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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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

the film growth produced on a set of copper samples exposed in the same way but in the absence of O_3. The presence of O_3 does not affect the sulfidation for short exposures but at longer exposures (> 10 ppm-hour) enhances the film thickness by up to a factor of 3. This is an important enhancement, since typical H_2S field exposures are about 10 ppm-hour per year [18].

Figure 2b shows the sulfide film growth on copper samples exposed to H_2S in highly humidified air without O_3 but under incident radiation approximat-ing one solar constant. Thermocouple measurements indicated no significant change in the temperature of the samples, which were cooled by the flowing air stream. The presence of incident radiation enhances sulfidation by a factor of between 1.5 and 2 at longer exposures (Fig. 2b). Figure 2c shows the results of exposures of copper samples to H_2S, O_3, and incident radiation in humidified air. The acceleration of sulfidation is approximately the same as that produced by exposures to H_2S and O_3 without incident radiation, as shown by the curve comparison in Fig. 2d.

Our results appear to be the first to demonstrate unambiguously that a trace oxidizing gas can enhance a specific corrosion process. The results of an earlier experiment involving a mixture of seven trace gases indicated that O_3 concentration was related to the weight gain of corroding copper and silver samples [1], so there is some precedent for our results.

Information on the mechanism of the sulfidation process is provided by the form of the kinetic data in Fig. 2. In the absence of O_3 and light, the copper sulfidation rate is known to be approximately parabolic once the initial corrosion layer forms [4, 19]. Such behavior indicates that the corrosion process is controlled by the rate of upward diffusion of copper ions [20]. In the presence of O_3, however-er, the rate becomes linear, an indication that gas-phase diffusion is the limiting process [21]. The implication, therefore, is that the surface film that forms in the presence of O_3 is subject to structural defects that provide efficient channels for ion diffusion. Our SEM micrographs of these samples are suggestive but not conclusive in this regard. It has often been remarked [22] that there are major differences in the compositional and contact resistance properties of tarnish films produced by laboratory exposure and those produced by field exposures. The lack of O_3 in the laboratory exposures is a possible cause of the discrepancy.

The effects of incident radiation on copper sulfidation can be accounted for by the semiconductor properties of the surface constituents. Copper forms a mixed surface film upon initial exposure to humidified air, with a layered $Cu/Cu_2O/CuO$, $Cu(OH)_2$ structure [23, 24]. Upon sulfidation, a mixed oxide-sulfide film will form. Photocorrosion of such semiconductor materials in oxygenated aqueous solution is known to occur [23, 25], and our data indicate that photocorrosion occurs within thin aqueous surface films as well. The rate of growth of the corrosion film under illumination is
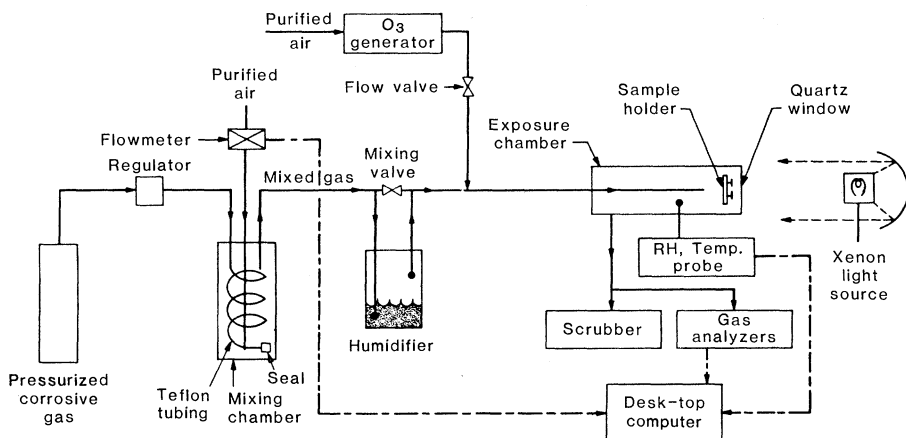

Fig. 1. The sample exposure apparatus used in the experiments. Solid lines indicate paths of gas flow, broken lines paths of data flow; RH, relative humidity.
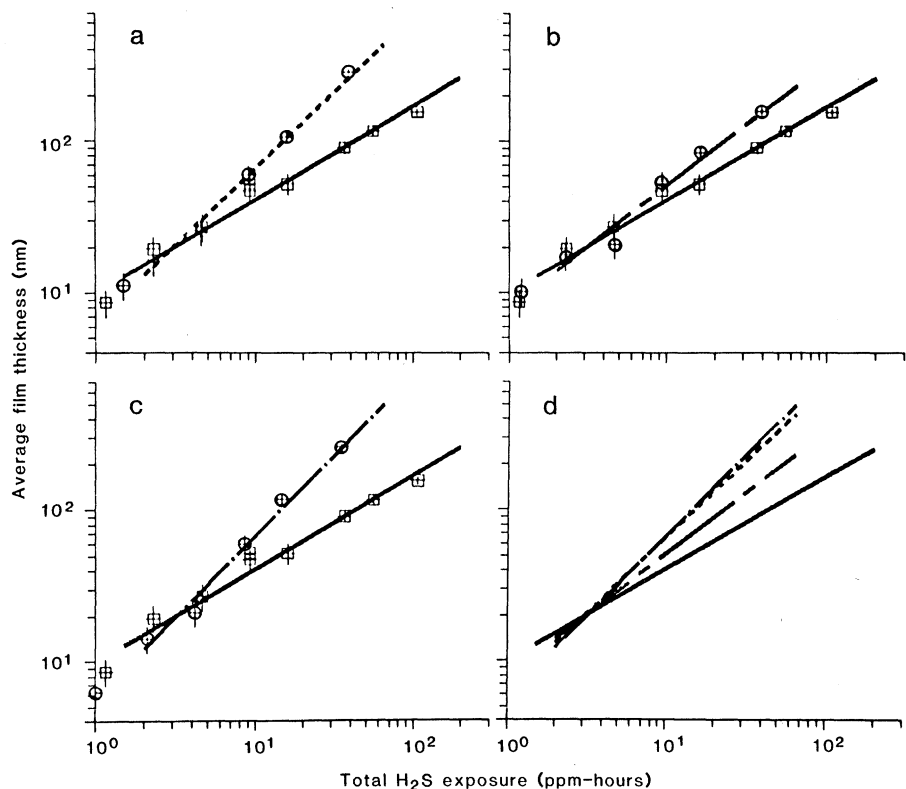

Fig. 2. Average thickness of the cuprous sulfide corrosion film as a function of total H_2S exposure (the product of H_2S concentration and exposure time): (a) exposure to H_2S (2.3 ± 0.2 ppm) and O_3 (0.17 ± 0.03 ppm); (b) exposure to H_2S (2.3 ± 0.3 ppm) and light; (c) exposure to H_2S (2.1 ± 0.2 ppm), O_3 (0.20 ± 0.03 ppm), and light; (d) fitted curves from (a) to (c). The solid lines and squares are for exposures to H_2S in the absence of both O_3 and incident radiation; the circles and broken lines are for exposures to H_2S in the presence of either O_3 or incident radiation or both. The estimated error limits for our determinations of total exposure and film thickness are indicated for each data point; the lines are least-squares fits to the points. For all experiments, the temperature was 21.0° ± 0.5°C and the dew point was 19.9° ± 0.6°C. The ± values given here are the standard deviations of the values throughout the exposure periods and indicate the ranges of the variables during those periods. The precision of each measurement is a negligibly small fraction of its range.

significantly less than that under O_3 exposure, however.

The concentrations of trace gases that we have used in these experiments are high but not unrealistic. Concentrations of H_2S of several parts per million occur in the vicinity of sources such as oil fields, pulp mills, and sewage treatment plants. In any case, our previous results demonstrate that sulfidation involving H_2S scales with total exposure over a wide range of concentrations (4), so that lower concentrations and longer exposure times produce equivalent sulfidation of copper. Ozone concentrations of 0.2 to 0.3 ppm do not often occur, but such concentrations have been measured in locations as diverse as Detroit (26), Houston (26), Los Angeles (26), New Haven (27), Sydney (28), and Toronto (29). High concentrations outside buildings can produce reduced but still high (~ 0.2 ppm) O_3 concentrations indoors (30). The high O_3 concentrations in urban areas are generally the result of photochemical generation from anthropogenic precursors (26), although high O_3 concentrations can occur anywhere as a result of the injection of stratospheric air into the troposphere (31). Once high concentrations of trace atmospheric gases are present in the air, they can be transported many hundreds of kilometers (32).

Our results and these considerations support the view that atmospheric O_3 participates in a wide range of corrosion processes on a variety of materials, both indoors and out. The diverse items affected must surely include open-wire telephone lines, copper roofing, and bronze statuary. With the involvement of O_3 in atmospheric corrosion now established, it is reasonable to anticipate that other atmospheric oxidizing species are involved as well. Among those species are H_2O_2 and the OH, hydroperoxyl (HO_2), and alkylperoxyl (RO_2) radicals. It is clear that atmospheric chemistry and atmospheric corrosion of materials are inextricably intertwined and that a new degree of complexity has been added to corrosion research.

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Amblyomma americanum: A Potential Vector of Lyme Disease in New Jersey

Abstract. Amblyomma americanum *is a likely secondary vector of Lyme disease in New Jersey. Ticks of this species were removed from the site of the characteristic skin lesion known as* erythema chronicum migrans *on two patients with the disease, and the Lyme disease spirochete was isolated from nymphs and adults of this species. That* A. americanum *is a potential vector is supported by its similarities to* Ixodes dammini, *the known tick vector, in seasonal distribution and host utilization. The extensive range of* A. americanum *may have great implications for potential Lyme disease transmission outside known endemic areas.*

Lyme disease, first described in Connecticut in 1975, is an inflammatory disorder with a characteristic annular lesion, *erythema chronicum migrans* (ECM), which may be followed by arthritic, cardiac, or neurological manifestations (1). Initial epidemiologic evidence suggested that Lyme disease was transmitted by the nymphal stage of the tick *Ixodes dammini* (2). That the etiologic agent of Lyme disease is a spirochete was first proposed in 1982 (3). Spirochetes were subsequently isolated from adult and immature *I. dammini* from New York, Connecticut, and New Jersey (4–6). Past evidence indicated that Lyme disease in the United States and cases of ECM in Europe were transmitted solely by ticks in the genus *Ixodes* (7). In New Jersey, populations of *Amblyomma americanum* ticks temporally coexist with *I. dammini* and equally infest a variety of mammalian hosts including the white-footed mouse (*Peromyscus leucopus*) and white-tailed deer (*Odocoileus virginianus*) (8–10).

We first became aware of the vector potential of *A. americanum* in May 1982 when a tick removed from the site at which ECM developed in an 87-year-old male from Medford, New Jersey, was identified as a female of this species. As this case predated the publication of the isolation of the Lyme disease spirochete (3), serological confirmation was not attempted at the time of illness. A serum sample drawn 4 months after the date of onset showed a titer of 1:128 by indirect immunofluorescence (IFA) (Table 1). In June 1983, a second *A. americanum* as-