Mercury Concentration in the Ocean*

Masakichi Nishimura†, Shigeki Konishi†, Katsuhiko Matsunaga†, Kohtaro Hata† and Tsuneo Kosuga†

Abstract: Seventy percent of 342 seawater samples collected in the Bering Sea, North and South Pacific, Japan Sea, East and South China Seas, and Indian Ocean had concentrations of "total" mercury ranging from 3 to 6 ng Hg l⁻¹ with an arithmetic mean of 5.3 ng l⁻¹ and a geometric mean of 5.0 ng l⁻¹. In some cases, a higher concentration was observed at the surface, at the halocline or thermocline, or in the bottom water. But in general, there was no consistent correlation between mercury concentration and depth, except for a statistical tendency for mercury concentration to be slightly higher in the surface water. This tendency suggests that mercury in the ocean is supplied from the atmosphere by rain washout. The latitudinal variation of surface mercury concentrations showed that the maximum concentration at each latitude decreased from 40°N to 30°S. This variation provides evidence that atmospheric mercury is emitted mainly from continental areas naturally or anthropogenically.

1. Introduction

Mercury is a volatile element and the mercury emitted from natural and anthropogenic sources is rapidly dispersed worldwide in the atmosphere. According to Lantzy and Mackenzie (1979), the atmospheric input of mercury to the ocean is about 8 times larger than that from rivers. Weiss et al. (1971) considered the natural vaporization of mercury from the land surface to be a significant source of mercury in the atmosphere, but Moore and Moore (1976) estimated that almost all the mercury moving over the surface of the globe is anthropogenic.

Since Stock and Cucuel (1934) determined mercury concentrations in seawater, mercury concentrations have been reported by many investigators. The oceanic mercury data, however, came from a limited number of sampling sites, and those reported prior to 1975 showed very large variations, 2 to 2,800 ng Hg l⁻¹, as reviewed in a previous paper (Nishimura and Konishi, 1976). In fact, the data were so widely scattered that a general picture of mercury concentration in the ocean could not be given. The scattering of the data did not seem to be due to real diversity in the nature of seawater in the oceans, but rather to inadequate analytical techniques, namely, contamination of mercury from reagents and bottles, loss of mercury during storage of sample, and inadequate pretreatment of water samples (Matsunaga et al., 1979).

2. Sampling and analysis

Water samples were collected with polyvinylchloride van Dorn or Niskin samplers in the areas shown in Fig. 1 and listed in Table 1. Immediately after collection, 500-ml aliquots of unfiltered seawater were transferred to carefully cleaned glass bottles (Matsunaga et al. 1979), and acidified to 0.2M with H₂SO₄. This acidification and the salt in seawater make the mercury in the sample solution stable for at least 60 days without any loss due to adsorption on the container wall. The analytical value for the mercury in the acidified sample increased gradually, and reached a maximum after 2 weeks. This value may be defined as the "total" mercury concentration because the value was not significantly different from that obtained after strong digestion of the sample with a mixture of H₂SO₄, HNO₃, KMnO₄ and K₂S₂O₅ (Matsunaga et al., 1979).

Stannous chloride was added to the sample solution after storing for more than 2 weeks after shipboard acidification. By passing N₂ through the solution, the reduced and vaporized

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mercury was collected on silver or gold metal particles held in a small glass tube. The metal was then transferred into a quartz tube held in an electric furnace, and heated to 500°C. The vaporized mercury was introduced into an absorption cell by passing N₂, and the absorption peak at 254 nm was measured with an atomic absorption spectrophotometer. A sharp peak for mercury was obtained (Nishimura et al., 1975). When a 500-ml aliquot was used, the relative standard deviation of analytical values was 13% for a 7 ng Hg l⁻¹ standard solution, while the relative standard deviations of 6 different seawater samples containing between 7 and 4 ng Hg l⁻¹ were between 9 and 20%, respectively.

3. Results and discussion

Matsunaga et al. (1975) briefly reported oceanic mercury concentrations in some areas around Japan. Since then we have carried out more extensive samplings (Table 1), and the analytical data are summarized in Table 2, including the previously reported data.

3.1. Concentration of mercury in the ocean

Although several papers gave very heterogeneous horizontal and vertical distributions of mercury in the oceans (e.g., Robertson, 1976), the data presented in this paper fall in a relatively narrow range. A histogram of the mercury concentrations of all the surface and vertical samples (Fig. 2) indicates that 72% of the 342
Table 2. Mercury concentrations (arithmetic means) in the oceans, ng l\(^{-1}\).

<table>
<thead>
<tr>
<th>Area</th>
<th>Surface</th>
<th>Below surface</th>
<th>All samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bering Sea</td>
<td>7.0±3.3(^b) (9)(^a)</td>
<td>5.6±1.8 (47)</td>
<td>5.8±2.2 (56)</td>
</tr>
<tr>
<td>Pacific Ocean</td>
<td>5.8±2.0 (64)</td>
<td>5.4±1.6 (75)</td>
<td>5.6±1.8 (139)</td>
</tr>
<tr>
<td>Japan Sea</td>
<td>5.9±1.8 (17)</td>
<td>4.5±1.5 (70)</td>
<td>4.8±1.6 (87)</td>
</tr>
<tr>
<td>East and South China Seas</td>
<td>5.7±2.3 (7)</td>
<td>5.0±1.8 (20)</td>
<td>5.2±1.9 (27)</td>
</tr>
<tr>
<td>Indian Ocean</td>
<td>4.4±1.6 (13)</td>
<td>4.5±2.6 (20)</td>
<td>4.4±2.2 (33)</td>
</tr>
<tr>
<td>Average of open seas</td>
<td>5.7±2.1 (110)</td>
<td>5.1±1.6 (232)</td>
<td>5.3±2.2 (342)</td>
</tr>
</tbody>
</table>

\(^a\) Standard deviation of the samples.
\(^b\) ( ) Numbers of samples analyzed.

seawater samples fall in the range of 3 to 6 ng Hg l\(^{-1}\) with an arithmetic mean of 5.3 ng l\(^{-1}\). The distribution, however, fits rather well to a log-normal distribution with a geometric mean of 5.0 ng l\(^{-1}\).

Higher values for oceanic mercury have been reported in books, e.g., 50 ng l\(^{-1}\) reported by Riley and Chester (1971), and a questionable value of 30 ng l\(^{-1}\) by Brewer (1975). Recent reports, however, have shown a tendency towards lower values for mercury in the oceans, e.g., 7 ng l\(^{-1}\) in the Northwest Atlantic (Fitzgerald and Hunt, 1974), 8 ng l\(^{-1}\) in the Northwest Atlantic (Fitzgerald, 1975), 5 ng l\(^{-1}\) in the Northwest Pacific and the Japan Sea (Matsunaga et al., 1975), 4 ng l\(^{-1}\) as reactive mercury in a vertical profile of the Gulf Stream (Mukherji and Kester, 1979), 6-46 ng l\(^{-1}\) for surface waters and 6.3 ng l\(^{-1}\) for samples below 400 m in depth in the Northwest Pacific (Takahashi et al., 1981), and 14 ng l\(^{-1}\) for surface waters and 6 ng l\(^{-1}\) for samples below 500 m in the Western North Pacific (Miyake and Suzuki, 1983). Broecker and Peng (1982) gave 1 ng l\(^{-1}\) after Bruland in their book as a highly uncertain average.

3.2 Vertical profile

Only 4 vertical profiles out of the 29 vertical stations are presented in Figs. 3, 4 and 5 as representative examples. In some cases, a higher concentration was observed at the surface, at the halocline or thermocline, or in the bottom water. But in general, there was no consistent correlation between mercury concentration and depth, except that the data displayed a statistical tendency (T-test, p<0.01) to be slightly higher in the surface waters as seen in the
average concentrations (Table 2) and in the relative frequency of concentrations given in Fig. 6. This suggests that mercury in the ocean is supplied from the atmosphere by rain washout.

Mukherji and Kester (1979) reported a correlation between vertical variations in mercury and silicate, but a correlation was not always apparent in the case of our observations.

3.3. Latitudinal variability

All the data for surface waters from 87°E to 170°E are plotted against latitude in Fig. 7. The maximum concentration at each latitude decreased from north to south, i.e., from 40°N to 30°S. This trend does not seem to be accidental, although the sampling stations covered a relatively wide longitudinal range. Rex and Goldberg (1958) reported that the quartz contents of pelagic clays from the Eastern Pacific Ocean showed a marked latitudinal dependence with a

![Graph](image)

**Fig. 6.** The relative frequency distributions of mercury concentrations in surface and deeper waters in the oceans, normalized at the level of 4 ng l⁻¹.
Fig. 7. Latitudinal variation of mercury concentrations in surface waters of the Pacific and Indian Oceans.

maximum at around 30°N and the quartz was interpreted to be atmospherically transported from the continental areas to the sea. Tsunogai and Nozaki (1971) reported that the highest concentration of $^{210}$Pb, the daughter of radon gas mainly emitted from the land, appeared in surface waters around 30°N in the North Pacific. The latitudinal variation of mercury concentration in the surface waters provides evidence that atmospheric mercury is emitted mainly from the continental areas either naturally or by man, and the mercury is added to the sea surface by rain. In fact, the average mercury concentration in rain collected by us over the northern North Pacific was 8 times higher than that in the seawater. The relationship between mercury concentrations in the air, rain and sea will be published elsewhere in detail.

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海洋の水銀濃度

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要旨: ベーリング海、北太平洋、南太平洋、日本海、東および南シナ海、インド洋で採取した342の海水試料について水銀を定量し、その70%は3～6 ng l⁻¹の水銀濃度範囲に入り、全試料の算術平均濃度は5.3 ng l⁻¹、幾何平均濃度は5.0 ng l⁻¹であった。時には塩分躍層、温度躍層や底層水にやや高い水銀濃度が認められる場合もあるが、全般的には深度と水銀濃度の関係は見られず、また、各鉛直層等では表面水に水銀濃度が常に高いとは限らないが、全試料について統計的に見れば、1%の有意水準で表面水（平均5.7 ng l⁻¹）は表面以下の水（平均5.1 ng l⁻¹）よりも水銀濃度が高い。このことは、水銀は大気圏から降水によって海洋へ供給されていることを示唆している。表面水の各鉛直における水銀濃度の最高値は40°Nから30°Sへと減少する。この傾向は標地面積や人類活動の大きさとの関連を示すものと言えよう。