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Sea-Air Partitioning of Mercury in the Equatorial Pacific Ocean

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The partitioning of gaseous mercury between the atmosphere and surface waters was determined in the equatorial Pacific Ocean. The highest concentrations of dissolved gaseous mercury occurred in cooler, nutrient-rich waters that characterize equatorial upwelling and increased biological productivity at the sea surface. The surface waters were supersaturated with respect to elemental mercury; a significant flux of elemental mercury to the atmosphere is predicted for the equatorial Pacific. When normalized to primary production on a global basis, the ocean effluxes of mercury may rival anthropogenic emissions of mercury to the atmosphere.

RECENTLY WE PRESENTED PRELIMINARY evidence for the evasion of mercury from the surface waters of the equatorial Pacific Ocean. This evidence supported model predictions of a low-latitude ocean source of mercury and suggested that the volatilization process may be mediated by marine biota (*1*). Here we report results confirming that biologically productive regions of the equatorial Pacific are a source of atmospheric mercury. Moreover, the principal species appears to be elemental mercury (Hg°). The largest dissolved quantities of Hg° were associated with cooler temperatures and higher nutrient and chlorophyll a levels, suggesting that Hg° efflux is tied to equatorial upwelling and phytoplankton activity.

Evidence for an atmospheric source of mercury in the equatorial Pacific was obtained on a research cruise of the O.S.S. *Researcher* from 8 June to 3 July 1984. The equatorial cruise track from 155° to 93°W and the track at 85°W from 4°30′S to 4°30′N are shown in Fig. 1. Seawater for measurement of dissolved gaseous mercury (DGM) was collected in the surface mixed layer at every 5° of longitude along the equator and at closer intervals (<2°) along the track at 85°W. Water samples were also obtained for determination of temperature, total mercury (*2*), nitrate plus nitrite, and chlorophyll a. Total gaseous mercury (TGM) and organic gaseous mercury (OGM) in the air were sampled at bow level (10 m above the surface) on both cruise legs while the ship was under way. The broad coverage of these two cruise tracks allowed quantification of the horizontal extent and range of DGM in surface water and TGM and OGM in the overlying air in the equatorial Pacific.

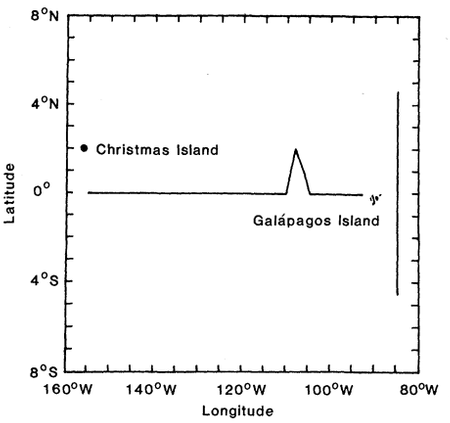

Fig. 1. Cruise track of the O.S.S. *Researcher* in the equatorial Pacific (June to July 1984).

Samples of DGM in surface seawater were collected in acid-cleaned, Teflon-lined, 30-liter Go-Flo bottles suspended on Kevlar line and anchored with a plastic-bagged concrete weight. The seawater was then purged with mercury-free air in a 4-liter flow-through glass bubbler that had been scrupulously acid-cleaned (*3*). The sparging efficiency for Hg° was 90 to 95 percent, as determined with dissolved oxygen as a tracer and a volatilization rate ratio of Hg° to dissolved oxygen of 0.94 (*4*). Total DGM was purged from 30- to 60-liter aliquots, trapped on gilded quartz sand columns, and analyzed by cold vapor atomic absorption spectrophotometry (*5*). Another 30- to 60-liter aliquot was used to separate the total DGM into an organic and an inorganic fraction with a silver-gold stack method (*6*). In this arrangement the silver column collects Hg° while passing volatile organic mercury species such as $(CH_3)_2Hg$ to be trapped on the gold column. Subsequent measurements are made with a two-stage gold amalgamation technique (*5*).

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Atmospheric concentrations of TGM and OGM were determined by the gold and the silver-gold stack procedure (*6*). Total mercury in surface seawater was collected in the Go-Flo bottles. Aliquots were acidified with ultrapure, sub-boiling distilled nitric acid and stored in acid-cleaned, 2-liter Teflon bottles for later analysis (*2*). Sea surface temperature was measured by a thermistor mounted on the hull of the ship at a depth of 5 m. Temperature profiles (250 m) were obtained with expendable bathythermographs or with reversing thermometers mounted on Niskin bottles in a rosette frame. The nutrient samples of nitrate plus nitrite were collected in acid-washed (10 percent HCl) polyethylene bottles and frozen for later analysis with a Technicon autoanalyzer (*7*). Chlorophyll a was measured fluorometrically (*8*).

The atmospheric measurements of TGM along the equatorial cruise track (Fig. 2A) and along the meridional cruise track at 85°W (Fig. 2B) ranged from 0.85 to 1.13 ng of mercury per standard cubic meter (SCM), with an average of 1.02 ± 0.08 (mean ± SD, n = 23). This variation corresponds to our estimate of overall experimental error associated with the collection, volume determination, and analysis of TGM at these concentrations. The value compares well with open-ocean results for the Southern Hemisphere of 1.05 ± 0.09 ng/SCM (n = 4) at latitudes greater than 10°S during our 1980 equatorial Pacific study (*1*) and with 1.07 ± 0.08 ng/SCM (n = 16) measured by us in the South Pacific westerlies at New Zealand. Values of 1.05 ± 0.22 ng/SCM (n = 64) have been reported for the South Atlantic (*9*). The predominant form of the mercury in the air is Hg° (80 to 96 percent), as defined by the silver-gold separation technique (Fig. 2, A and B).

Elevated atmospheric TGM (1.5 to 2.3 ng/SCM) found during our October 1980 study (*1*) at 160°W in the equatorial upwelling region was not observed. The differences in TGM between the cruises most probably reflect temporal and spatial variability in the processes affecting the volatilization of mercury in the equatorial zone. For example, equatorial upwelling can show significant short-term (10- to 20-day) variations in response to fluctuations in the strength of the trade winds (*10*). In addition, significant areal and temporal changes in equatorial primary production have been reported (*11*).

The total DGM in the surface seawater (Fig. 2A) generally increases along the equator from about 60 fM between 155° to 125°W to 225 fM near the Galpágos Islands (90°W). At the 85°W track (Fig. 2B), total DGM is about 50 fM at 4°30′N and gradually increases to 135 fM at 3°S. The silver-gold speciation experiments show that all the DGM is Hg°. The increasing trend of DGM coincides with decreasing surface sea temperature and increasing concentration of nitrate plus nitrite along the equator farther east toward the Galpágos Islands (Fig. 2A) and south of the equator along the 85°W track at 3°S (Fig. 2B). Cooler, nutrient-rich waters found east of 130°W are indicators of the upwelling of water from lower depths (*12*). The 20°C isotherm along the equator was at a depth of 100 at 155°W and 25 m at 93°W. This shallowing of the thermocline allowed cool water to be closer to the sea surface in the eastern part of the equatorial Pacific.

The chlorophyll a distribution, contoured every 100 μg/m^3 for the top 100 m (Fig. 2, A and B), is variable and reflects the patchiness of the phytoplankton populations. The sampling depths for DGM are superimposed on the chlorophyll a distribution. High concentrations of DGM and chlorophyll a occur along the equator at 95°, 100°, 105°, and 115°W (Fig. 2A) and at 2° and

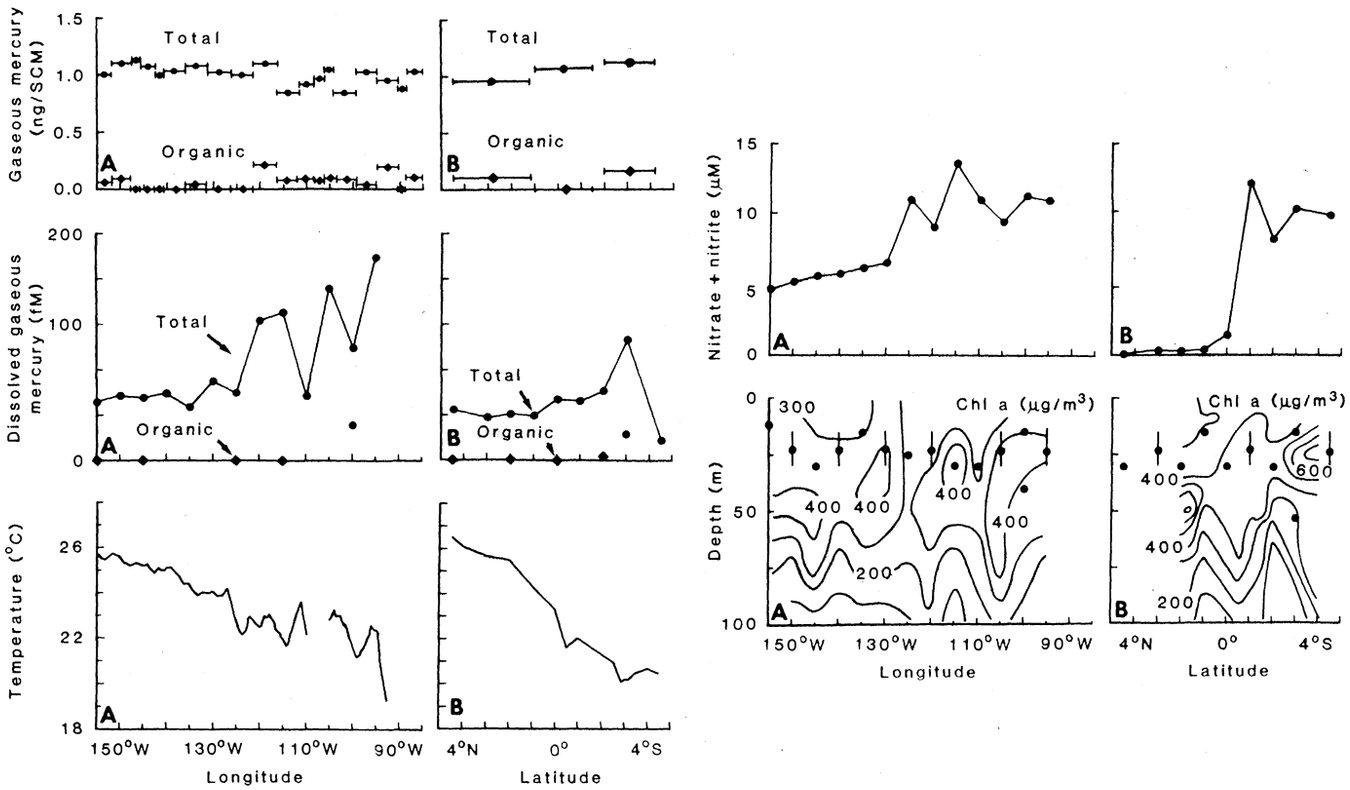

Fig. 2. Experimental results from the equatorial Pacific plotted versus longitude from 155° to 93°W along the equator (A) and versus latitude from 4°30′N to 4°30′S along 85°W (B). The parameters, in descending order, are: total and organic gaseous mercury concentrations in the atmosphere in nanograms per standard cubic meter; dissolved gaseous mercury in surface seawater in femtomoles per liter; sea-surface temperature in degrees Celsius; nitrate plus nitrite in micromoles per liter; and chlorophyll a, contoured every 100 μg/m^3. Superimposed on the chlorophyll a field are the sampling depths of the dissolved gaseous mercury. A circle denotes one sample, while a circle with a line indicates that two samples taken at 15 and 30 were combined for the dissolved gaseous mercury measurement.

3°S (15 m) along the 85°W track (Fig. 2B). Among all samples, DGM and chlorophyll a have a correlation coefficient of 0.448 ($P = 0.0415$, $n = 21$).

The correspondence between DGM and chlorophyll a, although weak, suggests that dissolved mercury in the surface waters of the equatorial Pacific may be volatilized by phytoplankton to an inorganic volatile form that is probably Hg°. Laboratory studies have shown that algae are able to convert dissolved mercury to Hg° (*13*). The elevated levels of DGM in cooler, nutrient-rich waters also suggest that DGM could be produced at depth, perhaps through bacterial activity, and subsequently be transported in upwelling waters to the sea surface. Dissolved gaseous mercury may also be formed from the reduction of dissolved mercury species by organic compounds. While the production of DGM is associated with biological activity, there is no specific information on the principal volatilization mechanisms.

Total mercury concentrations (*2*) in the surface water of the equatorial Pacific are low, ranging from 1.0 to 3.5 p*M*. These values compare well with our previous results in the equatorial Pacific (155°W) for reactive Hg in surface seawater of 0.7 to 2.0 p*M* (*1*). The concentrations of DGM range from 28 to 225 f*M* and represent a significant fraction of total mercury (2 to 12 percent).

Elemental mercury is the only inorganic gaseous form of mercury that is sufficiently volatile to be purged from seawater under the experimental conditions. Dissolved $HgCl_2$ gas, although predicted to be about 2.6 percent of the total dissolved mercury in seawater (*14*), is too soluble to be removed during the purging step. The Henry's law constant [$H = C_g/C_w$, where C_g and C_w are the concentrations for $HgCl_2$ in air and in fresh water ($Cl^- = 0.2 \times 10^{-3} M$), respectively] for $HgCl_2$ gas is 2.9×10^{-8} at 25°C (*15*). Only inorganic volatile mercury species with relatively large values of H are viable candidates for DGM, with Hg° ($H = 0.37$ at 25°C) being the prime candidate.

It is reasonable to assume that all the DGM in the surface water and all the inorganic gaseous mercury in the overlying air is Hg°. The degree of saturation of mercury in the seawater relative to air can be calculated by

$$S = \left[\left(\frac{C_w H}{C_g}\right) - 1\right]100 \qquad (1)$$

where C_w and C_g are the concentrations of Hg° in seawater and air, respectively, and H is the Henry's law constant for Hg° (*16*). Positive values of S indicate supersaturation in the water while negative values indicate undersaturation. Using the measured values of C_w and C_g obtained on the cruise and values of H as a function of temperature in seawater for Hg° (*17*), we calculate a range of values for S from 79 to 1669. The surface seawater is greatly supersaturated with Hg° for all stations. This indicates that the equatorial Pacific Ocean is a source of mercury to the atmosphere.

The flux of Hg° from the ocean to the atmosphere can be estimated with a thin-film gas-exchange model following the approach of Broecker and Peng (*18*):

$$F = \left(\frac{D}{Z}\right)(C_t - C_b) \qquad (2)$$

where F is flux of Hg° into (+) or out of (−) the ocean, D is diffusivity of Hg° in water, Z is water film thickness at the air-sea interface, and C_t and C_b are the concentrations of Hg° at the top and the bottom of the film, respectively. Using an average value of Z for this region of 50 ± 22 μm ($n = 11$) (*18*) and a value of D for Hg° (*19*) of $2.9 \pm 0.1 \times 10^{-5}$ cm²/sec at 23.6°C [the average sea-surface temperature ($n = 22$) of all the stations], we calculate a piston velocity (D/Z) for Hg° of 5.1 ± 2.2 m/day. This is comparable to piston velocities of other gases such as oxygen (4.0 ± 1.7 m/day, $n = 11$) and radon (2.4 ± 1.0 m/day, $n = 11$) in the equatorial region (*18*).

The calculated annual flux of Hg° ranges from 4.4 to 78.7 μg/m², with an average of 29 ± 19 μg/m² ($n = 22$). Taking the area of the equatorial Pacific Ocean (length from 82° to 172°W and width from 5°N to 5°S) to be roughly 1.1×10^{13} m², we estimate an average annual mercury flux from the equatorial Pacific to the atmosphere of $0.32 \pm 0.26 \times 10^9$ g/year ($n = 22$). This is about 4 percent of the total annual mercury flux to the atmosphere (8×10^9 g/year) (*1*).

We can estimate a flux of mercury from the world ocean to the atmosphere by assuming that the volatilization of mercury is proportional to primary production. About 11 percent of the total primary production occurs in the equatorial Pacific, on the basis of a primary production in the equatorial zone of 2×10^{15} g of carbon per year (*20*) and a primary productivity for the world ocean of 1.8×10^{16} g of carbon per year (*21*). This yields an annual mercury efflux of $2.9 \pm 1.8 \times 10^9$ g/year ($n = 22$) for the world ocean. This is about 36 percent of the yearly mercury flow to the atmosphere and is comparable to anthropogenic emissions estimated by Watson (*22*) at 2.4×10^9 g/year.

In summary, evasion is an important feature of the marine biogeochemical cycle of mercury in the equatorial Pacific ocean. On a broader scale, oceanic effluxes of mercury may significantly affect the global cycling of this metal. The exchange behavior of mercury between air and sea should be further investigated, particularly in differing ocean regimes, to elucidate the mechanisms responsible for the volatilization of mercury in the marine environment.

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