

Distribution of Heavy Metals and Inorganic Nutrients in Nagura Estuary, Ishigaki, Ryukyu Islands*

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Abstract

The concentrations of some heavy metals related closely to primary production in an estuarine ecosystem such as Mn, Fe, Co, Zn, Cu, and Ni, were measured in samples of filtered water, suspended particulate matter, and bottom sediments in Nagura River estuary, Ishigaki Island, Ryukyu Islands in 1980. The distributions of inorganic nutrients such as phosphate and silicate were also investigated in the same region. The concentrations of most of the heavy metals in the water were rather constant regardless of the tidal levels when the samples were collected or the different sampling sites. Manganese, to the contrary, was found in conspicuously higher quantity near river area suggesting its supply in soluble form is related to river water influx. The concentrations of metals in the sediments differed at various sampling sites and those in the suspended particulate matter were far higher in the samples nearer the river. Such a change at the river mouth regions was remarkably noted in Mn, Ni, Fe, and Cu. The distribution of phosphate and silicate indicated that the river is a major source of supply of these matters to the ocean.

Key Words: Heavy metals, Nutrients, Production, Estuary

Introduction

An estuary is the transitional region from a fresh water source to the saline ocean. The estuarine environment can be greatly modified by the conditions on both sides of this transition zone. The importance of the estuary in aquatic production is well known (see, for example, CRONIN et al, 1976). The discharged materials from the land, through rivers, are mixed with those in oceanic waters. The biota in the estuarine water differ from those in oceanic and fresh water. They are able to adjust to a wide range of en-

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vironmental stresses. The present study was designed to obtain the best possible estimates of some heavy metals and inorganic nutrients in one estuary. The significant roles of heavy metals in the aquatic environments were studied by several investigators. The biological importance of manganese was stated by SUNDA and HUNTSMAN (1985); the effects of the starved iron quantity on *Thalassiosira weissflogii*, a phytoplankton, by HARRISON and MOREL (1986); the effects of copper and zinc on a zooplankton by STOECKER et al (1986); and the distribution of nickel and its relation to primary production in the ocean by JONES and MURRAY (1984).

Ishigaki Island is situated near the south-western end of the Ryukyu Islands, Okinawa Prefecture, and has a subtropical climate. Nagura estuary is located on the west side of the island, and it is known to be an unpolluted zone (WATANABE et al, 1978). This survey was carried out between July 11 and 12 in 1980. The results obtained here comprise a part of the study entitled "The Water-Land Interactive Systems Project" headed by Professor IWAKIRI, Faculty of Fisheries, Kagoshima University and funded by the United Nations University. Other aquatic environmental parameters such as salinity, water temperature, and current were observed by CHAEN (1981).

Materials and Methods

1) Sampling stations

The 14 sampling sites are shown in Fig. 1. Stations 1 and 2 were located off-shore and stations 3 to 7 were along the coral reef edge. Station 12 was just at the mouth of the Nagura River while Stations 13 and 14 were in the river itself.

2) Collection and analysis of water samples

The surface water was collected by acid-washed plastic bottles at the above mentioned 14 sampling stations at high tide and at all but Station 14 at low tide. The difference between high and low tide was about 170 cm. The water samples collected thus were filtered by acid-washed millipore filters (0.45μ) as soon as possible at the laboratory of the Okinawa Prefectural Fisheries Station located very near the sampling sites and stored at -20°C .

The concentration of heavy metals was basically determined according to the procedure by Biechler (1965) using cation exchange resin. Water samples of 500 or 1,000 ml were passed through a 10×70 mm column of Chelex 100 (Bio-Rad) at a rate not exceeding 3 ml/min. After being dried, the column was washed by an aliquot of redistilled water which was followed by the addition of 4 N nitric acid to adsorb the metals. The eluted metals were measured directly with a Hitachi 208 Atomic Absorption Spectrophotometer using air-acetylene flame.

The additional water samples were used for the analysis of the concentrations of phosphate-P and silicate-Si as representative parameters of inorganic nutrients in the water. After 1 ml of HNO_3 was added to every 500 ml of filtered water, it was stored at

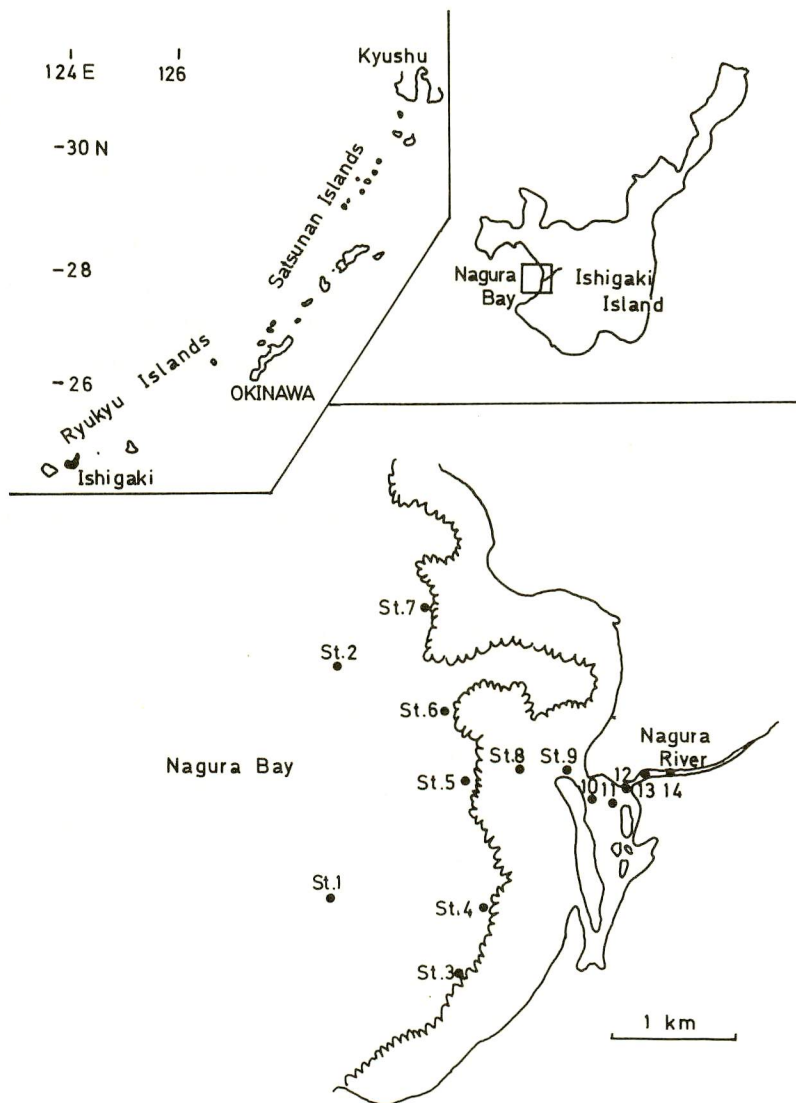


Fig. 1. Sampling stations in the Nagura Estuary.

–20 °C until analysis. The measurements were taken as in STRICKLAND and PARSONS (1972).

3) Analysis of heavy metal concentrations of suspended particulate matter

The residues on millipore filters were used for the measurements of heavy metals in the suspended particulate matter. The quality of the residues was not examined at this time. Both the filters and the residues on them were heated to the boiling point in 1 ml of HNO_3 and 3 ml of HCl for 25 min. After drying completely, the contents were dissolved in 4N HNO_3 and analysed by Atomic Absorption Spectrophotometry as adopted to water samples.

4) Collection and analysis of sediment sample

Sediments were collected at six sites at low tide level. In addition to Stations 5, 8, 9, 11, and 12 for water samples, Station 12', located close to St. 12 was added. The features of St. 12 and 12' were very different from each other. St. 12' seemed to be in a rather reduced condition having a black colour and a strong smell of H_2S . The top 5 cm of the sediments were collected in plastic tube samplers and used for the analysis of heavy metals. Some recognizable foreign matters such as shells and algae were excluded before the samples were homogenized in a mortar. They were then processed in the same way as the particulate matters above. After being completely decomposed, everything was filtered through acid-washed filter papers and washed thoroughly with redistilled water followed by HNO_3 . Both of the filtrates were combined to measure the heavy metal concentrations.

No sediment samples were taken from stations 1, 2, 3, 4, 6, 7, 10, 13, and 14 mainly because of the difficulty of getting them, for the bottom consisted of corals or sand.

Results and Discussions

In order to understand the mixing of river and oceanic water in the Nagura Estuary, the salinities at each station at sampling time, measured by CHAEN (1981), are shown in Fig. 2. At both tidal levels, St. 7 through St. 1 had rather consistent salinity values indicating that these seven sites accepted less or no influence of fresh water. A decrease of salinity of varying degrees was observed at St. 13 and 14 at high water level, and St. 13 through St. 8 at low water level, respectively. The degree of the salinity depended on the distance from the river mouth.

The heavy metal concentrations in filtered water samples are indicated in Fig. 3. No significant disparities were observed on copper and iron among different sampling sites and tidal levels. The concentrations of zinc and nickel, however, differed according to tidal levels and generally trended to be higher at the oceanic stations. No recognizable differences for manganese was observed in those samples from St. 1–12. Its concentrations at St. 13 at low tide and St. 13 and 14 at high tide were conspicuously higher,

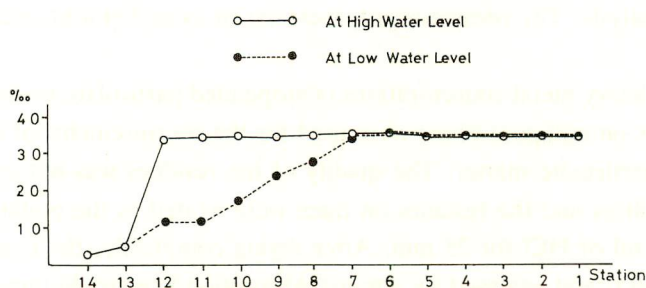


Fig. 2. Changes of salinities at sampling stations (by Chaen).

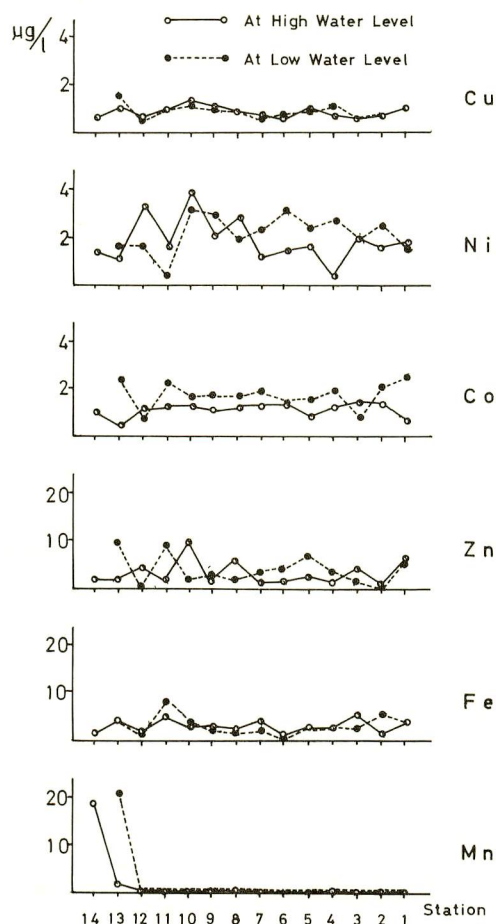


Fig. 3. Heavy metal concentrations in filtered water.

suggesting that the supply of this metal in soluble form is from the river. When heavy metal concentrations obtained here are compared with those in the coastal areas of Japan (INOUE, 1974; INOUE, 1977), copper, cobalt, and zinc are very similar. Manganese and nickel showed far less amount.

In Fig. 4 and Fig. 5 the concentrations of phosphate and silicate measured both at low and high tide levels are displayed. These two inorganic nutrients were observed to be supplied in a large amount from the river. The amount estimated from the results was $0.8 \mu\text{g-at P/l}$ and $70 \mu\text{g-at Si/l}$. These amounts were confirmed by other measurements of the concentrations of these nutrients on the fresh water samples obtained at ebbing and flooding tides which are not shown here. The amounts of the nutrients were at ordinary levels for the unpolluted shore water which could sustain enough the growth of phytoplankton population. For the total and better understanding of the primary production around the estuary, another nutrients, such as inorganic nitrogen, chlorophyll and water soluble vitamins would be required to be studied.

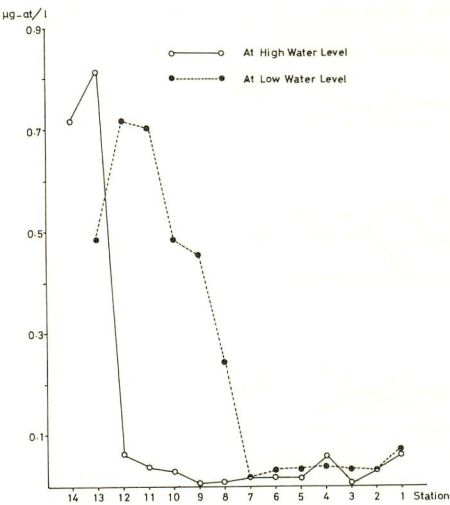


Fig. 4. Phosphate-P concentrations.

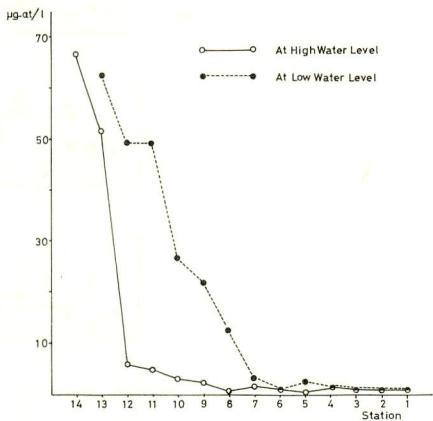


Fig. 5. Silicate-Si concentrations.

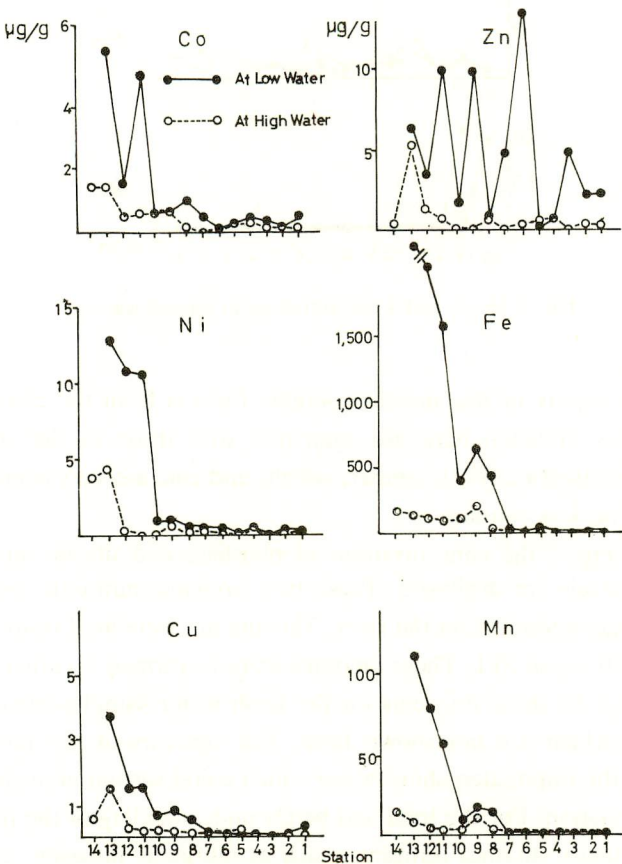


Fig. 6. Heavy metal contents in the suspended particulate matters.

The suspended particulate matter samples were analysed by using the residues on the millipore filters through which the water samples were passed. The results are shown in Fig. 6. From the results obtained by the analysis of manganese contents at low tide, combined with those values for the soluble fraction in Fig. 2, it was calculated that nearly 30 % of the total Mn supplied through the river water existed in particulate matters. The particulate manganese, however, decreased rapidly at the oceanic stations changing its form to a soluble or ionic one. A similar process was recognized at high tide exhibiting a clear decrease above those salinities of 34.5 ‰. These remarkable changes were observed also in nickel, iron, and copper. Such a sudden change noticed at the river mouth stations was conspicuous. The difference between two neighbouring stations were more apparent in samples taken at low tide. Further examination of the particulate matter of each water sample is needed to fully explain the processes.

Fig. 7 indicates the metal concentrations in the sediments. The analysis was done mainly on the samples taken at the river stations. The concentrations of each metal per dried matters were; 8–18 $\mu\text{g/g}$ for Zn; 2,000–7,000 $\mu\text{g/g}$ for Fe; 3–22 $\mu\text{g/g}$ for Mn; 2–4 $\mu\text{g/g}$ for Cu; 3–15 $\mu\text{g/g}$ for Ni and 2–12 $\mu\text{g/g}$ for Co respectively. Some metals such as Ni and Co were found to be higher in off-shore samples than river samples. To the contrary Zn and Fe decreased from upstream to the bay. These differences were probably due to the different absorption characteristics of each metal to particulate matters and use by living organisms. In Table 1 and 2 the correlation coefficients between metal concentrations in the sediments and particulate matters are indicated. Rather high nega-

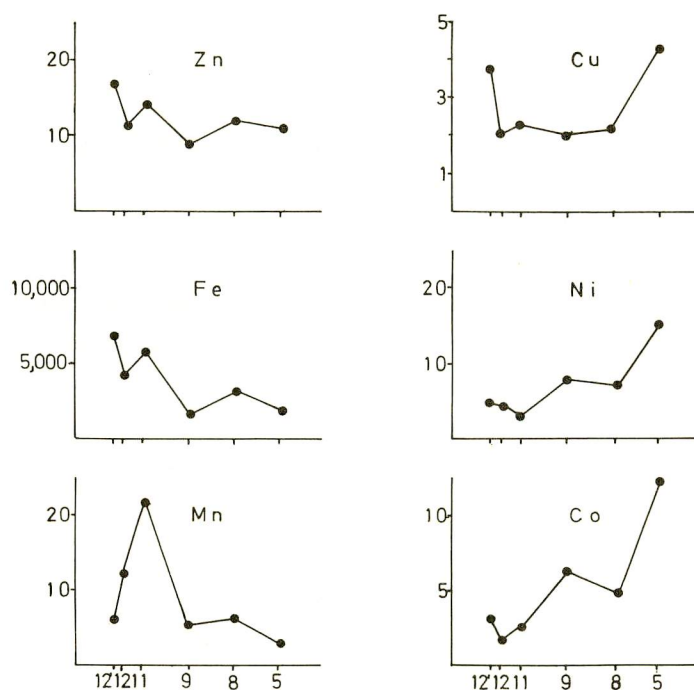


Fig. 7. Heavy metal contents in the sediments.

Table 1 Correlation among heavy metal contents in the sediments

	Cu	Ni	Co	Zn	Fe	Mn
Cu		0.64	0.66	0.44	0.10	-0.47
Ni			0.98	-0.22	-0.66	-0.65
Co				-0.23	-0.65	-0.61
Zn					0.85	0.26
Fe						0.52
Mn						

Table 2 Correlation among heavy metal contents in particulate matters

	Cu	Ni	Co	Zn	Fe	Mn
Cu		0.89	0.88	0.44	0.93	0.92
Ni			0.90	0.43	0.82	0.95
Co				0.44	0.84	0.86
Zn					0.34	0.38
Fe						0.94
Mn						

tive correlations were obtained between Ni and Fe, Ni and Mn, Co and Fe, and Co and Mn in the sediment concentrations, for reasons not yet understood. The manganese concentrations at St. 11 and 12 were exceptionally high and this was attributed to the reductive character of the sediments at these stations.

Estuary, a transitional region from fresh water to oceanic water, plays an important and peculiar role in aquatic ecosystem. The processes there, however, are complicated, and further studies on unplutted estuary were desired to understand the biological and chemical processes occurring in this region.

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