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Occurrence of Methylmercury in Lake Valencia, Venezuela

R. Jaffé,[1,2] Y. Cai,[3] J. West-Thomas[3] M. Morales,[4] R. D. Jones[3,5]

[1]Drinking Water Research Center, [2]Department of Chemistry, and [3]Southeast Environmental Research Program, Florida International University, Miami, Florida 33199, USA
[4]Departamento de Procesos, Universidad Simón Bolivar, Apartado 89000, Caracas 1080-A, Venezuela
[5]Department of Biological Scrences, Florida International University, Miami, Florida 33199, USA

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The presence of mercury in the environment has received renewed attention during recent years (e.g., Stein et al. 1996; Driscoll et al. 1994; Zillioux et al. 1993). This is in part due to the known human health and ecological effects of the highly toxic organomercury compounds, and to the fact that novel and improved analytical techniques such as atomic fluorescence spectroscopy (AFS) and capillary chromatography with AFS detection, have enhanced significantly the detection of trace amounts of mercury and organo mercurials in environmental samples (e.g., Bloom 1989; Alli et al. 1994; Jones et al. 1995). Such techniques have allowed for a better understanding of the biogeochemical cycle of mercury in the aquatic environment.

This paper reports on the presence of methylmercury in the water column and sediments of a hyper-eutrophic lake. Lake Valencia is a freshwater lake located in North-Central Venezuela's Aragua Valley. The lake's surface area covers approximately 350 km^2, with a mean depth of 19 m and a maximum depth of 41 m (Jaffé et al. 1993 and references therein). Due to the discharge of waste waters from the cities of Maracay and Valencia, as well as from other smaller villages and agricultural areas in its watershed (Jaffé et al. 1993), Lake Valencia has become hyper-eutrophic. The population of phytoplankton, particularly of blue-green algae, has increased dramatically during the last two decades resulting in anoxic conditions in the lower part of the water column during most of the year (Lewis, 1984). In addition, concentrations of anthropogenic chemicals, including heavy metals, have increased in the Lake during the last four decades (Jaffé et al. 1995).

Correspondence to: R. Jaffé

The anoxic/reducing environment in the hypolimnion of Lake Valencia, combined with the relatively high dissolved organic carbon (DOC) levels, are ideal conditions for the microbial transformation of mercury to organic mercury. However, the anthropogenic sources of sulfate to the lake have resulted in elevated sulfide concentrations in the anoxic waters and sediments of the lake. Therefore, the high affinity of mercury for sulfur (i.e., complexation and/or precipitation as sulfide) may compete with the microbial methylation process in both the hypolimnetic waters and the sediments. The data presented below address the issue of speciation.

MATERIALS AND METHODS

Water and sediment samples were collected in August of 1995 during the period when Lake Valencia presents anoxia in the deeper part of its water column. Water samples were collected at the central part of the lake, at a location where the water depth reaches 40 m. The water samples were collected in Teflon bottles, by pumping water through a polyethylene hose. The hose was cleaned by pumping lake water through it for at least 30 min., and also purged at each depth for 2 min. Samples were collected at 5 depths in the water column (1, 6, 12, 18 and 24 m). These depths were determined based on the dissolved oxygen (DO) profile. Only the deepest sample (24 m) was clearly anoxic (DO = 0.35 mg/l).

Sediments were collected also at the deepest part of the lake, using a gravity core sampler (Wildco model 2400). The core was sliced into 4 cm segments, placed in acid and solvent clean glass jars, and frozen immediately. Both sediment and water samples were analyzed for methylmercury by cold vapor AFS and GC-AFS following the procedures described by Jones and coworkers (Jones et al. 1995; Alli et al. 1994). Mercury reference material (Dorm-2 fish tissue, National Research Council of Canada) was analyzed in order to ensure adequate QA/QC. Certified and measured concentrations µg/g) for MeHg were 4.47±0.32 and 4.74±0.18, respectively, while those for HgT were 4.64±0.26 and 4.45±0.02, respectively. Detection limits for MeHg and HgT were 0.01 ng/g and 4.3 ng/g, respectively. Dissolved oxygen (DO) was determined on site using a DO probe. Suspended solids (SS) and particulate organic carbon (POC) were determined gravimetrically following standard procedures. Nutrients (ammonia and phosphorus) and dissolved organic carbon (DOC) were determined using automated nutrient analyzers (Alpkem R.F.A. 300 Series equipped with a Series 500 Autosampler) and a Total Organic Carbon Analyzer (Shimadzu T.O.C-5000A). Blanks were determined for all chemical parameters reported here.

RESULTS AND DISCUSSION

Figure 1 (a to f) shows DO, SS, POC, DOC, ammonia, total phosphorus and methylmercury data of the water column of Lake Valencia. The DO showed a steady decrease in concentration with increasing depth, with complete anoxia only in the sample taken at 24 m depth. This sample also showed the characteristic hydrogen sulfide odor when retrieved. The SS and POC profile suggested high abundances of phytoplankton in the surface waters of the lake, followed by a steady decrease with increasing depth. A similar profile was obtained for the DOC, however, with a substantially lower relative concentration decrease with depth compared to the SS and POC. The DOC concentrations were between 14.6 and 17.2 ppm throughout the water column. Both the high POC and DOC are indicative of abundant phytoplanktonic primary productivity at the surface waters. Their decrease with depth suggests early diagenetic degradation of this organic matter.

The degradation of the abundant planktonic organic matter in the water column is in agreement with the reduction in the DO levels and the steady increase of total dissolved phosphorus and ammonia with increasing depth (Fig. 1d and e). In agreement with these mainly sub-oxic and anoxic microbial processes in the deeper waters of the lake, the methylmercury concentrations increased steadily with increasing depth (Fig. lf). The decrease in methylmercury for the sample at 24 m compared to that at 18 m was lower than the standard deviation of the triplicate samples and, therefore, was not significant. However, the increase in concentration under increasingly reducing conditions was clearly observed.

Methylmercury concentrations in the sediments, however, were below the detection limit (10 pg/g of dried sediment). This was not surprising, since the sediments of Lake Valencia are anoxic and contain relatively high concentrations of sulfur. This suggests that the affinity of mercury for sulfur out-competes the microbial methylation process in this lake. In general terms, methylmercury is found in sediments that, although subject to anoxic or sub-oxic conditions, have limited sulfate availability. Diagenetic changes

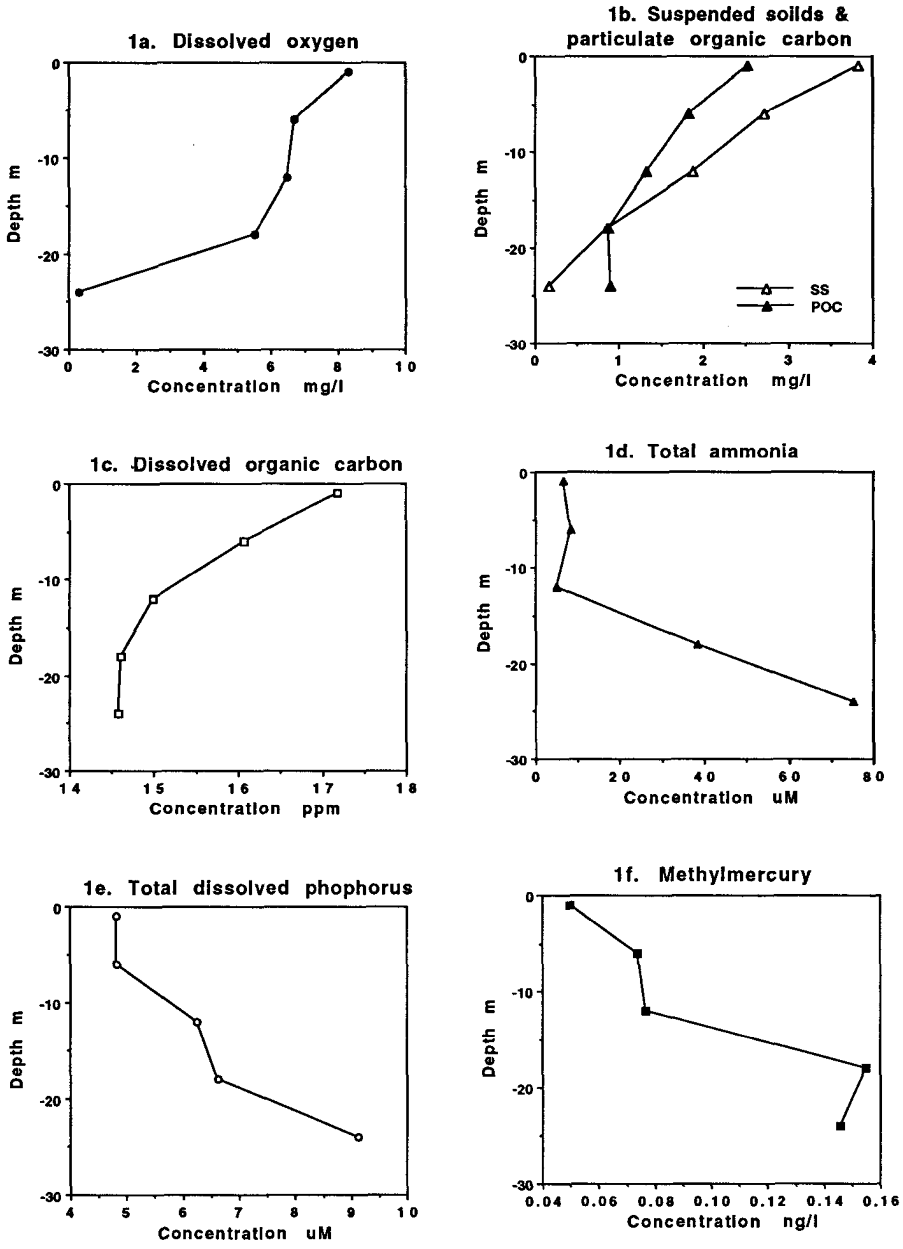

Figure 1. Depth profiles for (a) dissolved oxygen (DO), (b) suspended solids (SS) and particulate organic carbon (POC), (c) dissolved organic carbon (DOC), (d) ammonia, (e) total phosphorus and (f) methylmercury in the water column of Lake Valencia.

involving sulfate reduction, for example in marine sediments, have been reported to hinder the formation of methylmercury (Gagnon et al. 1996). Concentrations of total mercury were found to increase with water depth in a stratified lake environment, and were found to be mainly in the form of soluble sulfide-mercury complexes (Wang and Driscoll 1996). Other reports have shown that methylation of mercury is proportional to sulfide concentration, although only up to a concentration of approximately 2 mg/g, after which the methylmercury levels decreased sharply (Craig and Moreton 1983; Weber 1993; Stein et al. 1996). It is clear that high levels of sulfide can either precipitate the highly insoluble mercury sulfide or form soluble, although stable sulfide-mercury complexes, both resulting in dissolved mercury ion concentrations that are too low for biotic methylation reactions (Weber 1993). In addition, abiotical reactions between methylmercury and sulfide have been reported to produce both mercury sulfide and dimethylmercury (Craig and Bartlett 1978). This would result in a removal of mercury from the water phase to the sediments in the form of mercury sulfide via precipitation and sedimentation, and/or in the form of dimethylmercury via evaporation/volatilization to the atmosphere. Both scenarios are possible in the Lake Valencia water column. The present data suggest that initially the sub-oxic and in deeper samples the anoxic water conditions and the presence of hydrogen sulfide enhance the production of methylmercury. However, in the sediments mercury is likely to be present in association with sulfur. In addition, it has been suggested that in high DOC waters methylmercury could be prevented from entering the sediments (Miskimmin, 1991). Therefore, no methylmercury was detected in Lake Valencia sediments.

Although methylmercury was absent in Lake Valencia sediments, the core was analyzed for total mercury. As shown in Figure 2, the concentrations of total mercury were highest in the surface sediments. This general profile has been reported previously for other heavy metals in Lake Valencia cores (Jaffé et al. 1995). While Pb and Cu were found to increase in the lake sediments in the 1950’s, Ni and Cd were found to do so in the 1970’s. The Hg profile seems to suggest that mercury pollution in Lake Valencia has increased significantly in recent years. Although the core used in this study was not dated, extrapolating from previously determined sedimentation rates reported for the same sampling location (Jaffé et al. 1993), the mercury levels in the lake have increased significantly during the past 10 to 15 years.

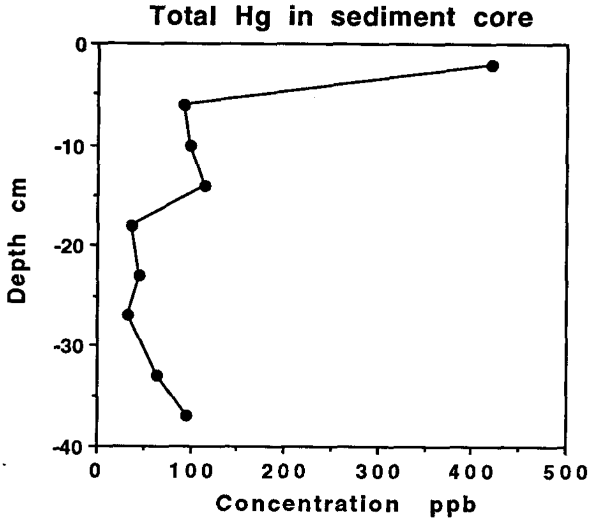

Figure 2. Depth profile of total mercury in a sediment core from Lake Valencia.

In summary, Lake Valencia's water column presents environmental conditions which seem adequate for the microbial transformation of mercury to methylmercury. However, the highly reducing conditions in the lake sediments, and the availability of sulfate for sulfate reduction, limit the presence or microbial production of methylmercury in the sedimentary environment due to its high affinity for sulfur compounds. The pollution chronology of mercury based on sediment core analyses suggests increased mercury pollution during the last decade.

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