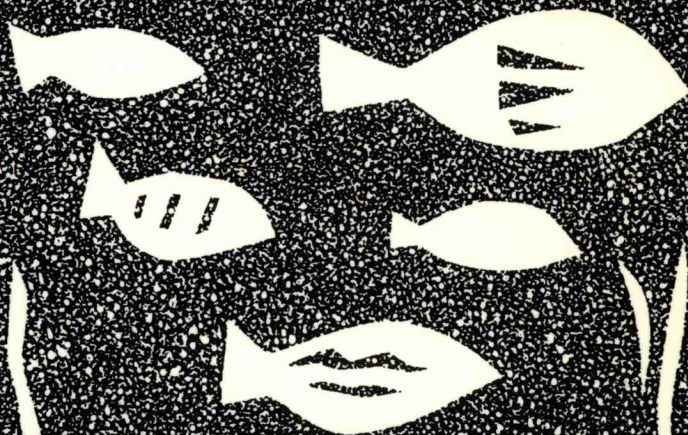
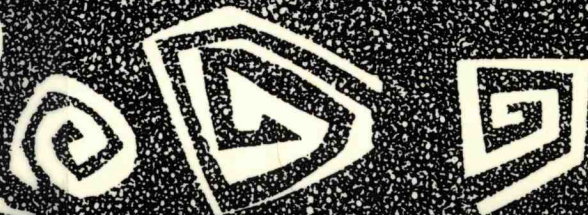


# Marine Ecosystem Enclosed Experiments

Proceedings of a symposium held  
in Beijing, People's Republic  
of China, 9-14 May 1987



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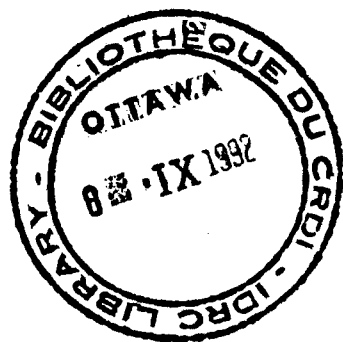


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Editor: C.S. Wong and P.J. Harrison



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## Abstract

This symposium on marine ecosystem enclosed experiments (MEEE) consists of nine review papers that describe various types of ecosystem enclosures and a series of papers resulting from enclosure experiments in Xiamen, People's Republic of China, and Saanich Inlet, BC, Canada. The reviews on types of enclosures include benthic enclosures for rocky and sandy shores and the effects of pollutants (primarily hydrocarbons) on bacteria, macroalgae, and invertebrates. The pelagic enclosures were used to study the control of phytoplankton blooms, the uptake and release of dissolved organic substances, and the effects of pesticides on freshwater ecosystems.

Six enclosure experiments were conducted in China and Canada from 1986–87. Some of these experiments examined the effects of contaminated sediments, primarily heavy metals, on bacteria, phytoplankton, and zooplankton and the pathways and fates of these heavy metals in the seawater. Other experiments studied the chemistry and biological effects of chemically dispersed oil.

## Résumé

Ce compte rendu du symposium sur les expériences faites en écosystèmes marins comprend neuf communications qui décrivent les écosystèmes retenus et les expériences faites à Xiamen en République populaire de Chine et à Saanich Inlet, C.-B., au Canada. Les communications portent, notamment, sur les écosystèmes benthiques des littoraux rocheux et sablonneux et sur les effets des polluants (surtout les hydrocarbures) sur les bactéries, les grandes algues et les invertébrés. Les expériences sur le contrôle des brutales pullulations ("blooms") du phytoplancton furent menées dans les écosystèmes pélagiques, ainsi que l'absorption et le dégagement des substances organiques dissoutes et les effets des pesticides sur les écosystèmes d'eau douce.

Six expériences ont été faites en Chine et au Canada entre 1983 et 1987. Certaines ont porté sur les effets des sédiments contaminés, principalement par des métaux lourds, sur les bactéries, le phytoplancton et le zooplancton et sur le cheminement et le sort de ces métaux lourds dans l'eau salée. D'autres expériences portaient sur la chimie et les effets biologiques du pétrole dispersé chimiquement.

## Resumen

Este simposio sobre Experimentos Marinos en Ecosistemas Cerrados (MEEE) consistió en nueve trabajos de análisis que describen varios tipos de enclaustramientos ecosistémicos y una serie de trabajos derivados de experimentos con estos enclaustramientos en Xiamen, República Popular de China, y en Saanich Inlet, Canadá. Los estudios incluyen enclaustramientos bentónicos para costas rocosas y arenosas, y los efectos de los contaminantes (fundamentalmente hidrocarburos) sobre bacterias, macroalgas e invertebrados. Los enclaustramientos pelágicos se utilizaron para estudiar el control de la reproducción del fitoplancton, la ingestión y expulsión de sustancias orgánicas disueltas y los efectos de pesticidas en los ecosistemas de agua dulce.

Se realizaron seis experimentos en ecosistemas cerrados en China y Canadá, de 1983 a 1987. Algunos de estos experimentos examinaron los efectos que ejercen los sedimentos contaminados, fundamentalmente los metales pesados, sobre bacterias, fitoplancton y zooplancton, y el ciclo y destino final de estos metales pesados en el agua de mar. Otros experimentos estudiaron los efectos químicos y biológicos de los aceites crudos dispersados por medios químicos.



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# Distribution of Heavy Metals in Xiamen Seawater and in the MEEE Enclosures

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*Distributions of dissolved, and weakly and strongly bound particulate heavy metals in surface seawater from Xiamen Bay and Jiulongjiang Estuary were determined in a clean laboratory. It was found that most previous measurements, particularly of Pb and Zn, from the same areas have been overestimated.*

*In Xiamen Bay seawater, Co, Fe, Ni, Pb, and Zn existed mainly in the particulate phase, whereas Cd and Cu existed mainly in the dissolved phase. The partition coefficient ( $K_d$ ) of each metal between the particulate and dissolved phases followed the order  $Fe > Co > Pb > Zn > Ni > Cu > Cd$ . In surface seawater from Jiulongjiang Estuary, dissolved Co, Cu, Pb, and Zn behaved conservatively, whereas Cd, Fe, and Ni did not. More than 90% of the riverborne suspended matter and its associated heavy metals settled in the estuary.*

*Advantages and limitations of the Marine Ecosystem Enclosure Experiment (MEEE) in studying the behaviour of heavy metals are discussed based on a comparison of field data with those obtained from the enclosure experiment.*

Since the mid-1970s, improvements on analyses of trace metals in seawater have revealed probable errors in previous measurements (Boyle and Edmond 1975; Wong et al. 1977; Kanamori 1981). Table 1 lists changes in the concentrations of trace metals measured in seawater over the last 40 years. Improvements in analytical techniques are the result of employing contaminant-free methods that provide a more realistic picture of background levels and a better distribution of various trace metals in the ocean (Moore 1978; Bruland 1980; Boyle et al. 1981; Bruland and Franks 1983; Flegal and Patterson 1983; Magnusson and Westerlund 1983).

In 1985, a clean laboratory was built in the Third Institute of Oceanography incorporating technology transferred from the Institute of Ocean Sciences in Canada. The laboratory makes it possible to monitor the concentration and distribution of trace metals in regional seawaters. Xiamen Bay connects with Jiulongjiang Estuary and faces the Taiwan Strait to the east. The annual flow of Jiulongjiang River exceeds  $11.7 \times 10^9 \text{ cm}^3$  and carries more than  $2.5 \times 10^6 \text{ t}$  of silt and clay to the estuarine area.

This paper presents the results of studies on the concentration and distribution of

Table 1. Changes in the concentration ( $\mu\text{g/kg}$ ) of trace metals in open ocean water over the last 40 years.

Reference	Cu	Pb	Zn	Cd	Co	Ni	Fe
Sverdrup (1942)	10	4	5	—	—	—	—
Goldberg (1965)	3	0.03	10	0.11	0.1	2	10
Riley (1975)	0.5	0.03	4.9	0.1	0.05	1.7	2
Kanamori (1981)	0.02–0.3	0.02–0.06	0.01–0.6	0.01–0.1	0.005	0.2–0.6	0.2–0.5
Bruland (1980)							
Surface	0.034	0.001	0.006	0.0003	0.007	0.146	0.008
Deep	0.130	0.0045	0.390	0.117	0.002	0.566	0.045

Table 2. Trace metal analysis of seawater (standard sample NASS-1) and blanks ( $\mu\text{g}\cdot\text{kg}^{-1}$ ).

Values	Cu	Pb	Zn	Cd	Co	Ni	Fe
Reference	0.099±0.010	0.039±0.006	0.159±0.028	0.029±0.004	0.004±0.001	0.257±0.027	0.192±0.036
Measured	0.102	0.032	0.156	0.029	0.005	0.280	0.225
Analytical blank <sup>a</sup>	0.0060±0.0022	0.001±0.001	0.040±0.023	0.0014±0.003	0.001±0.001	0.015±0.005	0.007±0.020

<sup>a</sup>  $n = 10$ .

dissolved and particulate Cd, Co, Cu, Fe, Ni, Pb, and Zn in surface seawater of Xiamen Bay and Jiulongjiang Estuary. In addition, field data are compared with the behaviour of trace metals in enclosed seawater from the Xiamen Marine Ecosystem Enclosure Experiment (MEEE).

## Methods

The 1985 MEEE data used in this study came from two 10 m<sup>3</sup> control bags (Li et al. this volume). Samples for the in-situ data (Fig. 1) were collected in August of the same year. Stations 1 and 2 were situated northeast of Xiamen Island (East Bay) where the input of industrial wastes is relatively low. Stations 3–8 were located on the western side of Xiamen Island (West Bay) where the annual input of industrial and domestic wastes is about  $30 \times 10^6$  t. The other stations were situated within Jiulongjiang Estuary. Stations 9–11 were at the freshwater end, with salinities of less than 0.5‰; stations 24–26 were near the open sea (Outer Bay), with salinities greater than 30‰; and stations 12–23 were within the brackish area. Details of the sampling procedure are given in Li et al. (1987).

Each seawater sample was filtered through a 0.4- $\mu$ m Nuclepore membrane filter under low vacuum. The filtrate was complexed with ammonium 1-pyrrolidine dithiocarbamate/diethyl ammonium diethyl dithiocarbamate (APDC/DDDC), extracted with Freon-TF, back-extracted with dilute nitric acid, and then analyzed using a graphite furnace flameless atomic absorption spectrophotometry (GFAAS) for dissolved metals (Li et al. 1987). Particulate matter retained on the filter was extracted with 0.5 N HCl for 24 h and the dissolved portion was analyzed using GFAAS for weakly bound metals. The remaining undissolved portion was further digested with aqua regia and HF to determine the strongly bound metals.

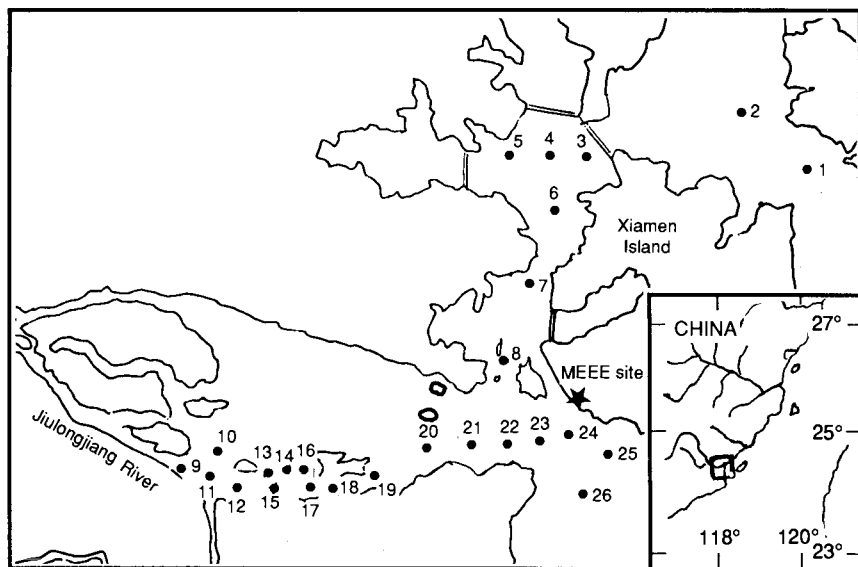


Fig. 1. Location of sampling stations (inset shows position of study area).

The results of the trace-metal analyses of the seawater standard and blank samples indicate that the analyses were reliable and that the blanks had very low levels of trace metals (Table 2).

## Results and discussion

### Concentration and distribution of dissolved metals

Characteristics of surface water from the Xiamen Bay area and concentrations of seven dissolved metals in the waters are presented in Table 3. All metal concentrations were fairly low. Regional variations were consistent with levels of pollution: the highest occurring in the West Bay and the lowest in the East Bay. The area including stations 3–8 was polluted by heavy metals, but at concentrations still within the ranges for coastal seawater. All values differed substantially from those reported earlier (Xu et al. 1986): i.e., before the clean laboratory procedure was used, Xu et al. (1986) could not detect any variation among the different regions. Compared with this study, their reported values for Pb and Zn were higher by two orders of magnitude, and Cu was four times higher; only the values for Cd were similar.

Changes in salinity, pH, and Eh were observed south of Xiamen Island at the mouth of Jiulongjiang River as fresh water mixes with seawater. There were corresponding variations in the speciation and concentration of heavy metals. Changes in the concentration of dissolved metals with salinity are shown in Fig. 2.

Dissolved Cu and Zn in the estuary behaved conservatively and their relations with salinity were

$$[1] \quad [Cu]_d = -0.015[S] + 0.79, (r = 0.95; n = 19)$$

$$[2] \quad [Zn]_d = -0.012[S] + 0.45, (r = 0.90; n = 18)$$

The concentrations of Co and Pb did not change significantly within the estuarine area, their values being  $0.016 \mu\text{g}\cdot\text{kg}^{-1}$  and  $0.008 \mu\text{g}\cdot\text{kg}^{-1}$  respectively.

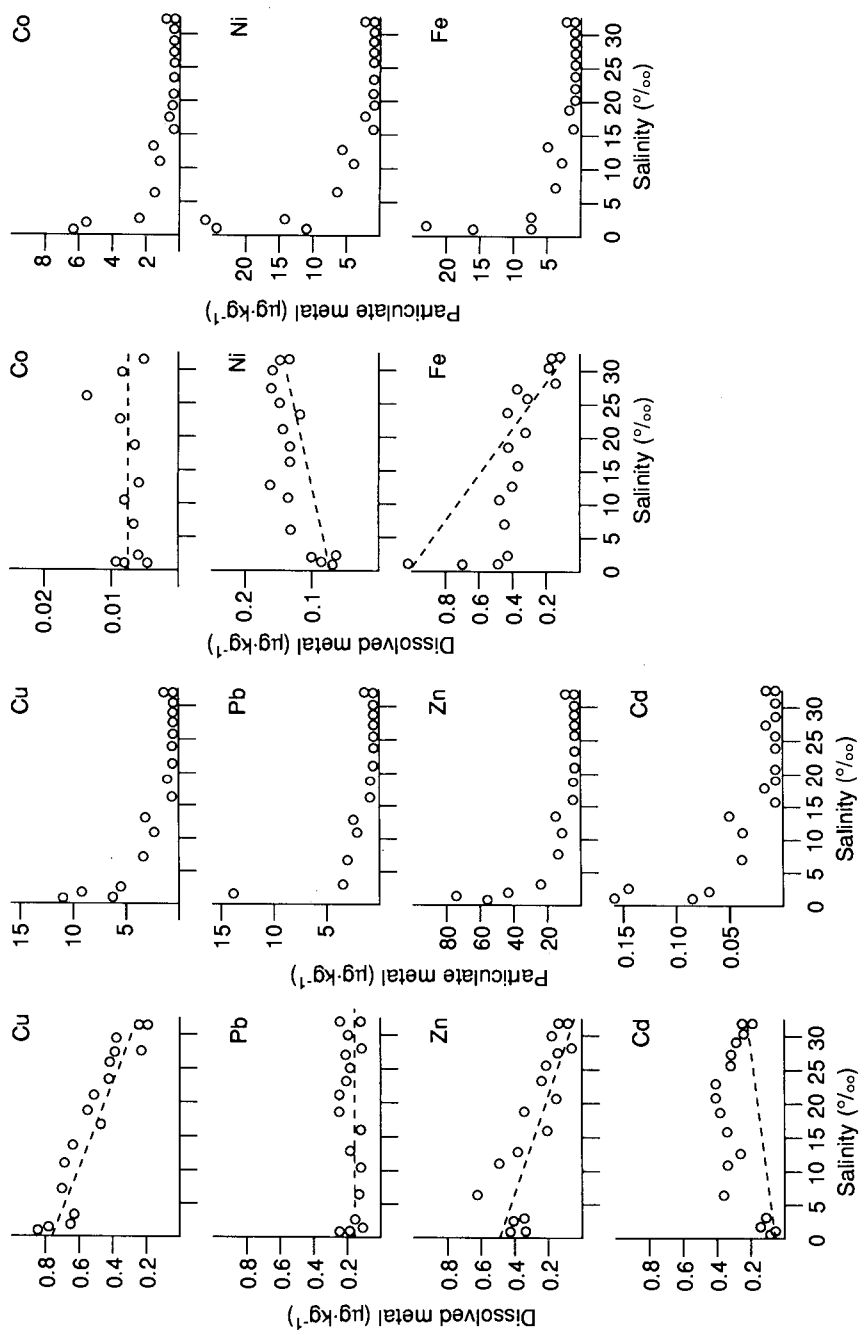
The concentrations of Cd at the freshwater end was about  $1.8 \text{ ng}\cdot\text{kg}^{-1}$ . Within the low salinity (<7‰) region, concentrations of Cd and Ni increased rapidly with increasing salinity — an order of magnitude for Cd and double for Ni. This indicated that with increases in chlorinity and the amount of cations, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$ , parts of the particulate Cd and Ni transferred to the dissolved phase. At pH 7, the concentration of dissolved Ni was about  $0.14 \mu\text{g}\cdot\text{kg}^{-1}$ , similar to that at the open sea end and with little variation in between. In the region with a salinity between 7 and 20‰, the concentration of dissolved Cd remained almost the same, indicating that particulate Cd was continuously transformed to the dissolved form. Beyond the region, where salinities were greater than 20‰, there was only a small amount of suspended particulates, and dissolved Cd also behaved conservatively, i.e.,

$$[3] \quad [Cd]_{d,S > 20} = -0.0021[S] + 0.084, (r = 0.90; n = 8).$$

In low-salinity water, dissolved Fe decreased sharply with increasing salinity. At a salinity of 2.5‰, the concentration of Fe was only half that measured in the fresh water. The decrease was probably caused by the precipitation of colloidal Fe as

Table 3. Physicochemical parameters and dissolved metal concentration for surface seawater from Xiamen Harbour.

Area	Station	Salinity (‰)	Temper- ature (°C)	pH	Total suspended matter (mg·kg <sup>-1</sup> )	Dissolved metals (μg·kg <sup>-1</sup> )						
						Cu	Pb	Zn	Cd	Co	Ni	Fe
Northeast Harbour	1-2	29.88	29.9	8.18	3.6	0.36	0.008	0.036	0.015	0.005	0.13	0.14
West Harbour	3-8	29.32	28.9	8.31	7.0	0.48	0.014	0.10	0.025	0.011	0.15	0.16
Entry to Estuary	9-11	0.31	30.2	7.48	103	0.81	0.017	0.47	0.0018	0.008	0.081	0.96
Middle of Estuary	12-23	0.5-29	30.5	7.5-8.3	300-7	—	—	—	—	—	—	—
Outside Harbour	24-26	29.85	28.5	8.35	6.3	0.30	0.014	0.087	0.020	0.010	0.14	0.14
Reported in 1982	—	—	—	—	—	1.6±1.1	2.7±2.6	7.2±5.8	0.25±0.020	—	—	—



**Fig. 2.** Correlation of dissolved metals and particulate metals in Jiulongjiang Estuary with salinity. The dashed lines represent theoretical dilution trends.



electrolytes in the water increased. For salinities greater than 12‰ and a pH greater than 8.1, dissolved Fe also behaved conservatively, i.e.,

$$[4] \quad [\text{Fe}]_{d,S>12} = -0.017[S] + 0.67, (r = 0.95; n = 9).$$

Because speciation of trace metals between dissolved and particulate phases varied greatly within the estuarine area, metal fluxes to the open sea should be computed using their effective input concentrations rather than their concentrations in river water (Boyle et al. 1982; Edmond et al. 1985). In this report, linear equations depicting the conservative behaviour of dissolved metals were extrapolated to their respective origins to obtain effective input concentrations ( $\mu\text{g}\cdot\text{kg}^{-1}$ ): Cd = 0.084, Co = 0.008, Cu = 0.79, Fe = 0.67, Ni = 0.14, Pb = 0.016, and Zn = 0.45.

### Concentration and distribution of particulate metals

In the various regions of Xiamen Bay, amounts of suspended matter were fairly similar. A close relationship could be established between the concentration of a given particulate metal and the total suspended matter (TSM).

Figure 3 shows the relationship between the relative amount of particulate metal in the water body and TSM. When TSM ranged from 3 to 10  $\text{mg}\cdot\text{kg}^{-1}$ , 90% of the particle-reactive elements, such as Co, Fe, and Pb (Santshi et al. 1980), and 70–90% of the Ni and Zn existed in their particulate forms; whereas most of the Cd and Cu existed in dissolved forms.

At the freshwater end of Jiulongjiang Estuary, TSM reached 300  $\text{mg}\cdot\text{kg}^{-1}$ . This value decreased with increasing salinity, dropping to 3–6  $\text{mg}\cdot\text{kg}^{-1}$  in the open-sea area (Fig. 4). The decrease was probably caused by rapid flocculation and precipitation of particulates when predominantly negatively charged particles composed mainly of organic matter were mixed with strong electrolytic seawater. Changes in the concentration of particulate metals with salinity were similar to those of TSM with salinity (Fig. 2).

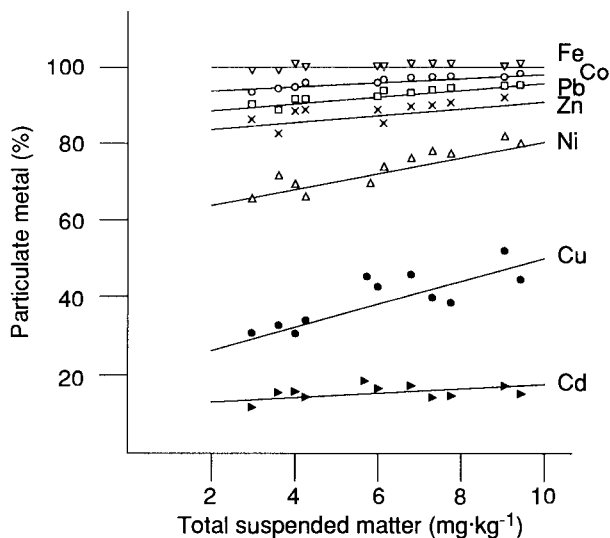
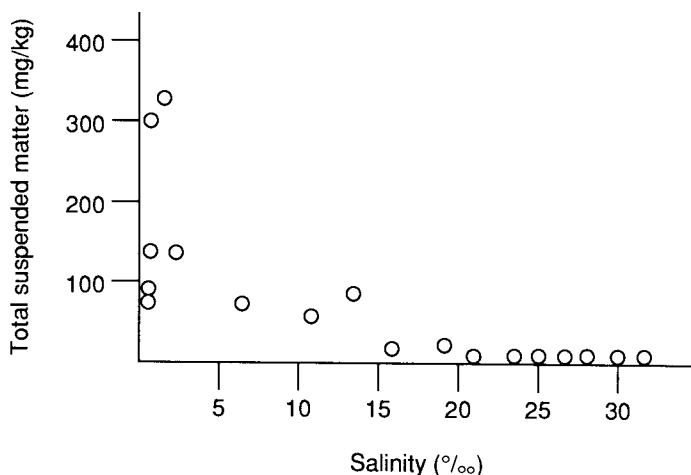


Fig. 3. Correlation between total suspended matter and the percentage of particulate metals in surface seawater from Xiamen Bay.



**Fig. 4.** Correlation between total suspended matter in surface seawater from Jiulongjiang Estuary.

Table 4 lists the relative amount of particulate metals observed at various salinities. In low-salinity water, 80% of the metals were in their particulate forms. At a salinity of 20‰, TSM was reduced to less than 5% of that in fresh water and there were some changes in the percentages of particulate metals. Now, Cd and Cu existed mainly in dissolved forms; there were slight decreases in the relative amount of particulate Ni and Zn; and 90% of Fe, Co, and Pb still existed in their particulate forms. Similar results were observed in high-salinity water.

As river water flows out to the coastal sea area, remaining particulate metals are precipitated further by various processes. Hence, the impact of particulate metals is limited to the estuarine and coastal areas, with only tiny amounts of these metals being carried to the open sea (Martin and Whitfield 1983).

## Comparison between field and MEEE enclosure data

The utility of the experimental ecosystem enclosure depends on how realistically the enclosure simulates field conditions and how effectively results observed can be applied to the sea area under consideration. In this study, data from the MEEE control bag were compared with in-situ sampling data (Table 5). For

Table 4. Changes in relative amounts (%) of particulate metals with salinity in the estuarine area.

Salinity (‰)	Total suspended matter (mg·kg <sup>-1</sup> )	% Particulate metal <sup>a</sup>						
		Cu	Pb	Zn	Cd	Co	Ni	Fe
0.5	159	85	99	98	97	99	99	99.99
20	7.5	40	94	85	15	95	79	99.97
30	6.1	42	93	87	16	97	75	99.96

<sup>a</sup> % Particulate metal =  $[M_p / (M_p + M_d)] \times 100$  where  $M_p$  = particulate metal and  $M_d$  = dissolved metal.

Table 5. Dissolved metal concentrations and partition coefficients ( $K_d$ )<sup>a</sup> in MEEE control bags and in Xiamen Harbour.

Source	Dissolved metal						
	Cu	Pb	Zn	Cd	Co	Ni	Fe
Bag C1 Bag C2 Harbour <sup>b</sup>	0.41±0.06	0.022±0.008	Dissolved metals (µg·kg <sup>-1</sup> )				
	0.42±0.04	0.017±0.007	0.20±0.05	0.032±0.004	0.019±0.011	0.25±0.07	0.22±0.11
	0.35±0.10	0.017±0.009	0.24±0.12	0.036±0.006	0.020±0.011	0.25±0.06	0.20±0.10
			0.10±0.05	0.022±0.003	0.008±0.002	0.14±0.02	0.14±0.02
Bag C1 Bag C2 Harbour <sup>b</sup>			log <i>K<sub>d</sub></i>				
	4.94	6.33	5.69	4.32	6.02	5.29	8.37
	4.91	6.48	5.73	4.25	5.94	5.42	8.11
	4.99	6.41	6.15	4.55	6.44	5.57	8.54

<sup>a</sup>  $K_d$  ( $\mu\text{g} \cdot \text{g}^{-1}$  dry suspended matter)/( $\mu\text{g} \cdot \text{kg}^{-1}$  seawater)  $\times 10^3$ .

<sup>b</sup> Average of stations 6–8 and 24–26.

dissolved metals, concentrations measured in the enclosures and in the field were the same order of magnitude. MEEE values were slightly higher, but not more than 1.1 times the concentrations observed in the field. Concentrations in the two control bags varied by less than  $\pm 25\%$ . These differences were probably caused by slight contamination during the experiment or as a result of sampling at different times.

Partition coefficients,  $K_d$ , in natural seawater and in the enclosures were the same magnitude, with slightly higher values being measured in the enclosures, probably because of higher concentrations of dissolved metals. In the controls,  $K_d$  for each metal decreased in the order Fe, Pb, Co, Zn, Ni, Cu, and Cd. As in the field survey, Cd and Cu existed mainly in their dissolved phases, whereas the other metals existed in their particulate phases.

Less than 2% of the total metal in the bag adheres to the bag wall (Li, J. et al. ("Pathways ..."), this volume). Thus, it is feasible to use MEEE enclosures to study the biogeochemistry of trace metals in coastal seawater. It should be possible to integrate the transfer model of metals and the dynamic transfer model in the enclosure to construct a transfer model of heavy metals applicable to field conditions.

Some limitations exist in applying enclosure results to the natural sea. For example, the hydrodynamics and conditions for water exchange in enclosures differ from those in the sea; the sediment–water interface is lacking in the enclosure; the plastic bag drifts easily; and observation time is limited. It is hoped that an improved enclosure will be designed in the near future to assist researchers in their studies of chemical oceanography.

## Conclusions

In monitoring marine trace metals, the accuracy of the data depends on eliminating contamination during sampling and analysis.

Concentrations of dissolved and particulate metals (Cd, Co, Cu, Fe, Ni, Pb, and Zn) in surface water from Xiamen Bay were within the normal ranges of coastal seawater, but with the West Bay slightly polluted by heavy metals. Cd and Cu existed mainly in dissolved forms, whereas the other metals existed in their particulate forms. There was good correlation between the concentration of particulate metals and TSM.

When fresh water from Jiulongjiang River mixed with seawater, the conservative behaviour of dissolved Cu and Zn increased with increasing salinity. Concentrations of Co and Pb followed the simple conservative rule of mixing. In the cases of Cd, Fe, and Ni, their behaviour was nonconservative, i.e., concentrations of Cd and Ni increased in low-salinity water, and Fe transferred from the dissolved phase to the particulate phase. In high-salinity water, all of the metals behaved conservatively. More than 90% of the suspended particulates carried by the river were deposited in the estuary.

The MEEE enclosure is an excellent tool for studying the biogeochemistry of trace metals. Concentrations of dissolved metals within the enclosures differed from those from the field by less than 1.1 times, and relative deviations between values from the two enclosures were within  $\pm 25\%$ .

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- Boyle, E.A., Edmond, J.M. 1975. Copper in surface waters south of New Zealand. *Nature*, 253, 107–109.
- Boyle, E.A., Husted, S.S., Jones, S.P. 1981. On the distribution of copper, nickel and cadmium in the surface waters of the North Atlantic and Pacific Ocean. *Journal of Geophysical Research*, 86 (C9), 8 048–8 066.
- Boyle, E.A., Husted, S.S., Grant, B. 1982. The chemical mass balance of the Amazon plume: II — Copper, nickel and cadmium. *Deep-Sea Research*, 29, 1 355–1 364.
- Bruland, K.W. 1980. Oceanographic distributions of cadmium, zinc, nickel and copper in the North Pacific. *Earth and Planetary Science Letters*, 47, 176–198.
- Bruland, K.W., Franks, R.P. 1983. Mn, Ni, Cu, Zn and Cd in the western North Atlantic. *In* Wong, C.S., Boyle, E., Bruland, K.W., Burton, J.D., Goldberg, E.D., ed., *Trace metals in sea water*. Plenum Press, New York, NY, USA. 395–414.
- Edmond, J.M., Spivack, A., Grant, B.C., Hu, M., Chen, Z., Chen, S., Zeng, X. 1985. Chemical dynamics of the Changjiang estuary. *Continental Shelf Research*, 4, 17–36.
- Flegal, A.R., Patterson, C.C. 1983. Vertical concentration profiles of lead in the central Pacific at 15°N and 20°S. *Earth and Planetary Science Letters*, 64, 19–32.
- Goldberg, E.D. 1965. Minor elements in sea water. *In* Riley, J.P., Skirrow, G., ed., *Chemical oceanography*, volume 1 (1st ed.). Academic Press, London, UK. 163–196.
- Kanamori, S. 1981. The species of trace elements in seawater. *Chemical Sphere*, 35 (4), 18–27. [In Japanese.]
- Li, J., Zhen, Z., Du, R., Zhang, G. 1987. The concentrations and distribution of trace metals in the surface waters of Xiamen Harbour. *Acta Oceanographica Sinica*, 6, 380–388.
- Magnusson, B., Westerlund, S. 1983. Trace metal levels in sea water from the Skagerrak and the Kattegat. *In* Wong, C.S., Boyle, E., Bruland, K.W., Burton, J.D., Goldberg, E.D., ed., *Trace metals in sea water*. Plenum Press, New York, NY, USA. 467–474.
- Martin, J.M., Whitfield, M. 1983. The significance of the river input of chemical elements to the ocean. *In* Wong, C.S., Boyle, E., Bruland, K.W., Burton, J.D., Goldberg, E.D., ed., *Trace metals in sea water*. Plenum Press, New York, NY, USA. 265–296.
- Moore, R.M. 1978. The distribution of dissolved copper in the eastern Atlantic Ocean. *Earth and Planetary Science Letters*, 41, 461–468.
- Riley, J.P., Skirrow, G., ed. 1975. *Chemical oceanography*, volume 1 (2nd ed.). Academic Press, London, UK.
- Santshi, P.H., Li, Y.H., Carson, S. 1980. The fate of trace metals in Narragansett Bay, Rhode Island: radiotracer experiment in microcosms. *Estuarine and Coastal Marine Science*, 10, 635–654.
- Sverdrup, J.U., Johnson, M.W., Fleming, R.H. 1942. *The oceans: their physics, chemistry, and general biology*. Prentice-Hall, Englewood Cliffs, NJ, USA.

- Wong, C.S., Cretney, W.J., Piuze, J., Christensen, P., Berrang, P.G. 1977. Clean laboratory methods to achieve contaminant-free processing and determination of ultra-trace samples in marine environmental studies. National Bureau of Statistics, Special Publication 464.
- Xu, Q., Huang, J., Yang, C., Huang, M., Chen, W., Lin, Y., Lin, L. 1986. Studies on the contents of metals and some other pollutants in sea water, sediments and organisms in the sea area near Xiamen Harbour. *Marine Environmental Science*, 5, 69–76. [In Chinese.]