# Research Brief 176: A New Analytical Method to Support Studies of Mercury Bioavailability/Bioaccumulation in Aquatic Ecosystems

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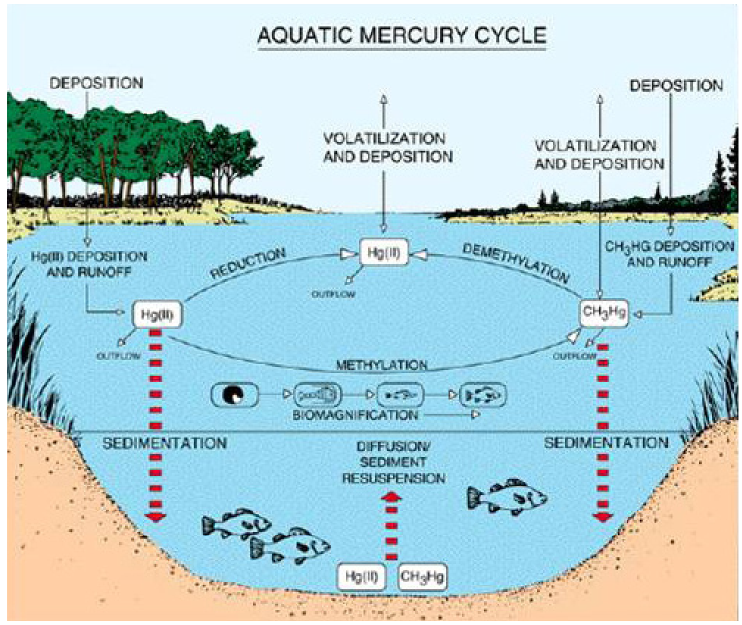
## Background

Mercury (Hg) enters the environment from natural and anthropogenic sources and readily moves into the biosphere, eventually making its way into all water bodies. An interdisciplinary team of ecologists, biogeochemists, trace metal chemists and modelers dDirected by Dr Celia Chen at the Dartmouth College SRP is investigating the natural processes regulating the fate of Hg and other metals across several orders of biological complexity. In a collaboration between the research project led by Dr. Celia Chen and the Trace Element Analysis (TEA) Core directed by Dr. Brian JacksonThe ultimate goal is to develop a mechanistic understanding of the vital links between human and environmental health. They are using extensive field surveys, mechanistic experiments, and detailed analytical and statistical models to discover the mechanisms underlying movement of Hg and methyl mercury (MeHg) through reservoir and estuarine foods webs into fish and shellfish and ultimately, humans.




These studies require quantification of total metals and of metal speciation in very low biomass samples such as zooplankton, polychaetes, amphipods, and snails. In a collaboration with Dartmouth Trace Element Analysis Core Director Dr. Brian Jackson and postdoctoral researcher Dr. Vivien Taylor, the team has developed methods to address these analytical challenges.

## Advances

Because Hg biomagnifies in aquatic ecosystems, mostly as MeHg, determination of Hg species is crucial to toxicity and uptake studies.

Determination of total metal concentration and Hg species in a sample are usually conducted independently on individual sub-samples. For low biomass samples it is not possible to sub-divide the sample for these two analyses. Drs. Taylor and Jackson built upon an acid leach method to develop a method capable of measuring MeHg as well as total metals (zinc [Zn], arsenic [As], selenium [Se], cadmium [Cd], Hg, and lead [Pb]) in low-mass samples by inductively coupled plasma mass spectrometry (ICP-MS).

Analysts first spike the sample with enriched stable isotopes of MeHg and inorganic Hg. The Hg species are extracted by a weak acid leach and are quantified by isotope dilution purge and trap gas chromatography coupled to ICP-MS. Because of the extremely high sensitivity of this approach it only uses 1% of the total acid leach extract. The remainder is then acidified with an equal volume of concentrated $HNO_3$ and microwave digested under high temperature and pressure. This digested solution is then analysed for total metal concentration by collision cell ICP-MS.

The researchers verified the method using five certified reference materials (lobster hepatopancreas, dogfish muscle, oyster tissue, mussel tissue, and plankton). Measured values for MeHg ranged from 93% to 114% of the certified value, suggesting that the extraction method is robust for a wide array of samples. Total metal concentrations were also in good agreement with certified values, with average recoveries from 97.1% to 103.5% of the reference values. The levels of accuracy and precision are well within the EPA-recommended quality control criteria.

The researchers then compared the sum of the Hg species determined from the speciation step of the analysis with total Hg determined from the total metals analysis. on 285 invertebrate and fish samples. The researchers found excellent agreement between the of the sum of mercury species and total mercury, indicating that the isotope dilution approach for Hg species quantification is effective for inorganic Hg in addition to MeHg.

## Significance:

This work provides a new avenue for sequential determination of MeHg and total Zn, As, Se, Cd, Hg, and Pb in biological samples with dry sample weight less than 250 50 mg. This method also requires less sample preparation time than previous methods.

This ability to analyze small samples is critical to ecological research like that conducted by Dr. Chen. For example, metal uptake in aquatic organisms varies with size and age, particularly when the diet of an organism changes throughout its lifecycle. This new method will allow researchers to analyze individual whole organisms or extremely small samples of organisms at the base of the food web. This will help us understand how metals move into aquatic food webs. In addition, differences between bioaccumulation of different heavy metals have been observed (e.g., Hg vs. As and Pb). Finally, determination of both MeHg and total heavy metal concentration in individual organisms will allow researchers to identify relationships between the uptake of different metals by aquatic organisms, their food sources, and their positions in the food web.

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## To learn more about this research, please refer to the following sources:

Jackson, Brian, Vivien F. Taylor, R.A. Baker, and Eric Miller. 2009. Low-level mercury speciation in freshwaters by isotope dilution GC-ICP-MS. Environmental Science & Technology. (http://pubs.acs.org/journals/esthag/) 43(7):2463-9. doi:10.1021/es802656p (http://dx.doi.org/10.1021/es802656p)

Taylor, Vivien F., Brian Jackson, and Celia Y. Chen. 2008. Mercury speciation and total trace element determination of low-biomass biological samples. Analytical and Bioanalytical Chemistry. (http://www.springer.com/chemistry/analytical/ journal/216) 392:1283-1290. doi:10.1007/s00216-008-2403-3 (http://dx.doi.org/10.1007/s00216-008-2403-3)