

# THE LOADS OF SELECTED HERBICIDES IN THE OHIO RIVER BASIN, 1997–2000

Load calculations based on National Stream Quality Accounting Network (NASQAN) data appear to indicate that the Cumberland and Green River Basins in Kentucky have the highest annual yields of atrazine, simazine, and metolachlor runoff in the country. These yields represent from 9 to 28 percent of the amount of these herbicides used in the Cumberland and Green River Basins on agricultural fields in 1997.

### NATIONAL STREAM QUALITY ACCOUNTING NETWORK PROGRAM

The U.S. Geological Survey (USGS) operates streamflow and water-quality sampling sites in the Ohio River Basin as part of the NASQAN program. The load (the mass of material passing a fixed point per unit of time) of selected herbicides in the Ohio River Basin was calculated using NASQAN data for 1997–2000. The streamflow and sampling stations are located on the main stem of the Ohio River and some of its major tributaries (the Wabash and the Tennessee). The stations are located above the confluences of major tributaries with the Ohio River or where the water quality in the Ohio River is expected to change.

### DESCRIPTION OF THE STREAMFLOW AND WATER-QUALITY SAMPLING NETWORK

Five NASQAN sampling sites were selected in the Ohio River Basin to monitor the loads of materials within the basin (fig.1 and table 1). Three sampling sites are located on the main stem of the Ohio River, and two sampling sites are on major tributaries to the Ohio River (the Wabash and the Tennessee). The Upper-Ohio River Basin is monitored at Greenup Dam, Kentucky (fig. 1, map number 1). Extensive coal mining is a major land-use activity in this part of the Ohio River Basin but the water quality in the Ohio



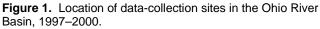


Table 1.	Data-collection sites in the Ohio River Basin, 1	997–2000
[km <sup>2</sup> , squ	uare kilometers]	

Map number (fig. 1)	Site number	Site name	Basin	Drainage area (km <sup>2</sup> )
1	03216600	Ohio River at Greenup Dam, Kentucky	Upper-Ohio	160,000
2	03303280	Ohio River at Cannelton Dam, Kentucky	Middle- Ohio	250,000
3	03378500	Wabash River at New Harmony, Indiana	Wabash	76,000
4	03609750	Tennessee River at Highway 60 near Paducah, Kentucky	Tennessee	106,000
5	03612500	Ohio River near Grand Chain, Illinois	Lower-Ohio	527,000

River also is affected by agriculture, forest, and large urban areas such as Pittsburgh, Pennsylvania. The Middle-Ohio River Basin is monitored at Cannelton Dam, Kentucky (fig. 1, map number 2), and represents predominantly forest and agricultural land uses, although the large urban areas of Louisville, Ky. and Cincinnati, Ohio also affect water quality. The Wabash River Basin is monitored at New Harmony, Indiana (fig. 1, map number 3), and the land use is largely agriculture with about two-thirds of the basin being devoted to row crops. The Tennessee River Basin—the largest Ohio River tributary basin—is monitored near Paducah, Ky. (fig. 1, map number 4). This site is located downstream of Kentucky Dam, and the flow is regulated. This site represents a large drainage area that reflects the effects of forest, agriculture, and highly urbanized land uses. The Ohio River near Grand Chain, Illinois (fig. 1, map number 5), integrates the effects of the many different types of land uses throughout the Ohio River Basin.

All sites were sampled 12 to 15 times per year with an emphasis on spring highflow conditions. Samples were collected every 2 weeks during peak pesticide-runoff periods (April–June), but only once every 4 to 6 weeks for all other months. Water samples were depth and width integrated and flow weighted as described in Edwards and Glysson (1988) and Shelton (1994). Pesticide samples were composited in a glass carboy, filtered immediately using a 0.7-micrometer pore-diameter glass fiber filter, and shipped on ice to the USGS National Water-Quality Laboratory (NWQL) in Denver, Colorado.

#### LOAD OF ATRAZINE, SIMAZINE, AND METOLACHLOR

The Ohio River Basin encompasses portions of 14 States (fig. 1) with an area of 526,000 square kilometers. Every year millions of pounds of herbicides are applied to crops throughout the Ohio River Basin to increase crop production (Ohio River Valley Water Sanitation Commission, 1997) and for safety and aesthetic purposes in urban areas. Storm-water runoff transports some of these herbicides to streams, sometimes causing their concentrations to reach levels that may have adverse ecological effects. Some of the most commonly applied herbicides in the Ohio River Basin are atrazine, simazine, and metolachlor (Kentucky Natural Resources and Environmental Protection Cabinet, 2000). All three herbicides are classified Federally as "restricted-use" herbicides.

The mean annual load (1997–2000) for atrazine, simazine, and metolachlor was estimated by interpolating between measurements and determining a mean daily concentration. To calculate the mean daily load, the mean daily herbicide concentration was multiplied by the mean daily flow table 2. Herbicide concentrations reported as being below the laboratory-reporting limit were set to zero for the calculation of the mean daily load.

Yields are defined as the amount of load per unit area and are useful for comparing basins with varying land use and agricultural practices. Incremental yields of a specific subbasin were determined by subtracting upstream loads from the subbasin outlet load and dividing by the basin area (Hooper and others, 2001; Kelly and others, 2001). Incremental yields for atrazine are presented in figure 2. Estimated yields of atrazine, simazine, and metolachlor for the Ohio River Basin are presented in table 2. The estimated yields of these herbicides in the Lower-Ohio River Basin are the highest in the country.

#### LOWER OHIO LOADS

The Lower-Ohio River is made up of the Green, Lower-Ohio (also referred to as Tradewater River Basin), and Cumberland River (GLOC) Basins and some smaller basins in southern Indiana. This region has a complex environmental setting that is affected by various natural processes and human activities. The basins in the Lower-Ohio River region are characterized by karst topography (eroded limestone, which creates sinkholes, springs, and caves). Land use among these basins is primarily agriculture.

Atrazine, metolachlor, and simazine were the most commonly used corn herbicides throughout the Lower Ohio during 1997 (Kentucky Agricultural Statistics Service, 1998) and are the three most frequently detected pesticides in the Lower-Ohio River Basin (Kelly and others, 2001). Based on estimated-use data from 1997 agricultural applications, a total of about 600,000 kg (kilograms) of atrazine, 430,000 kg of metolachlor, and 50,000 kg of simazine were applied in the GLOC Basins. These estimates were calculated from agricultural inputs obtained by multiplying the pesticide application rates, the percentage of crop receiving pesticide application, and the county-level, cropacreage data from the 1997 Census of Agriculture (U.S. Department of Commerce, website: http://www.nass.usda.gov/census/). Pesticide application rates and treatment percentages were obtained from a 1997 survey by the National Center for Food and Agriculture Policy (Gianessi and Marcelli, 2000). Atrazine, metolachlor, and simazine are used in urban areas for non-selective control of vegetation in rights-of-way; however, there are no reliable estimates of application amounts.

**Table 2.** Estimated mean loads and yields of atrazine, simazine, and metolachlor in the Ohio River Basin, 1997–2000

 [Load in metric tons; yield in grams per square kilometer]

	Herbicides					
	Atrazine		Simazine		Metolachlor	
Basin	Load	Yield	Load	Yield	Load	Yield
Upper-Ohio	7.68	48.2	1.42	8.93	3.82	23.9
Middle-Ohio	22.9	254	3.42	37.8	11.0	122
Wabash	61.2	806	5.16	67.8	25.6	337
Tennessee	6.54	61.7	.838	7.91	1.40	13.2
Lower-Ohio	107	1,120	14.2	148	38.9	406

#### NASQAN SUBBASIN MEAN ANNUAL YIELD, DEFINED INCREMENTALLY BY DIFFERENCE, OF ATRAZINE (39632) FOR WATER YEARS 1997–2000

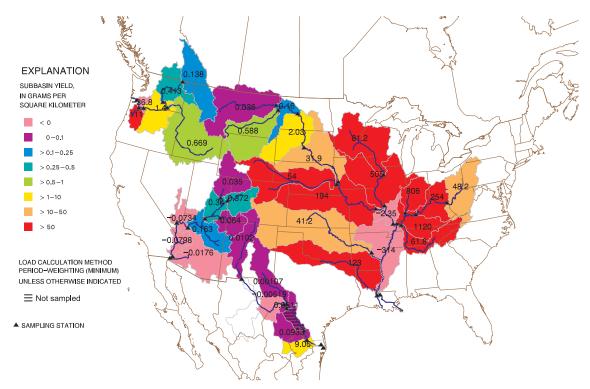


Figure 2. Atrazine yield from National Stream Quality Accounting Network (NASQAN) subbasins, 1997–2000.

Atrazine had the highest mean annual load from the Lower-Ohio River Basin with 107 metric tons (table 2); this amount represented about 18 percent of the atrazine applied to agricultural land in the Lower-Ohio River Basin. This percentage is much higher than earlier estimates of atrazine (1.13 percent) transported from the Lower-Ohio River Basin (Battaglin and others, 1993). Most literature indicates that losses on the order of 1 to 3 percent of the applied amount of herbicide can be expected. The percentage may increase to 5 or 10 percent during catastrophic events, such as a large rainfall event, soon after herbicide application. The percentage loss of simazine and metolachlor were similar to atrazine—28 and 9 percent, respectively.

The large percent losses of atrazine, simazine, metolachlor estimated for the Lower-Ohio River Basin is unusual and a concern, and there is no immediate explanation for these losses. Possible explanations include unusually large rainfall



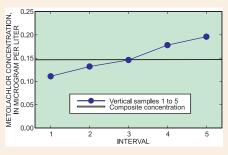
Agricultural land use in the Lower-Ohio River Basin near Leavenworth, Indiana.

events (there were some in 1997 and 1998), unusual agricultural practices or pathways for the movement of these herbicides (perhaps the karst topography), or measurement error. The load of herbicides from the Lower-Ohio Basin was not measured directly, but was estimated by subtracting the load from the Wabash, Tennessee, and the Middle-Ohio Basin from the load determined at the mouth of the Ohio. The difference was attributed to the GLOC Basins and the smaller basins in southern Indiana. These basins are the only other basins that discharge into the Ohio River between the two NASQAN Ohio River main stem sites (fig. 1, map numbers 2 and 5). It should be noted that the load from the Tennessee River at Highway 60 near Paducah, Ky., site is probably low because of the diversion of water to the Cumberland River. Little information is available on the occurrence of herbicides in the streams of these basins; therefore, there is a need for measuring the load directly. In 2001, the NASQAN program redirected some resources to begin directly monitoring the Cumberland River and also established a sampling site on the Ohio River near Pittsburgh to further define the load of material from the Upper-Ohio River Basin.

#### REPRESENTATIVE SAMPLING

The spatial variability of a constituent in a stream cross section is dependent upon a number of factors. If the constituent is in the dissolved phase, its distribution in the stream cross section depends upon how well mixed the stream is and the location of the source of entry of the constituent to the stream. If the constituent is associated with the particulate phase, in addition to the factors affecting constituents in the dissolved phase, there also is the vertical distribution caused by sinking of the particulate matter. This distribution has implications for the calculation of the constituent load. If the constituent concentration changes in the stream either horizontally or vertically, or both, then where and how the sample is collected will affect the concentration used to calculate the load.

The collection of a representative sample from the Ohio River near its confluence with the Mississippi River can be difficult (fig. 3). The concentration of constituents can vary considerably across the stream as the Cumberland and Tennessee Rivers enter the Ohio River from the south, and the Wabash River enters from the north above the sampling site. The water quality of the Wabash River reflects its intensive agricultural land use, whereas the Tennessee and Cumberland Rivers have more forest land use. This can be seen in the concentration of metolachlor in the Ohio River during July 1999 (figs. 3 and 4). The concentration of metolachlor in the stream nearly doubles from the south side of the river to the north side. These data were collected in July 1999 in an experiment to determine if representative samples were



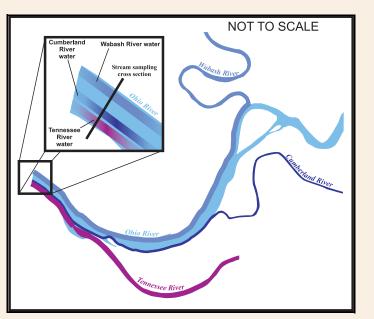
**Figure 4.** Cross-sectional variability of metolachlor concentrations during July 1999 in the Ohio River near Grand Chain, Illinois (map number 5).

being collected on the Ohio River. Other herbicides show the same pattern and some the reverse (tebuthiuron), with high concentrations on the Kentucky side of the Ohio River.

In order to ensure that a representative sample is collected, the NASQAN program collects all of its water samples using depthand width-integrating techniques and uses isokinetic (the velocity of the water into the sample bottle is the same as the velocity of the stream) sampling equipment.



U.S. Geological Survey personnel collecting water-quality samples on the Ohio River at Cannelton Dam, Kentucky (map number 2).



**Figure 3.** Schematic of the cross section of stream sampling on the Ohio River below Paducah, Kentucky.

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