

Keeping Tabs on Selenium

The question of whether or not a chemical in the environment is harmful is often hard to answer, particularly if the effects of that chemical vary depending on its chemical form — its speciation or oxidation state. Such is the case with selenium, an element that occurs naturally in varying concentrations, but has recently been observed to be on the increase in effluents from mining and milling operations.

“Humans are very tolerant [to selenium] and it is an essential nutrient for all living organisms,” says Dr. Cheryl Wiramanaden. “However, fish and birds are quite sensitive to selenium; that’s where the concern comes from.”

Researchers from several Canadian universities have recently partnered up with industry through a Natural Sciences and Engineering Research Council of Canada-funded collaborative effort to look at selenium accumulation downstream from mining operations, including analyses of selenium chemistry using the Canadian Light Source. Wiramanaden and Dr. Ingrid Pickering, both from the University of Saskatchewan, were the co-authors of two papers recently published that present the team’s preliminary observations.

The two studies looked at trace selenium in two aquatic ecosystems. One looking at uptake in fish surrounding a uranium milling operation at Key Lake in northern Saskatchewan, and the other focussed on the levels and speciation of selenium from coal mining found in two wetlands in Elk Valley in British Columbia.

“The interesting thing about selenium is that it has lots of oxidation states in the environment that can be present in all lakes, sediments and water bodies. Those different species all have different uptake and mobility,” says Wiramanaden. “That is why it is important to determine the species of selenium that are present within a system.”

For a complete profile of the different species of selenium found within the sediment, bottom-dwelling organisms and fish tissue, samples from the affected lakes as well as unaffected reference lakes were sent to the CLS for analysis using synchrotron light.

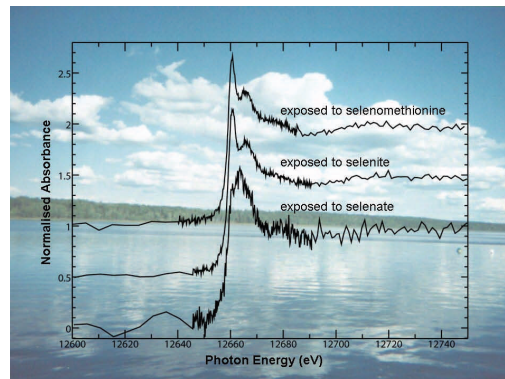
“We can look at anything because of the synchrotron: the sediment, bloodworms, and the fish that feed on the bloodworms. Even the smallest piece of tissue can be used,” explains Pickering. “Everything can be looked at using a much cleaner method and you can get all the different speciation.”

Wiramanaden did note that some of her samples posed some unique challenges. “The fish were collected by other members of our team and stored in freezers. When I asked for a fish tissue sample I got a 40 centimetre pike! I had to ask myself how do I get that into the beamline?”

While some of the beamlines at the CLS can accommodate specimens as large as her aquatic subject, the beamline being used by the team does not. How did they make it work?

“We ended up taking out organs and grinding them up,” Wiramanaden smiles.

In general, selenium is introduced into the environment in an inorganic form and is then reduced to an organic form that can enter the food chain. There are multiple types of selenium that can be taken up through an organism’s diet as it accumulates through a food chain. Organic selenide is one of the forms most commonly found in birds and fishes.



The spectra for the different speciation of selenium as determined using X-ray absorption spectroscopy.

Source: Phibbs J et al. 2011. *Selenium Uptake and Speciation in Wild and Caged Fish Downstream of a Metal Mining and Milling Discharge*

Fast facts:

- Using the CLS, researchers are tracking different forms of selenium in the food chains of lakes and wetlands to assess environmental impacts from mining activities.
- Selenium is a naturally occurring element that is essential to all living organisms, but is toxic in large quantities. Fish and birds are more susceptible to selenium toxicity than humans.
- There are multiple forms of selenium that build up in the food chain. Organic selenides such as selenomethionine is one of the forms of selenium that can easily accumulate.

References: Phibbs J et al., Selenium Uptake and Speciation in Wild and Caged Fish Downstream of a Metal Mining and Milling Discharge. 2011. *Ecotoxicology and Environmental Safety*, DOI:10.1016/j.ecoenv.2011.02.020

Martin A.J. et al., 2011. Biogeochemical Mechanisms of Selenium Exchange between Water and Sediments in Two Contrasting Lentic Environments. *Environmental Science & Technology* 45 (7), pp.2605-2612 DOI: 10.1021/es103604p



The change in concentration of the organic selenium found in the fish between the reference lake and the exposure lake is one observation that intrigued Wiramanaden. In the high exposure cases, selenomethionine was found to be the dominant form found in the fish in the Key Lake study. Wiramanaden and her colleagues found that they can use the proportion of selenomethionine to other selenium-containing compounds as a marker for exposure.

“There are problems in the sense that selenium is accumulating in fish, especially in the reproductive organs compared to the reference lake. They have more in them than they should,” states Wiramanaden as one of the reasons to monitor the element.

Since the start of this research in 2006, the mine company has introduced a system to remove selenium and other minerals from their effluent waste and the amount of selenium in the discharge has decreased.

Research is still ongoing; for Wiramanaden, who recently completed a NSERC Industrial Research and Development Fellowship at Minnow Environmental Inc, will continue to work on selenium looking to quantify selenium accumulation from water to fish ovaries by considering a site-specific food chain model.

“There is an elevated level of selenium, but what has been observed is that the effect of selenium has been borderline,” notes Pickering. “The focus of our study is to answer the question, is there an issue?”



Water samples are being collected by a Cameco employee at the Key Lake operation as part of the environmental management system. Since 2006, there has been a decrease in selenium found in the discharge as Cameco has developed and installed a system to enhance removal of selenium and other minerals from treated water released to the environment. *Source: Cameco*