Reconnaissance of Methylmercury in Water at Selected Sites on the Ohio River in 2010

a collaborative study by
the U.S. Geological Survey Indiana and Kentucky Water Science Centers
and the Ohio River Valley Water Sanitation Commission (ORSANCO)

Introduction. Mercury is a persistent bioaccumulative toxin. In its organic form of methylmercury, it can adversely affect human health and wildlife. The Ohio River could be listed under section 303(d) of the Clean Water Act as having impaired beneficial use because of mercury. Several reasons support the potential listing. Whole water and dissolved total mercury were detected in most water samples collected from the Ohio River by ORSANCO at 17 sites from 2001 to 2009. Concentrations frequently exceeded a freshwater chronic aquatic criterion for total mercury for states bordering the Ohio River Valley (for example, 12 nanograms per liter (Indiana Administrative Code, 2007). Total mercury concentrations in fish tissue samples collected from the Ohio River by ORSANCO at 12 sites in 2009 frequently exceeded the USEPA freshwater criterion for methylmercury of 0.3 milligrams per kilogram (USEPA, 2001).

Although extensive data for total mercury have been recorded from analysis of grab samples of the Ohio River water, additional data are needed to better evaluate the risks to humans and wildlife from methylmercury. Data on methylmercury in water are needed to evaluate whether a 303(d) listing is warranted and potentially indicate previously undocumented aspects of mercury transport and cycling in the Ohio River. These data include (a) collection of stream depth- and width-integrated water samples at selected sites; (b) analysis of these samples for dissolved and particulate total mercury and methylmercury; and (c) interpretations of the relations of flow, suspended particulates, and other constituent concentrations to total mercury and methylmercury concentrations.

Methods. The methods used for the reconnaissance sampling and analysis are consistent with other low-level mercury investigations by the USGS.

The <u>sampling sites</u> were selected in consultation with ORSANCO and are in the vicinity of some of the 17 sites sampled by ORSANCO since 2001 (table 1)—4 sites on the middle/ lower Ohio River near Indiana and Kentucky, and 2 sites on the upper Ohio River near Ohio and West Virginia. The lower river sites have the highest historical mercury levels. The upper river sites are in the vicinity of large point source discharges of mercury (fig. 1).

The <u>sampling schedule</u> was intended to include different seasons and flow conditions that could affect total mercury and methylmercury concentrations. Samples were collected during 2-week periods in May, July, and September 2010.

<u>Sample collection</u> was by an equal-discharge increment, depth-integrated, isokinetic method, using a US D-96 Teflon-bag sampler controlled with a reel-drive system on a boat-mounted crane. Methods were consistent with those for low-level mercury in the USGS National Field Manual for Collection of Water-Quality Data (Wilde and Radtke, 1998).

<u>Ancillary measurements</u> made at each sampling site included streamflow and water quality characteristics. Streamflow measurements were made with a boat mounted acoustic Doppler current profiler, following the USGS techniques (Mueller and Wagner, 2009) and Quality Assurance Plan (Lipscomb, 1995). Water quality characteristics were measured at multiple depths at each sampling vertical across the stream width, by use of a recording electronic multimeter.

Water sample analysis included mercury, supplemental, and particulate constituents (table 2). Water samples for mercury analysis were processed within 24 hours of collection using vacuum filtration and trace-metals protocols in a Class 100 laminar-flow, high-efficiency particulate-air filter work station in the Indiana Water Science Center trace metals laboratory. Water samples for determination of supplemental constituents were processed in a field laboratory van. Water samples for particulate analysis were processed within 24 hours of collection at the Indiana Water Science Center laboratory.

Future Work. Principal investigators from the USGS and ORSANCO intend to prepare an article for a scientific journal regarding the Ohio River study in 2010. The article will present and interpret the data, including comparisons with relevant historical water-quality and mercury data collected by the USGS and ORSANCO. Additional reconnaissance sampling may be planned in 2011.

Figure 1. Locations of mercury sampling sites on the Ohio River.

Table 1. Selected sites on the Ohio River for mercury sampling in 2010

Site name	Location and river mile	Description	Other Information	Identification
Mile 118	Upper; mile 118	Upstream of Hannibal locks and dam; Clarington, OH		USGS 394550080520501
Hannibal	Upper; mile 126.4	Upstream of Hannibal locks and dam; Hannibal, OH	USGS stream gage	USGS 03114275
McAlpine	Middle; mile 604.4	Upstream of McAlpine locks and dam; Louisville, KY	USGS stream gage	USGS 03294500
Cannelton	Lower; mile 720.7	Upstream of Cannelton locks and dam; Cannelton, IN	USGS NASQAN; USGS stream gage	USGS 03303280
JT Myers	Lower; mile 846.0	Upstream of JT Myers locks and dam; Uniontown, KY	USGS stream gage	**USGS 03322420**
Smithland	Lower; mile 918.5	Upstream of Smithland locks and dam; Brookport, IL	USGS stream gage	**USGS 03399801**

Table 2. Mercury and supplemental constituent determinations in water

[ng/L, nanogram per liter; mg/L, milligram per liter; MRL, Mercury Research Laboratory; NWQL, National Water-Quality Laboratory; KSL, Kentucky Sediment Laboratory; IWSC, Indiana Water Science Center]

Water-quality constituent or parameter	Method	Reporting limit	USGS Laboratory	Method Reference
Dissolved total mercury	Oxidation, purge and trap, and cold-vapor atomic fluorescence spectrometry (CVAFS)	0.04 ng/L	MRL	USEPA Method 1631 (2002)
Particulate total mercury preparation and analysis	Isolation on pre-baked quartz fiber filters (QFFs), oxidation, purge and trap, and CVAFS	0.04 ng/L	MRL	Olund and others, (2004). USEPA Method 1631 (2002)
Dissolved methylmercury	Aqueous phase ethylation, gas chromatographic separation with CVAF detection	0.04 ng/L	MRL	DeWild and others (2002)
Particulate methylmercury preparation and analysis	Isolation on pre-baked QFFs, distillation and aqueous phase ethylation, gas chromatographic separation with CVAF detection	0.04 ng/L	MRL	Dewild and others (2004) DeWild and others (2002)
Dissolved organic carbon	Shimadzu - catalytically-aided platinum 680°C combustion	0.1 mg/L[1]	MRL	
Dissolved sulfate	Ion chromatography	0.18 mg/L	NWQL	
Suspended sediment	Gravimetric from filtration	1.0 mg/L	KSL	Guy (1969)
Total particulate carbon	EPA 440.0 elemental analysis	0.1 mg/L	NWQL	USEPA (1997)
Particulate inorganic carbon	EPA 440.0 elemental analysis	0.06 mg/L	NWQL	USEPA (1997)
Particulate organic carbon	EPA 440.0 elemental analysis	0.12 mg/L	NWQL	USEPA (1997)
Total particulate nitrogen	EPA 440.0 elemental analysis	0.034 mg/L	NWQL	USEPA (1997)
Chlorophyll-a	Chromatography-fluorometry	0.0001 mg/L	IWSC	

[1]Estimated

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