Emerging Pathways

Mercury thermometers. Cadmium batteries. Lead shields. These metals are helpful in any number of technological devices. But thallium may be a new one to you. Nestled between mercury (Hg) and lead (Pb) among the p-block elements of the periodic table, thallium (Tl) is also a heavy metal with industrial uses. Discovered in 1861, thallium is more toxic to mammals than mercury, cadmium or lead.

Decades ago, thallium was commonly used in ant, rat and roach poisons. Currently, there is an increasing demand for thallium for use in the laser, optical, and other high-tech industries. Although not used to the extent it was in the past, thallium is still found in New York's Great Lakes region.

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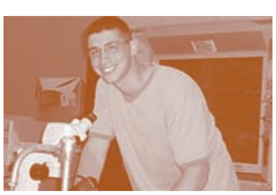

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Thallium enters the atmosphere through the combustion of coal, smelting of other metals, or other industrial processes. Once in the air, thallium particles can be deposited onto the lakes where they dissolve in water. Soluble thallium enters the food web through uptake by tiny plankton. They in turn are eaten by zooplankton which are eaten by inverterbrates and so thallium biomagnifies up the food chain.

Soluble thallium can be taken up by phytoplankton, then zooplankton, and so on up the food chain.

Artwork by Jan Porinchak

In the early 1970s, bald eagles and other wildlife populations around the Great Lakes basin displayed symptoms of thallium poisoning. For wildlife and people, signs of thallium poisoning include vomiting, hair-loss, neurologic and psychotic symptoms, liver and kidney damage.

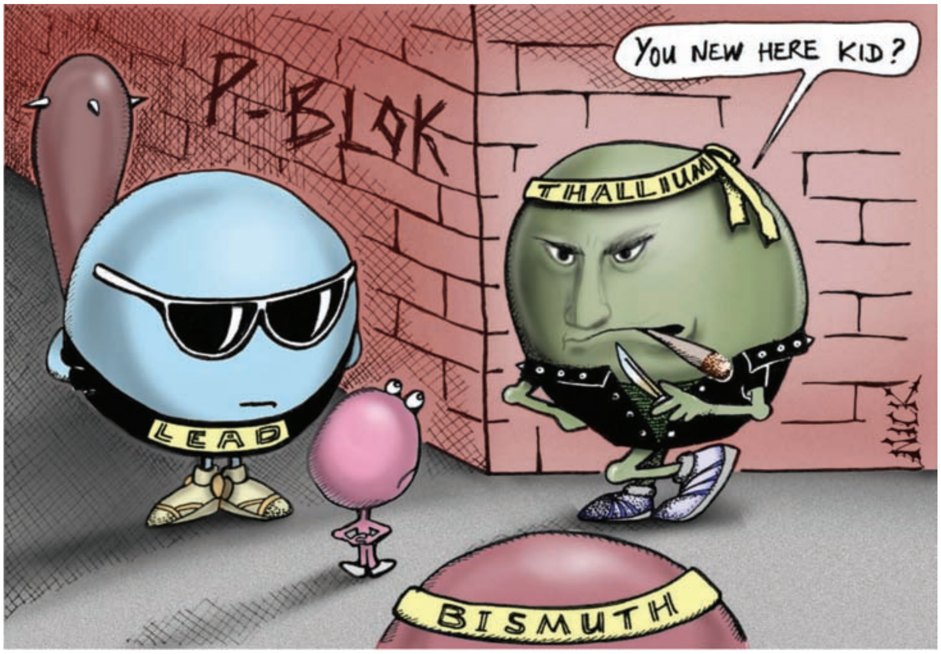
With little known about thallium uptake in lake food chains, researchers **Nicholas S. Fisher** from the Marine Sciences Research Center, Stony Brook University, and **Michael R.Twiss** of the Department of Biology, Clarkson University, set out to clarify these pathways. Their NYSG-funded project was to determine the degree of bioaccumulation of thallium in the freshwater microbial food web, focusing on key species of phytoplankton and zooplankton in Lakes Erie and Ontario.

Thallium in the Great Lakes

Previous research had shown that once thallium enters a lake, it can readily assume any of several different oxidation states depending on the environmental conditions. Thallium uptake by aquatic organisms may differ between the different oxidation states of the element. One oxidation state of thallium derived from coal ash, Tl^{+}, is thermodynamically stable and only weakly reacts with other inorganic or organic compounds. This form of thallium is accumulated intracellularly by aquatic organisms via the potassium ion channels in cell membranes and reactions with sulfur-containing proteins. Once in the cells, Tl^{+} is slow to leave, making it a very toxic form of thallium. Another oxidation state is an inorganic colloidal form, Tl^{3+}. This form is highly reactive and may accumulate on cell surfaces, but not to the extent of the more toxic Tl^{+}.

Over the last several decades, it had been reported that high levels of thallium accumulated in lake trout, a major sport fishery in Lakes Ontario and Erie. In 1987 to address this concern, New York State established an ambient water quality standard in order to protect fish, although there was no toxicity data to support this limit. Then in 1995, a Canadian study documented that dissolved thallium was on the increase across the Great Lakes; Lake Ontario had an average of 5.8 ng/L (nanograms per liter) of dissolved thallium and Lake Erie had 9.1 ng/L. Since that report there has been no ambient water quality standard established for thallium across the Great Lakes. Although the absolute amounts of thallium used in industry are relatively low, increasing use of thallium in high-tech manufacturing and the continued use of coal for energy will inevitably lead to its unavoidable dispersal and increased mobilization in the environment.

Utilizing state-of-the-art trace metal clean protocols and radioisotope methodologies, Fisher and Twiss assessed how thallium is transferred in plankton in the Great Lakes. The team collected phytoplankton and zooplankton from Lakes Ontario and Erie for bioaccumulation experiments both onboard research vessels and in university labs where thallium uptake and depuration rates



Unwittingly, and against his mother's advice, Vince the first-row transition metal had been lured far away from home, and now found himself surrounded by heavier elements of the P-block.

Original cartoon by Nick Kim, an environmental chemist from Hamilton, New Zealand with a great sense of humor and a serious interest in how thallium gets in the food chain.

within the lower food web were examined. The researchers looked at how resident plankton, including single-celled plants (phytoplankton), animals (protozoa), and bacteria, control the transformation of thallium into its various forms. They also examined the mechanisms by which phytoplankton take up and accumulate dissolved thallium. Since phytoplankton form the base of the aquatic food chain, they are an important entry point for toxic substances into the food web. The research also set out to determine the relative toxicity of Tl^{+} and Tl^{3+} to phytoplankton.

Thallium Pathways and Potential Impacts

Fisher and Twiss found that once thallium enters lake waters, it is converted into several different forms, including the two types described above (Tl^{+} and Tl^{3+}), as well as an organic form, dimethylthallium or DMT. Organic thallium, DMT, is also actively accumulated by phytoplankton, but apparently not by the same mechanism as Tl^{+} which is through potassium ion channels. The team found that aquatic bacteria are able to convert Tl^{+}, the form of thallium introduced by coal ash, to Tl^{3+}, the less toxic form of thallium. They also found that although Tl^{3+} is less toxic than Tl^{+}, Tl^{3+} has a much higher bioavailability than the more toxic Tl^{+}.

However, there was no consistent trend with respect to thallium uptake by different size classes of plankton. Once associated with phytoplankton, thallium can be assimilated with an efficiency of 40-50% from different phytoplankton species and by cladocerans, an important component of the zooplankton community. This relatively high assimilation can explain its passage up the food chain, leading to fish and other trophic levels in the Great Lakes ecosystems.

Considering these results, thallium is emerging as a pollutant of potential concern in the Great Lakes. Although it is not yet a prevalent problem in the lakes, these results suggest that industry be circumspect in its use of coal and consider rapid implementation of clean coal technologies. Since thallium oxidation states differ in their toxicity and bioavailability, this information will allow managers to more intelligently predict the ecological effects of dissolved thallium in lakes.

— Barbara A. Branca
and Patrick Dooley

See page 15 for a bibliographic list of journal reprints related to this project.