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Evaluation of Heavy Metal Pollution on the Coastal Marine Environments of Okinawa Island, Japan.

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Abstract

The distribution of heavy metals (Zn, Cd, Cu, Fe, Mn, Co, Ni and Pb) was investigated in surface sediment samples from Naha port, Tomari port and Nakagusuku bay in Okinawa Island. The total metal concentrations were in the range of Mn (155 -1840 mg/kg), Zn (86 - 2910 mg/kg), Pb (29- 460 mg/kg), Cu (0-945 mg/kg), Co (14 - 204 mg/kg), Ni (0-240 mg/kg) cd (0-2 mg/kg) and Fe (9650-11400 mg/kg). A sequential extraction procedure was carried out on the sediment samples to determine the chemical state of heavy metals in the sediments. All the elements analyzed except Cd were detected in several to 10% in the exchangeable fraction. Metals such as Zn, Pb and Co showed appreciable concentration in the carbonate fraction where they represented between 16-50 % of the total. In the reducible fraction most metals were found in appreciable percentages where Pb represented 36% of the total. In the oxidizable fraction, Cu, Mn, Co, Fe and Zn represented between 10-40% of the total while Ni and Pb represented less than 10%. The residual/ silicate fraction was the most abundant pool for most metals analyzed like Fe, Mn, Ni and Cd. The present results are indicative of the contribution of heavy metal pollution in the marine environments of Okinawa Island.

Key words: Heavy metals, Sequential extraction, Coastal Marine Environment, Okinawa Island.

1. Introduction

Heavy metals are among the most common environmental pollutants and their occurrences in water and biota indicate the presence of natural or anthropogenic sources (Singh *et al* 2005). At present, the anthropogenic contribution of heavy metals in the environment far exceeds natural inputs (Nriagu and Pacyna, 1988). Human activity has inevitably increased the levels of metal ions in natural water systems. The main sources of heavy metals in the aquatic system are weathering of soils and rocks and from anthropogenic

activities, whereby industrial and urban wastes are discharged into water bodies (Pardo *et al.*, 1990; Boughriet *et al.*, 1992; Yu *et al.*, 2001; Klavins *et al.*, 2000). Other sources such as mine drainage, off shore oil and gas explorations, industrial (pesticides, paints, leather, textile, fertilizers, pharmaceuticals), domestic effluents, agricultural runoff and acid rain have all contributed to the increased metal load in these waters being ultimately incorporated in to aquatic sediments (Ansari, *et al.*, 2004). The metals can be either adsorbed on to sediments or accumulated in benthic organisms, sometimes to toxic levels. Therefore, the bioavailability and subsequent toxicity of metals have been a major research area (Ankley *et al.*, 1996; Singh, 2001; Sharma *et al.*, 1999; Davies *et al.*, 1991; Klavins *et al.*, 2000; Gonzalez *et al.*, 2000; Srivastava *et al.*, 1994). Some heavy metals are essential for life and some are merely beneficial, however many are highly toxic (Ansari *et al.*, 2004). It is important to evaluate the chemical state and distribution of heavy metals in aquatic environments because the concentrations level of toxicity and essentiality are different among the chemical forms of elements.

One of most crucial properties of heavy metals is that they are not biodegradable in the environment (Florence, 1982). Therefore the determination and monitoring of specific chemical forms of the heavy metals in environmental samples is extremely important (Tokalioglu *et al.*, 2000). Furthermore, it is now widely recognized that the total dissolved metal concentration is often a poor indicator of toxicity to aquatic organisms. In many instances, biological toxicity is related more closely to the metal concentration of particular chemical forms (Florence, 1982, Tessier *et al.*, 1979).

Okinawa is a prefecture located in a subtropical climatic zone in Japan. The emerald-green Ocean is known as one of the most beautiful seas in the world and in particular there are lots of unique biological species. Light industries, fisheries, military bases and harbors are its economic and political importance and problem in this Island and by these activities and training in addition to the human's normal life, the marine environment may be contaminated. The objectives of this study were to determine the levels and characteristics of heavy metals in surface sediments in coastal zones such as Naha port, Tomari port and Nakagusuku bay in Okinawa Island and to discuss whether the levels can be considered to be a threat to the aquatic organisms.

2. Material and methods

2.1 Sampling sites

Naha port, Tomari port and Nakagusuku bay in Okinawa Island were chosen as representative sites for the polluted sediments and Sesoko Island as a representative site for less polluted sediments (Fig. 1). Naha port and Tomari port are located on the south-west of Okinawa Island and there are a lot of shipments at these ports. Nakagusuku bay is located on the south-east of Okinawa Island and there is a lot of agriculture which

takes place there. Sesoko Island sampling site is located at the home of the Tropical Biosphere Research Center of the University of the Ryukyus, which is dedicated to studying the diversity of tropical biota including coral reefs and mangroves.

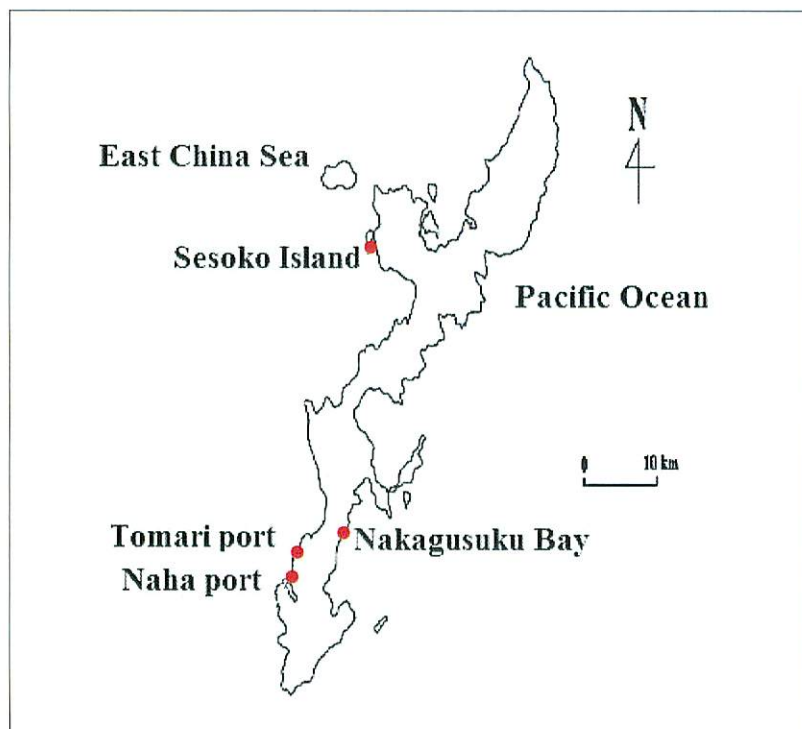


Fig.1 Map of Okinawa Island showing Sampling locations

2.2 Sample collection and storage

Sediment samples were collected from 7 sites at Naha port (NR & NP), 4 sites at Tomari port (TP), 6 sites at Nakagusuku bay (NKB) and 1 site at Sesoko Island (SI;) (Fig 1). All the samples were taken using a grab sampler, put in to acid rinsed polyethylene bottles and then transported to the laboratory. The samples were freeze-dried using a freeze drier (FRD 51 model), homogenized using a mortar and a pestle and then stored in polyethylene bottles at -5°C until required for analysis.

2.3 Total metal concentration procedure

Sediment samples were analysed using the "total digestion" method described by Fatoki and Mathambatha (2001). One g of freeze dried sediment was weighed into a Teflon beaker. Ten ml of conc. HNO_3 was added and then it was boiled gently for 30 minutes on a hot-plate. The beaker was cooled and 2 ml conc. HClO_4 , 10 ml conc. HNO_3 and 10 ml conc. HF were added. The mixture was heated to near dryness. The corners and walls of

the beakers were washed with about 5 ml Milli Q water, and the solution was again heated until dense white fumes developed. The beaker was cooled and 10 ml of 1N HCl was added to dissolve the salts. The solution was transferred into a 100 ml volumetric flask and then diluted to the with Mill Q water. The solution was analysed by means of atomic absorption spectroscopy (Thermal Elemental Solaar 969). A blank determination using the same procedure was performed.

2.4 Sequential extraction procedure

A Sequential extraction procedure according to IUPAC (technical report, 2004) was applied to seventeen surface sediments collected from Naha port, Tomari port and Nakagusuku bay in Okinawa Island in order to fractionate heavy metals (Cd, Cu, Ni, Co, Zn, Pb, Mn and Fe) into six operationally defined fractions; Water soluble (Milli Q water), Exchangeable (1M $\text{CH}_3\text{COONH}_4$ at pH 7), Carbonate bound (1 M CH_3COOH at pH 5), Reducible (1M $\text{NH}_2\text{OH}\cdot\text{HCl}$ at pH 2), Oxidizable (30% v/v H_2O_2 at pH 2), and Residual/Silicate (HF , HClO_4 , HNO_3). Each extraction procedure was carried out successively in three days at room temperature. After each successive extraction, the supernatant solution was separated by centrifuging the suspension at 4,500 rpm for 30 min and filtering through filter paper.

All extractions were carried out in acid-washed (5% HNO_3) labware. All chemicals used in this study were of analytical grade or better. Milli Q water was used through out the analysis. Metal concentrations of the supernatants from each step were analyzed by atomic absorption spectrophotometer (Thermo Elemental Solaar 969) equipped with a flame atomizer. Standards for calibration curves for all metals were prepared for each extraction. Reagent blanks were used for background correction.

3. Results and discussion

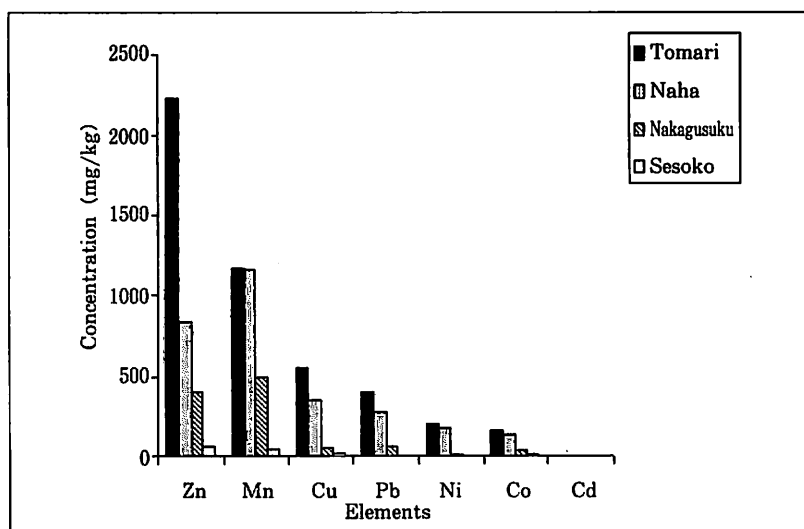
3.1 Total metal concentrations

Heavy metals were detected at all sampling sites as shown in Table 1. The concentration levels varied in the range of Mn (155-1840 mg/kg), Zn (86- 2910 mg/kg), Pb (29 - 460 mg/kg), Cu (0-945 mg/kg), Co (14-204 mg/kg), Ni (0-240 mg/kg), Fe (9650-11400 mg/kg) and Cd (0-2 mg/kg). The most abundant heavy metal in all the samples was Fe followed by Zn and then Mn. The mean metal concentrations of the heavy metals in the sediments were in the order $\text{Fe} > \text{Zn} > \text{Mn} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Co} > \text{Cd}$ (Table 1). Among the sampling sites, Mn and Ni showed highest concentration at Naha port while at Tomari port, Zn, Co, Pb and Cu were the highest. At Nakagusuku bay, Fe and Cd were the highest. Among the Nakagusuku bay samples, only NKB5 showed highest concentrations of the analyzed elements. From the mean metal concentration results as shown in Fig. 2, it can be seen that Tomari port is the most polluted area followed by

Table 1. Total metal concentration (mg/kg dry weight) in sediments from Naha port, Tomari port, Nakagusuku bay and Sesoko Island. (n = 17)

Sample		Fe	Zn	Mn	Cu	Pb	Ni	Co	Cd
NR1	Naha port, river side	53900	1540	1390	399	240	235	135	N.D
NR2		27400	613	982	262	374	77	122	N.D
NR3		60100	1720	1830	297	261	247	195	N.D
NP1	Naha port	10900	433	633	100	254	76	176	N.D
NP2		51500	195	1670	476	353	238	126	N.D
NP3		49000	1210	1210	790	287	235	140	N.D
NP4		10600	116	358	145	200	106	94	N.D
TP1	Tomari port	23900	2090	1250	409	327	187	130	N.D
TP2		41900	2200	1230	946	446	240	139	N.D
TP3		44700	2110	1020	492	460	187	198	N.D
TP4		37900	2530	1170	364	381	185	204	N.D
NKB1	Nakagusuku bay	63790	313	372	52	23	N.D	39	N.D
NKB2		30800	301	610	18	77	N.D	14	N.D
NKB3		13500	176	155	14	64	N.D	37	N.D
NKB5		114000	1340	908	235	115	45	41	2
NKB8		9650	86	339	N.D	75	N.D	28	N.D
NKB9		24200	157	607	N.D	29	N.D	28	2
Mean		39300	1010	925	333	233	172	109	0.2
S1- Sesoko		871	70	42	18	N.D	N.D	16	N.D

N.D: Not detected.

**Fig.2** Mean heavy metal concentrations in sediments at Tomari port, Naha port, Nakagusuku bay and Sesoko Island

Naha port and then Nakagusuku bay. Naha port is located in the capital City of Okinawa Island which is densely populated with sewage discharge to the coastal areas around Naha port. In addition there are several light industries and US military bases and thus the high concentrations of these metals at these sites can be attributed to the discharge from the residential areas and also discharge from the domestic and international ships which operate at this port. Tomari port which is located near Naha port there is high density of passenger and cargo shipping traffic around the Inter Islands, so the high concentration of the heavy metals are probably related to the potential discharges from the ships and sewage discharge from the residential areas. Similar results of high PCBs concentrations at these points were found by Sheikh *et al.*, (2002). Also comparing these results with that obtained from Sesoko Island (Fig. 2) it is evident that Tomari port and Naha port are highly polluted with these heavy metals as compared to Nakagusuku bay.

3.2 Chemical fractionation of Heavy Metals in sediments

The results of chemical fractionation of the heavy metals by sequential extraction are shown in Figs. 3a & 3b. Table 3 shows mean and percentage fractional concentration of each element. A significant proportion of Ni and Pb was present in the wash fraction representing between 15-28% of the total, while Co, Zn, Cu and Fe represented less than 4%

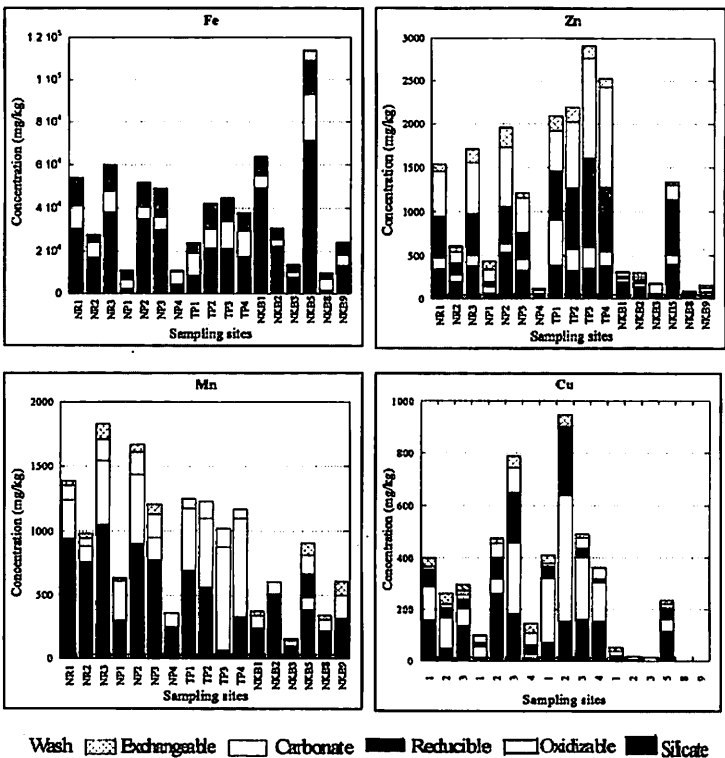


Fig.3a Concentration of Fe, Zn, Mn and Cu in each fraction

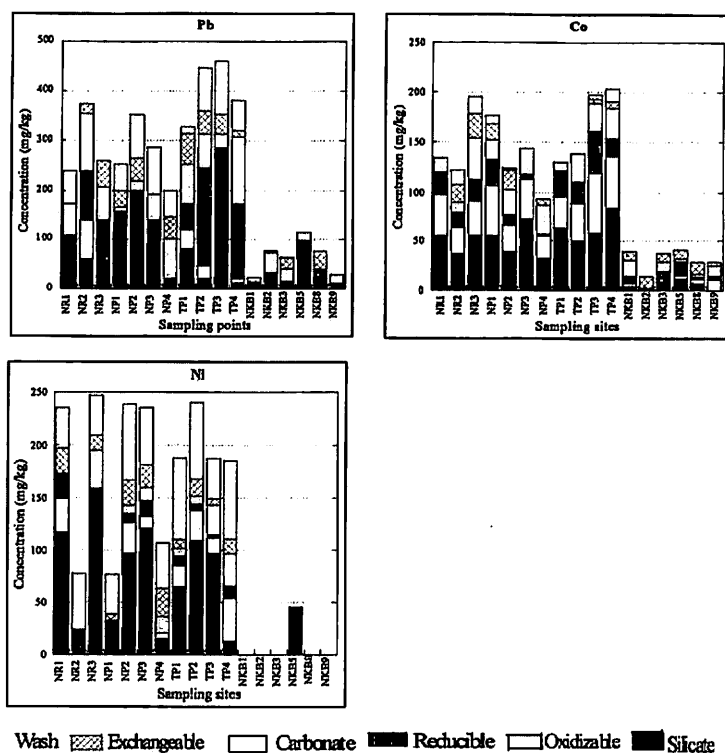


Fig.3b Concentration of Pb, Co and Ni in each fraction.

Table 2 Mean concentrations of heavy metals and their relative abundance in each fraction in the Coastal sediments. (Mean in mg/kg).

Element	Wash		Exchangeable		Carbonate		Reducible		Oxidizable		Silicate	
	Mean	%	Mean	%	Mean	%	Mean	%	Mean	%	Mean	%
Zn	3	0.2	80	7	376	33	331	29	120	11	247	21
Mn	0.4	0.04	37	4	106	11	64	7	279	30	439	47
Pb	37	15	24	10	49	21	92	39	9	4	27	11
Cu	2	1	18	6	24	8	52	18	110	37	89	30
Co	4	3	9	8	18	17	15	14	27	25	37	34
Ni	35	28	10	8	11	8	7	5	13	10	51	40
Cd	0	0	0	0	0	0	0	0	0	0	0.04	100
Fe	214	0.5	77	0.9	456	1	7558	19	8130	21	24065	58

Table 3 Risk assessment code (Perlin *et al*; 1985).

Classification of Risk	Relative abundance of Metals in carbonate and exchangeable fractions (%).
No risk	< 1
Low risk	1 - 10
Medium risk	11 - 30
High risk	31 - 50
Very high risk	> 50

of the total extracted metal. This indicated that these elements were soluble in the interstitial waters or are adsorbed on to the particulate surface. The relative abundance in the exchangeable fraction were low with Ni, Pb, Co, Cu, Mn, Zn, and Fe representing less than 10% of the total.

Zinc, Pb, Ni, Co and Mn showed appreciable concentration in the carbonate fraction, where Zn was highest with a relative abundance value of $\approx 33\%$ of the total. Lead and Co were found in appreciable percentages of 16-21% whereas Ni, Fe, Mn and Cu were detected but in low percentage of less than 10% of the total. Similar results were reported for these elements in carbonate fraction in Gomti river sediments, India (Singh *et al*, 2005) and they have special affinity for carbonate and may co-precipitate with carbonate minerals (Forstner and Wittmann, 1991). Carbonate fraction is also termed to be the most bioavailable fraction to the aquatic organisms since the elements are loosely bound to the sediments and can be released back to the environment (Tack and Verloo., 1995).

Lead was dominant in the reducible fraction, which has been proved to be sensitive to anthropogenic inputs (Modak *et al*, 1992), and it represented $> 39\%$ of the total. Iron and manganese oxide are known to have strong scavenging efficiency and may provide a sink for heavy metals and thus they can be said to be good scavengers of Pb. Similar results are reported by Tokalióglu *et al.*, (2000). Other metals like Zn, Fe, Co and Cu were also found in this fraction in appreciable percentages. Manganese in this fraction was detected in negligible concentrations in Naha and Tomari ports. This may indicate that it existed in anoxic state in sediments in these sites. However in Nakagusuku bay Mn was detected in 7% of the total extracted metal which indicates that it exists in oxic form in sediments in this site. Nickel and Cadmium were the least scavenged elements representing $< 10\%$ of the total.

Copper was dominantly associated with oxidizable fraction ($\approx 40\%$) where it is likely to occur as organically complexed metal species or sulphide minerals. Davidson *et al* (1994) found similar results of Cu being dominant in the oxidizable fraction in contaminated marine sediments. Other metals found in this fraction included Mn, Co, Fe, Zn, Ni and Pb indicating that the metals occurred in the forms of stable organic complexes and metal sulfides. Cobalt might probably be present as sulphide in this fraction.

The highest concentration $\approx 50\%$ for Fe, Mn, Ni and Co were found in the residual/silicate fraction. This indicates that these elements are tightly bound to the sediment minerals and that they are not easily released to the environment. This was the only fraction in which Cd was detected. Other metals like Zn, Cu and Pb were also detected but in low concentrations in all the samples.

Fractionation of heavy metal contents may give indications of the source of the metals. According to Tack and Verloo (1995), exchangeable, carbonate, reducible and oxidizable fractions are considered the fractions that are more available to aquatic biota where the bioavailability decreases in the order of exchangeable > carbonate > reducible > oxidizable. According to risk assessment code (Table 3) (Perin *et al.*, 1985), concentrations of the elements in the exchangeable and carbonate pose a risk to the environment. Relative abundance (%) of < 1 in these fractions (exchangeable and carbonate) poses no risk to the environment, 1-10 % poses low risk, 11-30 % poses medium risk, 31-50 % poses high risk and >75 % poses very high risk to the environment. From the present results (Table 2), all the analyzed elements were detected in these fractions which suggest that they may be from anthropogenic sources. Zinc was found in appreciable percentage of 33 thereby posing a high risk to the environment. Lead, Co and Mn were in appreciable percentages of 21, 17 and 11 respectively posing a medium risk to the environment. These heavy metals can thus be termed to be a threat to the aquatic organisms since they can be easily released

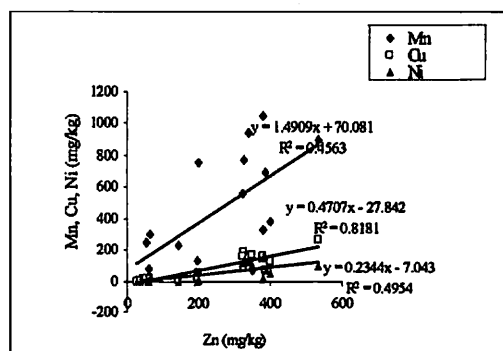


Fig.4a Correlation of Zn with Mn, Cu & Ni in the silicate fraction.

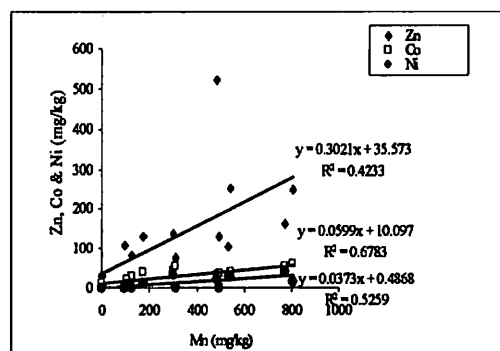


Fig.4b Correlation of Mn with Zn, Co & Ni in the oxidizable fraction.

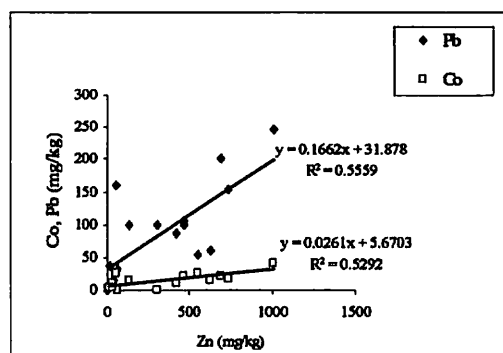


Fig.4c Correlation of Zn with Co & Pb in the reducible fraction.

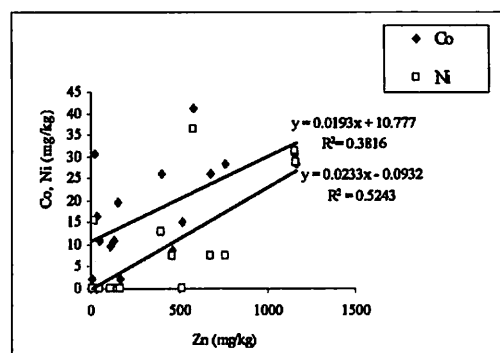


Fig.4d. Correlation of Zn with Co & Ni in the carbonate fraction.

n.g r=correlation Co-efficient
p=probability Co-efficient

back to the aquatic environment. Other heavy metals (Cu, Ni, and Fe) were found in < 10%.

3.3 Inter-element relationships

In the present study, statistical analysis was carried out to determine the correlation among the heavy metals in the sediments. Total Mn and Zn showed a significant positive correlation ($r^2 \geq 0.45$, $p \leq 0.005$) with other metals such as Pb, Cu, Co and Ni. Cobalt also showed a good positive correlation with Pb; Nickel correlated well with Cu and Co while no significant correlation was found between Fe and other metals such as Mn, Zn, Pb, Co, Cu, Ni and Cd. This may imply that Fe is from a different source from the rest of the metals.

In the silicate fraction, Mn, Cu and Ni showed high positive correlation ($r^2 \geq 0.45$, $p \leq 0.005$) with Zn (Fig. 4a). This suggests that these metals probably has a similar source or have a similar behavior. Manganese showed a high positive correlation ($r^2 \geq 0.42$, $p \leq 0.005$) with Zn, Ni and Co in the Oxidizable fraction (Fig 4b). This high correlation found between metals in this fraction (oxidizable) suggests the possibility of formation of strong complexes with organic matter. Zinc correlated well ($r^2 \geq 0.52$, $p \leq 0.005$) with both Pb and Co in the reducible fraction, which indicates that Fe and Mn may provide sinks for these metals (Fig 4c). Zinc correlated well ($r^2 \geq 0.38$, $p \leq 0.005$) with Ni and Co in the carbonate fraction (Fig 4d) and this indicates that these metals have a special affinity for carbonates and thus they precipitate with carbonate. It also indicates that these elements are loosely bound to the sediments and therefore can be released back posing a risk to the aquatic environment. No significant correlation was found between the metals in the exchangeable fraction. Further in the wash fraction, significant positive correlations between Pb and Ni and between Zn and Co were found suggesting that they may be soluble in the interstitial waters ($p \leq 0.005$).

4. Conclusion

The metal concentrations in sediments from Naha port and Tomari port are indicative of pollution from point sources in and around the ports and from diffuse sources as urban runoff. The chemical fractionation of the heavy metals provided information's on their bioavailability and mobility which showed that most of the metals are bioavailable indicating that they can be released, therefore posing risk to the environment and thus they should be monitored oftenly. The correlation of the concentrations of the metals in the fractions and also in the total concentration suggested similar origin or similar behavior of the pollutant metals.

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