Biochemical cycles

Natural volatilization of tin

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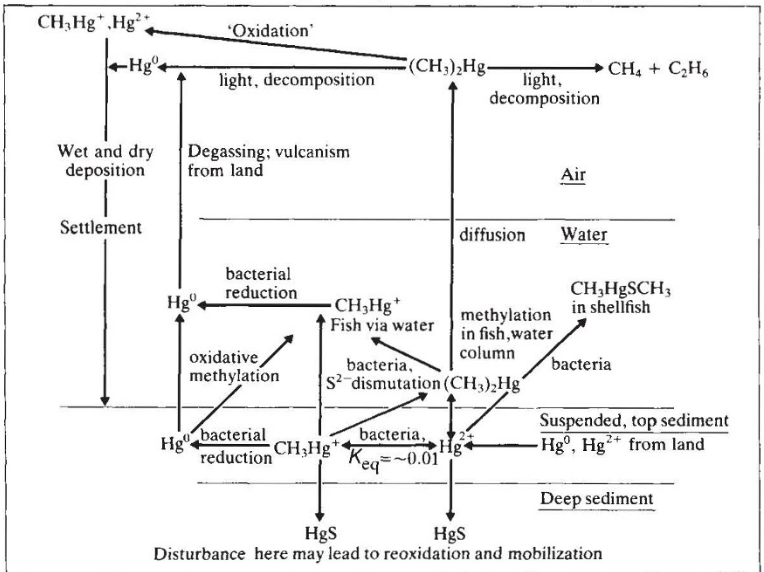
It is well known that there are natural biochemical cycles for carbon and nitrogen, and recent work has shown that there is analogous biogeochemical cycling of some metallic and metalloidal elements[1]. Best known among these are the cycles for arsenic and mercury (see figure), involving substantial chemical transformation of these elements to volatile methylated forms which diffuse to the atmosphere. Donard and Weber's work, reported on page 339 of this issue[2], significantly extends our knowledge about metallic cycles in the biosphere in revealing a new pathway for volatilization for one metal, tin, from aqueous to atmospheric phases. This pathway, which does not involve methylation, may be of significance for other metals.



Proposed biogeochemical cycle, involving methylation, for mercury (from ref. 6).

In Donard and Weber's experiment, inorganic tin compounds ($SnCl_4$ and tin metal) incubated for 6 months in an anoxic medium containing decaying algal material, were slowly converted to hydrophobic volatile stannane (SnH_4). This stannane then diffuses through the water above, without being oxidized, into the head space of the environmental chamber used in the experiment, in a way that could plausibly occur in real environments. One source of tin for such a process in the natural environment is the tributyltin antifouling paint common in harbours and marinas.

Interest in metal methylation (biomethylation) first arose because of pollution incidents in the late 1950s. For example, reductions in Canadian and Swedish bird populations occurred because of poor hatching rates due to eggshell thinning induced by anthropogenic methyl mercury from seed dressings[3]. Fish in various locations were found to have parts per million levels of methyl mercury, despite having had no apparent contact with this compound[4]. It was soon demonstrated that inorganic mercury added to aquarian sediments is partially but quickly methylated to methyl mercury[5]. Although the pollution levels in sediments are very low, food-chain effects that increase the concentration of the stable methyl mercury compounds led public-health authorities to impose maximum permissible levels of mercury in fish for human consumption.

More recently, interest has moved from pollution effects to the role of methylation in assisting the bulk transport of metals in the environment. For mercury, methylation to long-lived, non-volatile CH_3Hg^+ can be followed by dismutation to volatile, diffusable hydrophobic $(CH_3)_2Hg$ by interaction with sulphides in sediments. It has been estimated that up to 12 per cent of the methyl mercury per year could be removed from a sediment and diffused through the water layer to the atmosphere[6]. No natural alkylation by groups other than methyl has yet been observed. Metal hydride formation has only recently been discovered.

Increasingly sophisticated analytical techniques are being developed to identify the methyl metals. Gas chromatography, mass spectroscopy, atomic absorption spectroscopy and other techniques can analyse methyl metals at concentrations of a few parts per billion (10^9) or below in various environmental matrices. Naturally methylated elements thus identified include mercury, tin, arsenic, antimony, germanium, thallium, selenium, tellurium and, less clearly, lead and silicon[7]. Much work has been carried out on lead, but the data are not easy to interpret, and biomethylation is hard to recognize, because of general environmental contamination by methyl-lead gasoline additives.

The latest twist in the ability of the environment to synthesize unusual inorganic compounds is revealed by the work of Donard and Weber in this issue[2], showing that certain algae can convert inorganic tin compounds to stannane. This is the first demonstration of the environmental production of a simple metal hydride, and several issues are raised by this observation. As tin is a Group IV element, as is carbon, it could be that the production of stannane arises by the substitution of tin for carbon at critical points in the pathway of methane biosynthesis. It is significant that methanogenic activity was also observed in this experiment, as this result suggests that methanogenic organisms are responsible for stannane formation. That some methyl tins are also formed adds to this suspicion.

The existence of these apparently unstable compounds under natural conditions (normally they oxidize quickly in air) could be explained by the fact that they originate in anoxic environmental compartments, and also because their low concentration reduces the rate of intermolecular collisions leading to oxidation. Donard and Weber's work also appears to be the first demonstration of the natural formation of a simple heavy metal hydride, although the mixed metalloidal species $(CH_3)_2AsH$ can be formed microbially from inorganic arsenic compounds. This has important implications for tin transport in the environment.

Naturally occurring mixed organometallic hydrides have been identified[8] in Baltimore harbour. These compounds, $(CH_3)_nSnH_{4-n}$ ($n = 1$–3) and $(CH_3)_4Sn$, could have biogenic or anthropogenic origins. The highest levels found for the methyl stannanes are up to about 0.5 μg l^{-1} for each species, well within the limits of detection by modern equipment. Up to about 1.0 μg l^{-1} $(CH_3)_4Sn$ is also found. Laboratory experiments confirm[8] that inorganic tin can be methylated and reduced to a methyl tin hydride by an aerobic strain of *Pseudomonas* 244 which was isolated from Chesapeake Bay, and small quantities of $(CH_3)_4Sn$ and $(CH_3)_3SnH$ were also detected in the incubation. It will be interesting to see if there are other simple metal hydrides that occur naturally. □

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