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**THE POSSIBLE CHANGES IN ORGANO-METAL COMPLEXES ON COASTAL SUSPENDED PARTICULATE
MATTER DURING EXPOSURE TO RAINFALL**

by

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CONTENTS

	Page
Abstract	1
I. Introduction	1
II. Materials and Methods	2
III. Results	3
IV. Discussion	4
Acknowledgements	5
References	6

ABSTRACT

The investigation aimed to assess the possible effect of rainfall on heavy metal levels in suspended particulate matters (SPM) around the sea of Pun Wa Peninsula during August-November, 1981. SPM samples were trapped in 3-liter jars and were analysed for heavy metal levels in SPM loads. Similar SPM samples were collected and reacted with filtered rainwater for 48 hours as the rain water treated SPM prior to heavy metal analysis. The results show the concentration ranges for cadmium, copper, lead and zinc to be 1.80-2.40, 13.20-19.80, 28.20-55.00 and 201.00-252.00 $\mu\text{g/g}$ dry SPM load respectively. After treatment with rain water, the levels in all heavy metals decreased 13.4-29.8% due to the desorption of metal from organo-metal complex under lower pH values. Zn was the exception as it varied greatly over time. In contrast, the levels in heavy metals in sediments were relatively lower than those in SPM.

I. INTRODUCTION

The experiment was conducted in the sea around Pun Wa Peninsula which is located on the southern coast of Phuket Island where the offshore water meets the southern flow of coastal water during falling tides and northern flow during rising tides (Charoenlaph, 1982, Yasaki and Jantarapagdee, 1982, Limpsaichol, 1984). The sea on the east coast of this peninsula appeared rough during the northeast monsoon and alternatively calm during the southwest monsoon. The coastal water was rather turbid due to the relatively high level of suspended particulate matter (SPM). Apparently it was mainly generated from the two mangrove forests nearby, namely Ao Nam Bor and Ao Chalong on the southeast and southwest coasts of the island respectively, together with mining discharges, resuspension of clay particles

and sewage from Phuket town. The resulting SPM consists of a relatively high level of organic compounds associated with clay and siliceous and calcareous components from remineralized phytoplankton cells (Khanna and Stevenson, 1962, Tyler, 1972, Brown and Holley, 1982, UNEP, 1983). The contained organic component has been shown to be capable of actively chelating some minerals in sea water, especially heavy metals to form an organo-metal complex (Rashid and Leonard, 1973). The metals in complexes are not available for combination with sulphides, hydroxides, carbonates, etc. to form insoluble salts but keep the complexed metal in solution (Dissanayake, 1983). Thus, relatively high heavy metal concentrations were confined to such complexes and were distributed away by currents and tidal dispersion. Such behaviour of heavy metals has already been described in aquatic

systems (Donard, et al. 1983). Finally, they would gradually settle in some coastal regions where tidal action was weak and conditions favoured sedimentation (Chareonlaph, 1982).

The aim of this study was to investigate the possible dissolution of chelated metals such as Cd, Cu, Pb and Zn from the organo-metal complex into its surrounding water during the heavy rainfall which may last for several days. Under such circumstances, cation exchange processes may predominate between the SPM-Water interface.

II. MATERIALS AND METHODS

Samples of suspended particulate matter (SPM) were collected monthly at 3 stations; station A, B and C during August-November, 1981. Sediment samples were also collected on a transect of station C (Fig. 1).

SPM collection: Four 3 litre jars were attached with a pole which was securely fixed at the substrate. The jars were located about 1 m above the bottom substrate, to avoid substrate resuspension of previously settled particles, they were left for about one week to allow adequate settlement of SPM in the jars. All the samples were taken to the laboratory and left standing over night for complete settlement. One litre of sea water was siphoned out from the jar, and replaced with one litre of clean, filtered rain water. The treatment with rain water was carried out over 48 hours with occasionally stirring with a fresh replacement of rainwater after 24 hours. Such procedure to simulate the prolonged exposure to heavy rainfall for a couple of days. The 48 hours treated SPM was dried at 100°C over night prior to heavy metal and organic matter analysis. Four SPM samples were also collected which were not treated with rain water, the overlying sea water was siphoned

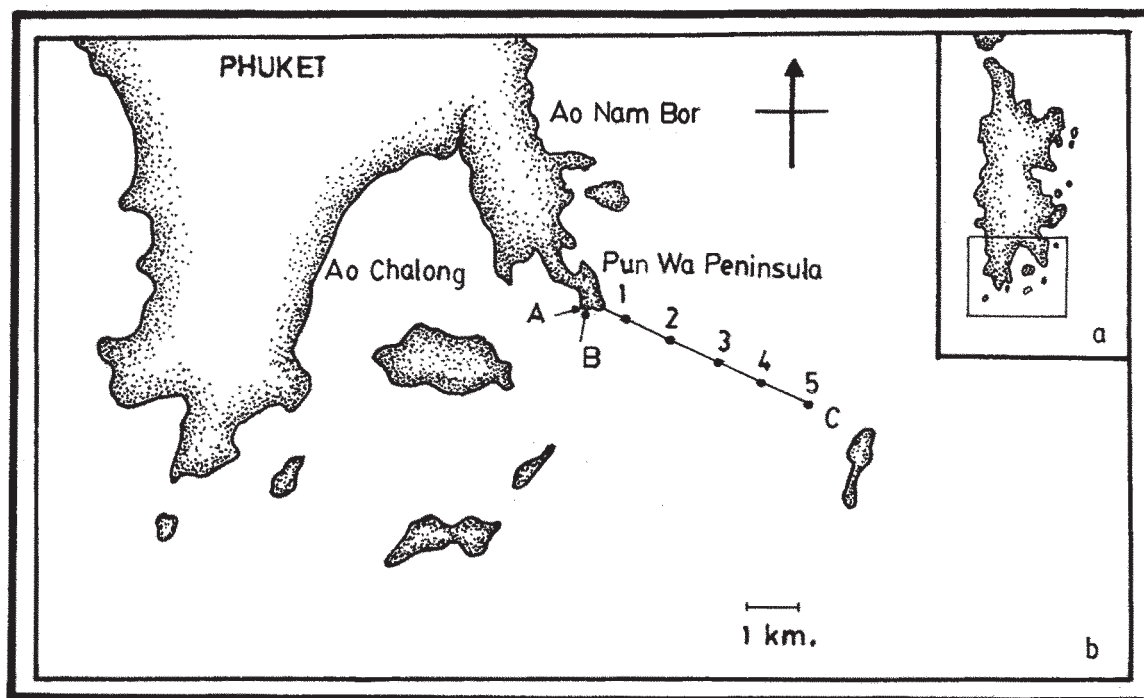


Fig. 1. (a) Phuket Island, Thailand, insert showing Pun Wa Peninsula (lat. $7^{\circ} 47' 55''$, long. $98^{\circ} 24' 45''$)
(b) Enlarged map of the Pun Wa Peninsula showing sampling localities: A, B and C and site number of locality C.

out as far as possible, and then the SPM was dried as untreated SPM prior to heavy metal and organic matter analysis. About 1 liter of subsurface sea water (1 m) was filtered with a membrane filter (0.45 μ) and particulates so retained were dried at 100°C over night for SPM load (mg/l). The substrate sediments were also taken by Vanveen grab at 400 m from shore and every 1 km along a transect to 5 km offshore. They were dried at 100°C for 24 hours and ground and sieved through 0.5 mm mesh size prior to heavy metal and organic analysis.

Heavy metal analysis:

Approximately 0.5 g of sediment and SPM samples were weighed and digested with HNO₃-H₂O₂ in the proportion of 10:3 by volume (Krishnamurty, et al., 1976). The levels of heavy metals were measured with an atomic absorption

spectrophotometer, Perkin-Elmer model 372. The metal concentrations were compared and calibrated with the standard reference samples from Denmark.

Organic fraction analysis:

Sediment and SPM samples were analysed by wet oxidation with K₂CrO₄-H₂SO₄ and back titration with ammonium ferrous sulfate solution (HMSO, 1973).

III. RESULTS

The results of SPM load, heavy metals and organic fraction did not show any significant difference ($P > 0.05$) between stations and times and thus they are presented in terms of mean value with standard deviation in fig. 2(a-d).

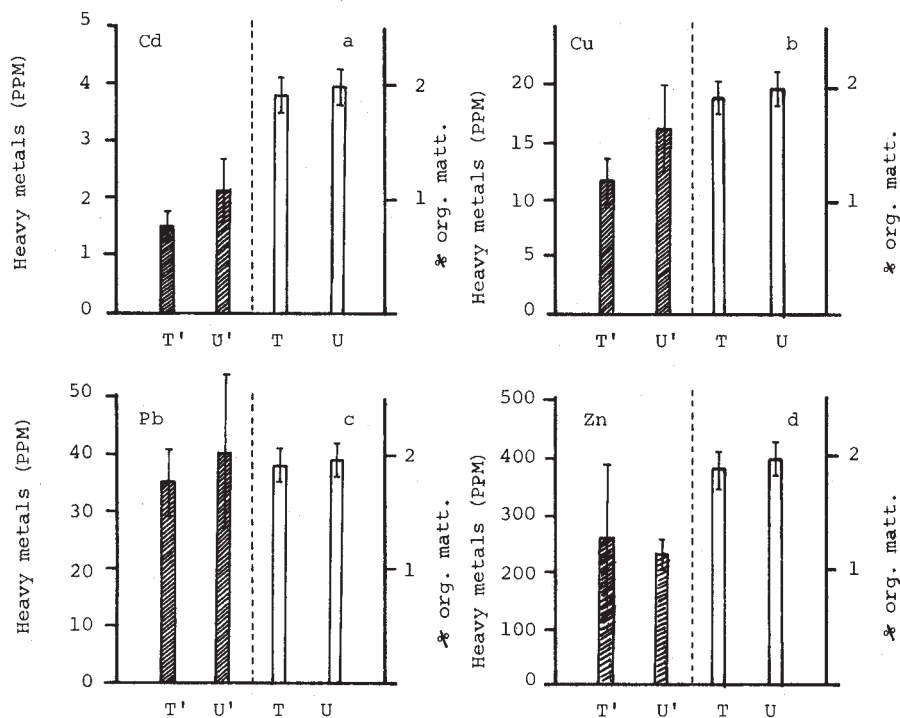


Fig. 2. (a-d) Heavy metals in rain water treated and untreated SPM are presented in shadow bars and denoted as T' and U' respectively. The rainwater treated and untreated organic fraction of SPM are presented in blank bars and are denoted as T and U respectively.

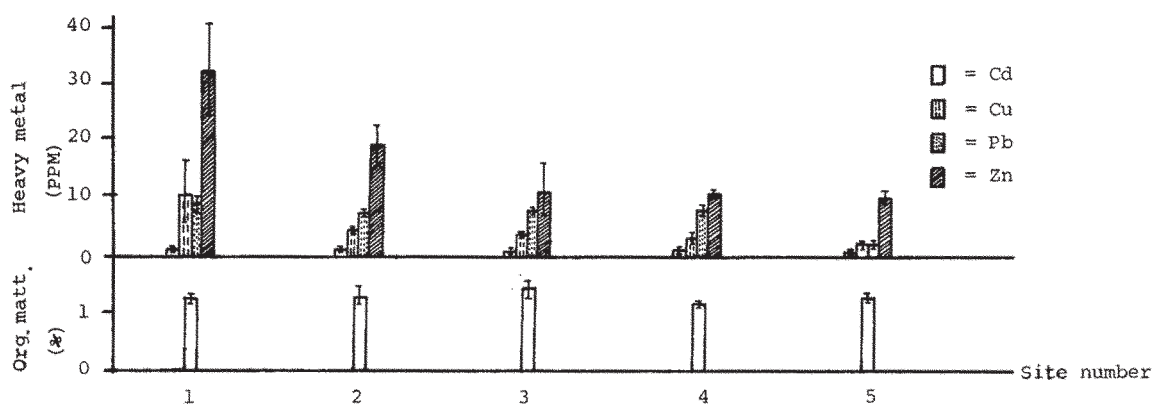


Fig. 3. The variations in levels of heavy metals $\mu\text{g/g}$ dry sediment and organic matter % in sediments along a seaward transect at sampling locality C.

The heavy metals and organic fraction incorporated in sediments are presented in fig. 3.

The SPM load of 28.8 ± 3.5 (25.2-32.1) mg/l consisted of 1.97 ± 0.16 (1.80-2.13)% of organic matter capable of chelating metals in seawater of pH value 8.2. Cadmium showed the lowest concentration in comparison with zinc, which was relatively variable, i.e. 2.11 ± 0.30 (1.80-2.40) and 228.00 ± 25.00 (201.00-252.00) $\mu\text{g/g}$ dry SPM respectively. The rain water treated SPM showed lower levels of metal and organic fraction with relatively low pH values of 7.5. The levels of Cd, Cu, Pb and organic fraction were apparently decreased 29.8%, 26.9%, 13.4% and 5.58% respectively. The levels of metals in both treated and untreated SPM of station A showed no significant difference ($P > 0.05$) from station B. However, the level of Zn in treated SPM was clearly unpredictable with great variations of 268.00 ± 107.00 (139.00-378.00) $\mu\text{g/g}$ dry SPM.

The organic loads in sediments of all sites along the transect were similar with values of 1.30 ± 0.08 (1.17-1.41)%. In contrast, all metal levels appeared to decrease offshore along the transect and were much lower than those values in SPM. The level of Zn in sediment particularly revealed a considerable decrease from near shore to offshore sites, they were 32.30 ± 8.20 and 10.20 ± 1.06 $\mu\text{g/g}$ dry sediment respectively.

IV. DISCUSSION

The results of heavy metals and organic load in SPM shown insignificant differences ($P > 0.05$) between stations and times because of a wide standard deviation on the significant tests.

The relatively high levels in Cd, Pb, Cu and Zn in SPM resemble the high levels of those metals in particulates of Tasmania Bay, Australia (Cooper and Langlois, 1982). Such high metal levels were confirmed with the results obtained by Brown and Holley (1982), who studied a nearby location to the present study site and reported that the levels of Cu, Fe and Zn in particulates were relatively high when compared with those in the mudflat sediments. However, their results appear higher than the present result; this is probably due to the stirred up sea condition during their sampling period in the southwest monsoon (July-August). The present sampling period was during mostly calm sea in pre-northeast monsoon (August-November). It has been observed that during a stirred up sea, more particulates were presented in sea water resulting relatively high levels in metals recorded.

The relatively high levels in metals incorporated in SPM and sediments can be explained by the formation of a complex between metal ions and humic components which may be incorporated on the surface of organic or clay particles through the cation exchange or chelation processes (Rasid,

1969, Tyler, 1972). However, great variations in Zn was considered to be due to the fact that its stability in forming complexes tends to be much weaker than other metals (Dharmvanij and Van den Berg, 1983). Special interest was concentrated on the humic components which were capable of enhancing insoluble salts, for instance, metal-sulfate, carbonate, etc. resulting in high metal levels incorporated in the humic fraction (Rashid and Leonard, 1973). It seems that heavy metals were closely chelated more specifically to the humic fraction rather than the total organic matter. The humic component consists of various functional groups, i.e. carboxyl, phenolic hydroxyl, carbonyl, amino groups and others. The stability of these functional groups are crucially important as they depend upon the surrounding water conditions (Rashid, 1972). Considering the present results, it was thought that the capability of cation exchange processes was altered by a drop in pH on mixing with rain water. This effect was predominant during a prolonged period of heavy rainfall. Cadmium was generally undetectable in rain water whereas Cu, Pb and Zn were lower than 0.10, 0.02 and 0.47 mg/l respectively with a pH around 7 (Department of Health, 1983). It would be likely that in a shallow coastal or estuarine sea, the pH of the surface layer may drop occasionally from the normal value of 8.2 to 7.5 encouraging active cation exchange processes to occur in the functional groups particularly those incorporated H ions in carboxyl and phenolic hydroxyl groups (Kononova, 1966). Normally the phenolic hydroxyl group (although present in relatively small concentrations in humic component in sea water) presented a high capability of cation exchange in sea water or alkali solution (Sieven et. al. 1965). It was also found that such capability of cation exchange diminished when the pH dropped to about 7.2-7.7. In turn, the carboxyl group, which is present in humic components, becomes active in cation exchange processes (Sieven et al., 1968; Rashid and King, 1970). Consequently, the release of metal from

the organo-metal complex in the SPM was probably due to the desorption of metal on the carboxyl group when the SPM was treated with rain water resulting a drop in pH of the water.

The drop in heavy metal levels in sediments further offshore was in contrast to the relatively uniform distribution in organic matter offshore. It could be seen that the factors involved were rather complicated. However, it was considered that the nearshore site was favourable for sedimentation resulting in the settlement of SPM together with other suspended solids. Resuspension likely occurred occasionally when the water movement became stronger. When such processes reoccured and were repeated over time relatively high levels of metals in nearshore sediment were recorded. At the further offshore sites, the marked drop in metal levels indicated increasing distance from the source and the inactive sedimentation processes. Those previously sedimented humic and other organic compounds may be affected by microbial processes. As a result the anaerobic condition was produced together with a lowering of the redox state would cause a release of metal ions from chelating in organo-metal complex (Kamp-Nielsen, 1973). In the present study, the levels of metals (Cd, Cu, Pb and Zn) in sediments were also compatible with those metal levels previously recorded in the offshore sediments of the Andaman sea (Hungspreugs and Yuangthong, 1982).

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