Reports

An Equatorial Pacific Ocean Source of Atmospheric Mercury

Abstract. *Pronounced increases in total gaseous mercury (TGM) in the near surface marine atmosphere were found in the equatorial region (4°N to 10°S) of the Pacific Ocean at 160°W. The atmospheric enhancement of TGM corresponded closely to sea-surface manifestations of equatorial upwelling as reflected in measured changes of temperature and nutrient concentrations as well as to variations of reactive mercury in surface seawater. The elevated atmospheric TGM levels most probably result from oceanic mercury evasion associated with upwelling and increased biological production that occurs in the equatorial Pacific Ocean. This evidence of sea-to-air mercury transfer supports model predictions of an oceanic source of atmospheric mercury and suggests that marine-derived mercury emissions should occur in other biologically productive regimes.*

Mercury and many of its compounds are toxic, quite volatile, and readily cycled at the earth's surface. Various global scale geochemical models for the cycling of Hg in the environment (*1*) suggest that atmospheric processes must significantly affect the global distribution of Hg and provide a means for Hg transfer between the continents and oceans. Moreover, such simulations, in general, predict the oceans to be a source of atmospheric gaseous Hg. The postulated prominence of the atmosphere and the interaction of the air and sea in the Hg cycle has focused interest on the atmospheric behavior of Hg and toward the marine environment. Nevertheless, limited information is available concerning the role of the oceans in the Hg cycle, and few studies have addressed air-sea Hg exchange (*2*).

We report experimental data indicating that biologically productive regions in the equatorial Pacific Ocean may be a source of gaseous Hg species to the marine troposphere. This evidence for Hg evasion from the ocean is based on a study of Hg in the near surface marine atmosphere and in surface seawater on a cruise track along 160°W from 20°N to 20°S. These results, which confirm model predictions of the sea as a source of atmospheric gaseous Hg, also demonstrate that Hg interactions between the oceans and atmosphere are more complex than geochemical mass balance estimates suggest.

The primary evidence for Hg evasion from the surface ocean was obtained on an interhemispheric research cruise of the R.V. *T. G. Thompson* (University of Washington) in the tropical Pacific Ocean during October 1980. The meridional cruise track at 160°W and the air sampling locations are summarized in Fig. 1. Shipboard determinations were made of total gaseous mercury (TGM) (*3*) in the marine atmosphere at bow level (~ 10 m). In addition, mixed-layer water samples from the surface were collected and analyzed on shipboard for reactive Hg (*2*). Nutrient concentrations were measured, and standard hydrographic determinations of salinity and temperature were also obtained (*4*) (Fig. 2).

We found pronounced increases [> 0.5 ng per standard cubic meter (scm)] of TGM in the equatorial region approximately defined by the latitudes 4°N and 10°S (Fig. 2). Moreover, these maxima appear to be superimposed on a background concentration of TGM that decreases interhemispherically going north to south. A relatively smooth transition from higher concentrations of TGM in the Northern Hemisphere to lower concentrations in the Southern Hemisphere had been anticipated. That pattern would be similar, for example, to the one exhibited by another trace gas, carbon monoxide, whose primary sources are continental (*5*). Indeed, such an interhemispheric distribution for TGM in the near surface atmosphere over the Atlantic Ocean has been reported (*6*). Initially, we suggested that the localized enhancement of TGM in the atmosphere over the equatorial Pacific was caused by evasion of Hg species from the oceans to the atmosphere (*2*). We can now demonstrate that this hypothesis is supported by the ancillary sea-surface measurements and other studies of trace gases in the equatorial Pacific Ocean.

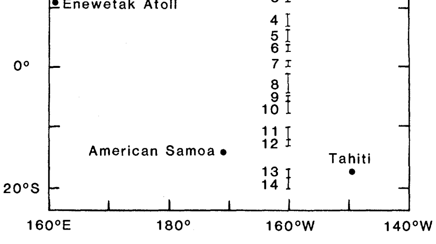

Fig. 1. Cruise track of the R.V. *T. G. Thompson* (1 to 21 October 1980). Each bar represents the latitudinal distance traversed during a period when atmospheric Hg was collected.

The increases in TGM are defined by measurements in which we have a high degree of confidence. The overall analytical uncertainty in any one measurement is about 10 percent, and the determinations at the extremes of latitude agree with other results. For example, the TGM concentrations (~ 1.5 ng/scm) at latitudes north of 10°N are similar to our earlier observations at Enewetak Atoll, the Marshall Islands, and in the northwest Atlantic Ocean (*2*) as well as to the average TGM concentration of 1.56 ng/m^3 reported for the North Atlantic Ocean (*6*). At latitudes south of 10°S smaller concentrations of TGM (~ 1.0 ng/scm) were observed and these results are almost identical to the average concentrations of TGM (1.05 ng/m^3) reported for the South Atlantic Ocean (*6*). This agreement at the extremes of latitude corresponds satisfactorily with the Intertropical Convergence Zone (ITCZ) as defined by cloudiness at or near 160°W. During the cruise period (1 to 21 October 1980) this transition region, which serves to inhibit interhemispheric exchange in the troposphere, varied between 5°N and 15°N (*7*). Thus, Southern Hemispheric chemical distributions in the troposphere would be expected south of 5°N.

The equatorial Pacific regime is hydrographically and biologically dynamic. Westward currents flowing north and south of the equator are intersected by an eastward equatorial countercurrent resulting in a strong but variable zonal water flow (*8*). Significant wind-driven equatorial upwelling (Ekman divergence) occurs in the South Equatorial Current, which flows between ~ 4°N to ~ 10°S. The diverging surface waters are replaced by cooler, nutrient-rich water from depths of about 100 to 200 m, supporting primary production and biological activity at the surface (*9*).

The observed TGM fluctuations are distributed over the same latitudinal range as the oceanographic features. Indeed, the increased TGM in the atmosphere coincides with sea-surface manifestations of equatorial divergence and upwelling as reflected in measured changes of temperature and nutrient concentrations (Fig. 2). The temperature of the sea-surface mixed layer can be used as an indicator of upwelling along the equator and the concentrations of nitrate plus nitrite show that the cooler waters reaching the surface are enriched in nutrients. This reasonably good correlation between the near surface atmospheric changes in Hg and hydrographic variability suggests, first, that Hg evasion is enhanced within the equatorial upwelling region and, second, biological mediation is probably involved in the process.

The day to night variability observed for TGM as a function of latitude (Fig. 2) provides additional support for an equatorial oceanic source of gaseous Hg and further evidence for the role of biota in the process. In the upwelling region (4°N to 10°S) the TGM concentrations are about 0.7 ng/scm higher during the day than in the night. Although we do not have day and night data from the same site, we assume this difference to reflect temporal rather than spatial variability. No significant difference in TGM from day to night was observed at the higher latitude stations in either hemisphere. This pattern is consistent with the distribution of biological productivity in the region. That is, primary biological production in upwelling zones is considerably higher than in the oligotrophic open ocean regimes to the north and south (*10*). Laboratory studies indicate that both algae (*11*) and bacteria (*12*) can convert dissolved inorganic Hg to volatile vaporous forms. Our work, while suggesting biological mediation in the Hg emission process, cannot specify what kinds of organisms may be involved.

Emission of gaseous Hg species from the equatorial Pacific Ocean does not appear to be an anomalous process. For example, enhanced concentrations of the trace gases ethylene, propylene, and nitrous oxide (N_2O) in association with increased biological productivity have also been observed in the Pacific equatorial upwelling region. A source of ethylene and propylene was observed between 9°N and 20°S on a cruise track from Hawaii to New Zealand (*13*). The excessive concentrations of these unsaturated hydrocarbons in the surface seawater were assumed to be of biological origin. Nitrous oxide has been found between 4°N and 6°S in the surface seawater of the eastern equatorial Pacific Ocean (*14*). This N_2O was also associated with primary production (nitrate reduction) in the upwelling zone. Photochemically induced nitric oxide production was observed in samples of nutrient rich equatorial surface water from the central Pacific Ocean near 170°W (*15*). Most recently, Andreae and Raemdonck (*16*) reported finding evasion of dimethyl sulfide (DMS) from equatorial Pacific water as well as a variation in the atmospheric DMS concentrations from day to night caused by photooxidative destruction. Thus, the elevated but small atmospheric concentrations of TGM may be a reflection of more significant gaseous emissions in the equatorial region.

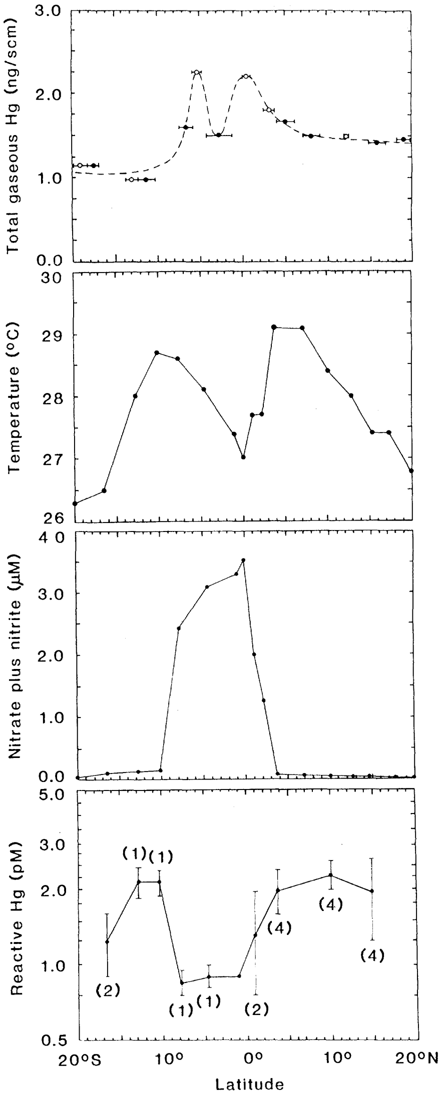

Fig. 2. Interhemispheric shipboard study of Hg in near surface marine atmosphere and in surface sea water at 160°W. Latitudinal distributions plotted are: Total gaseous Hg, where open circles represent collections during daylight hours and filled circles represent night collections (the bars refer to latitudinal sampling intervals as indicated in Fig. 1); temperature of the mixed layer at 5 m below the sea surface; nitrate plus nitrite concentration in the sea-surface mixed layer; reactive Hg concentrations in the sea-surface mixed layer with the 2σ experimental error limits indicated for replicate samples where the number of collections = N and for duplicate analyses of a single sample where $N = 1$. Only one determination was made at 1°S.

Additional supporting evidence for Hg evasion from the equatorial zone is the coincidental reduction in reactive Hg concentrations in surface water between 4°N and 10°S (Fig. 2). A decrease in reactive Hg of about 65 percent occurred in this equatorial region. While we have not yet measured dissolved gaseous Hg species directly, part of the decrease in reactive Hg may represent conversion of dissolved species to volatile gaseous forms that can escape from the sea surface.

We estimated the regional precipitation transport of Hg to the tropical Pacific Ocean at 3 μg/m^2 per year from our rainfall studies at Enewetak Atoll (11°20′N, 162°20′E) (*2*). Wyrtki (*9*) estimates the transport of newly upwelled water in the Pacific Ocean equatorial zone at 50×10^6 m^3/sec or 1.6×10^{15} m^3/year. If just 10 percent of the decrease of 1 nmole/m^3 in reactive Hg observed between 4°N and 10°S was converted to TGM in newly upwelled waters, then about 30 metric tons (MT) of Hg per year would be released to the atmosphere. This flux would correspond to an emission of ~ 3 μg/m^2 per year for the Pacific Ocean equatorial area (95°W to 165°E) taken as 10×10^{12} m^2 by Wyrtki. This estimate, while conservative, is comparable to the precipitation flux of Hg at Enewetak and demonstrates the potential for geochemically significant Hg evasion in the equatorial Pacific Ocean.

On a larger scale, this Hg efflux, obtained from an independent measure of equatorial upwelling, can be contrasted with other Hg emissions to the atmosphere. Anthropogenic Hg emissions, for example, have been assessed at about 2000 to 3000 MT/year (*17*), whereas we have estimated total Hg emissions (natural plus human-related) at 8000 MT/year (*18*). We suspect that other biologically productive regions of the oceans may also be sources of Hg to the atmosphere. If oceanic Hg emissions to the atmosphere were proportional to the biological activity in the water, a correspondingly greater amount of Hg would emanate from the sea surface. Since the Pacific Ocean equatorial productivity represents approximately 2 percent of the total oceanic carbon production (*19*), an ocean-wide sea to air Hg flux may be of the order of 50 times the equatorial release to the atmosphere. In terms of the global cycling of Hg, and given the limitations of our estimate, oceanic sources of Hg would probably not substantially perturb the predominant Hg transfer between the continents and the oceans. However, ocean to atmosphere Hg flows could potentially rival anthropogenic fluxes of Hg to the atmosphere.

While no information on the composition of Hg in the vapor phase was obtained, the increases in TGM may be caused by the emission of a Hg species other than elemental Hg. The effluxing phase may include an organomercury component, such as dimethyl mercury, which can be synthesized biologically (*20*). The Hg-containing compounds in the atmosphere may be related to the regional source of Hg, and thus a measure of the Hg-containing compounds in the local atmosphere may reveal the local relationship of the atmospheric Hg speciation imprint to physical and biological oceanic processes. Information on the Hg-containing compounds in the atmosphere may also benefit meteorologists concerned with mixing processes and oceanic air mass trajectories. Clearly, further exploration will be required to evaluate the significance of air-sea interaction and exchange of gaseous Hg species to the Hg cycle in the environment.

In summary, our data provide evidence of an oceanic source of atmospheric Hg in the equatorial Pacific Ocean. Elevated atmospheric TGM concentrations were evident locally, and this regional effect was apparently produced by an oceanic evasion process that is related to upwelling and biological productivity in the equatorial Pacific Ocean.

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21. We thank the captain and crew of the R.V. *T. G. Thompson* and our colleagues in the SEAREX Program for their assistance. We particularly thank Kenneth Bruland for allowing us to participate in his field sampling program and for providing the nutrient and hydrographic data. John Merrill provided us with meteorological insight. Supported by National Science Foundation grants as part of the Sea-Air Exchange Program (SEAREX).

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Ozone- and Photon-Enhanced Atmospheric Sulfidation of Copper

Abstract. *The sulfidation of materials upon exposure to the atmosphere has traditionally been attributed entirely to reactions with sulfur-containing gases and water vapor. New laboratory results demonstrate that the sulfidation of polycrystalline copper can be markedly enhanced both by solar radiation and by the ubiquitous atmospheric ozone, thus indicating that the high rates of corrosion in urban areas are a result of a complex sequence of multicomponent photochemical processes.*

Copper and its alloys corrode in the ambient air in the presence of reduced sulfur-containing gases (*1, 2*). The mechanism of the sulfidation is not understood, although the process is known to be sensitive to humidity (*3, 4*) and its activation energy is consistent with the involvement of a radical or ion intermediate (*4*).

In normal field use, materials are exposed to a multiplicity of trace gases, not just those containing sulfur. Among these gases is the strong oxidizer ozone, which is of interest in the context of this study because it is known to enhance the oxidation of silver in the solid state (*5*) and in aqueous solution (*6*) and that of iron in the solid state (*7*) and in aqueous solution (*8*). Since exposed metal surfaces are covered by several monolayers of water at high relative humidities (*9*), the surfaces of most materials in field use appear to be intermediate between that of a dry solid and that of a solid with a water overlayer.

It is not clear whether under ambient conditions the principal metal oxidation reactions will involve ozone or one of its reactive products. Ozone hydrolyzes in solution to produce hydroxyl (OH) radicals (*10*), which are known to react directly with a number of metals (*11*). In addition, ozone photolyzes in solution at wavelengths typical of solar radiation (*12*), a process that generates OH radicals through the H_2O_2 intermediate (*13*).

These considerations suggested that experiments in which materials are exposed to mixtures of ozone and a sulfur-containing gas might enable us to increase our understanding of atmospheric corrosion. Accordingly, we exposed samples of polycrystalline oxygen-free, high-conductivity copper (99.999 percent pure) to corrosive atmospheres of hydrogen sulfide (H_2S) and ozone (O_3) in humidified, prepurified air. The samples were prepared by a sequential polishing technique described in detail elsewhere (*4*). The exposures were performed with the apparatus shown in Fig. 1, which adapts techniques previously developed for sulfidation studies not involving light or O_3 (*14*). The apparatus is designed to permit continuous monitoring of all relevant experimental parameters, the values of which are stored and subsequently analyzed by a dedicated desk-top computer. After exposure, the thickness of the sulfide film grown on each sample is determined by energy-dispersive x-ray analysis, with the use of a scanning electron microscope (SEM) (*15*).

One set of samples was exposed to the environment containing mixed H_2S and O_3, with no incident radiation present. The gases were mixed just prior to injection into the exposure chamber. The H_2S concentrations were of the order of 2 ppm, the O_3 concentrations of the order of 0.2 ppm. Although H_2S and O_3 react with each other, the rate of reaction is slow (*16*). Calculations of system flow rates demonstrate that gas-phase removal of these species by mutual reaction is unimportant in our studies. The possibility that surfaces may heterogeneously catalyze the reaction (*17*) increases the potential relevance of our experiments. The results of the exposures are plotted in Fig. 2a, where they are compared with