CHAPTER IV

DISCUSSION AND CONCLUSION

4.1 Reproducibility and Reliability of the Results.

Since this study was undertaken using samples of the natural

occurrence, the reproducibility and the reliability of the results are

seemingly more affected by variables which operate in the system

underinvestigation than the choice of the techniques used. Such variables

are sample collection date, level and location of the collection, salinity

and pH.

In this study, samples were collected twice, in October and

December 1979 at and near the Tha Chin River estuary. Although the two

sampling times were only two months apart, they had a significant

difference in salinity since in December fresh water runoff from the up

river was much less than normal whereas the amount of the direct drainage

of rain water preceeded the first sampling time, was exceptionally high.

Hence, samples from the first sampling had lower salinity and were

different in both chemical speciation and quantity of metals of interest

from the second sampling samples.

Difference in sampling sites which stretched from inner river to

the river mount causes a great difference in salinity owing to difference

in the degree of mixing of sea water with river water and also in the

chemical speciation. At the same station but different level, difference

in salinity can be expected since the mixing process is not homogeneous, sea water which is heavier. will flow under the fresh water. It is interesting to see the trend of the concentration dependent on salinity of abundant ions in sea water as shown in Fig. 5.1. The concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} increase with increasing of salinity while HCO_3^- and CO_3^{2-} concentrations are unchanged. Consequently, the ionic strength as well as chemical speciation of metals of each sample vary with salinity. Tables 3.15 and 3.16 show the influence of salinity on the percentage chemical speciation of cadmium lead and copper.

4.2 Chemical Speciation Model for Cadmium, Lead and Copper

Chemical speciation model for cadmium, lead and copper in water has been worked out by assumming that only Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^- and OH^- form complexes with metals ions of interest. The quantities of these anions in each sample were determined and included in the calculation for the percentage chemical speciation of cadmium, lead and copper. Results are shown in Tables 3.15 and 3.16 from which it is evident that cadmium ion is strongly associated with chloride ion. The predominant species are $CdCl^+$ $CdCl_2$, $CdCl_3$, CdOHCl including $Cd(OH)_2$ and Cd^{2+}. Chloro-complexes of cadmium ion were also found by Zirino and Yamamoto (27) and Dyrssen and Wedborg (33) in similar studies to this work, to predominate in open sea water of 35% salinity. Fortunately that chloro-complexes of cadmium is not harmful to organisms such as grass shrimp (19). It is interesting to observe from Tables 3.15 and 3.16 that the percentage of free cadmium ion which is the most toxic species vary from 17.35 to 59.95 % at salinity ranging from 26.95 to 3.02 %. Since the figures
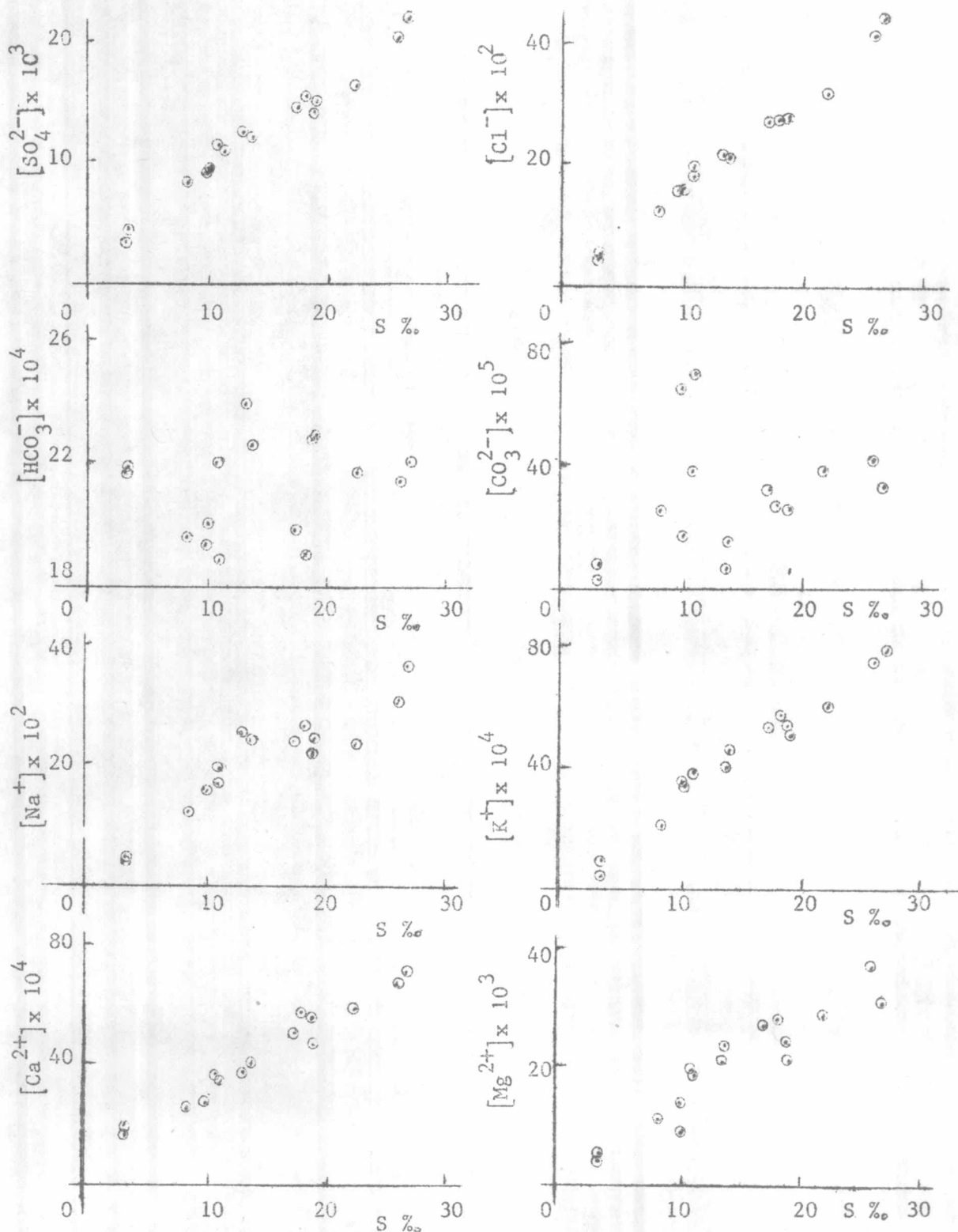
Figure 4.1 Relationship of $[Cl^-]$, $[SO_4^{2-}]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[Na^+]$, $[K^+]$, $[Ca^{2+}]$ and $[Mg^{2+}]$ with salinity of sample

represent Cd^{2+} content relate reciprocally with chloride ion concentrations or salinity, it can be concluded unambigously that river water should contain more Cd^{2+} than sea water.

The predominant species of lead are found to be Pb^{2+}, $PbOH^{+}$, $PbCl^{+}$, $PbHCO_3^{+}$, $Pb(OH)_2$ and PbOHCl. By examining Tables 3.15 and 3.16, 23.52 to 40.51% of lead species are $PbOH^{+}$ and 18.88 to 52.21% are Pb^{2+}. It is also found that in river water the lower is the salinity, the higher is the percentage of Pb^{2+}.

Results presented in the mentioned two tables also reveal the fact that almost all of copper species exist in the form of $Cu(OH)_2$ with only small amount of $CuCO_3$, $CuOH^{+}$, CuOHCl and Cu^{2+}. It should be aware however that for copper, not only copper free ion but also $Cu(OH)_n$ can equally cause mortality of organisms in water (14,18). Hence, the high percentage of $Cu(OH)_2$ in the samples should be regarded as a bad sign for the survival of aquatic life. Unlike cadmium and lead, the speciation of copper species is influenced more by the alkalinity and the pH of the samples than by the salinity (Tables 3.15 and 3.16).

This chemical speciation model is applicable if the assumption that in the Tha Chin River only certain inorganic anions can effectively interact with the cations concerned is true. Though the assumption is not groundless results from DPASV in Tables 3.7-3.12 are worth considering At natural pH, cadmium, lead and copper ion concentrations are all lower than those determined at pH below. There are two explanations, one is due to Duinker and Kramer (58) who had observed a similar effect of pH on the concentrations of metal species using DPASV. They concluded that at

natural pH all inorganic metal complexes in the sample were non labile

and detectable but as the pH was lowered by acidification, the labile

fraction was increased due to the dissolved organic metal complexes.

The second group, Batley and Florence (52) seemed to think slightly

different. They proposed that both inorganic and organic complexes of

metals could be found labile as well as non-labile regardless of pH.

Though it is difficult to judge which explanation is right, their

explanations can both be applied to the discrepancies found in this work

in the percentages of cadmium, lead and copper ions (at natural pH) obtained

by DPASV and those from calculations which were used in the computation

of the chemical speciation. While the latter confined its consideration

only to the complexation of Cd^{2+}, Pb^{2+} and Cu^{2+} to Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}

and OH^-, the former measured those species as well as those resulting from,

for example metals complexed with organic ligands. These ligands can

easily enter the river from domestic discharges but cannot be equally

easily detected and controlled. This is the reason why results from DPASV

were deliberately not used in the computation of the chemical speciation.

It was intended to use such results as an indicator of the possible

presence of other ligands than those included in the calculations.

4.3 Conclusion

From the present study, it can be concluded that the amount of

free cadmium and lead ions increases with decreasing of salinity, while

that of Cu^{2+} and $Cu(OH)_2$ depends on pH of the sample. The levels of

labile and non-labile or bound complexes in each sample vary from one

sample to the others depending on the amount of unaccounted organic ligands. The proposed chemical speciation model for the complexation of cadmium, lead and copper can at least be used to indicate the extent of the formation of the toxic forms of metals. Included in the suggested speciation are metal ions and inorganic anion–metal complexes. A more complete model can be developed by taking into account organic ligands. This is by no means an easy task.