Behavior of Heavy Metals and Particulate Matters in Seawater
Expected from that of Radioactive Nuclides

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Abstract: Vertical profiles of $^{210}$Pb and $^{238}$Th in the deep water were analyzed by using a simple one-dimensional model. Both nuclides are considered to settle down with the velocity of $1 \times 10^{-4}$ cm/sec. The diameter of particle corresponding to the velocity is calculated to be 5 $\mu$m, while only about 10% of the nuclides can be collected on filter paper with a pore size of 0.5 $\mu$m. It is supposed that the nuclides exist in particulate materials which is changeable in size. This suggestion is supported from the following evidences. (1) The directly observed behavior of marine snow and the size distribution of particles observed with a coulter counter. (2) The existence of many chemical elements of which residence time is about 150 years. (3) Their possible existence as eutectic solid phases in the seawater. (4) The consistency of the observed accumulation rate of pelagic sediments with that estimated from the settling velocity. (5) The consistency of the decomposition rate of organic matter in the deep water estimated from the oxygen consumption with that from the settling velocity.

1. Introduction

Since Sillén (1961) applied an equilibrium model to the system of seawater, the form and the concentration of chemical elements in seawater have been actively discussed from the physicochemical aspects. This model was succeeded in some cases especially in those of the major constituents in seawater (e.g. Garrels and Thompson, 1962; Kramer, 1965). Sillén (1961), however, could not account the existing state of some minor constituents in seawater such as iron and manganese which are major constituents in the earth’s crust.

Broecker (1971) emphasized the importance of kinetic effects on the concentrations of chemical elements in the ocean water. The chief difference between the physicochemical equilibrium model and the real ocean may be caused by the activities of living organisms and their products in the ocean. In the surface water living organisms are responsible for the production of solid particles from dissolved constituents, a part of which settles down and is decomposed in the deep water. Thus seston may act as an important conveyor of materials from the surface to the deep. The main purpose of this study is to clarify this role of seston in the behavior of heavy metals as well as biophile elements in seawater.

In the first step we tried to use radioactive nuclides, isotopes of thorium and lead, as tracers of slightly soluble heavy metals. The nuclides, $^{210}$Pb and $^{230}$Th are daughters of $^{226}$Ra and $^{234}$U, respectively, which exist as dissolved species in seawater, though lead and thorium are elements of rather short residence time in the ocean (Goldberg and Arrhenius, 1958; Tsunogai and Nozaki, 1971). The decay scheme with half lives of the long lived nuclides in the uranium series is as follows:

$^{238}$U $\rightarrow 4.5 \times 10^{10}$y $\rightarrow ^{234}$Th $\rightarrow ^{234}$U $\rightarrow 2.5 \times 10^{4}$y $\rightarrow$

$^{230}$Th $\rightarrow 8.0 \times 10^{4}$y $\rightarrow ^{226}$Ra $\rightarrow 1022$y $\rightarrow$

$^{210}$Pb $\rightarrow 21.4$y $\rightarrow ^{206}$Pb (stable)

Judging from their half lives, $^{210}$Pb and $^{230}$Th seem to be mostly useful to discuss the behavior of lead and thorium in deep water.

2. The vertical distribution of $^{210}$Pb and $^{230}$Th in deep water

Figures 1 and 2 show the vertical distributions
of $^{210}$Pb at stations in the western North Pacific Ocean (KH–71–3 S and N stations) determined by NOZAKI and TSUNOGAI (1972a). The radioactivity of $^{210}$Pb in the deep water is 10 to 30% lower than that of $^{226}$Ra (NOZAKI and TSUNOGAI, 1972b), although the analytical error of the determination was 5 to 10%. Nearly the same results were obtained in the eastern North Pacific by CRAIG, KRISHNASWAMI and SOMAYAJULU (1973).

The vertical distributions of $^{230}$Th are shown in Figure 3 where data used are compiled from MOORE and SACKETT (1964), SOMAYAJULU and GOLDBERG (1968), and MIYAKE, SUGIMURA and YASUJIMA (1970). The activity of $^{230}$Th in the deep water is only 0.01 to 0.1% of that of $^{234}$U.

These facts may be caused by the effect that $^{210}$Pb and $^{230}$Th are incorporated in or adsorbed on particulate materials and removed by settling.

3. The estimation of “mean settling velocity”

A simple one-dimensional diffusion advection model is used to analyze the vertical profiles of these nuclides. The model has been successfully applied to the deep water of the Pacific Ocean by many researchers (e.g., MUNK, 1966; CRAIG, 1969; TSUNOGAI, 1972a). We introduce a term representing settling into the balance equation for a constituent in particulate materials as follows:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - (W+S) \frac{\partial C}{\partial z} + P - \lambda C \quad (1)$$

where $C$ is the concentration of a constituent, $D$ is the eddy diffusion constant, $W$ and $S$ are the vertical advection velocity of water and the mean settling velocity (positive to downward), respectively, $t$ is time, $z$ is depth, $P$ is the production rate from a parent nuclide and $\lambda$ is the radioactive decay constant. For simplicity, $D$, $W$, and $S$ are assumed to be constant with time and depth, and $W$ can be often neglected because $W$ is much smaller than $S$.

Strictly speaking, Equation (1) is applicable only for a constituent contained in particles identical in size and density. However, if the constituent is contained in particles of changeable size, the equation can be used. The validity of the assumption will be discussed later. Thus, we designate the settling term as “mean settling velocity”. The term $P$ is different from nuclide to nuclide, thus Equation (1) is solved separately for $^{210}$Pb and $^{230}$Th in deep water.

a) $^{210}$Pb

The production rate of $^{210}$Pb which is equal to the disintegration rate of $^{222}$Rn in seawater is approximately expressed as

$$P = P_1 - P_2 \exp (-\mu z)$$

$$= 6.8 \times 10^{-6} - 6.0 \times 10^{-8} \exp (-5.6 \times 10^{-6} z)$$

with units of atoms/cm$^2$ (2)

where $P_1$, $P_2$, and $\mu$ are constants. This equation is cited from TSUNOGAI and NOZAKI (1971) with a slight modification by the data obtained by NOZAKI and TSUNOGAI (1972b) at the station (KH–71–3–S, 28.5°N, 145°E) where $^{210}$Pb shown in Figure 1 was determined.

![Fig. 1. Vertical distribution of $^{210}$Pb at the KH–71–3 S station (28.5°N, 145.0°E). The solid curves are the calculated distribution of $^{210}$Pb by putting given settling velocities (S) and the vertical eddy diffusivity (D) of 1.2 cm$^2$/sec into Equation (3). The dashed lines indicate the distribution of $^{226}$Ra at the KH–71–3 S station.](attachment:image_url)
The solution of Equation (1) is written by
\[
C = C_0 \exp(-\sigma z) + \left(\frac{P_1}{\lambda}\right)[1 - \exp(-\sigma z)] + [\frac{P_2}{(D\mu^2 + \mu S - \lambda)}] \\
\times [\exp(-\mu z) - \exp(-\sigma z)] \quad (3)
\]
where
\[
\sigma = \frac{(S/2D)}{(\sqrt{1 + 4D\lambda/S^2} - 1)}
\]
The eddy diffusion constant \(D\) of the Pacific deep water has been estimated to be 1.2 cm\(^2\)/sec by TSUNOGAI (1972b). The surface concentration \(C_0\) is calculated from the flux at the surface, \(I\), which is the same as the input rate from the atmosphere.

\[
I = -D\left(\frac{dC}{dz}\right)_{z=0} + SC_0
\]
\[
= SC_0 + D\sigma \left(\frac{P_1}{\lambda}\right) + \frac{DP_2(\mu - \sigma)}{D\mu^2 + S\mu - \lambda}
\]
(4)

We use the value \(I = 0.22\) atoms/cm\(^2\)-sec which has been obtained by FUKUDA and TSUNOGAI (1972).

In Figure 1 the solution for given \(S\) values are plotted and compared with observed data at the KH-71-3-S station. The observed values in the deep water seem to fit the curve of \(1 \times 10^{-4}\) cm/sec of settling velocity better than other curves, although the velocity may be uncertain by a factor of 2. The settling velocity at the KH-71-N station (Figure 2) also fits rather well with the \(1 \times 10^{-4}\) cm/sec curve, although the \(^{228}\)Ra distribution used is that observed at the station KH-71-3-S. The settling velocity obtained is one order of magnitude larger than the advection velocity of the deep water (MUNK, 1966; TSUNOGAI, 1972b).

b) \(^{230}\)Th

The concentration of \(^{234}\)U is virtually uniform in the ocean because of the sufficiently long residence time of uranium and the long radioactive mean life time of \(^{234}\)U as compared with global circulation of the deep water. Thus the production rate of \(^{230}\)Th (\(P\)) is constant, and the solution of Equation (1) is expressed by using the activity ratio \(R\) as follows:

\[
R = \frac{A_{230}}{A_{234}} = \frac{\lambda_{230}C_{230}}{\lambda_{234}C_{234}} = \frac{iC_0}{P}
\]
\[
= 1 - \exp(-\sigma z) \left[1 - \frac{iC_0}{P}\right] \quad (5)
\]
where
\[
\sigma = \frac{(S/2D)}{(\sqrt{1 + 4D\lambda/S^2} - 1)}
\]

In the second and third terms of the above equation, \(A\) is activity and subscripts 230 and 234 indicate \(^{230}\)Th and \(^{234}\)U, respectively. The activity of \(^{234}\)U \((A_{234})\) is assumed to be 2.8 dpm/l which is based on the facts that the concentration of uranium is 3.3 \(\mu\)g/l in seawater and the activity ratio of \(^{234}\)U to \(^{238}\)U is 1.15 (MIYAKE, SUGIMURA and MAYEDA, 1970).

The ratio, \(R\), is calculated for given \(S\) and \(D\) (1.2 cm\(^2\)/sec) values as a function of depth (\(z\)) and shown in Figure 3. The best-fit curve of the Figure 3 means the settling velocity of \(^{230}\)Th of \(1 \times 10^{-4}\) cm/sec although the uncertainty seems to be larger than that of \(^{210}\)Pb because the data of \(^{230}\)Th are compiled from various sources observed at various location. The settling velocity does not sensitively depend on
an eddy diffusivity, if the diffusivity is less than 100 cm$^2$/sec.

4. The mechanism of removal of heavy metals in the ocean

The settling velocity of $^{210}$Pb in the deep water coincides fairly well with that of $^{230}$Th. In the surface water, the settling velocity of $^{210}$Pb (NOZAKI and TSUNOGAI, 1973) is also comparable with that of $^{234}$Th (MATSUMOTO, 1972; TSUNOGAI et al., 1974) or that of $^{229}$Th (BROECKER, KAUFMAN and TRIER, 1973), although the settling velocity in the surface water is one order of magnitude larger than that in the deep water. The concentrations of these nuclides or stable isotopes of these nuclides are too low to make pure solid phases of these metals which spontaneously settle down with a significant speed. Therefore, the conveyors of these nuclides must be found in the ocean, which may be common for these nuclides.

According to Stokes' law, the settling velocity of $1 \times 10^{-4}$ cm/sec indicates the particle diameter of 5 or 1.4 $\mu$m of which density is 1.1 or 2.0 g/cm$^3$, respectively. Thus, if seawater is filtered with a membrane filter paper such as Millipore type HA (pore size, 0.45 $\mu$m), a substantial part of lead or thorium in seawater is expected to be left on the filter paper. We, however, can collect only about 10% for each of nuclides in seawater with the filtration method (MIYAKE, SUGIMURA and YASUJIMA, 1970; TSUNOGAI et al., 1974; CRAIG, KRISHNASWAMI and SOMAYAJULU, 1973).

If only the 10% of the nuclide is settling and the rest remains in seawater at that time, the velocity for sinking particles is expected from the net flux to be $1 \times 10^{-2}$ cm/sec which corresponds to the particle diameter of 16 or 4.5 $\mu$m. Moreover, the mean settling velocity in the surface water is about $10^{-3}$ cm/sec (MATSUMOTO, 1972; TSUNOGAI et al., 1974). Thus the settling velocity of the particulate materials in the surface water collected on the filter must be about $10^{-2}$ to $10^{-3}$ cm/sec, which agrees with that of particulate organic carbon estimated by NAKAJIMA and NISHIZAWA (1972). The settling velocity corresponds to that of the particle larger than 10 $\mu$m in diameter. This is also supported by the observation on particles with a coulter counter at the KH-71-3 S and N stations (MATSUMOTO, 1972). As shown in Figure 4, the flux-mean diameter which is obtained as a weighted mean for particulate flux (mass $\times$ settling velocity) is certainly larger than 10 $\mu$m, because the curve does not converge at the right hand side. The results on the particle size and settling velocity are not so different from those on marine snow observed by KAJIHARA (1971), where the settling velocity is $5 \times 10^{-2}$ cm/sec for particles of diameter of 100 $\mu$m giving a density of 1.1 g/cm$^3$ from Stokes' law in his Figure 4.

TSUNOGAI et al. (1974) found that the inorganic portion of particulate materials in the ocean water is about one third of total dry weight and most of the inorganic portion consists of water soluble sea salt and calcium and silica in biological skeletal parts. It is natural
Further works are necessary for discussing quantitatively the size of sinking particles and the reversibility of the size. Of course, if there were no change of the existing state, the depression of the \(^{210}\text{Pb}\) content observed by Tsunogai and Nozaki (1971) would not be found. This is the reason why we express the relation of radioactive disequilibrium between a soluble parent and its insoluble daughter by using the mean settling velocity.

When \(^{210}\text{Pb}\), \(^{228}\text{Ra}\) disequilibrium in the deep water was analyzed, Craig, Krishnaswami and Somayajulu (1973) did not adopt the concept of settling velocity but they used scavenging rate (\(\varphi\)) as follows:

\[
\frac{\partial C}{\partial t} = 0 = D \frac{\partial^2 C}{\partial z^2} - W \frac{\partial C}{\partial z} + P - (\lambda + \varphi) C
\]  

(6)

They also attributed the scavenging process to the removal by settling but they ignored the amount of \(^{210}\text{Pb}\) in particles. This concept of scavenging rate is virtually applicable to a radionuclide in the surface water, the upper most layer. The concept, however, seems to be unsuitable or not valid for an isotope of lead or thorium in the deep water, because the scavenged lead or thorium must be irreversibly incorporated in (i.e. must not be regenerated from) sinking particles and transported to the bottom with the rate much sooner than the scavenging rate. In the surface layer (200 m), the scavenging residence time (1/\(\varphi\)) is 0.6 yr for \(^{234}\text{Th}\) (Matsumoto, 1972; Tsunogai et al., 1974) or 0.7 yr for \(^{228}\text{Th}\) (Broecker, Kaufman and Trier, 1973) or 0.6 yr for \(^{210}\text{Pb}\) (Nozaki and Tsunogai, 1973), which is much smaller than that in the deep water (100–150 yr converted from the settling velocity of \(1 \times 10^{-4}\) cm/sec). Therefore, if the scavenged lead or thorium in the surface layer is not regenerated in the deep water, the net flux of lead or thorium from the deep to the surface must be much more than the scavenged amount in the deep. This may not be the case, but our Equation (1) satisfies the condition that the removal in the upper layer is the source in the lower layer.

to consider that these nuclides produced in water or constituents in fine particles supplied to the ocean are attached to neighboring particulate materials comprised substantially of seston of which nature was discussed by Tsujita (1956). Nishizawa (1966, 1969) stated that seston, organic aggregate, is formed from the “dissolved” material and is decomposed biologically or broken physically.

These nuclides, thus, are considered to exist practically in one phase of “particulate” state, seston, where their existing forms in seawater change rather reversibly among particles of various sizes and “dissolved” species which may be fine particles, and the seston sinks only when it forms aggregates larger than a few microns. This idea does not contradict with the finding of Nakajima and Nishizawa (1972).
5. The form of chemical elements having short residence time in the ocean

Goldberg and Arrhenius (1958) estimated the residence times of many elements in the ocean water from the mean chemical compositions of seawater and of crustal materials, and the accumulation rate of pelagic sediments. At present, the residence times seem to be generally reliable excluding some elements of which concentrations in seawater have been newly determined (Riley and Chester, 1971; Spencer et al., 1970). Many elements such as iron, aluminum, cobalt, thorium, titanium, zirconium, beryllium, gallium, scandium, yttrium and lanthanoids are belonging to the class of the shortest residence time (100–200 yrs). The existence of many elements having nearly the same residence time suggests that these elements are transported to the bottom by the same conveyor. Manganese and lead have somewhat larger residence times than the above-mentioned elements. The former two elements, however, seem to be also belonging to the same class, because the source of manganese is considered to be other than river input (Horn and Adams, 1966).

When particles settle down with the velocity of $1 \times 10^{-4}$ cm/sec, the time necessary for settling through 4,500 m is about 150 years, which can be regarded as the residence time of constituents in the particles in the open ocean. If it is probable to assign 150 years to the residence time of an element belonging to the shortest residence time class, the sedimentation rate turns out to be $2.8 \text{ mm} / 10^8 \text{ yr}$ for the sediment of density of 2.0 g/cm$^3$ or 1.2 mm/$10^8$ yr for water-free basis. The calculated rate agrees fairly well with the mean sedimentation rate of pelagic sediments (Lisitzin, 1971). Thus, a new table of the residence time is in preparation, which is based on our conclusion that particles in the ocean are settling with a rate of $1 \times 10^{-4}$ cm/sec.

6. The possibility of existence of eutectic solid phases

As shown in Table 1, the calculated concentrations of manganese in seawater being in equilibrium with the thermodynamically stable solid phase are much lower than observed one. Contrary to manganese, the calculated equilibrium concentration of lead which makes the same solid phase with manganese is much higher than observed concentration. This can be explained as follows: 1) the major constituents, manganese, exists as particles (solid phase) in seawater; 2) the equilibrium concentration of the minor constituent, lead, is lowered by making eutectic solid phase (solid solution) with its host element, manganese. As also shown in Table 1, the observed concentration of lead in seawater is saturated if the activity of lead in solid phase is reduced by the ratio of lead to manganese in crustal material (solid phase). Sillén (1961) stated that this assumption is probable in practical use.

The similar relation is recognized in the relation between iron and cobalt (Table 1). In contrast to cobalt, nickel does not make the solid phase of MOOH type, the residence time of which exceeds that of cobalt by a factor of a few tens. It is necessary to know about

<table>
<thead>
<tr>
<th>Solid phase</th>
<th>Element</th>
<th>Calculated* ($\mu$g/l)</th>
<th>Seawater observed ($\mu$g/l)</th>
<th>Cald./Obsd.</th>
<th>Earth’s crust observed ($\mu$g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOOH</td>
<td>Fe</td>
<td>$2 \times 10^{-6}$</td>
<td>3</td>
<td>—</td>
<td>$5.6 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>1.2</td>
<td>0.03</td>
<td>400</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Fe/Co (atomic)</td>
<td></td>
<td></td>
<td>2300</td>
<td></td>
</tr>
<tr>
<td>MO₂</td>
<td>Mn</td>
<td>$5.5 \times 10^{-8}$</td>
<td>2</td>
<td>—</td>
<td>950</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>10</td>
<td>0.03</td>
<td>300</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>Mn/Pb (atomic)</td>
<td></td>
<td></td>
<td>300</td>
<td></td>
</tr>
</tbody>
</table>

* In equilibrium with its pure solid phase.
activity coefficients of metals in solid phases for the closer examination of this problem.

7. Radionuclides as tracers of particulate organic material

The following evidence shows the similarity in the behavior of thorium or lead to that of seston. The settling velocity of particulate organic matter (POC) in the deep water is assumed to be $1 \times 10^{-4}$ cm/sec and the decomposition rate of organic matter at depths greater than 1 km has been estimated to be 5 gC/m$^2$.yr from the consumption rate of oxygen by Tsunogai (1972a). Although the amount of dissolved organic matter (DOC) is about 10 times as great as that of POC in seawater, the decomposition of DOC in the deep water seems to be negligibly small as compared with that of POC, because the DOC content in the deep water below 0.5 km, 0.5 mgC/l, is nearly constant (e.g. Menzel, 1972; Ogura, 1970) and the $^{14}$C age of this material, about 3,400 years, is very old (Williams, 1970). The sedimentation rate of organic carbon in pelagic sediments is also negligibly small as compared with the particulate flux. Thus, the concentration of POC in the deep water is estimated as follows:

$$\text{POC} = \frac{5 \text{ gC/m}^2 \text{-yr}}{1 \times 10^{-4} \text{ cm/sec}} = 160 \mu\text{gC/l}$$

Menzel and Goering (1966) determined POC content which was invariably about 18 $\mu$gC/l in the deep water and at the KH-71-3 stations the POC content was 40 $\mu$gC/l (Ocean Research Institute, 1973). The POC content estimated above is a few to ten times greater than the observed POC contents which were determined by collecting particles on glass fiber filter of about 0.8 $\mu$ pore size. This fact supports our suggestion that a substantial part of particulate matter is so small as to pass through the filter paper or exists sometimes in the form of “dissolved” state. Recently, Ogura (1973) proved by using a ultra-filtration technique that a substantial part of DOC comprises organic compounds of molecular weight more than 1,000. Though there are some studies which shed light on the formation of organic aggregates (Riley, 1963; Sheldon, Evely and Parsons, 1967; Nishizawa, 1969), further attempts are necessary to solve this problem.

8. Concluding remarks

In this discussion, emphasis has been placed to the role of seston, biogenic particulate matters, in the vertical transport of some heavy metals. The size of seston transporting the metals can not be evaluated accurately by using the present data. It is, however, supposed from Figure 4 that large particles like faecal pellets of zooplankton or marine snow may be important as the conveyor.

The state of these metals in filtered seawater can not be also assessed. They may be contained in fine particles or may exist in a certain form which is liable to grow large.

Acknowledgment

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放射性核種より推定される海水中の重金属及び懸濁物の挙動

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要旨：深層水中の$^{210}$Pb及び$^{230}$Thの鉛直分布を一次元モデルを用いて解析し、これらの沈降速度として$1 \times 10^{-4}$ cm/secを得た。この速度に対応する粒径は5μで
ある。ところが、海水を孔径1μ以下のろ紙でろ過して
もこれらの核種は10％程度しか集められない。この事
実から次のように推論される。これらの核種は粒子とし
て存在し、その粒径は大は$10^{-3}$ cm/secで沈降するも
のから小は事実上溶けているものとの間を変換可能で
ある。この結論を支持する証拠として次のものがある。
1. マリンスノーやクールタカウンターによって観測
された粒子状の挙動や粒径分布、2. 平均滞留時間150年
程度の多数の元素の存在、3. 海水中に固溶体の存在の
可能性、4. 沈降速度から推定される堆積速度と実測値
との一致、5. 沈降速度及び酸素消費速度から推定され
る深海での有機物の分解量の一一致。