remain one of the world's most productive and diverse coral reef ecosystems. But however, all indicators (e.g., UNEP;1997;PERSGA, 2002 and present work) are showing that the coral reefs of Aqaba are increasingly threatened because of anthropogenics entering the gulf and also due to the isolation from other oceanic processes, since the northern section of the Gulf of Aqaba is far from the flushing dynamics of open ocean circulation patterns, which means that pollutants and sediments accumulate rapidly and have nowhere to go.
- The potential hazard to the marine environment of pollutants depends mostly on their concentration and persistence. Persistent pollutants, such as heavy metals, can remain in the environment unchanged for years and may thus pose a threat to man and other organisms, (Howard, and Brown, 1984).

However, the term "Future" which is used in this chapter corresponds to the year 2002 and onward. This is because in that year, Aqaba region was transformed into a special economic zone, which means that most imported merchandise, mainly capital goods, are not subjected to declaration. The purpose was to attract more investments to the region utilizing the geographical location of the city and the existence of marine access. Such investments include of course wide varieties, industrial, tourist and other routine commercial ones.

It should be noted here that the following reading of the future trend is only a descriptive one. Quantifying such prediction will be needing some calculations, statistical analysis, modelling and would include identifying of specific indicator for further assessment and monitoring, the thing which could be a purpose of further researches in the future,

Reviewing of both the human impact on the marine ecosystem during the last 20 years and the potential impacts from recent development (2002-2004) including some of planned projects were the base of identifying the future trend.

10.1.1 Human Impact on the Marine Ecosystem: the Past, the 1980s and Beyond

Human activities in the Gulf of Aqaba used to be minimal until the 1960’s, when Jordan and the other surrounding countries; Egypt, Saudi Arabia and Israel began to develop their ports at the northern Gulf. Although the ports of Aqaba and Eilat in particular became economically significant, they still remain minor ports on a larger scale. Jordan relies on Aqaba as its only outlet to the sea, while Israel imports the majority of its petroleum through Eilat ports.

Development in the Jordanian sector of the Gulf of Aqaba has taken place mainly in the last three decades and more intensively during the last two decades. During this relatively short period, maritime activities have increased substantially. However, the rhythm of development has not been steady. In 1993, the World Bank published a report stating that “ during the last 25 years the nutrient levels, turbidity, and productivity of the seawater have increased”.

The developments included the construction of port and storage facilities, power generation stations, fertilizer production industries, hotels and restaurants. However, approximately 30 percent of Jordan’s coastline is currently occupied by port-related facilities.

In chapter nine, all potential sources of pollution and threats were listed. It is always necessary to remember that these threats have become increasingly more salient in recent years, as there is an exponential growth in the usage of coast for different purposes.

An associated day-to-day basis impact of such exponential development, include small, recurrent leaks from cargo and pleasure boats, land-to-sea transfers, and the discharge of oily ballast water produce more pollution and do more environmental damage overall than one-time events like a large spill.

Industrialization around the Gulf of Aqaba adds significantly to the pollution of the marine environment. The exportation of phosphate from Jordanian industries is a major type of pollution from the port of Aqaba. Approximately one percent of phosphate is lost into the atmosphere during the loading process. The dust settles in the Gulf of Aqaba, increasing the water born phosphate concentration. The increase of phosphate in the sea leads to several possible consequences, the most serious being "phosphate poisoning." Phosphate dust can bring about the death of corals through stress caused by reduced light intensity and increased sediment load .

Industries in the Gulf of Aqaba often use water for cooling and other manufacturing processes. Power generation and fertilizer production are currently the primary sources of heated effluents released into coastal marine water from the city of Aqaba. Several thousand cubic meters of water are released per hour in the form of jets 200 meters off shore and at a depth of 20 meters. A consequence of the discharge into the Gulf is that the water is 3C° higher than that of the surrounding water, which has an average temperature of 23.1C°. Considering that the Gulf of Aqaba marine organisms live within a few degrees of their upper thermal limits, an increase in temperature of about one or a few degrees can have profound affects on these organisms .

Industrial discharges into the gulf also contain suspended particles. Identifying the effects of these contaminants on the marine environment is important; any factor that reduces light penetration, such as a continuous thick film of oil, interrupts the photosynthetic cycle of specific coral reefs, leading to secondary effects, (Literath,1993). Corals need sunlight because they depend for their survival on tiny algae that live in their tissues. The photosynthetic algae provide the polyps with carbon, and benefit in return from nitrates and phosphates produced as waste by the polyps. The lack of sunlight also upsets the relationship between the polyps and their algae. When there is an ample supply of nutrients in the water, the algae no longer depend on their host for these materials. Although the algae proliferate in the host cells, they begin to withhold the products of photosynthesis from the polyp, which starves. Eventually the algae either leave or are expelled by the host (Guzman and Jimenz,1992). Heavy metals also pose a serious threat to the environment in the Gulf of Aqaba.

10.1.2 Potential Impacts from Recent Development

Since the date of transforming Aqaba into special economic zone in 2002, doors were opened for more investments. Nothing was mentioned on the capacity of the region to host such investments. No figures on the numbers or the type of the investment that are allowed to take place in Aqaba.

The following is a briefing of the major investments launched in Aqaba since the transformation into free zone, provides an idea that would help to envisage the future trend. This is the only method which could be used to predict the future, simply by modifying the what so called; “the present is the key to the past” into “the present is the key to the future “.

A) The new Kemira Arab Potash Company KEMAPCO; a joint venture between Jordan and Finland which is considered now as Jordan's largest fertilizers and animal feed production plant. This industry utilizes the phosphate and potash raw material to produce different kinds of fertilizers and other related products. The major environmental concern here is that the plant is using the seawater for cooling. The heated return water is being discharged again into the gulf. Right now, things seem to be controlled; at the discharge area (personal observation and survey).

B) Two new big storage facilities have been constructed along the coast since 2002; the first belongs to the Jordan Bromine Company, and the Second is of the Jordan Magnesia company. Both have been subjected to environmental impact assessment studies, and supposed to be monitored by the concerned authorities.

C) A large lagoon (marina) is being constructed along the south coast within the marine park boundary. The lagoon will be part of a big resort, and this lagoon will serve the leisure boats and other marine-sport activities.

D) A storage facility is also being constructed for glass sand, which is supposed to be exported via Aqaba main port.

E) Finally, the huge and the well-known Red Sea-Dead Sea Conduit project. This project is still being proposed, but all indications reveal that it is right on the way in the coming two years, since all of the concerned parties are negotiating over its feasibility and other related issues, and some preliminary environmental studies are being conducted nowadays (MWI, 2004 and *person. comm.*). However, as this project might be of special interest and consideration from an environmental point of view and also as it provides a milestone for any proposed scenario for the future of the gulf , we provide a brief summary below:

E1. General Background to the Project

The Dead Sea basin is a unique ecosystem to the world. The Dead Sea, a terminal lake, is the lowest place on earth and the saltiest large water body on the planet. Over the last forty years however, the Dead Sea water level has dropped by some 25 meters. The current yearly water level decline is by over one meter in depth, due to both water diversion and industrial activity. The building of a conduit for the purposes of bringing marine waters from the the Gulf of Aqaba/Red Sea to fill the Dead Sea, has been proposed by the governments of Jordan and Israel as the solution to the declining Dead Sea water level.

The Red-Dead Conduit is a water conduit that would convey sufficient water from the Red Sea to the Dead Sea. The conduit represents the only viable measure to mitigate all the negative environmental impacts of the declination of the Dead Sea.

The project is bold and visionary. It needs to be bold in order to solve the enormous Dead Sea situation. It consists of a water conduit (a combination of tunnel arid canal sections) to convey almost 1.8 billion cubic meters per year of sea water some 180 kilometres from the Gulf of Aqaba to the vicinity of the Dead Sea. The project itself would reverse the decline in the Dead Sea and gradually promote an increase in the level back to historic levels, (MWI,2004)

The Conduit implementation unlocks the ability to develop power/desalination projects. The 1.8 cubic billion meters per year of seawater brought from the Red Sea will utilize the 400 - meter elevation difference to generate a renewable source of power This power will be used to operate reverse osmosis units that will transform seawater to fresh water

There will be two enormous products from the fully realized project. A portion of the water (1.00 billion cubic meters per year) will be directed to the Dead Sea. This quantity will be sufficient to reverse the decline of the Dead Sea level and restore it at an ecologically prudent rate.

A great quantity of fresh water: (850million cubic meters per year) will be produced and directed to satisfy the fresh water demands in Jordan, Israel and Palestine. The quantity would be sufficient to meet the region's needs for fresh water for the foreseeable future.

E2. Future Environmental Effects of the Conduit on the Gulf of Aqaba

Although discussing such topic is totally beyond the objectives of the present research, it was necessary while talking about the future trend regarding the environmental conditions in the Gulf of Aqaba to include this project as an example which is expected to affect the gulf's pysiochemical characteristics. However, what is included already under this section is the more related issues to the metal inputs which is ultimately the main concern and scope of the present work.

The extent to which construction and operation of the proposed conduit might affect the gulf depends upon a number of variables, which might include one or more of the following:

- Magnitude and frequency of operation or activity,
- Presence of sensitive habitats and species and their proximity to the site,
- Hydrodynamic conditions (tidal range, depth, tides, currents),
- Sediment characteristics (size, density and quality),
- Background environmental quality (seawater and sediments),
- Seasonal variability,
- Channel size and depth,

- Characteristics of the intertidal area,
- Proximity of the marine feature to the activity.

The large number of variables that need to be considered in determining whether an operation or activity is likely to have an adverse effect on marine environment, means that this judgement will have to be made on an area by area (within the site) basis, and will often be specific to individual habitats.

Prediction of the potential effects that might be caused by the construction works cannot be made with any degree of confidence if these parameters are not known .

However, the main concern of constructing this conduit which might be related to the metal inputs include the following:

- Once operating, the water flow from the gulf will help in facilitating the movement of pollutants when occur offshore specially from the non-point sources like oil spills, or the discharged ballast water, therefore any existing pollution in the gulf will be eventually withdrawn to the shore of Aqaba.
- Dredging and operations may under certain conditions have adverse effects on releasing heavy metals that have already sunk and trapped by sediments.
- Construction and operations in intertidal areas usually associated with changes to hydrodynamic regime and geomorphology which usually have an impact and effects on shoreline wave action, tidal range, tidal currents, suspended sediment load. This will ultimately affect any possible diffusion of pollutants including metal inputs that might enter the coastal area.

The expectations which could be made based on the outcomes of the present work reveal that all the problems associated with heavy metal pollution will increase considerably in the years to come if measures for control and management are not created.

Among all of the literature and reports reviewed, it was clear that many authors were admitting that coral reefs are threatened worldwide by anthropogenic, in particular heavy metals, but it seems that the effects of such pollution on the ecosystem are still not well understood. This however might affect passing and clarifying the relevant message to the decision makers.

10.1.3 The Expected Scenarios

All records of heavy metals have shown that concentrations have been at least doubled at some sites during the last 20 years. Accordingly, the first scenario which comes up is, if the development continues with the same trend and momentum observed in the last 20 years, automatically the magnitude reported here will be doubled. This prediction is considering the physical and chemical characteristics of the Gulf of Aqaba. Being semi-closed system, low rainfall and absence of streams discharging means that any pollutants enter the system will not be flushed away or even diluted. The ultimate route is to sink either in sediments or in coral reefs and in turns taken up by organisms eventually reach the human beings. The other direct consequence is the deterioration of the marine ecosystem including death of corals and the associated marine life which will on long run affect the tourism industry in the region. This in fact summarizes the first scenario.

Second Scenario, is the development (in all different fields; industry, tourism, infrastructure) to continue taking place, and this is the most probable, but along, a raising in awareness, understanding and appreciation of the sensitivity of the ecosystem by decisions makers and public exist. The thing will lead to a sound management and control over such development. This of course include strict enforcement for environmental regulations for example, the standards that controlling discharging of cooling water into the gulf, or that controlling discharging ballast water by large vessels in the regional water. However this definitely will not eliminate the impact totally, but at least assists in minimizing and mitigating the potential impacts.

The third scenario, which is unthinkable to consider by the authorities. This option hypothesizes to halt the ongoing development for the sake of conserving the marine environment allowing and designating the coastal areas only for tourist industry. Many examples worldwide have shown that tourism revenues generated by coral reefs are significant. For example, according to the reports by international concerned agencies, tourists visiting the Florida Keys generate at least US3 billion dollars in annual income, and the Great Barrier Reef well over US1 billion dollars per year (UNEP1998).

10.2 Discussion and Conclusions

The present work represents the first detailed geochemical –heavy metal- survey of the Jordan's Gulf of Aqaba. It provided baseline data on both vertical and lateral variability in metal concentration across the coastline.

10.2.1 Benefit of Using Coral Reef as Environmental Indicator

The coral reef can function as environmental indicators for heavy metal. A comparison with a natural background of the area can then provide the basis for identifying influences of local human activities on coral reefs.

The results obtained here by using coral reef coincide with other conclusions made by many authors who have used other different methods (i.e. sediments, seawater or organisms),with respect to the identification of potential sources of pollution, (Abu-Hilal,1985,1987,1993; Abu-Hilal, and Badran,1990, Wahbeh,1990).

The models established using the data of the present work have also confirmed the usefulness of coral reef in determining the spatial distribution of metal pollution, this of course is benefiting from the original good distribution of reef communities along the Aqaba's coast.

Studying reef cores also has another benefit, since it helps in identifying the historical input of certain pollutants, in turn, this help in establishing a baseline to be used while planning and setting management and landuse plans.

Finally, it is noteworthy here that researchers should focus their efforts in the future to establish specific guidelines for metal content in coral reef, because till now no such guidelines exist.

10.2.2 Metal Pollution in Similar Ecosystems

It was necessary to compare the outputs of the present research with other similar cases, so it becomes easier to understand the magnitude of the impact and the pollution status in Aqaba. Several examples and case studies as well as reports have been reviewed during this research (see List of References). However, a major distinct for the study area is that it is not influenced by rivers or wadi influx. Therefore one can expect that the ecosystem; in case of continental influx, has adapted the existence of such conditions.

Among the reviewed cases, the interesting results of Guzman *et al.*,(1992) is briefly discussed here.

The authors studied the contamination of coral reefs using heavy metals along the Caribbean coast of Central America. Besides sediment samples, coral samples were collected from the top of the colonies where the subsamples of coral skeleton contained at least the last 4 years of skeletal growth, based on growth rates of 5-6mm y^{-1}.

The authors concluded that most of metal levels measured in coral skeletons along the Caribbean were higher than the range observed in corals from Thailand and Hong Kong with which they were compared.

According to the results obtained, the metal concentrations observed along the Caribbean showed no consistent differences among all study reefs. Even the remote reefs are influenced by metal pollution, although at lower levels than the other reefs. This suggests that a wide range of pollution sources; both natural and anthropogenic are probably influencing the entire region.

Several pollution sources have been identified through the research. According to the authors, possible point sources were refineries, oil terminals, power plants, ports and domestic and industrial sewage. Non-point sources include agricultural activities and soil erosion. The concentrations range in the reef samples of Cr, Cu, Zn, Cd, Pb and Ni were; 6.3-32.4, 1,7-19.6, 5.3-26.2, 18.6-40.5, 65.4-141.8 ppm respectively.

The overall conclusion of the authors was; the area is exposed to larger range of metal pollution, natural and anthropogenic as a result of the increasing environmental contamination from sewage discharges, oil spills, the misuse of agricultural chemicals and fertilizers and topsoil erosion.

10.2.3 Verification of Results and Conclusions Obtained Throughout the Present Work:

It was stated earlier that few studies and investigation have been carried out on the environmental quality of the Aqaba coast environment . But however, each was conducted based on different method and/or indicators (see literature review and chapter seven).

With all of these different method-based studies, it was noticed that some of them have common conclusions and results that are very interesting and in agreement with the main outputs of the present work concerning the identification of hot spots (impacted sites) along the coast. The following summarizes briefly these studies where Fig.30 depicts both the outputs of the present work and that of the mentioned previous works.

Badran and Foster,(1998): Through fine temporal resolution monitoring of the ambient water temperature, dissolved oxygen concentration and percent saturation, the inorganic nutrients ammonia, nitrate, nitrite, phosphate and chlorophyll *a* concentrations were generated to assess seawater quality. Four coastal stations were designated for sampling. According to their results, the area of the main port and the industrial area both show significant positive modification with respect to the measures parameters.

In the present work, the area of the main port has shown significant enrichment with respect to the metal content which has been identified as highly impacted area (Fig. 27 and 28).

Abu-Hilal,(1987) has studied the distribution of trace elements in nearshore sediments along six sampling stations. He concluded that the area opposite to the old sewage plant is highly impacted. Concentrations of Cd, Co, Cu and Pb recorded at that site were higher (3-9times) than the other stations. The significant correlation between these trace elements and the organic carbon suggests that such high content of metal is most probably attributed to the discharge of untreated swage effluent from the treatment plant into the Gulf's water in that area.

Comparing this conclusion with the present work, it is totally in agreement when compared with samples taken from around the old sewage plant. For example, Cd, Pb and Zn recorded to have concentration of 0.78,6.2 and 8.9 µg g-1 respectively.

The same conclusion was also made by Wahbeh,(1990), who investigated the concentrations of Zn, Mn, Cu, and Cd in soft body tissues of some Intertidal molluscs in Aqaba. The results indicated that species collected from the intertidal area opposite to the old sewage plant have higher concentration than other sites. He attributed this to the discharge of untreated water into the sea.

Abu-Naseer, (2004) in a qualitative study to detect pollution and damage of the coral reef by using remote sensing technique as a tool has concluded that the reef south of the Marine Science Station (MSS) suffer from changes in its area and spectral characteristics in last decade (from 1990 to 2000). He attributed such deterioration in coral health to the pollution hypothesis. However, this conclusion coincides partly with the conclusions made out of this present work. The area south of MSS, described by Abu-Naseer as being suffering deterioration is geographically part of the marine park in Aqaba. According to the present work, this area was considered as less impacted compared with the other parts of the coast.

Noteworthy is to mention that the conclusion of Abu-Naseer explains not only the deterioration of coral reef that result from pollution but also -as understood from the method he has used- the physical damage that is common by boat anchoring and break down of reefs by tourists.

10.2.4 Discussion and Conclusion on the Metal Concentrations along the Coast

The concentration of metals observed showed consistent differences among all study sites. Even what could be described as pristine reefs were influenced by metal pollution. This suggests that wide range of pollution sources (natural and anthropogenic) and probably sometimes an effective mechanism for distributing metals southward are influencing the entire area.

All records have shown that there are significant fluctuations when moving southward with general increasing trend in concentrations, this is due to the fact that the coast is not well-segmented in terms of land use system. For example the main port is located between the protected areas of the marine park and the marine reserve and the north recreational beach. South of these protected area, the oil port and the industrial area are located. This is attributed mainly to the fact that the main port was constructed prior to getting the extra 12 km from Saudi Arabia in 1966 through a land-exchange agreement between the two states. Before this agreement, the whole coast of Aqaba was only for about 15km in length.

Studying the distribution of all metals in the collected samples have shown that the offshore and deeper samples have in general lower concentrations of metals. This indicates that the closer sites are being more impacted by the metal discharge as well as indicating that pollutants had not the chance to move further as the gulf is characterized by low tide and weak currents. The exception was in few offshore samples which showed some relatively high and unexpected concentrations of metals. This is in principle attributed to non-point sources including oil spills and the discharge of ballast water by vessels navigating the gulf.

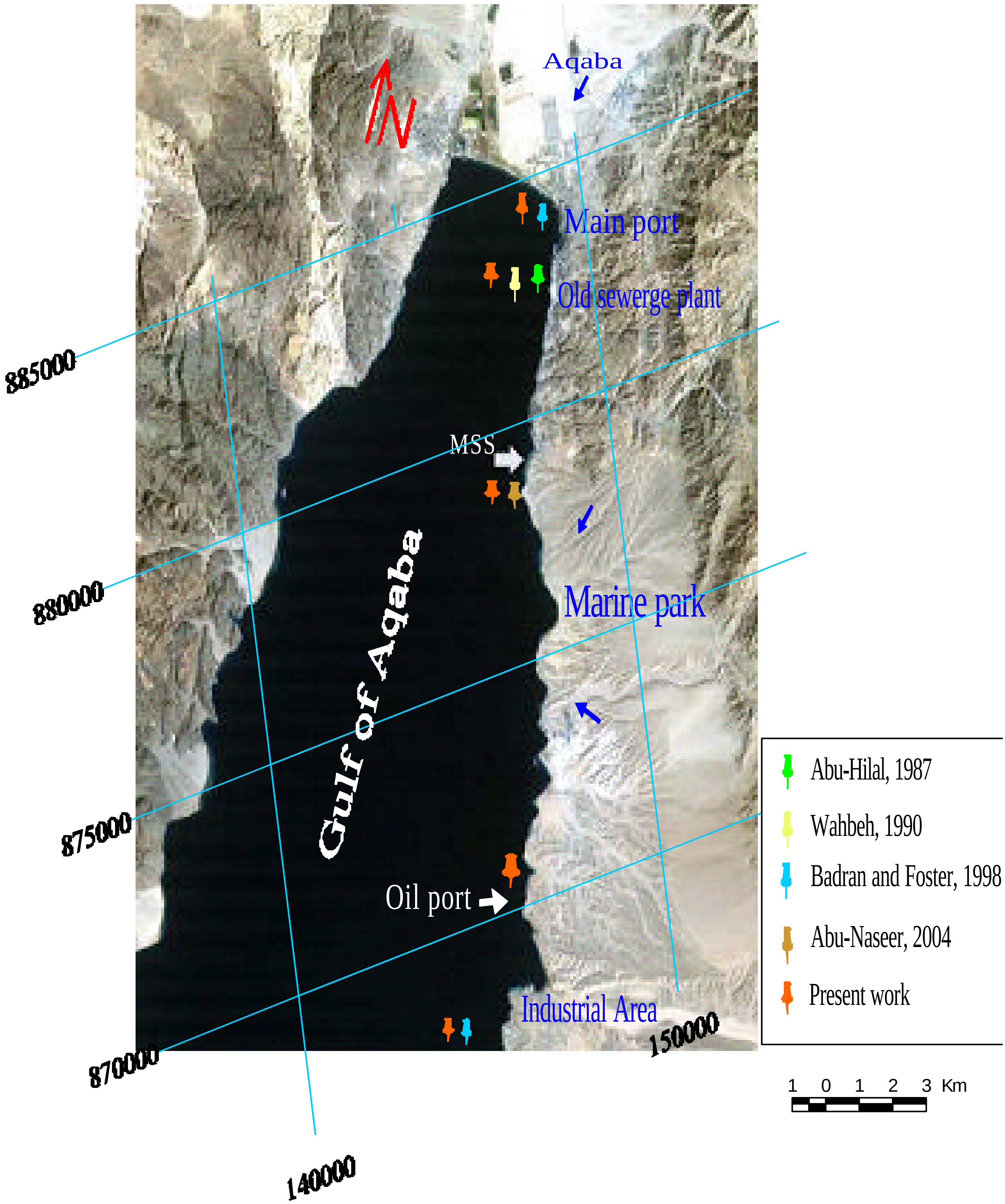


Fig. 30.Landsat Image showing the Jordanian coastline and the main hot spots (highly impacted) sites identified by the present work and other several authors.

Furthermore, investigations of the correlation between heavy metals recorded in this work revealed the presence of strong and significant relationships between several pairs of trace elements in the gulf. All metals were positively correlated to each other, indicating that the appearance of local high concentration for one metal by possible contamination correlates with high values for other metals. Such relationship might reflect similar sources and/or similar biogeochemical behaviors (Saad and Kandeel,1988).

The presence of metal enrichment in some samples taken from sites assumed to be protected and not exposed to human activities, reflect the fact that not only the closeness to the industrial and other main facilities (i.e. ports, marina, etc.,), determines the sample metal concentration but also the daily human routine activities might also contribute to the metal enrichment such as boating, skiing, littering and driving close to the shoreline. Such minor sources could be sorted among the other non-point sources.

As for the high metal content observed in the area of the oil port, the positive and strong correlation among these metals, suggests obviously that they were introduced by mainly, one common source. The port is mainly used for crude oil (and some other derivatives products) loading and unloading. Therefore, this high concentration of metals is attributed to either spills or leakages during loading and unloading processes. This calls for more strict controlling and patrolling on the operations at this site.

In contrary to what could be expected, the results of metal content recorded at the north beach, have confirmed a status of relatively intermediate impact, but, however, there is still a need to explain some relative high content of metals recorded in some samples. Reviewing and researching all activities usually taking place at that area have raised the following:

- The beaches and near-shore reef and sea grass areas of Jordan's Gulf of Aqaba ,in particular that of the north beach are heavily polluted by discarded plastic and other refuse material. This is, in principle due to the fact that most of the area is accessible by foot, so it receives thousands of local and national tourists specially in weekends and national holidays and –due to lack of awareness- much solid wastes are being dumped close to the beach and eventually carried by winds and tides into the gulf.
- As part of the extensive development in the whole area of Aqaba, construction of new hotels and tourist facilities close to the north beach area has increased over the last 10-15 years. The inappropriate disposing of both solid and liquid wastes from these constructions has, undoubtedly contributed to metal enrichment in this site. Constructions and generated solid and liquid wastes have been confirmed to be among metal sources (Leal *et al.*,1997, Gunzman, *et al.*,1992).
- The area of the north beach is the closest to the city center and to the recreational facilities in the town of Aqaba and Eilat. The hotels of Aqaba which are located mainly along the north beach are connected to the main sewer system which does not drain into the sea. However, the possibility of uncontrolled sewage discharge from either Eilat or Aqaba reaching the sea could not be ruled out.
- Prior1986, treated waste water was being discharged into the gulf through the north beach area, therefore the building and growth of some reefs was associated with this discharge, this explains, at least some of the enrichment found in this area.
- Although not much is available on the environmental conditions at the existing nearby Israeli in-sea fish farms, some reports have confirmed eutrophication due to excess of nutrients usually added to the seawater through fish-feed (MoI,2001). Such pollutants are drove to the Aqaba coast by the prevailing north winds, and the whole

issue is being negotiated by the local authorities in Aqaba and Eilat. The possibility for some metals to travel along, much probably exists.

- The seaside opposite to the north beach is used during rush-time at the main port as a waiting zone for vessels usually waiting to load/unload the cargo. These vessels, in the of absence of any control would discharge or dump their wastes.
- Another comment concerning the north beach area, is the very low recorded concentration of lead. The interpretation beyond this, is that bedsides that there are no industries there, the area is not accessible by vehicles and the shoreline is located at least 200m from the main roads and hence the possibility of being impacted by traffic exhausts is limited.

10.2.5 Discussion and Conclusions on the Reef Cores

Concerning the metal content and distribution in the three studied cores, A,B, and C at the industrial area, the following can be pointed out:

- It was easily noticed, that all metals in the three cores share one clear increasing trend towards the surface, where significant enrichment during the period of 1980-2000, more markedly in the last 5-7 years has taken place. This is supported by high (and relatively high) positive correlations among most of these metals (Table 14). This eventually indicates that the overall activities usually take place at the industrial zone, including shipping, oil porting and manufacturing which are all contributing to this enrichment and should be continuously monitored and controlled.
- The available records have shown that there two major oil spills have occurred. The first in 1995, but no details are available, and the second in 1998, where 20 tones of oil were released into the gulf opposite to the industrial area, (APO,2002). Therefore, and since high concentrations coincide with the period of the importantly increase of metal content (1993-2000) when these events occurred, this suggests that at least part of this enrichment is due to these two major spills.
- Studying the whole profile of metals in Core C of the oil port, common distinct peaks were observed for Pb, Cu, Zn, and Cr in layers representing the period of 1984-1989. These relative high values are much probably attributed to the heavy use of the port for the export of Iraqi oil during the first Gulf War (APC, 2002).
- Metal peaks observed in the bottom layers of the three cores correlate with years of high and upnormal precipitation (Fig.29) which resulted in increased sediment transport into the sea, but comparing such high values with the other reference values (offshore or literature), suggests that there might be a pronounceable enrichment which has been taking place even before 1980's, the year corresponding to the core bottom.
- The overall conclusion on the metal distribution in core samples and hence the status of pollution in the industrial area can be made based on the EF calculated for these cores (Table18). Since EF for Cd, Pb and Zn is >1, the area is considered as intermediately polluted with respect to these metals and highly polluted by Ni and Cr where EF for both is >3. Among the whole group; Pb is the less enriched, Cr is the highest enriched. This conclusion is made clear in Fig. 22.

However, the direct reasons and interpretation for such high content of metal can be easily interpreted, as the area is occupied by several industries where several and different varieties of raw materials are being used and transported to this area, and on the other hand some other products are being exported via this area, which means that the area is heavily navigated by large vessels. In addition, all facilities in this are continuously being subjected to development and expansion.

10.2.6 Conclusion on the Metal Sources

There was an attempt to identify the potential sources (both; point and no-point) that contribute to the enrichment of metals in the gulf ecosystem. However, in general, point-sources can be identified and some actions can be taken to manage the problem, but as for that of non-point sources, more research and continuous monitoring should be carried out along with enforcing the existing regulations, as well as to work on conservative principle rather than reacting on certain event. The following represent some main points and conclusions on the metal sources identified earlier:

- The issue of vessels sewage is usually raised while talking about pollution sources. Considerable amounts of sewage are, however, being discharged into the gulf seawater from cargo vessels, tour boats, ferries and private yachts. This is in addition to the vessels operated by the Arab Bridge Maritime Company, servicing the Aqaba-Nuweiba ferry route, which have no on-board sewage treatment systems. Untreated sewage generated from the 1.2 million passengers who travel this route annually is dumped directly into the gulf. This issue to be immediately considered and controlled by the concerned authorities.
- The other issue of concern is the unpredictable amount of pollution caused by the discharging of ballast water into the regional water of Jordan. Ballast water is defined as water used to maintain stability during transit along coasts and on the open ocean, and is taken from coastal port areas and transported with the ship to the next port of call where the water may be discharged or exchanged. Such type of waste water is almost oily and rich in pollutants, in particular heavy metals. Two main sub-issues are related to this; first is the absence of reception facility for such type of water at the port, and the second is the regulations controlling such process of the discharge and the exchange of this type of water.
- Oil spills on the other hand is one of the main sources of pollution in the Gulf of Aqaba. Oil is known to be the most important cargo poses a catastrophic threat to reefs. Several concerns can be pointed out here:
  - A large oil spill would decimate the reefs by blocking sunlight and disabling the symbiotic relationship between the photo-synthetic algae and the coral. Oil also impedes reproduction, growth and regeneration of corals (Salvat,1987).
  - Although most of oil and toxic pollution spills usually occur around port areas and decrease with distance from there, their effects are spreading nonetheless.
  - The seasonal tidal changes in Aqaba are an important consideration in determining oil spill distribution and sensitivity and calculating spill risk. In addition, low summer tides have significance with respect to the thermal stress in intertidal/shallow water corals (Hulnigs,1989).
- Large amounts of fertilizers are shipped from the Aqaba Port facility, posing threats of large spills or series of minor accidents. Although there have been no major spills to date, approximately 0.1% of phosphate dust coming through the port blows away as dust into the immediate marine environment during loading and shipping, (PERSGA, 2001).Between 1978 and 1985 phosphate pollution increased by a factor of ten (UNEP, 1999). This pollution has caused a gradual deterioration in water quality in the vicinity of the Port that could worsen as phosphate exports increase. The major

concern related directly to the present work is the metal content in this phosphate, which will continue to reach the marine ecosystem as long as the dust of the phosphate raw material (and fertilizers) still exists.

- Regarding the lead exhausted by vehicles, several authors (*inter alia* Smith,1976 in Facchinelli *et al.*,2001) have demonstrated that Pb derived from car exhausts does not extend appreciably beyond 30m from the road. This is actually in agreement of the earlier conclusion on the high content of lead in some samples of the marine park area which was attributed to such exhausts. In Aqaba, people used to drive very close to the beach, just few meters from the land-water mark, and this has lasted for many years until the marine park authority has prohibited and blocked any access to the 50m-zone from the water mark, only three years ago. The fringing reef type of Aqaba is distributed widely in shallow waters close to the beach (Plate 9), therefore any pollutants will have very short rout before sinking into the gulf.

  Furthermore, lead aerosols and industrial fames can be carried over longer distance, where they ultimately sink into the seawater (Facchinelli *et al.*,2001). This is applicable also in the present case of industries in Aqaba, but however such mechanism for lead transport if exists would affect the nearby sites further south, since the prevailing wind in Aqaba comes from north. This of course does not imply by any mean to neglect such source. The gulf is eventually one ecological unit, and any impact at one site will automatically affect the others.

- The early conclusion made regarding the area of the main port and the pollution status was also in agreement with the results of (Badran and Foster, 1998). The authors have recorded high concentration of NO-3, NH+4 at different sites of the main port. They have attributed these high values to accidental spillage from ships and geographic isolation due to the design and orientation of the harbor jetty. The jetty is a solid concrete pavement that isolates the water behind it over the entire depth (~10m) from the open water body. It is about 200m long and projects from south to north. Currents along the Jordanian coast move mainly against the jetty projection, from north to south (Hulings,1979 in Badran, 1998) forming the area into a trap. The capture and the subsequent decomposition of trapped material were the most likely reason for the elevated values. Tidal flushing counter balances the current action and helps prevent complete water stagnation.

- The accelerated economic growth in Aqaba consequently promoted demographic expansion in which the population increased from 45000 in 1980 to 85000 by the year 2002 (ASEZA,2002). Part of the increasing metal concentration could be attributed to the increments in population, in which such increasing is met with expansion of the infrastructures and consequently in raw domestic wastes that were used to be discharged (after primary treatment) directly to the sea

10.2.7 Contamination (Enrichment) of Specific Heavy Metals:

Although, all metals recorded along the coast have shown both significant and relative enrichment over the background, no signs that specific metal was enriched over another (or over the whole set) was observed.

However, some general notices and comments can be made while considering the general distribution (trend) of all metals along the coast.

Both Cd and Cu have shown relatively more prominence in their increasing towards the south than the others, (Fig.30). The trend starts relatively low at the northmost of the coast, and increase at the main port area, Where it goes down at around the marine park before it continues its sharp increase southward.

In core samples it was a bit difficult to figure out enrichment of specific metal over another. In core A all metal profiles were very similar and the enrichment rates along the core as well.

The only fact that can be noticed in that same regard is the mean concentrations of Cd and Pb in this core when compared with other cores. Both were almost doubled, therefore the core could be considered relatively enriched specifically with respect to Cd and Pb.

Core B and C show somewhat a slight difference, where Pb and Cu can be considered less enriched in these cores compared with the other metals, indicated from the relative low EF along the core axis, and when compared with their mean concentrations in core A.

10.2.8 Overall Conclusion:

Considering together all results of the present work, the following are pointed out:

- Comparing the concentrations found here with those reported in the literature, it is concluded, on the whole, that most of the samples examined were higher than the range observed of metals in many other places, e.g.; Cu, Zn in Thailand, (Brown et al.,1987); Cu, Zn, Ni, Cd in the Red Sea (Hanna et al.,1990) and Cd, Pb in Hong Kong (Scott,1990), they are also relatively higher than those compiled by most workers in the Mediterranean Sea and are relatively higher than the typical open ocean water (Hamza, and Amierh,1992; Shriadah, and Emara,1999; Emara, and Shriadah,1991; Leal et al.,1997).
- The dramatic increases in heavy metals are related to anthropogenic resources. The measured metal concentrations are many times higher than what natural fluxes would apply to the various environments. This is very clear in this work as there is no considerable and continuous natural influx due to the absence of rivers and the low rainfall in the study area.
- Noteworthy is that, even in areas that contain several pollution sources i.e. industries, refineries or power plants and expected to be described as heavily polluted, some literature found that some of these areas have relatively moderate and not severe pollution. Researchers have attributed this to the high assimilation capacity of the coral reef ecosystem and marine systems in general, (Lough and Barnes,1990). Although corals as they are well known to be very fragile and delicate for the external disturbance, but still they do have high capability to adapt such big changes in the surrounding environment. This of course does not imply/justify ignoring the long term changes, and to go ahead towards the non-sustainable development.

The sources of pollution were generally identified and discussed in chapter nine. It is worthy to note here that each of these sources above should be investigated in details as to get details on their actual contribution(in terms of quality and quantity) to the metal budget in the ecosystem. This is in turn would be of great help to enhance the decision making on land use planning and management aspects.

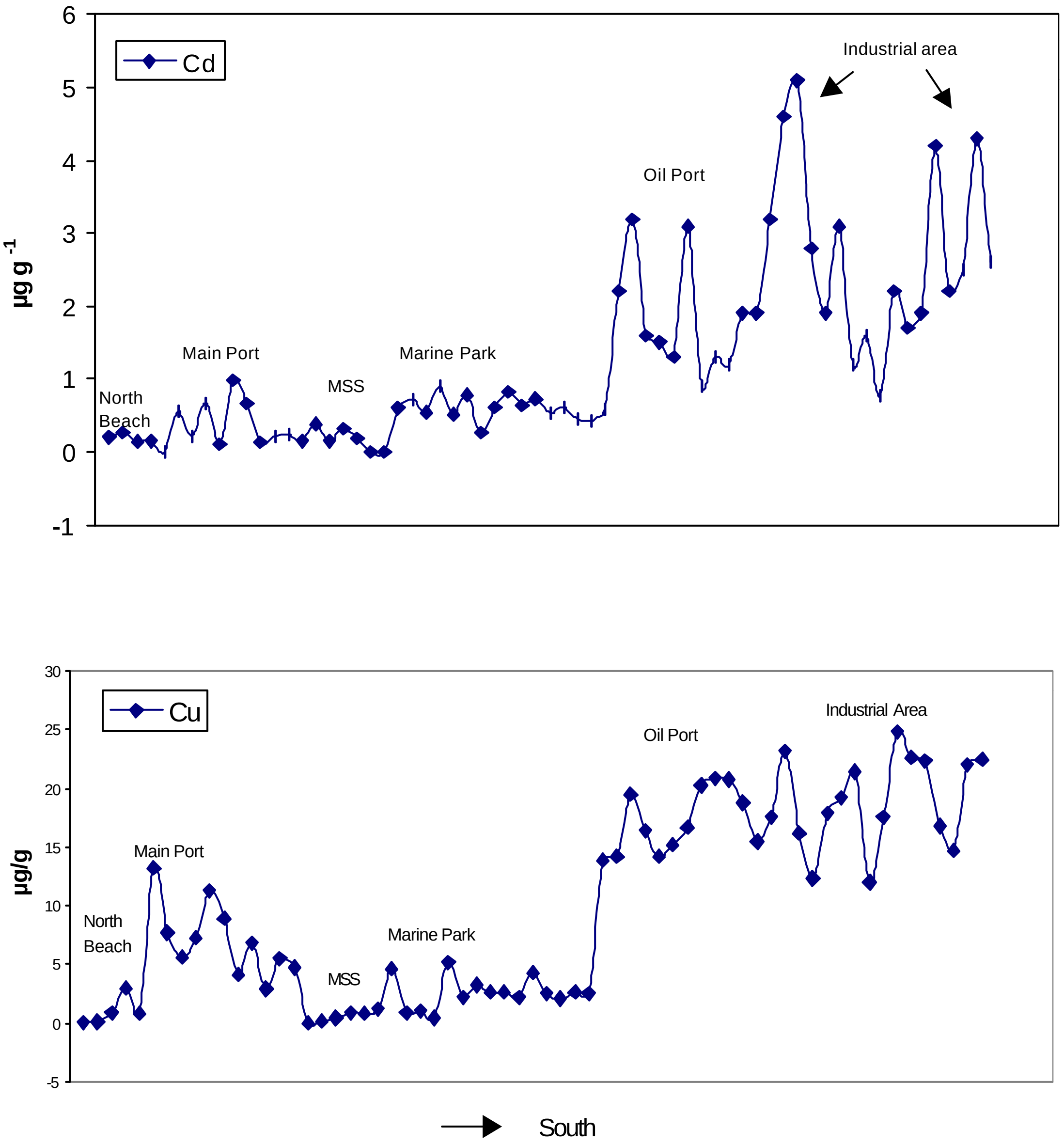


Fig.31.The general increasing trend of Cd and Cu along the coastline.

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Appendix 1. Metal concentration in coral reef grouped by samples (in µg g^{-1}).

Sample No.*	X	Y	**Cd**	**Pb**	**Cu**	**Zn**	**Ni**	**Cr**
NB1	148900	882000	0,2	0,08	0,06	1,1	0,4	0
NB2	149000	881350	0,27	0,5	0,1	0,71	0,65	0,9
NB3	149000	881475	0,14	0,11	0,9	0,65	1,1	0
NB4	149000	879050	0,15	0	3	0,81	0,38	0
NB5	149150	877025	0	0,4	0,8	0,64	0,45	1,1
MP1	148020	877500	0,56	1,1	13,2	18	1,2	13,7
MP2	148050	877235	0,22	11,2	7,7	18	2,3	8,9
MP3	148000	877000	0,67	5,3	5,6	16	1,7	14,2
MP4	147935	877615	0,11	10,2	7,2	17	1,9	4,2
MP5	147900	878050	0,98	7,5	11,3	22	2,2	13,5
MP6	147900	878200	0,67	8,2	8,9	9	2,8	11,8
MP7	147755	877500	0,12	3,2	4,1	12,2	1,5	3,8
MP8	147750	877235	0,22	3,2	6,8	12,1	2,2	6,1
MP9	147685	877000	0,24	5,4	2,9	11	1,4	4,7
MP10	147645	877615	0,15	3,6	5,5	12,4	2,2	3,9
MP11	147630	878050	0,38	2,9	4,7	11,1	3,1	5,1
MSS1	147435	874800	0,15	0,1	0	0,58	0,9	0,6
MSS2	147470	874800	0,31	0,35	0,17	0,55	0,6	0,6
MSS3	147430	874750	0,19	0	0,4	0,48	0,2	0
MSS4	147525	874350	0	0	0,9	0,5	0,25	0,6
MSS5	147525	874895	0	0,48	0,8	0,58	0,48	0
MPK1	146500	870500	0,6	0	1,2	0,97	0,2	1,8
MPK2	146440	870500	0,72	0,46	4,6	0,64	0,62	2,2
MPK3	146500	870585	0,54	3,1	0,88	3,7	0,77	0,4
MPK4	146500	870320	0,9	0,62	1	0,25	0,86	0,6
MPK5	146480	870050	0,52	4,2	0,4	0,82	0,92	0,86
MPK6	145850	865650	1,6	5,9	19,5	13,5	5,4	20,1
MPK7	146000	864510	1,5	3,8	16,4	21,2	3,7	21,8
MPK8	146200	864700	1,3	5,8	14,2	21,4	3,8	15,6
MPK9	146535	868820	0,78	6,2	5,2	5,4	0	4,2
OP1	146715	866200	0,26	0,3	2,2	11	0	7,1
OP2	146800	866520	0,62	0,9	3,2	18,6	0	12,3
OP3	146815	866220	0,82	6,3	2,6	12,3	1,9	18,2
OP4	146800	866165	0,64	3,5	2,6	14,4	2,1	28,2
OP5	146815	865820	0,73	6,6	2,2	16	1,5	11,9

Appendix 1. *cont*.

OP1a	146435	866200	0,53	3,5	4,3	10,2	0,2	5,6
OP2a	146435	866520	0,62	2,5	2,5	5,9	0	4,2
OP3a	146450	866220	0,45	3,8	2,1	8,9	1,2	8,4
OP4a	146445	866165	0,42	6,2	2,6	12,5	1,1	3,3
OP5a	146450	865820	0,58	4,5	2,5	8,4	1,1	6,4
IC1	144850	864950	2,2	6,2	13,9	21,1	6,2	22,3
IC2	144850	864870	3,2	5,2	14,2	19,9	5,1	24,1
IC3	145000	864950	3,1	2,4	15,2	11,8	3,8	18,6
IC4	146100	870500	0,9	2,3	16,7	18,1	3,7	14,4
IC5	144845	865000	1,3	3,8	20,3	18,2	3,9	14,8
IC6	144845	864850	1,2	7,2	20,9	8,8	3,9	14,7
IC7	144845	862825	1,9	5,8	20,8	11,2	4,8	14,5
IC8	144845	864415	1,9	11,1	18,8	21,3	4,7	19,6
IC9	144845	864570	3,2	5,7	15,5	14,4	3,2	15,4
IC10	145150	865115	4,6	5,8	17,6	17,5	2,1	21,2
IC11	145150	870170	5,1	5,9	23,2	18,5	4,8	15,5
IZ1	146000	864950	2,8	3,7	16,2	16,2	3,5	18,1
IZ2	146000	864870	1,9	8,4	12,3	16,8	4,3	23,3
IZ3	146000	865650	3,1	2,8	17,9	9,8	3,5	22,7
IZ4	146150	864510	1,2	6,6	19,2	19,4	2,8	19,8
IZ5	146050	864700	1,6	6,8	21,4	18,7	1,9	11,9
IZ6	146220	864950	0,76	6,6	12	8,5	4	11,2
IZ7	147000	870500	2,2	5,2	17,6	20,1	3,6	10,2
IZ8	145050	865000	1,7	4,8	24,9	18,4	4,1	13,7
IZ9	145050	864850	1,9	6,2	22,6	5,3	4,2	12,5
IZ10	145100	856825	4,2	4,3	22,4	9,3	4,9	11,3
IZ11	145775	864415	2,2	9,6	16,8	17,5	2,8	14,6
IZ12	145215	864570	2,5	5,1	14,7	12,2	1,9	14,5
IZ13	145370	865115	4,3	8,5	22,1	16	3,1	19,5
IZ14	146600	870170	2,6	5,3	22,5	21,1	4,8	18,7

*NB= north beach, MP= main port, MSS= Marine science station, MPK=marine park, OP= oil port, IC= area between oil port and industrial area, and IZ=industrial area. X-values in blue refer to deeper samples ~>11m.

Appendix 2. Descriptive statistics calculated by sampling site (basic unit µg g^{-1}).

Site	Cd	Pb	Cu	Zn	Ni	Cr
North beach						
Mean	0,152	0,218	0,972	0,782	0,596	0,4
Standard Deviation	0,099	0,218	1,197	0,190	0,301	0,552
Range	0,27	0,5	2,94	0,46	0,72	1,1
Minimum	0,01	0,01	0,06	0,64	0,38	0,01
Maximum	0,28	0,51	3,0	1,1	1,1	1,11
Main port						
Mean	0,392	5,616	7,088	14,43	2,045	8,177
Standard Deviation	0,283	3,237	3,093	3,984	0,582	4,334
Range	0,87	10,1	10,3	13,0	1,9	10,4
Minimum	0,11	1,1	2,9	9,0	1,2	3,8
Maximum	0,98	11,2	13,2	22	3,1	14,2
Marine Science Station						
Mean	0,13	0,186	0,454	0,538	0,486	0,36
Standard Deviation	0,132	0,217	0,389	0,046	0,283	0,328
Range	0,11	0,43	0,8	0,1	0,7	0,5
Minimum	0,20	0,05	0,1	0,48	0,2	0,1
Maximum	0,31	0,48	0,9	0,58	0,9	0,6
Marine park						
Mean	0,676	2,43	2,213	1,963	0,561	1,676
Standard Deviation	0,1493	2,484	2,106	2,088	0,376	1,422
Range	0,38	6,2	4,8	5,15	0,89	3,8
Minimum	0,52	0,01	0,4	0,25	0,03	0,4
Maximum	0,9	6,21	5,2	5,4	0,92	4,2

Appendix 2. cont.

Site	Cd	Pb	Cu	Zn	Ni	Cr
Oil port						
Mean	0,567	3,81	2,68	11,82	0,91	10,56
Standard Deviation	0,160	2,182	0,647	3,791	0,808	7,645
Range	0,56	6,3	2,2	12,7	2,1	24,9
Minimum	0,26	0,3	2,1	5,9	0,01	3,3
Maximum	0,82	6,6	4,3	18,6	2,11	28,2
Industrial area						
Mean	2,35	5,99	18,75	14,95	3,52	15,85
Standard Deviation	1,01	1,92	4,06	4,98	0,946	4,41
Range	3,54	6,8	12,9	15,8	3	13,1
Minimum	0,76	2,8	12	5,3	1,9	10,2
Maximum	4,3	9,6	24,9	21,1	4,9	23,3

Appendix 3. Showing descriptive statistics of the six measured metals along the whole coast (basic unit µg g^{-1}).

	Cd	Pb	Cu	Zn	Ni	Cr
Mean	1,252	4,266	9,767	11,408	2,290	10,522
Standard Deviation	1,236	2,957	8,104	7,1376	1,667	7,787
Range	5,0	11,2	24,9	21,75	6,1	28,2
Minimum	0,1	0,08	0,06	0,25	0,1	0,4
Maximum	5,1	11,28	24,96	22	6,2	28,2

Appendix 4. Descriptive statistics calculated for core samples.

	Cd	**Pb**	**Cu**	**Zn**	**Ni**	**Cr**
Core A						
Mean	1,92	6,05	9,67	4,20	2,07	10,90
Standard Deviation	0,963	2,583	6,056	4,399	1,203	5,077
Range	3,13	8,67	21,47	17,21	3,88	15,96
Minimum	0,68	2,94	0,98	0,39	0,34	2,94
Maximum	3,81	11,61	22,45	17,6	4,22	18,9
Core B						
Mean	0,7985	3,495	3,41	8,235	2,71	8,17
Standard Deviation	0,368	1,576	1,321	3,677	1,015	3,707
Range	1,43	5,7	6,3	10,3	3,9	14,4
Minimum	0,19	0,9	1,9	2,2	1,3	2,9
Maximum	1,62	6,6	8,2	12,5	5,2	17,3
Core C						
Mean	0,8125	3,55	3,21	8,25	2,30	7,145
Standard Deviation	0,476	1,984	1,354	4,680	0,846	3,374
Range	2,11	6,8	5,4	16,1	3,1	10,4
Minimum	0,23	0,8	1,1	1,3	1,2	2,9
Maximum	2,34	7,6	6,5	17,4	4,3	13,3

Appendix 5. Standardized data used in PCA (transformation of data was made by subtracting each value from mean and dividing it by the standard deviation).

Sample No	Cd	Pb	Cu	Zn	Ni	Cr
NB1	-0,851227084	-1,41537679	-1,19780887	-1,44430718	-1,13391371	-1,35119947
NB2	-0,794619612	-1,27337096	-1,19287345	-1,4989472	-0,983961744	-1,2356296
NB3	-0,899747774	-1,40523352	-1,09416493	-1,50735336	-0,714048202	-1,35119947
NB4	-0,891660992	-1,44242552	-0,835055072	-1,48493694	-1,14590987	-1,35119947
NB5	-1,01296272	-1,30718187	-1,10650349	-1,50875439	-1,10392332	-1,2099474
MP1	-0,560102942	-1,07050549	0,423478521	0,923427176	-0,654067415	0,408030789
MP2	-0,83505352	2,34439662	-0,255142534	0,923427176	0,00572124432	-0,208341856
MP3	-0,471148344	0,349552813	-0,514252392	0,643221927	-0,354163479	0,472236273
MP4	-0,924008119	2,0062875	-0,316835358	0,783324552	-0,234201904	-0,811873405
MP5	-0,220458111	1,09339288	0,189045793	1,48383767	-0,0542595429	0,382348595
MP6	-0,471148344	1,33006926	-0,107079759	-0,337496446	0,30562518	0,16404995
MP7	-0,915921338	-0,360476338	-0,699330861	0,110831953	-0,474125053	-0,863237792
MP8	-0,83505352	-0,360476338	-0,366189616	0,0968216908	-0,0542595429	-0,567892566
MP9	-0,818879957	0,383363725	-0,847393637	-0,0572911964	-0,53410584	-0,747667921
MP10	-0,891660992	-0,22523269	-0,526590956	0,138852478	-0,0542595429	-0,850396695
MP11	-0,705665013	-0,461909074	-0,625299474	-0,0432809339	0,485567542	-0,696303534
MSS1	-0,891660992	-1,40861461	-1,20521201	-1,51716055	-0,834009776	-1,27415289
MSS2	-0,762272485	-1,32408733	-1,18423645	-1,52136362	-1,01395214	-1,27415289
MSS3	-0,859313866	-1,44242552	-1,15585775	-1,53117081	-1,25387529	-1,35119947
MSS4	-1,01296272	-1,44242552	-1,09416493	-1,52836876	-1,22388489	-1,27415289
MSS5	-1,01296272	-1,28013314	-1,10650349	-1,51716055	-1,08592908	-1,35119947
MPK1	-0,527755816	-1,44242552	-1,05714924	-1,46252052	-1,25387529	-1,12005973
MPK2	-0,430714435	-1,28689533	-0,637638038	-1,50875439	-1,00195598	-1,06869534
MPK3	-0,576276506	-0,39428725	-1,09663264	-1,08004036	-0,9119848	-1,29983508
MPK4	-0,285152364	-1,23279787	-1,08182637	-1,56339441	-0,858002091	-1,27415289
MPK5	-0,592450069	-0,0223672187	-1,15585775	-1,48353592	-0,822013619	-1,24076604
MPK6	-0,382193745	0,65385102	-0,56360665	-0,841865894	-1,37383686	-0,811873405
MPK7	1,57480743	0,48479646	0,707265508	0,419057727	0,545548329	0,626329434
MPK8	2,70695687	0,518607372	0,966375365	0,853375864	-0,11424033	1,37111305
MPK9	3,11129595	0,552418284	1,65733498	0,993478489	1,50524092	0,639170531
OP1	-0,802706394	-1,34099278	-0,93376359	-0,0572911964	-1,37383686	-0,439481598
OP2	-0,511582252	-1,13812731	-0,810377943	1,00748875	-1,37383686	0,228255434
OP3	-0,349846618	0,687661932	-0,884409331	0,124842216	-0,234201904	0,985880144
OP4	-0,495408689	-0,259043602	-0,884409331	0,419057727	-0,11424033	2,26998982
OP5	-0,422627653	0,789094668	-0,93376359	0,643221927	-0,474125053	0,176891047

Appendix 5. *cont*.

OP1a	-0,584363287	-0,259043602	-0,674653732	-0,169373296	-1,25387529	-0,63209805
OP2a	-0,511582252	-0,597152722	-0,896747896	-0,771814582	-1,37383686	-0,811873405
OP3a	-0,649057541	-0,157610866	-0,946102154	-0,351506708	-0,654067415	-0,27254734
OP4a	-0,673317886	0,65385102	-0,884409331	0,152862741	-0,714048202	-0,927443276
OP5a	-0,543929379	0,0790655172	-0,896747896	-0,42155802	-0,714048202	-0,529369276
IC1	0,766129258	0,65385102	0,509848473	1,35774531	2,34497194	1,51236511
IC2	1,57480743	0,315741901	0,546864167	1,18962216	1,68518329	1,74350485
IC3	0,280922355	0,552418284	1,20080809	0,292965365	1,86512565	1,22986098
IC4	0,200054538	-0,157610866	0,818312589	1,37175558	0,845452265	1,44815963
IC5	0,0383189041	0,518607372	0,546864167	1,3997761	0,905433052	0,652011628
IC6	1,49393961	-0,630963634	0,670249814	0,0547909034	0,905433052	1,03724453
IC7	-0,285152364	-0,664774546	0,855328283	0,937437439	0,845452265	0,497918466
IC8	0,0383189041	-0,157610866	1,29951661	0,951447701	0,965413839	0,549282853
IC9	-0,042548913	0,99196014	1,373548	-0,365516971	0,965413839	0,536441757
IC10	0,523525807	0,518607372	1,36120943	-0,0292706714	1,50524092	0,510759563
IC11	0,523525807	2,31058571	1,11443814	1,38576584	1,44526014	1,1656555
IZ1	1,25133616	-0,191421778	0,79363546	0,671242452	0,725490691	0,973039047
IZ2	0,523525807	1,39769108	0,312431439	0,755304027	1,20533699	1,64077608
IZ3	1,49393961	-0,495719986	1,00339106	-0,225414346	0,725490691	1,5637295
IZ4	-0,042548913	0,789094668	1,1637924	1,11957085	0,30562518	1,19133769
IZ5	0,280922355	0,856716492	1,43524082	1,02149901	-0,234201904	0,176891047
IZ6	-0,398367308	0,789094668	0,275415745	-0,407547758	1,02539463	0,0870033695
IZ7	0,766129258	0,315741901	0,966375365	1,21764269	0,785471478	-0,0414075982
IZ8	0,361790172	0,180498253	1,86709058	0,979468226	1,08537541	0,408030789
IZ9	0,523525807	0,65385102	1,5833036	-0,855876157	1,1453562	0,253937628
IZ10	2,3834856	0,0114436933	1,55862647	-0,295465658	1,56522171	0,0998444663
IZ11	0,766129258	1,80342203	0,867666848	0,853375864	0,30562518	0,52360066
IZ12	1,00873271	0,281930989	0,60855699	0,110831953	-0,234201904	0,510759563
IZ13	2,46435342	1,43150199	1,52161077	0,643221927	0,485567542	1,1528144
IZ14	1,08960053	0,349552813	1,57096503	1,35774531	1,50524092	1,05008563