

Migration of Trace Heavy Metals at the Sea Water/Sediment Interface

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Migration of Trace Heavy Metals at the Sea Water/Sediment Interface

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Abstract Migration behavior of some trace heavy metals such as Co(II), Cu(II), Mn(II) and Zn(II) at the sea water/sediment interface was investigated by tank experiments. The sea water which was doped with these metal ions (ppb to ppm levels) allowed to contact with the raw-, ignited- and autoclaved-marine sediments and the change of the concentration of each metal was traced at definite time intervals. At the end of the experiments, a core sample of the sediment was taken and analyzed for each metal in every 1 mm thick segment. On the other hand, the surface sediment was submitted to partial extraction with various kinds of reagents to estimate the chemical species of the metals captured in the sediment. While every metal ion was quickly adsorbed on surface of the raw sediment, a concentration gradient from surface to bottom of the water phase occurred in the ignited sediment system. The migration of manganese to the sediment phase was assumed to be concerned with bacterial activity in the sediment. Copper and zinc seemed to be adsorbed very quickly onto some fine sediment particles by the formation of organometallic complexes with some organic materials existing in the sediments. Cobalt migrated relatively fast downward within the sediment phase after its deposition.

Introduction

The trace metals carried to the ocean from a number of sources through streams or meteoric precipitation are subjected to chemical and biological actions, and finally sink and deposit in the sediment through various pathways. A number of studies concerned with removal mechanism of various trace elements from sea water have been performed and it has been revealed that the removal of them is related to some surface phenomena on suspended particulates such as hydrous metal oxides¹⁾, clay or detrital organic substances²⁾.

The behavior of these trace metals in ocean has been explained by applying several models^{3), 4)}. Craig suggested the scavenging model in which especially clay minerals play an important role for migration of the dissolved heavy metals⁵⁾. Tsunogai et al.^{6), 7)} proposed the settling model as a removal mechanism. In their model, the vertical trans-

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port of the trace metals is principally achieved by giant particles whose diameter is usually larger than a few tens μm . While, Bacon et al.⁸⁾ suggested the importance of scavenging process at sea water/sediment interface.

From the view of adsorption and redissolution of trace metals according to their liquid-solid equilibrium, the sea water/sediment interface seems to possess very attractive feature^{9), 10)}. The purpose of this study is to clarify the behavior of trace metals at the sea water/sediment interface. A model of an environment near the sea water/sediment interface was set by means of a tank experiment in laboratory and the concentration change of some trace metals in sea water was followed under several conditions. Furthermore, in order to obtain the information on the chemical forms of trace metals transferred into sediment, a partial extraction procedure¹¹⁾ was applied.

Experimental

Samples. Marine sediment was collected by dredging from 20 m depth at Tsukumo Bay, Noto Peninsula. The sediment was sieved through a stainless steel sieve (42 mesh) in sea water in order to avoid air contact, then was stored in a refrigerator at 4°C. This sediment was greenish dark gray silt. The fundamental data on the original sediment are shown in Table 1. Surface sea water was also collected at Tsukumo Bay and stored in a refrigerator at 4°C.

Table 1. Properties of original sediment

Content of water	65.3%
Ignition loss	35.2%
TOC	4.86%
TON	0.43%
Particle size	<42 mesh

Reagents. Manganese(II) and zinc(II) standard solutions were prepared by dissolving their pure metals in hydrochloric acid to make a solution of 1,000 ppm. Copper metal was dissolved in nitric acid and evaporated to dryness, then the residue was dissolved in 1 M hydrochloric acid to make 1,000 ppm solution. Cobalt(II) standard solution was prepared by dissolving cobalt chloride 6 hydrate of guaranteed reagent grade in deionized water and standardized gravimetrically as cobalt(III) oxide. All chemicals used were of guaranteed reagent grade. The radioactive tracer, Co-60, was purchased from the Radiochemical Centre, Amersham, England, whose specific activity was 84 mCi mg^{-1} .

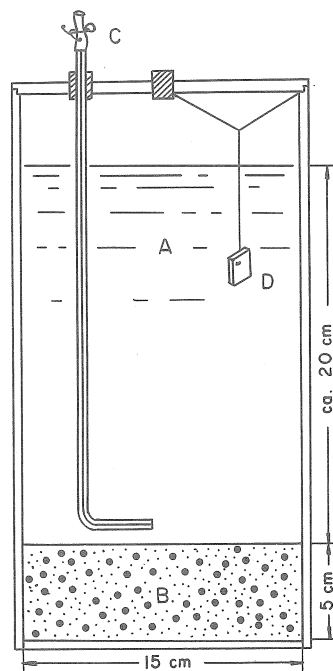


Fig. 1. Experimental setup. A : sea water, B : sediment, C : glass capillary tube, D : small plate of resin

Apparatus. A setup for tank experiment is shown in Fig. 1. A cylindrical container of 15 cm in diameter and 30 cm in height was made of acrylic acid resin of 2 mm in thickness. The tank was tightly covered with an acrylic resin plate of 5 mm in thickness. Several small holes were made on the plate, through one of which a glass capillary tube (inner diameter, 1 mm) was mounted for sampling bottom water at 1 cm over the surface of the sediment. The bottom water was sampled by a pipet connected with the capillary tube. Other holes were for pipetting the surface water and for air supply to the system.

Atomic absorption measurements were done with a Hitachi 170-50 type. Gamma activity measurements were performed with a Kobe Kogyo STL-200 well-type scintillation counter, and X-ray diffraction was measured with Rigaku Denki Geiger Flex. A MOM Derivatograph TYP-D-102, a Hitachi-Horiba M-50 pH meter and Iwaki KM shaker were used.

Pretreatment of sediment sample. Ignited sediment- - - The raw sediment was ignited at 550°C for 24 hrs to remove any organic substances completely. This was reddish brown color. X-ray diffraction analysis for the powder samples showed some peaks corresponding to montmorillonite, calcite and dolomite in the patterns of both raw and ignited sediments. Therefore, it seems that the mineral composition is little affected by ignition. Moreover, the two kinds of samples were submitted to differential thermoanalysis. In the derivatogram of the raw sediment, there was an exothermal peak at 200-500°C corresponding to combustion of organic substances. However, this peak disappeared in the derivatogram of the ignited one. This means that complete decomposition of organic substances in the raw sediment was achieved by simple ignition.

Autoclaved sediment- - - The raw sediment was placed in a beaker which was covered with watch glass, and the beaker was put into an autoclave to sterilized at 1.2 atm. and 100°C for 30 min.

All the sea water samples used were filtered through 0.45 μm Millipore filter and a part of the filtered sea water was irradiated with 15 W mercury lamp (Toshiba) for about 100 hrs to decompose organic substances in sea water.

Procedure for tank experiments. Known amounts of heavy metal ions (manganese, copper, cobalt and zinc) were added to 3 ℓ of the sea water and pH was adjusted to 7.7 ± 0.1 with 1 M sodium carbonate solution. After the sea water was allowed to stand for 2-5 days at 25°C, it was filtered through 0.45 μm Millipore filter, then carefully poured into a cylindrical container which contained a sediment sample in 5 cm thickness as shown in Fig. 1. In order to cause no disturbance in the sediment on adding sea water, a circular thin film of plastics which was made many small holes and hung with thin nylon strings, was slowly lifted according to elevation of surface of the water. The containers were placed in a thermostat regulated at $25 \pm 1^\circ\text{C}$.

At intervals, the bottom water sample was taken from a layer of 1 cm above the surface of the sediment through the capillary tube (C). At the same time, the surface water sample was pipetted out from a layer of 1 cm below the water surface. By using a definite volume of the samples, the metal concentration was determined by γ -ray

counting for cobalt, or by atomic absorption spectrometry for manganese, copper, cobalt and zinc.

Finally, vertical distribution of metal ions in the water and sediment phases were measured after the period of 20-30 days. After siphoning off all water in the container, a core sample of the sediment was taken with a thin plastic tube, and was immediately frozen as it was. Then, the frozen core sample was cut into some segments in the order of depth. In the case of cobalt, γ -counting of each segment was measured. For the other metals, each segment was decomposed by heating with nitric acid-perchloric acid mixture (1 : 1 v/v) and after filtration the filtrate was submitted to atomic absorption spectrometry.

In order to estimate the adsorption of trace metals onto the container wall during the experiment, a small plate (D) of the same resin whose surface area was about 6 cm², was suspended in the sea water containing Co-60. After 30 days, the activity adsorbed onto the plate was counted and it was calculated that only 2% of the original activity was adsorbed on the container wall. Therefore, loss of metal ions from sea water was estimated to be negligible.

Besides, redissolution behavior of metals from the sediment phase was examined on converting the system from aerobic to anaerobic conditions. About 20 days later, when oxidation and consequently metal fixation were found to be fairly well advanced, the sample was transferred into a 50-ml syringe shown in Fig. 2. The sample was kept air-tight with rubber stopper, and was allowed to stand for some days at room temperature in the dark, so that the milieu changed becoming anaerobic. After ascertaining that the anaerobic condition was achieved, the water sample was taken from the syringe and analyzed.

Partial extraction procedure. At the end of the tank experiments, the surface sediment of about 2 mm thick was sucked into a syringe together with small amount of sea water, transferred in a polyethylene bottle and mixed well. An adequate amount of this sample was taken into a centrifuge tube and centrifuged at 3,500 rpm for 15 min to remove sea water and interstitial water. Washing of the sediment with about 15 ml of deionized water was carried out one time. Then, methanol-acetone mixture (1 : 1 v/v) was added to the sediment and the tube was shaken for 4-5 hrs. The extract was separated by centrifugation (3,500 rpm, 15 min) and evaporated to dryness on a hot plate. The contents were decomposed by heating with an acid mixture (HNO₃ + HClO₄, 1 : 1 v/v) and diluted with deionized water. The solution was submitted to atomic absorption measurements of metals.

Next, a definite amount of 0.5 M magnesium chloride solution was added to the

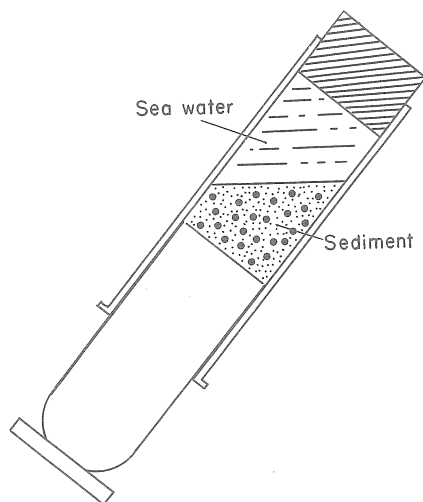


Fig. 2. Apparatus for air-shielded experiment.

sediment fraction resulted from methanol-acetone extraction and they were shaken for 4-5 hrs. After centrifugation, the concentration of metals in the supernatant was determined as same as described above. This procedure was repeated until no more leaching of metals from the sediment was observed. In the same way, the successive extraction of metals was carried out with 0.5 M sodium hydroxide solution, 0.01 M, 0.1 M, and 1 M hydrochloric acids. After these procedures, 10 ml of 1 M hydrochloric acid and 5 ml of 30% hydrogen peroxide were added to the residue and the mixture was heated in a boiling water bath. The supernatant was separated by centrifugation, followed by atomic absorption measurement. Then, the residue was transferred to a 30-ml Erlenmeyer flask with 5 ml of an acid mixture ($\text{HNO}_3 + \text{HClO}_4$) and heated until it becomes colorless. Finally, it was brought to dryness, and the residue was dissolved in 0.5 M nitric acid and filtered off. The filtrate was submitted to atomic absorption spectrometry.

Results and Discussion

In addition to the X-ray diffraction and the derivatographic analyses, adsorption isotherms of some trace metals were examined for the raw and ignited sediments. With respect to manganese, copper, cobalt and zinc, the adsorption isotherms are shown in Fig. 3. The adsorption of metals was found to increase in the order of $\text{Mn(II)} < \text{Co(II)} < \text{Zn(II)} < \text{Cu(II)}$. This order is corresponding to Irving-Williams order for the complex

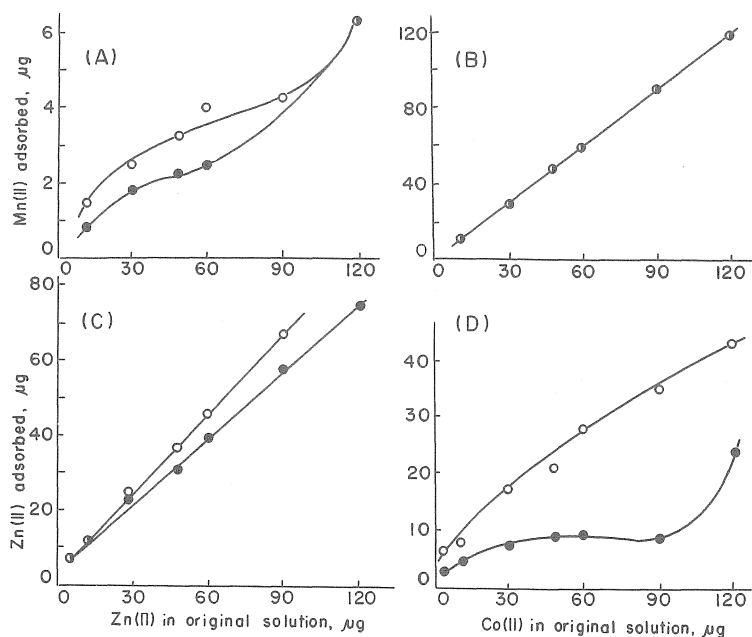


Fig. 3. Isotherms of (A) Mn (II), (B) Cu (II), (C) Zn (II) and (D) Co (II) adsorption by the raw and ignited sediments
(○) raw sediment, (●) ignited sediment

formation. Hence, the adsorption of these metals by the sediments is assumed to be related to the complex formation.

The isotherms for copper and zinc reveal the Henry-type adsorption for the raw and ignited sediments. On the other hand, that of cobalt seems to be Henry-type for the raw sediment and BET-type for the ignited one. This difference may be attributed to the existence of organic substances in the former sediment. The quantities of manganese adsorbed were only 5-7% of the initial content in both sediments.

Concentration change of trace metals in sea water phase. Fig. 4 shows the radioactivity change of Co-60 in aqueous phase for the raw and ignited sediment systems. In each system, UV-irradiated and unirradiated sea waters were used as aqueous phase. A remarkable difference in removal process of cobalt was observed in both cases. In the former system, at first the radioactivity in bottom layer decreased more rapidly than surface layer, but after 9 days the radioactivity in both surface and bottom layers became equal. On the other hand, in the ignited system, the radioactivity in surface water layer scarcely changed, although that in bottom layer decreased to about 28% of initial radioactivity. Furthermore, by comparing two curves, UV-irradiated and unirradiated, it is shown that in the raw sediment system for former case a little higher quantity of Co-60 was lost than the latter case. This suggests that some organic ligands in sea water was

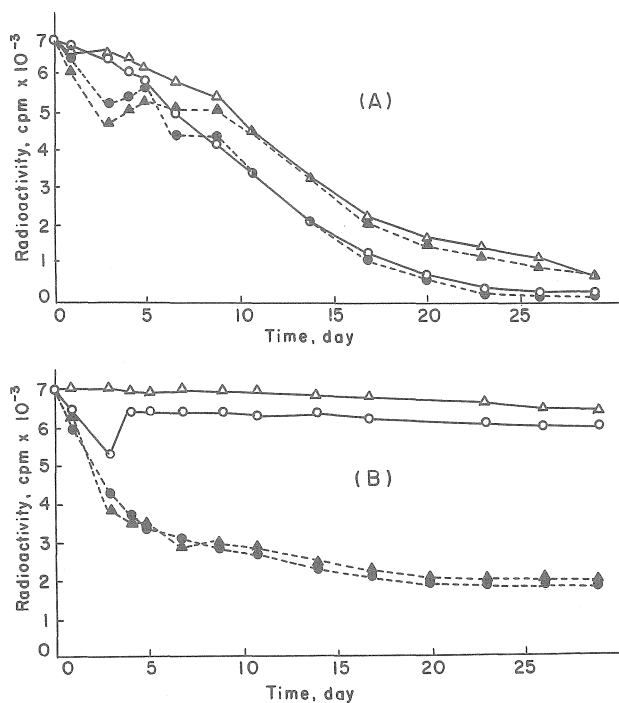


Fig. 4. Radioactivity change of Co-60 in aqueous phase.
 (A) raw sediment system, (B) ignited sediment system
 (O) UV-irradiated sea water, —○— surface
 (Δ) UV-unirradiated sea water ---●--- bottom

decomposed by UV-irradiation lowering resistability against the scavenging action for metals.

Fig. 5 shows vertical distribution of Co-60 in the water column after 30 days-standing for the ignited system. This profile indicates that the transfer of Co-60 into the sediment occurred in the neighborhood of the sea water/sediment interface.

When about 2 mg of non-radioactive cobalt (II) ion spiked with Co-60 tracer was added into the sea water, a similar concentration change of the element in the aqueous phase as shown in Fig. 4 (ppb level) was observed and the uniform distribution of the element in the aqueous phase appeared after standing for 7 days. Therefore, it may be concluded that the behavior of trace metals in ppb level can be evaluated from the results obtained by the experiments carried out in ppm level of metals. Furthermore, it was confirmed that concentration change of each metal in ppm level was negligibly small in the absence of the sediment throughout the experiment period under the same conditions as the tank experiment. Fig. 6 shows the concentration change of manganese, copper, cobalt and zinc for the raw and ignited sediment systems. As was observed in the Co-60 tracer experiment, an uniform distribution of each metal was established in the raw sediment

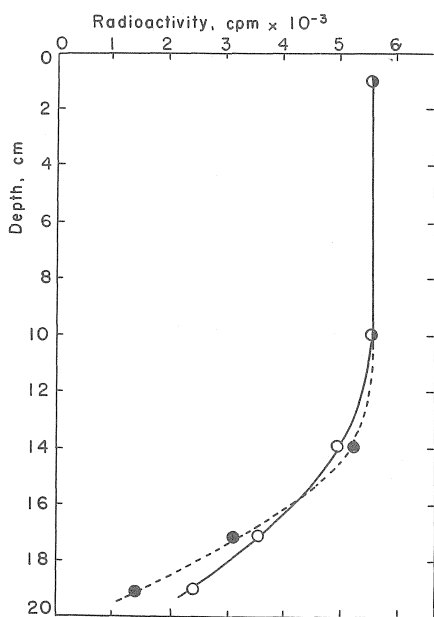


Fig. 5. Vertical distribution of Co-60 in aqueous phase after 30-days of contact with the ignited sediment.

—○— observed
 ---●--- calculated

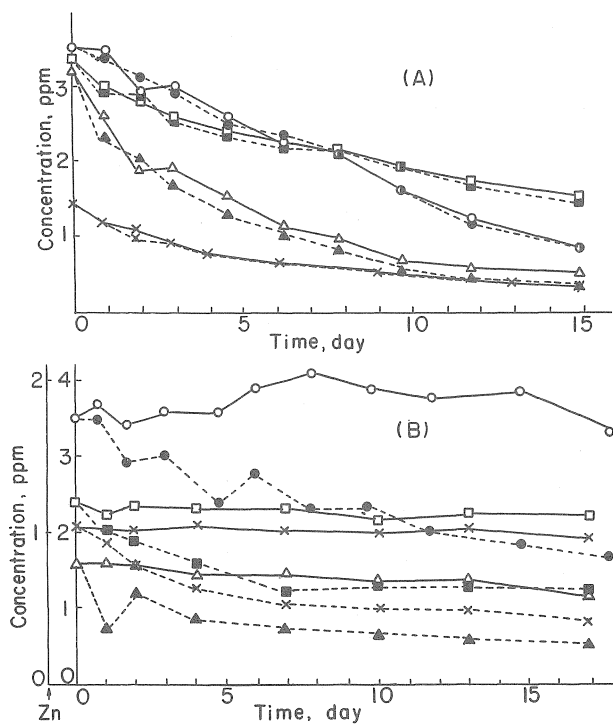


Fig. 6. Concentration change of Mn, Cu, Zn and Co in aqueous phase.

(A) raw sediment system, (B) ignited sediment system
 (○) Mn, (△) Cu, (×) Zn, (□) Co
 —○— surface, ---●--- bottom

system, while in the ignited sediment system a vertical gradient of concentration of metals appeared.

Fig. 7 shows a profile of the vertical distribution of the metals in the aqueous phase at the end of the experiments. This again indicates that the migration of the trace metals into the sediment is dominant at the sea water/sediment interface.

Various kinds of factors such as, the presence of particulate materials and some organic substances, the bacterial activity, and diffusion or convection effects were assumed to influence on the migration of the metals at water/sediment interface.

First, the influence of bacteria existing in the sediment was tested by using an autoclaved sediment. The concentration changes of manganese, copper and cobalt are shown in Fig. 8. The concentration of copper and cobalt decreased in the same manner as in the case of the raw sediment system. Therefore, it can be assumed that bacterial activity is not responsible for the uptake of these metals by the sediment. On the other hand, manganese again scarcely migrated into the sediment phase as it behaved in the experiment without sediment. In comparison of Fig. 8 with Fig. 6, it can be expected that deposition of manganese may be related to the bacterial activity in the sediment.

Next, in order to evaluate the effect of the organic substances in sea water on migration of the metals into the sediments, the experiment using the humic acid-doped sea water and the ignited sediment as a solid phase. The results obtained were not distinguishable from that shown in Fig. 6. This fact may suggest that the organic compounds such as humic acid in sea water give little effect on the removal of metals from the sea water. However, the rapid transfer of copper to the sediment may be partially due to co-deposition with the coagulated humic acid molecule in water phase.

Diffusion process of cobalt in sea water. Now let's consider the diffusion process of some chemical species in sea water. In the ignited sediment system, it is assumed that the

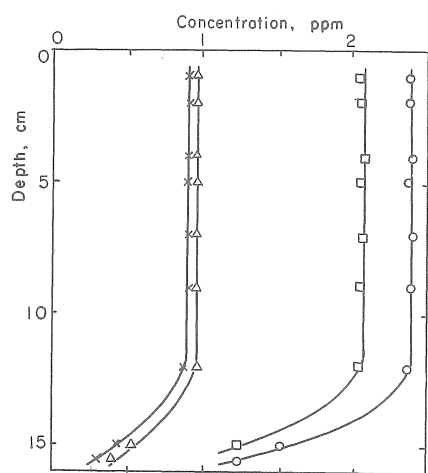


Fig. 7. Vertical distribution of Mn, Cu, Zn and Co in aqueous phase.
(○) Mn, (△) Cu, (×) Zn, (□) Co

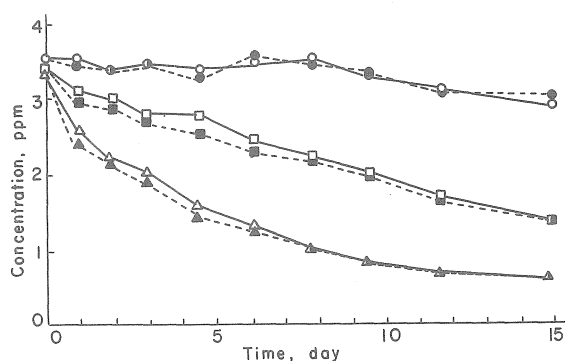


Fig. 8. Concentration change of Mn, Cu and Co in aqueous phase for the autoclaved sediment system.
(○) Mn, (△) Cu, (□) Co, —○— surface,
---●--- bottom

gradient of metal concentration occurred in water layer (Fig. 5) is attributed to a simple diffusion in laminar flow.

In general, Fick's second law is written as follows^{12, 13},

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where C is the concentration of metal, x is the distance from the surface of sediment and D is the diffusion coefficient. The solution of this equation can be put as

$$C_{(x,t)} = \frac{C_0}{\sqrt{\pi Dt}} \exp \left[-\frac{x^2}{4Dt} \right] \quad (2)$$

where C_0 is the initial concentration of the metal.

Here the rate-determining step is postulated to be the diffusion in sea water. According to this assumption, D is calculated by substituting the experimental data in the equation (2).

$$D = 1.2 \times 10^{-6} \text{ cm}^2/\text{sec}$$

The vertical distribution of Co-60 calculated by using this D value coincides with the observed one as shown in Fig. 5. Therefore, it can be concluded that the diffusion in laminar flow in water column is the most important process for the migration of metals in the ignited sediment system. On the other hand, in the cases of the raw and autoclaved sediment systems, it seems that the rate of diffusion is so fast and adsorption process may be the rate-determining step. Such diffusion process should be regarded as diffusion in turbulent flow which may be occurred in the aqueous phase by certain mechanism.

In fact, a convection current was visually observed by watching a movement of small resin particles which was matching in gravity with the sea water used and suspended in the aqueous phase. The particles sunk down to the bottom through the center of the water column, and then moved horizontally toward the wall of the container. Then, along the wall it ascended to the surface and repeated this motion. The movement was relatively fast taking about 17 min in one cycle. Since the temperature of the whole system was kept constant in a thermostat over the period of the experiment, a convection current must be caused with the heat generated by some reaction occurring in the sediment or at water/sediment interface. Although the same test was examined in the ignited sediment system, the particle did not move vertically during the observation for 2 hrs. Therefore, it seems that some exothermal reaction occurred in the raw or autoclaved sediment but not in the ignited one. Next, the similar experiments were carried out under cooling at 5-6°C. As was expected, a vertical gradient of concentration occurred in the water column of the raw sediment system as shown in Fig. 9. This indicates that the heat generated by some reaction in the sediment was immediately consumed by the cold surroundings, or that the exothermal metabolic activity of the organisms existing in the sediment might be reduced

at such a low temperature. However, taking into account the occurrence of an uniform distribution of metals in the autoclaved system at room temperature, such a metabolic activity of the organisms may be considered to be little significant for production of the convection current.

Furthermore, a similar experiment with the raw sediment was performed under acidic condition (pH 4.2) in spite of pH 7.7 ± 0.1 at 25°C. The results are shown in Fig. 10. It is evident that the concentration gradients appeared for every metal. From these results, it is postulated that the reaction accompanying some heat which contributes to produce a convection current in thermostated water column is nonbiological and takes place at the sea water/sediment interface of rather higher pH. There are many kinds of reactions which depend on pH in solution, e.g., chelate formation, acid-base reaction, oxidation and reduction, ion-exchange etc., but it will be quite difficult to ascertain which reaction

principally occurred. In fact, in the experiments using powdered kaolinite or some chelating resins such as Dowex A-1 or Uniserex UR-120H as the solid phase in the place of the sediment, the homogeneous distribution of the metals was quickly achieved and also a convection current was observed suggesting the reaction between metals and these materials was exothermal. While copper was rapidly transferred to both chelating resins, manganese was adsorbed by Dowex A-1 (functional group: iminodiacetic acid), but not UR-120H (functional group: thiourea). These results are considered to be reasonable because manganese belongs to the hard metal but copper is rather soft.

Effect of redox condition of the system. The behavior of metals at sea water/sediment interface, especially iron and manganese, is said to be subject to the effect of redox condition in the system^{14,15}. Table 2 shows the concentration changes of manganese, copper and cobalt in sea water when the system was converted from the aerobic to anaerobic conditions using a syringe as described above. After standing for 5 days, the concentration of copper and cobalt in aqueous phase gave no change, while that of manganese increased about ten times the initial concentration. This result suggests that

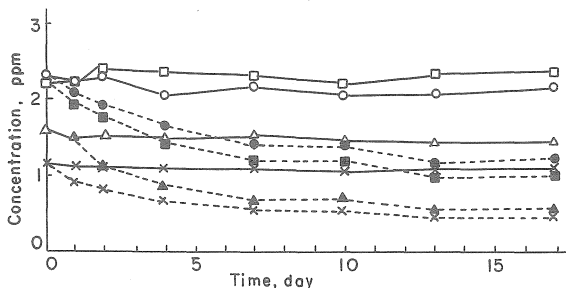


Fig. 9. Concentration change of Mn, Cu, Zn and Co in aqueous phase for the raw sediment system at 5-6°C.

(○) Mn, (△) Cu, (×) Zn, (□) Co
—○— surface, ---●--- bottom

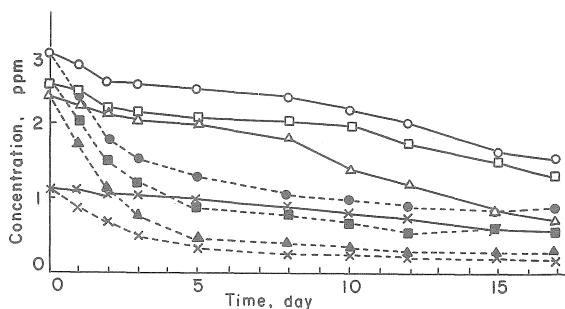


Fig. 10. Concentration change of Mn, Cu, Zn and Co in aqueous phase adjusted to pH 4.2 for the raw sediment system.

(○) Mn, (△) Cu, (×) Zn, (□) Co
—○— surface, ---●--- bottom

manganese has been fixed to the sediment as oxidized form and redissolved in aqueous phase according to a drop of the redox potential in the system.

Vertical distribution of metals in sediment. Where does take place the uptake of metals by the sediment from sea water, and are they retained? To clarify these

question, the vertical distribution of the metals in the sediment layer was surveyed. According to the method mentioned previously, core samples of the sediment freshly concentrated the metals were taken and analyzed along the depth. The results are shown in Fig. 11. The abscissa indicates the amount of metals contained in each 1-mm length of the core samples.

As it is clear from Fig. 11, among the metals surveyed, manganese exhibited a particular distribution, concentrating in the first 1 mm surface layer and steeply decreasing in the next 1 mm layer. On the other hand, zinc, copper and cobalt decreased more gradually from the top to 3-7 mm depth of the core. From these results, the reaction between these metals and the sediment seems to take place at a very thin surface layer of the sediment and then the metals except for manganese may diffuse downward through the interstitial water. Up to date, a numerous studies on migration of manganese in interstitial water have been reported^{16,17}. For the comparison, the same sediment was sur-

Table 2. Concentration change of Mn, Cu and Co in aqueous phase in anaerobiosis

Ion	Initial concn.	Concn. after 5 days
	ppm	ppm
Mn (II)	0.37	3.89
Cu (II)	0.18	0.18
Co (II)	1.21	1.00

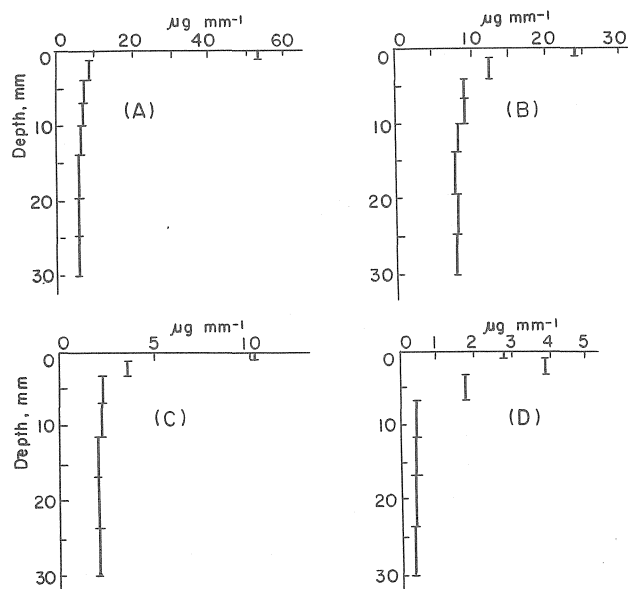


Fig. 11. Vertical distribution of (A) Mn (II), (B) Zn (II), (C) Cu (II) and (D) Co (II) in the raw sediment taken up the metals.

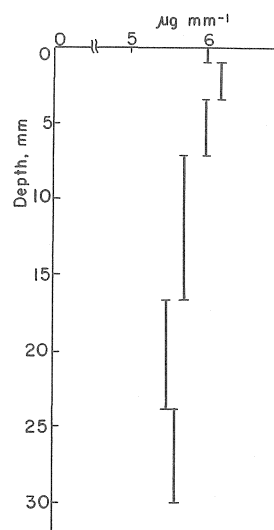


Fig. 12. Vertical distribution of Mn in the original sediment after 20-days of contact with sea water.

veyed for vertical distribution of manganese after contact with the original sea water undopted with any metals for 20 days. The result is shown in Fig. 12. The vertical distribution of manganese is looked as rather uniform through the whole depth. Therefore, a higher concentration of the element in the 1 mm top of the sediment indicates that newly deposited manganese can be retained in very thin surface portion of the sediment for certain time interval.

Speciation of the metals in the sediment. Partial extraction procedures were performed to survey the metal species transferred in the sediment. First, no metal was detected in the methanol-acetone extract. Hence, these metals seem not to be associated with such organic substances as extractable by the solvent mixture. The next extraction with magnesium chloride solution was performed to leach the ion-exchangeable metal species. This implies the metals electrostatically bound to clay minerals such as montmorillonite, or to organic substances. Sodium hydroxide solution was expected to dissolve the metal associated with humic and fulvic acids. And the metals leached with a series of hydrochloric acids of different concentrations are probably in the form of hydrous oxide, carbonate and partly the metals associated with organic substances. Next fraction obtained by digestion with hydrogen peroxide and hydrochloric acid may contain not only the metals combined with organic part but also the oxidative component such as manganese dioxide. And the last fraction contained the residual metals except for that of silicate.

The results are shown graphically in Fig. 13, in which the result for the original sediment is presented in (A) and in (B) that for the sediment allowed to contact with the sea water added a certain amount of the metal ions for 20 days. Data on each fraction are given in percentage of total amount of the extracted metal.

About 40% of manganese was extracted with magnesium chloride from the metal-captured sediment, while from the original sediment no manganese was extracted at all with this reagent. This suggests that large part of manganese exists as manganese (II) in the sediment after subjecting to methanol-acetone extraction. This result seems to conflict with the result shown in Table 2,

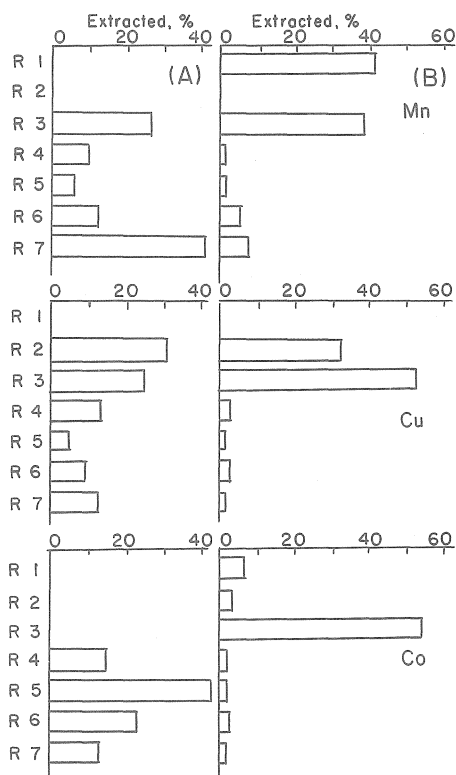
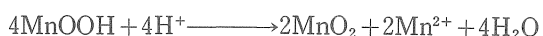


Fig. 13. Partial extraction of the metals from sediment. R-1: 0.5M $MgCl_2$, R-2: 0.5M $NaOH$, R-3: 0.01M HCl , R-4: 0.1M HCl , R-5: 1M HCl , R-6: 1M HCl +30% H_2O_2 , R-7: HNO_3 + $HClO_4$

which indicated that redissolution of manganese trapped in the sediment only started when the system was brought to an anaerobic condition. Therefore, if manganese which initially had been supplied to the sea water as bivalent ion, migrates to sediment as oxidized form, it can be assumed to be its hydrous oxide such as MnOOH or $\text{MnO}(\text{OH})_2$. In order to extract the oxidized manganese with magnesium chloride solution, these tri- or tetravalent manganese should be subject to some reduction. The possible reductant in this case is methanol which was used prior to the magnesium chloride extraction. In fact, when the same sediment was treated at first with magnesium chloride solution, it gave no manganese in the extract. Alternatively, the disproportionation of MnOOH is considered as possible mechanism¹⁸⁾.



In this reaction, proton might be supplied from methanol.

Although further investigation will be desired to explain this process, it is obvious that the chemical form of manganese which has been freshly uptaken in the sediment from the sea water is different from that of the manganese originally existed in the sediment. The former can be regarded as unstable form which will easily be subject to reduction or disproportionation.

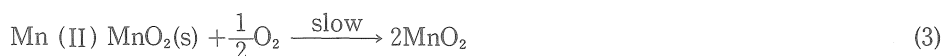
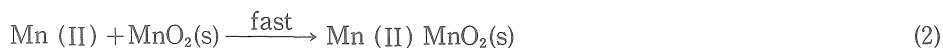
With respect to copper, the data shown in Fig. 13 (B) indicates that most of copper appeared in the sodium hydroxide and 0.01 M hydrochloric acid fractions. Generally, the stability constants of organo-copper complexes are very high. Indeed, it has been reported that above 80% of copper may exist as organic complexes in sea water¹⁹⁾. Therefore, the organic species of copper is expected to occupy large portion of the total copper in marine sediment. Stoffers et al.²⁰⁾ found that 20% of copper was present as the form associated with humic acid and/or fulvic acid in the sediment collected from Bedford Bay. Hence, the result obtained by the present study seems to be reasonable.

For cobalt, a part of cobalt was leached in both magnesium chloride and sodium hydroxide fractions and most of cobalt was dissolved in 0.01 M hydrochloric acid from the sediment freshly retained this element from sea water. In contrast to this result, for the original sediment no cobalt was extracted with these reagents. This means that the chemical form of cobalt freshly deposited in the sediment is quite different from that of originally existing in the sediment. Furthermore, as shown in Fig. 11 (D) cobalt seems to move within the sediment relatively fast compared to the other element. From these results, it is assumed that after transferring into the sediment, cobalt may migrate downward and is subject to some diagenetic reaction, then it may be converted to more stable forms. These phenomena are very attractive and more detailed investigation will be desired.

Scavenging mechanism of trace metals at sea water/sediment interface. Manganese: As described above, the data relating to the uptake of manganese suggest that the bacterial activity may be concerned with the behavior of this element at sea water/sediment interface. Ehrlich²¹⁾ reported that he had isolated both manganese-oxidizing and-reducing

bacteria from deep sea nodules, and when organic nutrients were maintained in optimal concentration, these cultures increased experimental deposition of Mn(II) ion onto pulverized nodule. Crerar et al.²²⁾ also suggested that bacteria can accelerate manganese deposition within organic marine environment.

Generally, oxidation of manganese by dissolved oxygen in an aqueous solution is very slow at or below pH 8.5. Stumm²³⁾ has suggested the following process for the oxidation of manganese,



Furthermore, he expressed the oxidation kinetics as follows:

$$\frac{d [\text{Mn(II)}]}{dt} = K_0 [\text{Mn(II)}] + k [\text{Mn(II)}] [\text{MnO}_2]$$

$$k = k' [\text{OH}^-]^2 p_{\text{O}_2}$$

Then, the data obtained in the present study will be represented as log [Mn(II)] vs. time plot for the raw and ignited sediment systems as shown in Fig. 14. From these plots, it is evident that the reaction taken place at the time of manganese deposition is not simple first order but of second order or two-step reaction. According to the Stumm's model, the following process can be estimated for the raw sediment system. First, Mn(II) ion is oxidized slowly to MnO₂ by dissolved oxygen in aqueous phase, then the formation of MnO₂ accelerates the removal of Mn(II) from sea water since MnO₂ has an autocatalytic ability as shown in equation (2). In this process, bacteria may catalyze the first reaction. This is the reason that manganese was hardly transferred to the autoclaved sediment where any bacteria was absent.

On the other hand, in spite of the absence of bacteria, manganese was deposited to the ignited sediment. This can be attributed to the catalytic effect of hydrous ferric oxide on the oxidation rate of manganese²⁴⁾. This mechanism was revealed by Van der Weijden²⁵⁾ according to the laboratory studies. However, it was also reported that the catalytic oxidation of manganese by hydrous ferric oxide is not so effective in contrast with the autocatalytic effect of preexisting manganese oxide.

Copper and zinc: The behavior of zinc at the sea water/sediment interface can be regarded as similar to that of copper. Besides the experiment mentioned above, the following experiment was complementally carried out. Under the same conditions as in the raw sediment system, sediment was completely suspended in sea water by vigorous stirring for 1 min. The sea water was taken together with the suspended sediment particles at a definite interval of the time and filtered through 0.45 μm Millipore filter.

The concentration changes of the metals were determined by atomic absorption spectrometry.

As a result, 100% of copper, 97% of zinc, 70% of cobalt, and 30% of manganese were removed from the sea water by adsorbing on the particulates. It seems that adsorption rate of copper and zinc on to the particulates is very fast. In the tank experiment suspending of a small amount of fine particles of the sediment was unavoidable in aqueous phase although sea water was very carefully introduced on the sediment. Therefore, a fast removal of these metals in earlier stage of the experiment might be principally due to adsorption and sedimentation with such fine particles.

Fig. 14 (c) and (d) show the $\log [M]$ vs. time plot where the data were obtained from the tank experiments. It is obvious that the rate of initial change was slightly faster than that of subsequent step. In order to ascertain the mechanism of this process, the data obtained from the chelate resin system are plotted in the same manner (Fig. 14 (e)).

Comparing the straight line (e) with that of (c) and (d), it becomes clear that the initial steep gradient observed in (c) and (d) is attributed to the sedimentation with some fine particles.

Therefore, it can be concluded that copper and zinc are liable to be removed by suspended particles in sea water, and that their kinetics of adsorption by sediment are governed by the first order reaction.

Cobalt: The $\log [Co(II)]$ vs. time plot is shown in Fig. 14 (f). Also in this case, cobalt was removed principally by adsorption onto the suspended particulates at the first process. After the sedimentation of the particulates cobalt may be removed from sea water exclusively at the sea water/ sediment interface and its distribution in aqueous layer becomes uniform with the aid of convection current.

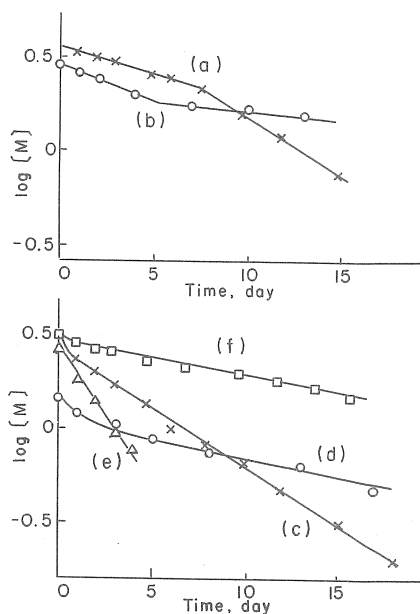


Fig. 14. Log $[M]$ -time plot
 (a) Mn for the raw sediment system,
 (b) Mn for the ignited sediment system,
 (c) Cu for the raw sediment system,
 (d) Zn for the raw sediment system,
 (e) Cu for Uniselex UR-120H system,
 (f) Co for the raw sediment system.

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References

- 1) J. A. Davis and J. O. Leckie, *Environ. Sci. Technol.*, **12** (1978) 1309.
- 2) M. A. Rashid, *Chem. Geol.*, **13**(1974) 115.
- 3) Y. Nozaki, *Chikyu Kagaku*, **12** (1978) 27.
- 4) S. Tsunogai, *Shizen*, **34** (1979) 48.
- 5) H. Craig, *Earth Planet. Sci. Lett.*, **23** (1974) 149.
- 6) S. Tsunogai and M. Minagawa, *Geochem. J.*, **12** (1978) 47.
- 7) S. Tsunogai, *ibid.*, **12** (1978) 81.
- 8) M. P. Bacon and D. W. Spencer, *Earth Planet. Sci. Lett.*, **32** (1976) 277.
- 9) J. G. S. Lu and K. Y. Chen, *Environ. Sci. Technol.*, **11** (1977) 174.
- 10) J. C. S. Lu, *Chemistry of Marine Sediment*, (1977) Ann Arbor Sci., Ann Arbor, p. 181.
- 11) R. Chester and M. J. Hughes, *Chem. Geol.*, **2** (1967) 249.
- 12) Y. Miyake, *Kaisui no Kagaku*, (1970) eds. M. Iwashita, Y. Komaki, T. Hoshino, Y. Horibe and J. Masuzawa, Tokai Univ. Press, Tokyo, p. 176.
- 13) Y. Miyake, K. Saruhashi and Y. Sugimura, *Kaiyo Mukikagaku*, (1975) ed. Y. Horibe, Tokyo Univ. Press, Tokyo, p. 140.
- 14) E. A. Jenne, *Trace Inorganics in Water*, Advances in Chemistry Series, 73 (1968) Amer. Chem. Soc. Publ., Washington D. C., p. 337.
- 15) B. J. Presley, R. R. Brooks and I. R. Kaplan, *Science*, **158** (1967) 906.
- 16) S. E. Calvert and N. B. Price, *Earth Planet. Sci. Lett.*, **16** (1972) 245.
- 17) Y. H. Li, J. Bischoff and G. Mathieu, *ibid.*, **7** (1969) 265.
- 18) J. D. Hem, *Chem. Geol.*, **21** (1978) 199.
- 19) Y. Sugimura, Y. Suzuki and Y. Miyake, *J. Oceanogr. Soc. Japan*, **34**(1978) 93.
- 20) P. Stoffers, C. Summerhayes, U. Forstner and S. R. Datchineelam, *Environ. Sci. Technol.*, **11** (1977) 819.
- 21) H. L. Ehrlich, *Appl. Microbiol.*, **16** (1968) 197.
- 22) D. A. Crerar and H. L. Barnes, *Geochim. Cosmochim. Acta*, **38** (1974) 279.
- 23) W. Stumm and J. J. Morgan, *Aquatic Chemistry*, (1970) Wiley, New York, p. 536.
- 24) J. D. Hem, *Geochim. Cosmochim. Acta*, **41** (1977) 527.
- 25) C. H. Van der Weijden, Ph. D. Thesis, State Univ. Utrecht, (1975) Utrecht, Neth.,