

Variations of Heavy Metals Concentration in Suspended Matter and Physiochemical Properties in the Coastal Surface Water of the Gulf of Aqaba.

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Abstract

Variations of heavy metals concentrations (Pb, Zn, Ni and Cd) in suspended matter as well as the physical properties (temperature, salinity, dissolved oxygen and pH) at five coastal sites and one reference station (offshore) were measured on seasonal base of the year 2005. Seasonal variations of seawater temperature, salinity, pH and dissolved oxygen were significant different, meanwhile; spatial variations among different stations were not significant. Temporal variations of heavy metal concentrations were significantly different ($P < 0.001$); the highest concentrations were detected in spring 0.003 and 0.137 ppm for Pb and Zn respectively. Very low concentrations of Cd (not exceed 0.001 ppm) were detected in autumn and winter. Very low concentrations of Pb, Zn and Cd metals were detected in all sampling stations except Ni the concentrations were ranged between 0.12 and 0.108 ppm; however, variations among different sampling sites were not significant ($p = 0.84$)

الملخص

لقد تم دراسة التغير في تراكيز العناصر النزرة (Pb, Zn, Ni, Cd) في المواد العالقة وكذلك الخصائص الفيزيائية للمياه (درجة الحرارة، الملوحة، الاكسجين الذائب و درجة الملوحة) في خمس مناطق ساحلية و منطقة واحدة مرجعية (المياه المفتوحة) على اساس فصلي للعام 2005, لقد اظهرت نتائج الدراسة تغيرات معنوية في درجة الحرارة، الملوحة، الحموضة و الاكسجين المذاب للفصول المختلفة بينما لم تظهر اي تغيرات جوهرية بين الاماكن المختلفة. التغير الزمني لتراكيز العناصر المختلفة كان جوهريا ($P < 0.001$) بينما التغير المكاني لتراكيز العناصر المختلفة لم يكن جوهريا ($P = 0.84$). اعلى تركيز تم رصده خلال فصل الربيع 0.137 جزء في المليون لعنصر Zn و 0.003 جزء في المليون لعنصر Pb, اقل تركيز تم رصده خلال فصلا الخريف والشتاء لعنصر Cd (0.001 جزء في المليون). لقد اظهرت الدراسة تراكيز قليلة للعناصر (Cd, Zn, Pb) في جميع مناطق الدراسة ما عدا عنصر Ni فقد تم رصد تراكيز تراوحت ما بين 0.108 - 0.12 جزء في المليون.

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1. Introduction

Considerable evidence in the scientific literature that contaminants such as trace metals can be taken up and concentrated by sediments and suspended matter in the Aquatic systems (Forstner and Wittman, 1979; Hart, 1982). Transportation of these contaminants in association with particulate matter represents a major pathway in the biogeochemical cycling of trace contaminants (Hart, 1982).

The vertical and horizontal distributions of many trace elements in the ocean are determined by association with the cycle of growth, sinking and demineralization of

marine phytoplankton. Phytoplankton in the oligotrophic northern Red Sea and Gulf of Aqaba is characterized by a low biomass ($< 0.8 \text{ mg chlorophyll } 1^{-1}$ of seawater), in which the water were dominated by prochlorophytes during early summer and fall, meanwhile, during winter Eukaryotic algae were dominate (Sommer *et al.*, 2002; Al-Najjar, 2000). Phytoplankton, which serves as food for herbivorous fishes and higher organisms, is found to absorb significant amounts of dissolved organic matter from seawater. Hence, phytoplankton is found to be highly susceptible to various contaminants, such as, hydrocarbon, crude oil, metals and industrial effluents (Cushing and Walsh, 1976). Several Authors (Martin *et al.*, 1990; Grotti *et al.*, 2001)

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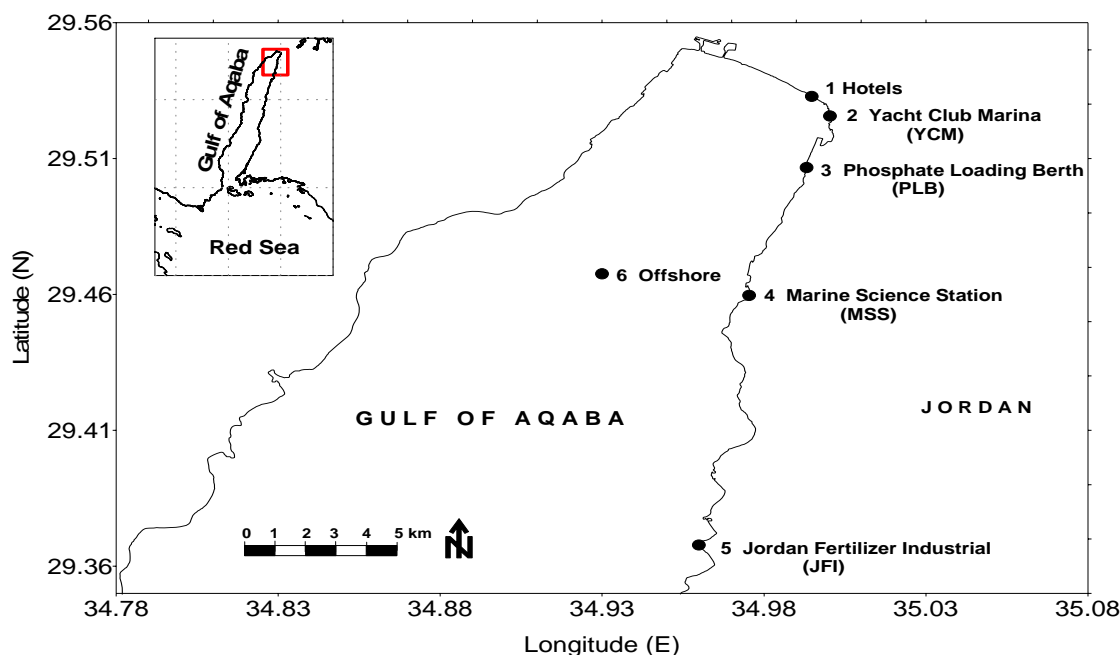


Figure 1. Study area and sampling sites in the northern Gulf of Aqaba.

Reported that the suspended matter of the coastal waters characteristically have much higher concentrations of trace metals such as Fe, Mn, Co, Cu, Cd and Zn than offshore waters, probably due to the input of atmospheric dust from land, nutrient availability, and plankton ecology. Physical and biological processes in the coastal areas have been reported to affect the concentration of their trace metals (Martin *et al.*, 1990; Sedwick *et al.*, 1997; Sohrin *et al.*, 2000).

No information is available on the levels of heavy metal in suspended matter of the coastal areas of the Gulf of Aqaba, which is subjected to different types of human activities, development and uses. The aim of this study is to fill a gap in the information on the levels of Cd, Ni, Pb, and Zn in suspended matter of the five coastal stations and one offshore station in the Gulf of Aqaba.

2. Materials and methods

2.1. Study Area

The Gulf of Aqaba is a partially enclosed water body that constitutes the eastern segment of the V-shaped northern extension of the Red Sea (Figure 1). It is located in a sub tropical arid area between 28°29'-56° north and 34°30'-35° east. The Gulf of Aqaba is 180 km long and has a maximum width of 25 km, which decreases at the northern tip to about 5 km. It is connected to the Red Sea through the Strait of Tiran, which has a depth of about 252 m (Hall, 1975; Por and Lerner-Seggev, 1966). The present study area lies within the Jordanian portion of the Gulf of Aqaba, which extended for about 27 Km to the north of the border with Saudi Arabia, and constitutes the most northern and northeastern side of the Gulf.

2.2. Temperature, Salinity, Ph and Dissolved Oxygen Measurements

Temperature, salinity, pH and dissolved oxygen were measured seasonally (winter, spring, summer and autumn, 2005) down to 30 m depth from five coastal sites; Hotels, Royal Yacht Club (YCM), Phosphate Loading Berth (PLB), Marine Science Station (MSS) and Industrial Complex/Jordan Fertilizer Industry (JFI), and one Reference station (Offshore) (Figure 1), using Conductivity, temperature and depth meter (OC 7316-Idronayt, CTD). These sites embrace various habitats such as fringing coral reef, seagrass beds and unconsolidated sandy bottom areas. In addition, the selected sites represent portions of the coastal zone where major development, and maritime, industry and tourism activities are taking place.

2.3. Suspended Matter Collection and Treatment

Suspended matters were collected on a seasonal base of the year 2005 from the five coastal sites, and one offshore station. Two liters of seawater were sampled using 5 liter Niskin bottle; samples were put in a pre-cleaned plastic bottles with 1% HCL, and brought to the laboratory immediately collection, where each sample was filtered on a GFC filter paper 0.45µm. Filters were then dried at 85°C to constant weight for about 24 hrs, and stored in a plastic bag for future trace metal analysis.

2.4. Samples Digestion and Heavy Metals Measurement

The filters were placed in pre-cleaned small capacity (100 ml) glass beakers, and oxidized by the addition of 8ml of 69.5% ultra-pure nitric acid at room temperature for 4 hrs. Beakers were put on a hot plate at 100°C for 6 hrs, and then allowed to cool to room temperature. The samples were heated again to near dryness in order to remove the nitric acid. The residue was dissolved in 8ml of 1% nitric acid and kept on a hot plate for about 1 hr to enhance dissolution. The samples were allowed to cool to room temperature and then filtered on a Whatman filter paper

number 43. Samples were finally diluted to 25ml with 1% nitric acid. Concentrations of Mg, Cd, Cu, Ni, Pb, Fe and Zn were measured by the use of Jena AA 300 atomic absorption spectrophotometer. Duplicate measurements were made for each sample, by direct aspiration into air-acetylene flame. The instrument was instructed to give the mean value and standard deviations of three readings as the final reading of each sample. The precision of the whole procedure was assessed by 10 replicates for a sample and the results agreed to within 3%. Duplicate

blanks were used for each batch of digested samples. The mean value of the blank was subtracted from the readings of the sample to give the final reading. In addition to the blank solution, three standard solutions were prepared to cover the expected range of the element concentrations in the samples and within the linearity of the procedure (within the linear portion of the calibration curve of the procedure). The final element concentrations were interpolated as ppm unit.

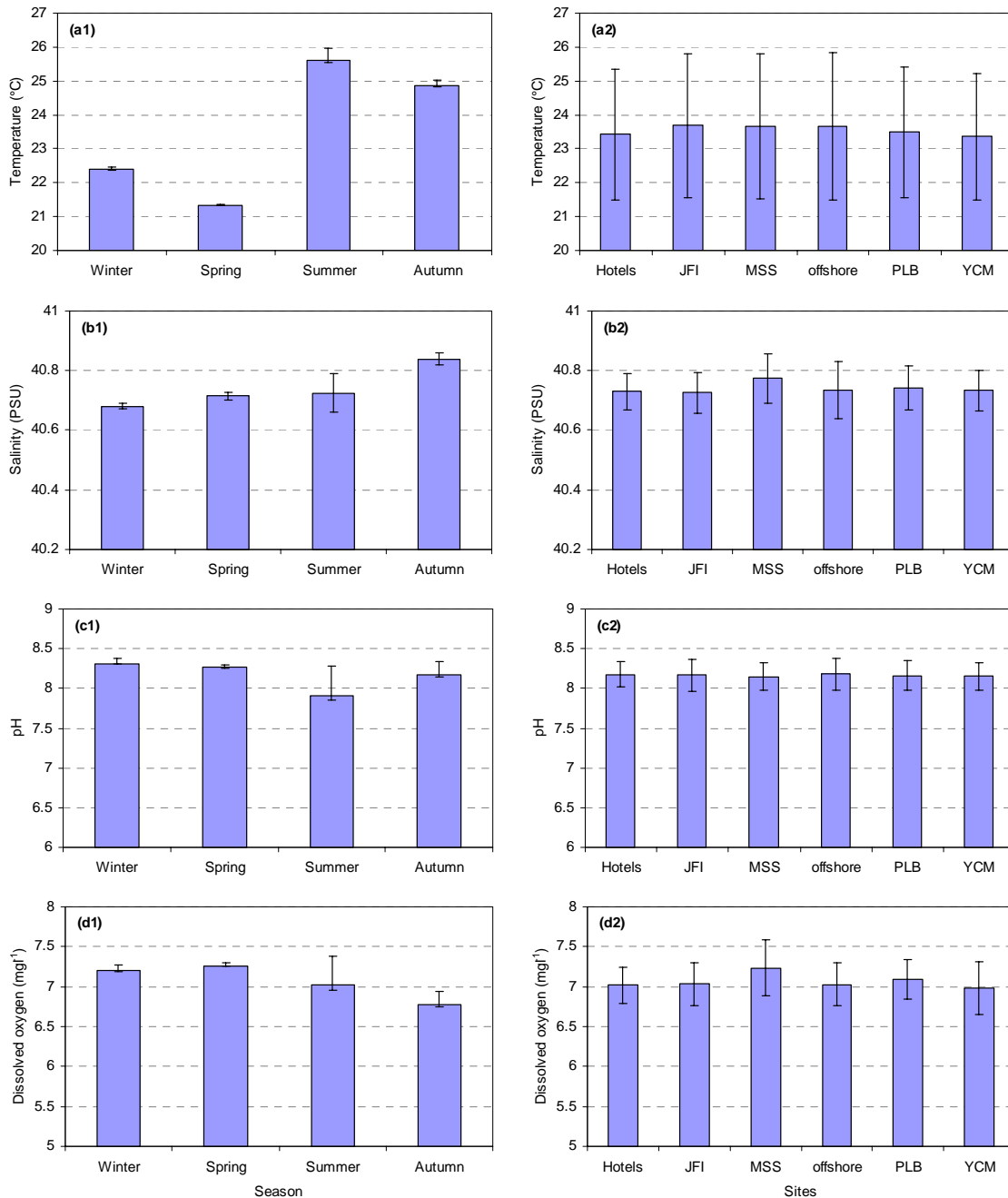


Figure 2. Spatial and temporal variations of (a) temperature (°C), (b) salinity (PSU), (c) pH and (d) dissolved oxygen (mg l⁻¹) of water column along the study area in the northern Gulf of Aqaba, Red Sea. Standard deviation are the bars ?.

3. Results

3.1. Water Temperature, Salinity, Ph and Dissolved Oxygen

Seasonal variations of seawater temperature were significant ($p = 0.0001$). The highest mean value ($25.61\text{ }^{\circ}\text{C}$) was recorded in summer, whereas the lowest mean ($21.33\text{ }^{\circ}\text{C}$) was recorded in spring. Spatial variations among different stations were not significant ($p = 0.90$), where the mean temperature values ranged between $23.36\text{ }^{\circ}\text{C}$ at YCM and $23.68\text{ }^{\circ}\text{C}$ at JFI (Figure 2. a).

Temporal variations of seawater salinity were significant ($p = 0.001$). The highest mean salinity (40.84 PSU) was recorded in autumn, whereas the lowest mean (40.68 PSU) was recorded in winter. In comparison, spatial variations in salinity between different stations were not significant ($p = 0.95$), whereas the mean value was 40.73 PSU at JFI and 40.77 PSU at MSS (Figure 2b).

Similarly, temporal variations in pH were also significant ($p < 0.0001$), with the highest mean value (8.32) was winter, while, the lowest in mean value (7.91) occurred in summer. Variations of pH among the sampling

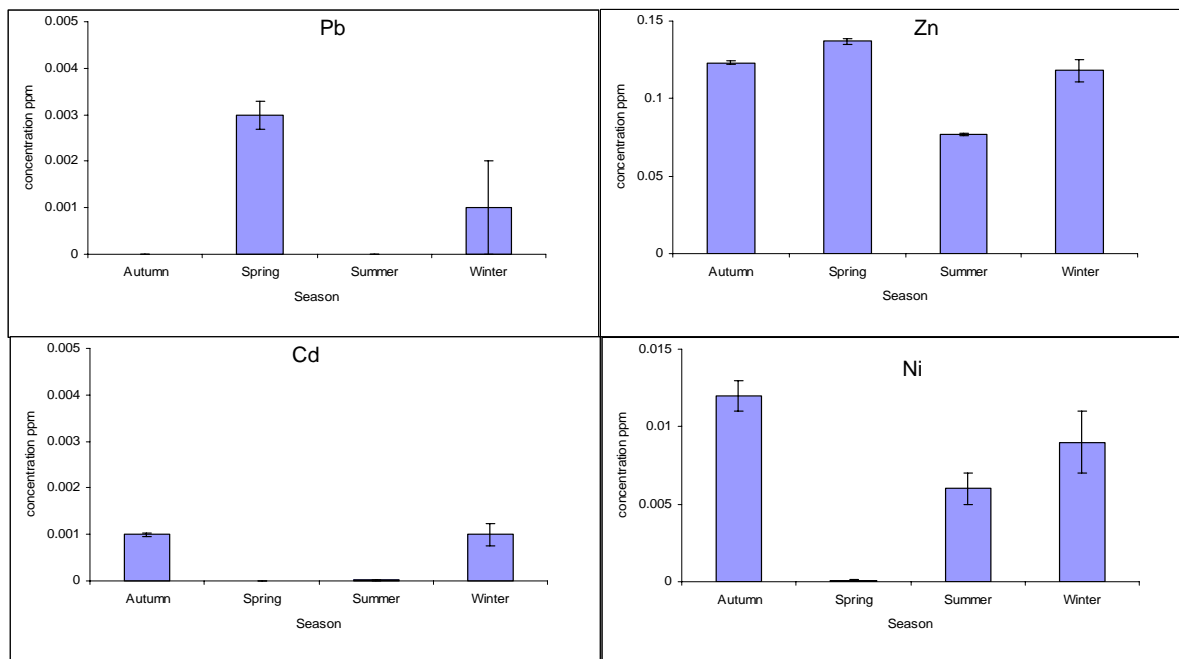


Figure 3. Temporal mean concentrations \pm SE of Pb, Zn, Ni, and Cd in phytoplankton from the Jordanian coast of the Gulf of Aqaba, Red Sea.

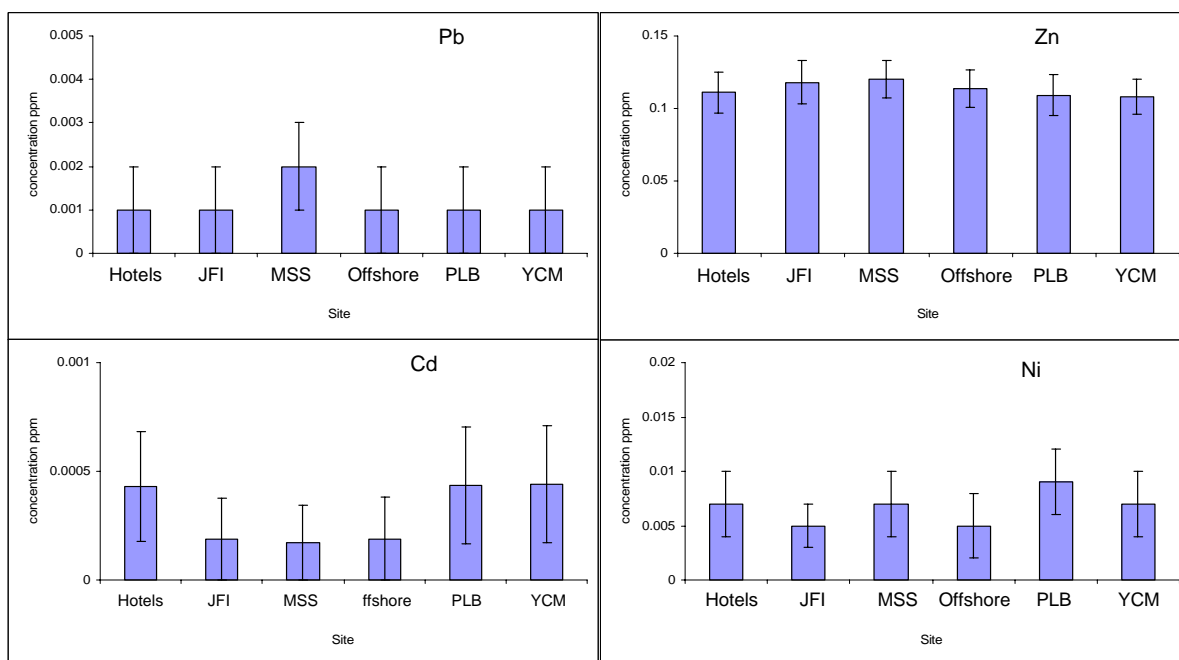


Figure 4. Spatial mean concentrations \pm SE of Pb, Zn, Ni, and Cd in phytoplankton from the Jordanian coast of the Gulf of Aqaba, Red Sea.

sites were not significant ($p=0.99$), where the mean pH value ranged between 8.15 at MSS and 8.18 at Offshore (Figure 2c).

Temporal variations ($p=0.0013$) in dissolved oxygen occurred during sampling dates; highest value was recorded in spring with mean value of 7.26 mg. l^{-1} , whereas the lowest value was in autumn with mean value of 6.77 mg. l^{-1} . Spatial variations of dissolved oxygen were not significant ($p=0.833$), the mean value was 7.24 mg. l^{-1} at MSS and 6.98 mg. l^{-1} at YCM (Figure 2d).

3.2. Heavy Metals in Suspended Matter

3.2.1. Temporal Variations

The mean concentration of Pb for spring and winter were 0.003 ppm and 0.001 ppm, respectively. However, no Pb was detected in autumn and summer. The season highest Zn concentration (0.137 ppm) occurred in spring, compared to a concentration of 0.077 ppm which was found in summer. The highest Ni concentration was obtained in autumn (0.01 ppm) while, lowest concentrations 0.0001 ppm were obtained in spring. The Cd concentrations did not exceed 0.001 ppm in both winter and autumn, while no Cd was detected in summer and spring. However the one way ANOVA test showed significant temporal variations between different seasons ($P<0.001$) (figure. 3).

3.2.2. Spatial Variations

The Pb concentrations at all sites were in the range of 0.001- 0.002 ppm. Concentrations of Zn in all sampling sites ranged between 0.12 ppm at the MSS and 0.108 ppm at the Yacht Club site. Ni concentrations were low at all sampling sites and ranged between 0.005 ppm at the JFI and 0.009 ppm at offshore, and Phosphate sampling sites. Very low concentrations of Cd were measured at all sampling sites, where it ranged between 0.00017 ppm at the MSS and 0.0004 ppm at the Yacht Club sampling site. The statistical test using one way ANOVA showed no significant differences among different sampling sites ($P=0.84$) (Figure. 4).

4. Discussion

4.1. Physical Conditions

The main temperature differences were recorded at the surface with mean values of $25.61 \text{ }^{\circ}\text{C}$ in summer and $21.33 \text{ }^{\circ}\text{C}$ in spring. The interannual variation of surface temperature is mainly linked to variation in the net heat flux (Genin *et al.*, 1995). The main trend of variation in the present study is in a good agreement with those reported in previous studies from the Gulf of Aqaba. Paldor and Anati (1979) reported a maximum surface water temperature of $26.7 \text{ }^{\circ}\text{C}$ in July and a minimum of $20.8 \text{ }^{\circ}\text{C}$ in March. Badran (1996) found a maximum surface water temperature 27.5°C and a minimum of $20.8 \text{ }^{\circ}\text{C}$. Manasrah (1998) reported a maximum surface water temperature of $25.48 \text{ }^{\circ}\text{C}$ in August and a minimum of $21.25 \text{ }^{\circ}\text{C}$ in April which is in agreement with the results obtained in the previous study. Moreover, Manasrah and Badran (2008, in press) found that the minimum and maximum surface temperature was 21.16 in February 2001 and 27.99 in August 1999.

In the present investigation, the salinity of surface water varied between 40.84 PSU in autumn and 40.68 PSU in winter. The temporal and spatial variations of surface salinity were very small and not significant compare the high value of salinity itself. Al-Najjar (2000) found that very small variations in surface water salinity, which ranged from 40.62 PSU in September to 40.33 PSU in April. Manasrah and Badran (2008, in press) reported that the minimum and maximum surface salinity value during 1997-2003 was 40.2 PSU and 40.7 PSU, respectively.

4.2. Spatial and Temporal Variability in Metal Concentrations in Suspended Matter

A considerable amount of trace metal has been concentrated by suspended matter in different locations along the Jordanian coast of the Gulf of Aqaba. The suspended matter contents of Zn are relatively high at the Marine Science Station. By comparison, the suspended water samples from the Yacht club and phosphate loading port showed apparently high concentration of Cd, Mg and Fe. Those from Phosphate Loading Port showed apparent high concentration of Fe and Ni. However, the statistical examination did not show any significant differences among the six sampling sites. The higher concentrations of suspended metals in the Marine Science Station can be explained in view that the site is exposed to the effects of different anthropogenic activities on the passenger port (Abu-Hilal and Al-Najjar, 2004). The high concentration of Cd in Yacht Club is mainly due to the relatively high activity of boats and their maintenance which includes painting and cleaning. The present results are in general agreement with the results of previous works (Al-Batainih, 2004; Ababneh, 2004) on bioaccumulation of trace metals in the tissue of bivalves (*Modiolus auriculatus*) at different locations along the Jordanian coast. However, in an overall view of the study have been made by Bu-Olayan *et al.*, 2001 concerning the distribution of different trace metals in different sites along the coast of Kuwait supporting our finding in which the elevation of some trace metals have been attribute to the input of metals from dust and industry, associated with pollution activities were found susceptible to environmental hazards in the marine ecosystem and mankind. Examination of the results of the present study showed that the phytoplankton metal concentrations was in the following order $\text{Zn} > \text{Ni} > \text{Pb} > \text{Cd}$. It is obvious that the Zn occurred in highest concentration. This is to be expected and could be explained in the view that this element is considered as essential trace element for cell growth and differentiation in several species of marine organisms such as an integral part of respiratory protein, and required for the activity of diverse enzymes and the healthy living of plankton organisms (Bryan, 1968; Ghidalia, 1995; Aaseth and Norseth, 1986; Adams *et al.*, 1982; Senkebeil and Wriston, 1981; Toma, 1984; Gherardi, *et al.*, 2001). However, it is known that at elevated concentrations these metals become toxic to organisms (Phillips, 1980). By comparison, the concentrations of the non essential highly toxic metals such as Cd and Pb are the lowest in availability (Gouvea *et al.*, 2005).

The careful examination of the result indicate that seasonal variation of metal in suspended particles have been observed in this study for all measured elements

where higher concentrations were detected mainly during autumn and spring. This variation could be related to the changes in the pollution load of the studies sites as suggested by Ritterhoff and Zauke (1997).

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