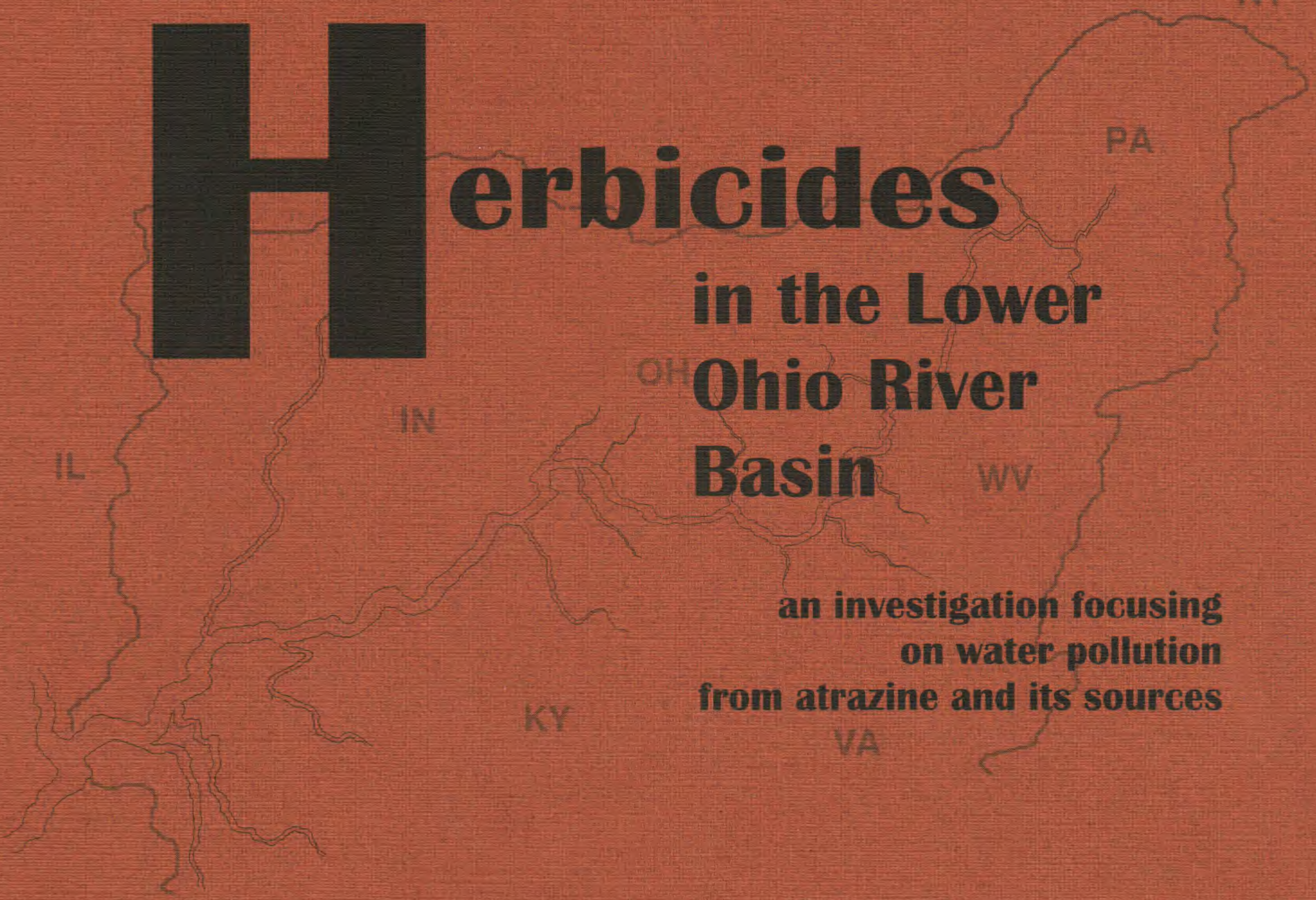
Herbicides in the Lower Ohio River Basin



an investigation focusing on water pollution from atrazine and its sources

Ohio River Valley Water Sanitation Commission

Herbicides in the Lower Ohio River Basin

An Investigation Focusing on Water Pollution from Atrazine and its Sources

The Ohio River Valley Water Sanitation Commission
5735 Kellogg Avenue
Cincinnati, Ohio 45228-1112
(513) 231-7719
http://www.orsanco.org

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EXECUTIVE SUMMARY

During the spring and summer of 1995, the Commission conducted water quality surveys in the lower half of the Ohio River Basin to characterize the presence of atrazine and certain other herbicides (a class of pesticides used to control broad-leafed plants) in the main stem and major tributaries. Primary objectives of the survey were to determine the degree of water quality degradation in the Ohio River caused by atrazine, and to identify significant tributary watersheds as sources of atrazine to the River. Secondary objectives were to identify heavily used herbicides in the lower Basin, characterize water quality conditions with respect to certain other herbicides (alachlor, metolachlor, cyanazine, and simazine), and to evaluate the immunnoassay analytical technique. The entire effort was conducted under the Commission's Tributary Assessment Program. All study objectives were met.

During the early 1990's, the Commission became aware of water pollution concerns in the lower Basin regarding the herbicide atrazine as a result of stream monitoring conducted by the Louisville Water Company and the United States Geological Survey. After reviewing this data, it became evident that additional information was necessary concerning atrazine in surface waters within the lower Ohio River Basin. An initial survey was conducted in 1994 which provided information necessary to design an efficient, comprehensive water quality sampling program for 1995. The 1994 work demonstrated the utility and cost effective nature of the immunoassay analytical technique which is performed in-house by ORSANCO staff producing analytical results with defined precision and accuracy.

Atrazine is the most heavily used herbicide in the lower Ohio River Basin. An estimated 23 million pounds was applied to corn and soybean crops in lower Ohio River Basin states in 1994. Rounding out the top five pesticides in terms of pounds applied to crops in 1994 in states within the lower Ohio River Basin include: metolachlor (20 million lbs./yr.), alachlor (13.8 million lbs./yr.), cyanazine (11.2 million lbs./yr.), and pendimethalinn (5.5 million lbs./yr.). Atrazine usage in the lower Basin has remained relatively steady over the last five years, as well as cyanazine and simazine. At the same time, alachlor usage has been steadily declining with metholachlor increasing to replace it.

Twenty-nine large direct tributaries to the Ohio River were sampled every other week, and 10 Ohio River sites (located at drinking water intakes) were sampled weekly from April through early July. The study was limited to the lower half of the Basin from Cincinnati, OH to the Mississippi River. A two-person field crew traveled more than 1000 miles of Ohio River shoreline over a three-day period, collecting tributary samples from bridges and Ohio River samples at water intakes. Samples were brought back to ORSANCO headquarters and analyzed for atrazine in-house using magnetic particle, enzyme-linked, immunoassay tests supplied by Ohmicron. These tests required multiple pipetting procedures to produce a color change which is measured with a spectrophotometer. Samples were analyzed in triplicate to minimize error. More than 10 percent of samples were analyzed by a contract laboratory using U.S. EPA Method 507 (gas chromatography). These "confirmation" samples also produced results for alachlor, metolachlor, cyanazine, and simazine.

Results from main stem sampling indicate an increasing trend in atrazine levels in a downstream direction to the highest levels which are found at Cairo, IL. However, it appears that an atrazine sink exists on the Ohio River somewhere between Henderson, KY and Sturgis, KY as evidenced by consistently lower concentrations at Mt. Vernon, IN and Morganfield, KY intakes. Ohio River atrazine concentrations occasionally exceed the drinking water maximum contaminant level (MCL = 3 µg/L) established to protect human health from long-term exposure from water ingestion, based on immunoassay results (which tend to be higher than by GC methods). Peak atrazine concentrations in 1995 were moderate as compared with higher levels in 1993 and lower concentrations in 1994. The times at which peak concentrations occurred in the Ohio River changed between locations, while initial detections generally occurred in mid-April and tailed off by the end of 1995. Such annual characteristics of atrazine levels in the Ohio River are expected to vary from year to year.

Atrazine concentrations on certain tributaries were occasionally quite high, with levels in excess of 60 µg/L (20 times the MCL) on Highland Creek. Tributaries inputting the greatest quantities of atrazine to the Ohio River and their relative contribution to the total loading were: Wabash River (38 percent), Great Miami River (11 percent), Little Wabash River (nine percent), and Green River (seven percent). By far, the Wabash River is the greatest source of atrazine (and possibly other pesticides and agriculturally related contaminants) to the Ohio River. All sources upstream of Cincinnati, OH combined accounted for 10 percent of the total atrazine loading in the Ohio. Only 14 percent of the total Ohio River load was not accounted for in the mass balance, an exceptional performance when considering the number of small tributaries which were not included in the survey.

Based on data from Evansville, IN water utility, treatment with activated carbon was effective in removing atrazine from source water. Evansville has implemented a policy to add carbon when atrazine levels in the Ohio River exceed half the MCL (1.5 µg/L). Data also indicate that routine, standard surface water treatment scenarios are generally ineffective toward atrazine removal (i.e., no carbon treatment).

In addition to atrazine, confirmation samples were analyzed for alachlor, metolachlor, cyanazine, and simazine. The cyanazine MCL was exceeded in approximately 20 percent of the raw water confirmation samples. None of the other pesticides exceeded their drinking water MCL in untreated water samples. The average composition of 49 confirmation samples analyzed for the five herbicides was as follows: atrazine (61 percent), cyanazine (15 percent), metolachlor (11 percent), simazine (11 percent), and alachlor (two percent).

The immunoassay analytical technique consistently produced atrazine results higher than by U.S. EPA Method 507 (by GC). For samples with atrazine concentrations at or below 5 µg/L, results by the immunoassay on average were approximately 0.7 µg/L higher than by gas chromatography. A correlation of atrazine concentrations produced by the immunoassay method versus the GC method resulted in a correlation coefficient (r) of 0.85 indicating a strong relationship. In light of costs per sample, $20 for immunoassay tests and $150 for results by GC, the immunoassay technique appears to be a desirable method for certain applications.

Recommendations

1. Monitor trends in pesticide use and replacement products to identify emerging water quality issues.
2. Install a long-term monitoring station for atrazine at Cairo, IL.
3. Provide early warning to water utilities concerning pesticide levels in the source water.
4. Facilitate exchange of information between water utilities concerning effective treatment techniques for pesticides.
5. Consider/prioritize watersheds for state nonpoint source control programs regarding pesticide reductions.

INTRODUCTION

Throughout the lower Ohio River Basin, an estimated 70 million pounds of five herbicides — atrazine, cyanazine, simazine, alachlor, and metolachlor — were applied to crops in 1994. Particularly during spring and summer, large quantities of these substances are transported, by runoff and atmospheric deposition, to streams which ultimately flow to the Ohio River. At the same time that these herbicides are found in the Ohio River and many of its tributaries, over one million people consume tap water supplied by utilities which use the lower Ohio River as a raw water source. Some of these herbicides have been classified as probable or possible carcinogens and are regulated under the federal Safe Drinking Water Act (SDWA). While routine drinking water treatment technologies are relatively ineffective, substantial removal of herbicides can be achieved with carbon. However, most drinking water utilities along the Ohio River do not routinely apply carbon treatment (although most utilities have the capability) and are unaware of the times at which high levels of these herbicides are present in the source water. This is partially due to the SDWA which requires monitoring by water utilities at a frequency insufficient to identify concentrations of concern (some utilities monitor for pesticides in their source water on a routine basis). As a result, populations are exposed to some level of pesticides through their drinking water. The problems are similar, if not worse, throughout other waters in the Corn Belt region of the United States.

During the early 1990's, the Commission became aware of the presence of herbicides in the lower Ohio River as a result of sampling efforts by the Louisville Water Company and the United States Geological Survey. A number of commonly used herbicides were detected frequently, sometimes at high levels, at certain stations within the watershed. Of those monitored and detected, atrazine was found to be of most concern due both to its frequent detections and concentrations with respect to its drinking water Maximum Contaminant Level (MCL). As a result, the Commission conducted a preliminary water quality survey in 1994, which included a one-time sampling of 60 tributaries and 13 water intakes from Huntington, WV to Cairo, IL (River Miles 300 to 981). Results indicated that only a handful of tributaries, those with the greatest flows, had an identifiable impact on Ohio River atrazine levels. Results also indicated that a small percentage of the total Ohio River atrazine load originates from sources upstream of Cincinnati (River Mile 460). With these observations in mind, a comprehensive sampling program was organized for the spring/summer of 1995 as described below.

Objectives

This report details what is known about prevalent herbicides use in the lower Ohio River Basin, their occurrence in the Ohio River at selected drinking water intakes, a determination of the prominent tributary sources to the Ohio River, and an assessment of the performance of the magnetic particle, enzyme-linked, immunoassay analytical technique. A water quality survey was conducted in 1995 with two primary objectives in mind.

1. Characterize atrazine levels in the Ohio River during the spring and early summer when annual peak concentrations are expected.
2. Determine which tributaries represent the largest atrazine sources to the Ohio River.

Secondary objectives were to evaluate the immunoassay technique in relation to results achieved by U.S. EPA approved gas chromatography (GC) methods, and to obtain water quality data on other commonly used pesticides.

Scope

While the survey was focused on atrazine, confirmation samples analyzed by gas chromatography also provided results for cyanazine, simazine, alachlor, and metolachlor. The survey was conducted from April through early July of 1995. Samples were collected weekly from 10 drinking water intakes and every other week from 28 tributaries from Cincinnati to the Mississippi River. In the process of conducting this survey, more than 7000 miles of shoreline were traveled, more than 400 water samples collected, and some 2000 individual analyses performed in-house using the magnetic particle, enzyme-linked immunoassay technique. Analytical costs for the survey were reduced, from $140 to approximately $20 per sample, through the use of the immunoassay technique. The investigation could not have been completed otherwise.

The Commission

The Ohio River Valley Water Sanitation Commission (ORSANCO) is an interstate water pollution control agency that was established as a provision of and to implement the Ohio River Valley Water Sanitation Compact, signed in 1948 by the governors of Illinois, Indiana, Kentucky, New York, Ohio, Pennsylvania, Virginia, and West Virginia. The Commission consists of three members from each state, appointed by their respective governors, and three members representing the federal government appointed by the President. A guiding principle of the Compact is that pollution originating in one state shall not injuriously affect the waters of another state. ORSANCO manages and operates programs for water quality monitoring and assessment, assists in emergency response management, has established pollution control standards for the Ohio River enforcing them when necessary, and facilitates interstate cooperation and coordination through an extensive committee structure. Because of the interstate nature of current water quality problems and sources of pollution concerning pesticides in the lower Ohio River Basin, the Commission was uniquely positioned, and thus implemented this survey.

The Basin

The Ohio River Basin encompasses portions of 14 states in an area of more than 200,000 square miles, which constitutes over five percent of the total United States land mass (Fig. 1). The Ohio River itself, formed in Pittsburgh at the confluence of the Allegheny and Monongahela Rivers, is 981 miles long and flows through or borders six states — Illinois, Indiana, Kentucky, Ohio, Pennsylvania, and West Virginia. Over 25 million people reside in the Ohio River Basin, or approximately 10 percent of the total U.S. population. Of these, nearly three million people use the Ohio River as a source of drinking water. The Ohio River conjoins with the upper Mississippi River at Cairo, IL and provides approximately two-thirds of the total flow of the Mississippi River at the confluence. As such, the Ohio River watershed may have a substantial influence on water quality of the lower Mississippi River, and subsequently the Gulf of Mexico.

From an economic standpoint, approximately 600 businesses employing 35,000 people with a combined annual payroll of $1 billion, are directly dependent on the Ohio River. Electric utilities using the Ohio River constitute over five per-cent of the nation's power generating capacity, while an estimated $43 billion in commodities are transported annually along the River system. Festivals and special events generate an estimated $100 million annually in communities along the River, including an increasing number of fishing and boating events. More than 100 species of fish live in the Ohio River. Given these important attributes, it is clear that protection and improvement of the water quality of this great resource is vital to the health and economic prosperity of the region and the nation.

HERBICIDE USE AND HUMAN HEALTH IMPLICATIONS

Herbicide Usage

Herbicides are used extensively throughout the lower Ohio River Basin to control weeds in croplands. Atrazine, metolachlor, alachlor, cyanazine, and simazine are five of the most heavily used pesticides within the Basin (see Table 1). Nationally, 84 percent of all corn acreage receive at least one of these five herbicides and 51 percent is treated with two or more[1]. In the states that make up the lower half of the Basin (OH, IN, KY, IL), these five herbicides accounted for an estimated 70 million pounds applied to corn and soybeans in 1994, over 65 percent of the total pesticides applied to these two crops[*]. Corn and soybeans are the predominant crops in this region, with approximately 80 percent of the crop land being used for the production of corn and soybeans[*].

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*Pesticide use statistics calculated using the agricultural chemical use and county crop acreage reports for corn and soybeans provided by the Agricultural Statistics Services of OH, KY, IN, IL and pesticide sales data from the KY Division of Pesticides.

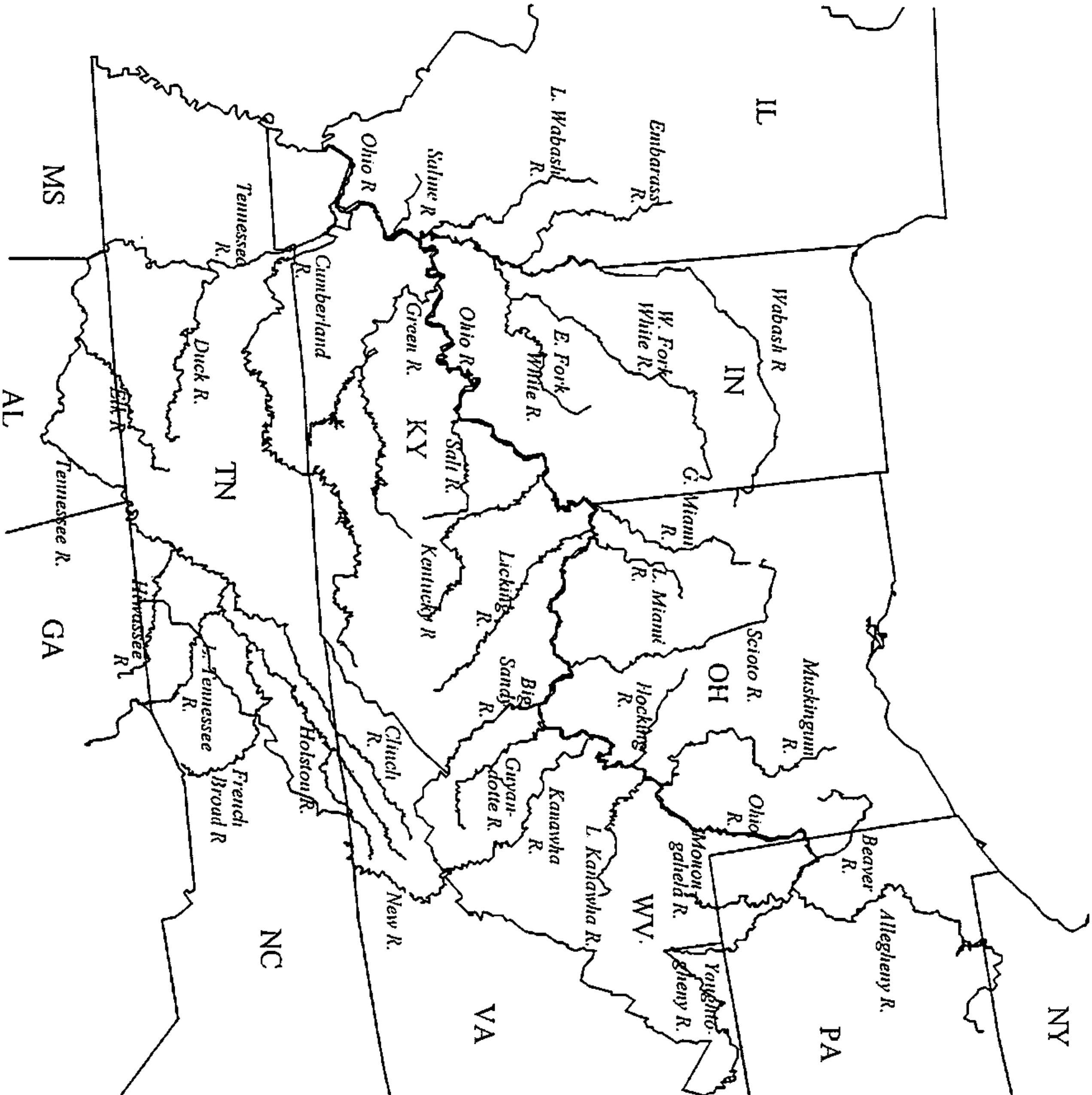

Figure 1. Ohio River Basin

Ranking	Pesticide	in 1000 lbs.
1	Atrazine	23850
2	Metolachlor	20071
3	Alachlor	13772
4	Cyanazine	11259
5	Pendimethalinn	5461
6	Glyphosate	3504
7	2,4-D	2851
8	Bentazon	2564
9	Chloryrifos	2154
10	Dicamba	1816
11	Trifluralin	1604
12	Acetochlor	1474
13	EPTC	1460
14	Terbufos	1302
15	Simazine	1149

Table 1. The 15 most used pesticides in the lower Ohio River Basin states (OH, IN, IL, KY) for corn and soybeans-1994 (Figures include quantities applied outside the Ohio River Basin).

Atrazine, registered in 1958 by Ciba Corporation, is from the triazine family of herbicides. It is used as a pre-and post-emergent herbicide for corn to control broad-leaf and grassy weeds. Atrazine is the most commonly used herbicide in the Basin with an estimated 11.6 million pounds applied in 1994[*]. Within the Basin, atrazine is used most heavily in the central portion of Indiana and southeast section of Illinois (Fig. 2). Nationally, 66 percent of all corn is treated with atrazine[1], while the percentage of corn acreage treated in the Basin is considerably higher. In the lower Basin states, between 81 percent and 91 percent of all corn is treated with atrazine.

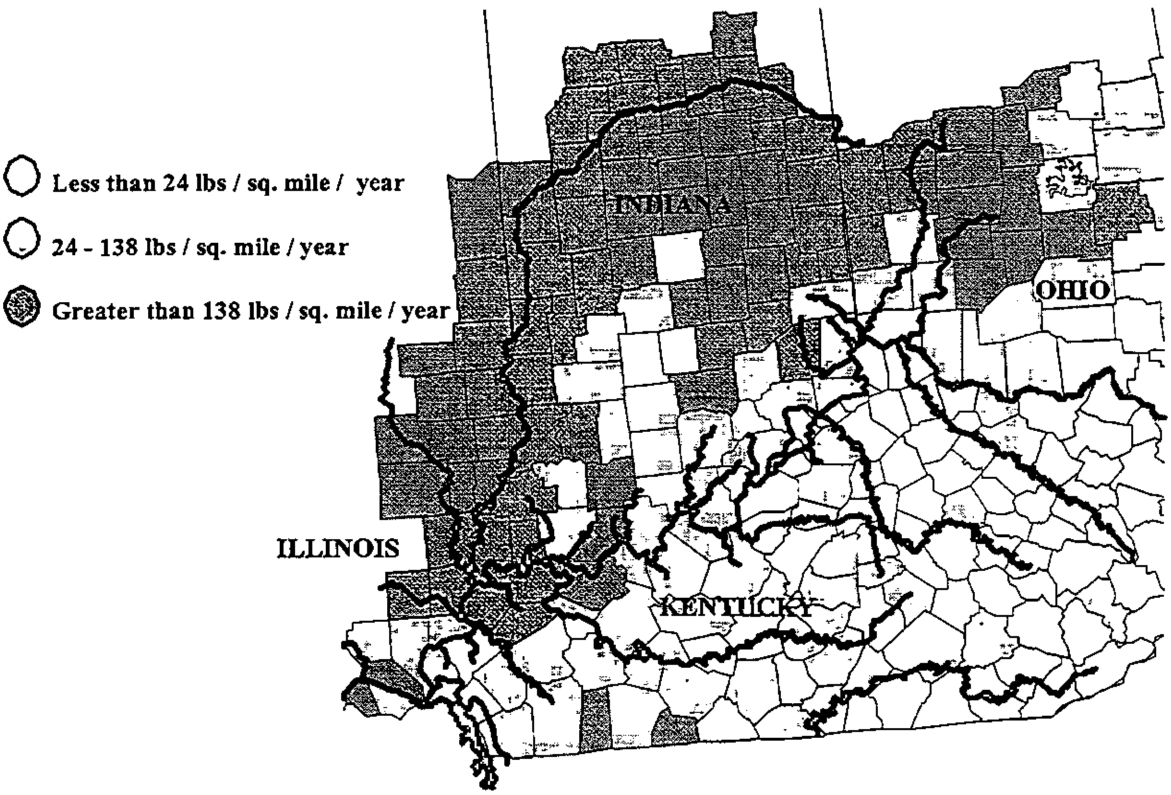

Figure 2. Atrazine Usage in the Lower Ohio River Basin (1993)
(Quantities may be based on data other than actual use, such as sales data).

In the past four years atrazine usage has remained fairly steady (Fig. 3) despite the manufacturer's reduction of the recommended application rate. Since 1989, the recommended application rate has decreased from 4.0 lbs./acre/yr. to a range between 1.6-2.5 lbs./acre/yr. depending on soil characteristics[2]. Decreasing the recommended application rates has had little effect on atrazine applied within the Basin because most corn growers in the Basin apply atrazine at rates below the manufacturer's reduced recommended rate. All four of the lower Ohio River Basin states have average application rates below the recommended rate[*].

In recent years, metolachlor has seen a steady increase in usage. In the last five years metolachlor usage in the Ohio River Basin has increased 32 percent from an estimated 7.2 million pounds in 1990 to 9.5 million pounds in 1994[*]. (Fig. 3) Metolachlor has become the substitute for alachlor in areas where alachlor has been banned[1], and appears to be replacing alachlor in the Basin as well.

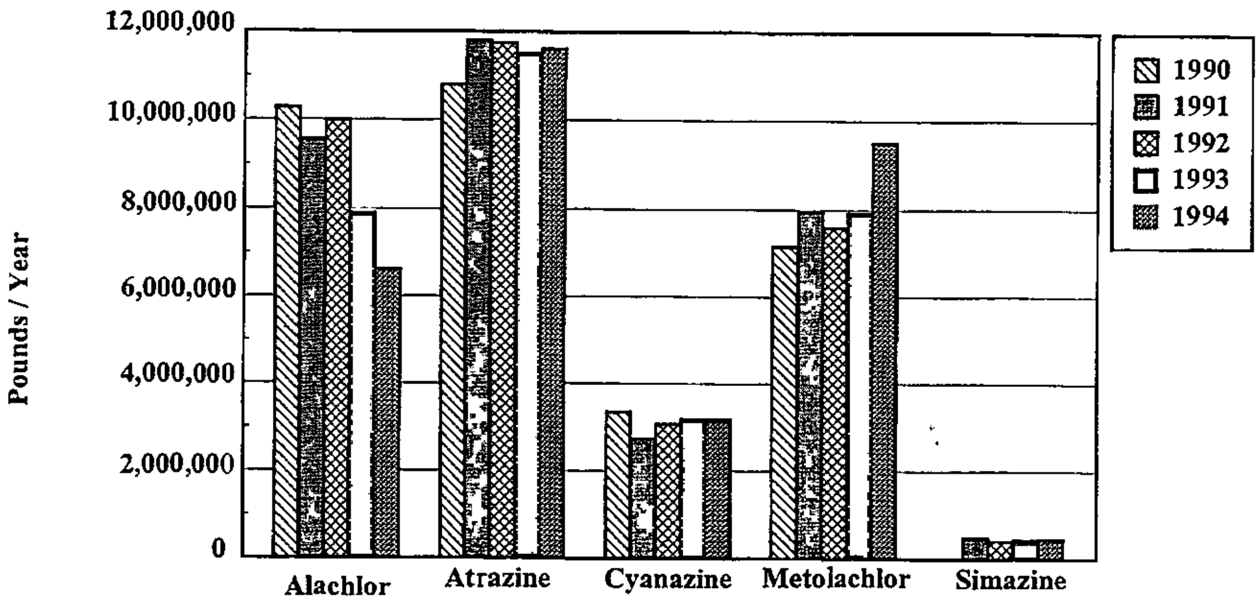

Figure 3. Total Herbicide Usage in the Lower Ohio River Basin (OH, KY, IN, IL) *.

Metolachlor, an acetanilide herbicide, was first produced in 1976 by Ciba Corporation. It is a pre-emergent pesticide used to control weeds in corn and soybeans. Metolachlor, commonly referred to as Dual, is the second most heavily used herbicide in the lower Ohio River Basin with an estimated 9.5 million pounds applied in 1994. Among the lower Basin states, the percentage of corn acreage treated ranged from 28 percent to 37 percent and for soybeans from two percent to 21 percent[*].

Alachlor, an acetanilide herbicide, is the third most used herbicide in the lower Ohio River Basin with over 6.6 million pounds applied in 1994 to corn and soybeans[*]. The acetanilide herbicide was first introduced by Monsanto in 1969 under the trade name Lasso. It is primarily used as a pre-emergent pesticide to control grasses and broad-leaf weeds in corn and soybeans. Within the Basin, the percentage of corn acreage treated ranged from 14 percent to 35 percent, and for soybeans between five percent and 17 percent. In recent years, the use of alachlor has significantly declined in the lower Ohio River Basin (Fig. 3). Usage has gone from an estimated 10.3 million pounds in 1990 to 6.6 million pounds in 1994, nearly a 36 percent decrease[*].

Cyanazine, commonly known as Bladex, is also from the triazine class of herbicides. It was developed by DuPont in 1971 for use on corn to control broad-leaf and grassy weeds. Cyanazine is the fourth most heavily used herbicide in the lower Ohio River Basin with an estimated annual usage in 1994 of 3.1 million pounds. The percentage of corn acreage treated with cyanazine within the lower Basin states ranged from 21 percent to 22 percent[*].

For the past several years, cyanazine usage within the lower Ohio River Basin has remained relatively steady (Fig. 3). However, recently the U.S. EPA announced that an agreement was reached with DuPont Agricultural Products to completely phase out cyanazine. A special review of cyanazine was in progress by the EPA due to concern that chronic exposure may pose a cancer risk. The manufacturer chose to withdraw cyanazine from the costly review process and voluntarily phase out the herbicide. The phase out will begin by reducing the manufacturer's recommended application rates. All sales and distribution by DuPont will be banned after December 31, 1999. Retailers will be permitted to sell existing stocks through September 1, 2002, with all use prohibited after December 31, 2002[3].

Simazine is a triazine herbicide developed by Ciba Corporation in 1956. Simazine, commonly known as Princep, is a pre-emergent pesticide used to control broad-leaf weeds and grasses in corn, fruits and vegetables. The herbicide is also used on lawns to control weeds, and as an algaecide in ponds[1]. The percentage of corn acreage treated with simazine in the lower Ohio River Basin states ranged from two percent to 18 percent. Simazine usage has not significantly changed (see Fig. 3) in Ohio and Kentucky (the only two Basin states with sufficient simazine data) in the past four years with 490,000 pounds applied in 1991, as compared to 465,000 pounds in 1994[*].

One key similarity among all five of these herbicides is persistence in the environment. Factors such as solubility, half-life in soil, and organic carbon partition coefficients (K_{oc}) are important for understanding the transport and fate of these herbicides in a riverine system. Becker and Associates found herbicides with solubilities greater than 30 mg/L, K_{oc} less than 300, and half-lives in soil longer than 21 days to be mobile and persistent in water[4]. Atrazine meets all three criteria (see Table 2), and has been found to persist in soils and water for up to a year after application[5]. Cyanazine and alachlor also may remain in soils and water up to one year. Though simazine is fairly insoluble at 6.2 mg/L, residues have been found to remain in soils for three years after application. Metolachlor has the shortest life in the environment, lasting weeks to months in soil[1].

Herbicide	Solubility, mg/L	Soil Half-Life days	K_{oc}
Atrazine	33	60	100
Cyanazine	170	14	190
Alachlor	240	15	170
Simazine	6.2	75	138
Metochlor	530	20	200

Table 2. Physical characteristics of atrazine, cyanazine, alachlor, simazine, and metolachlor[4].

Human Health Concerns

Atrazine is considered a possible human carcinogen. It has been found to cause tumors in mammary glands and other reproductive organs in laboratory animals. Some epidemiological studies indicate a possible association between atrazine exposure and occurrence of lymphomas, leukemias, and ovarian cancer in humans[1]. Other epidemiological studies suggest atrazine exposure may cause cardiac, urogenital and limb reduction birth defects[1]. Due to human health concerns, atrazine is banned in several European countries.

Both the Maximum Contaminant Level (MCL) and the Maximum Contaminant Level Goal (MCLG) have been set at 3 µg/L for atrazine.

An MCL is an enforceable drinking water standard established under the federal Safe Drinking Water Act. It is the maximum allowable level of a contaminant in finished drinking water. MCLs take into account both human health and the ability of removal technologies to provide effective treatment. An MCLG is a non-enforceable concentration of a drinking water contaminant that is protective of adverse human health effects allowing for an adequate margin of safety. The MCL and the MCLG for atrazine are not based on the carcinogenicity of the herbicide, but rather its potential to cause other non-cancer related health problems such as birth defects.

Metolachlor is considered to be a possible human carcinogen. Exposure to metolachlor has been found to increase the incidence of lung tumors in laboratory rats[1]. An MCL of 100 μg/L has been proposed and is currently under review, however no drinking water standard for metolachlor currently exists.

Alachlor is banned in Massachusetts, Canada and the Netherlands due to human health concerns. The EPA classifies alachlor as a probable human carcinogen. In laboratory studies alachlor exposure resulted in an increased incidence of lung tumors in mice and stomach, thyroid and nasal tumors in rats[1]. An MCL of 2 μg/L has been established for the protection of human health. The MCLG for alachlor, as with all carcinogens is 0 μg/L.

Cyanazine is classified as a possible human carcinogen. An MCL of 1 μg/L has been proposed for cyanazine. The EPA has deemed cyanazine a developmental toxicant and teratogen, and requires all herbicides containing cyanazine to bear a warning label. In laboratory tests, cyanazine has been found to cause eye abnormalities, malformations of the diaphragm and brain, cleft palates, and altered skeletal development[1].

Simazine is considered by the EPA as a possible human cancer risk. Laboratory tests on rats have shown simazine exposure can cause tumors in mammary glands, pituitary, kidneys, and liver[1]. The current MCL and MCLG for simazine is 4 μg/L.

SAMPLING PROGRAM

Sampling was conducted at 10 Ohio River locations and 29 of the largest tributaries to the Ohio River within the lower half of the Ohio River watershed from Cincinnati, OH to Cairo, IL (Fig. 4, Table 3). Ohio River samples were collected from water supply intakes because atrazine is a human health concern with drinking water as the main route of exposure.

Samples were collected weekly from Ohio River intakes and every other week on tributaries from April 10 through July 5, 1995. This sampling frequency amounted to a total of seven samples from each tributary and 13 samples from each Ohio River location over the sampling period. Originating in Cincinnati, a two-person field crew traveled down-river by vehicle, collecting tributary surface grab samples from bridges and intake samples from raw water taps at drinking water treatment facilities. Tributary samples were collected far enough downstream to measure the largest portion of the watershed, but upstream far enough from the Ohio River to be outside the Ohio/tributary mixing zone. Completed every other week, 1000 miles of shoreline was traveled collecting these samples over a three day period. During alternate weeks, water utility personnel collected the intake sample and refrigerated it until the ORSANCO field crew would pick it up the following week.

ANALYTICAL PROCEDURE

All water samples were analyzed in-house by the magnetic particle, enzyme-linked, immunoassay technique supplied by Ohmicron Corporation. Immunoassays are used extensively in the medical field where it is estimated that over one billion clinical tests are performed annually in the United States. Test kits to measure concentrations of certain compounds in water utilizing this technology are available from a number

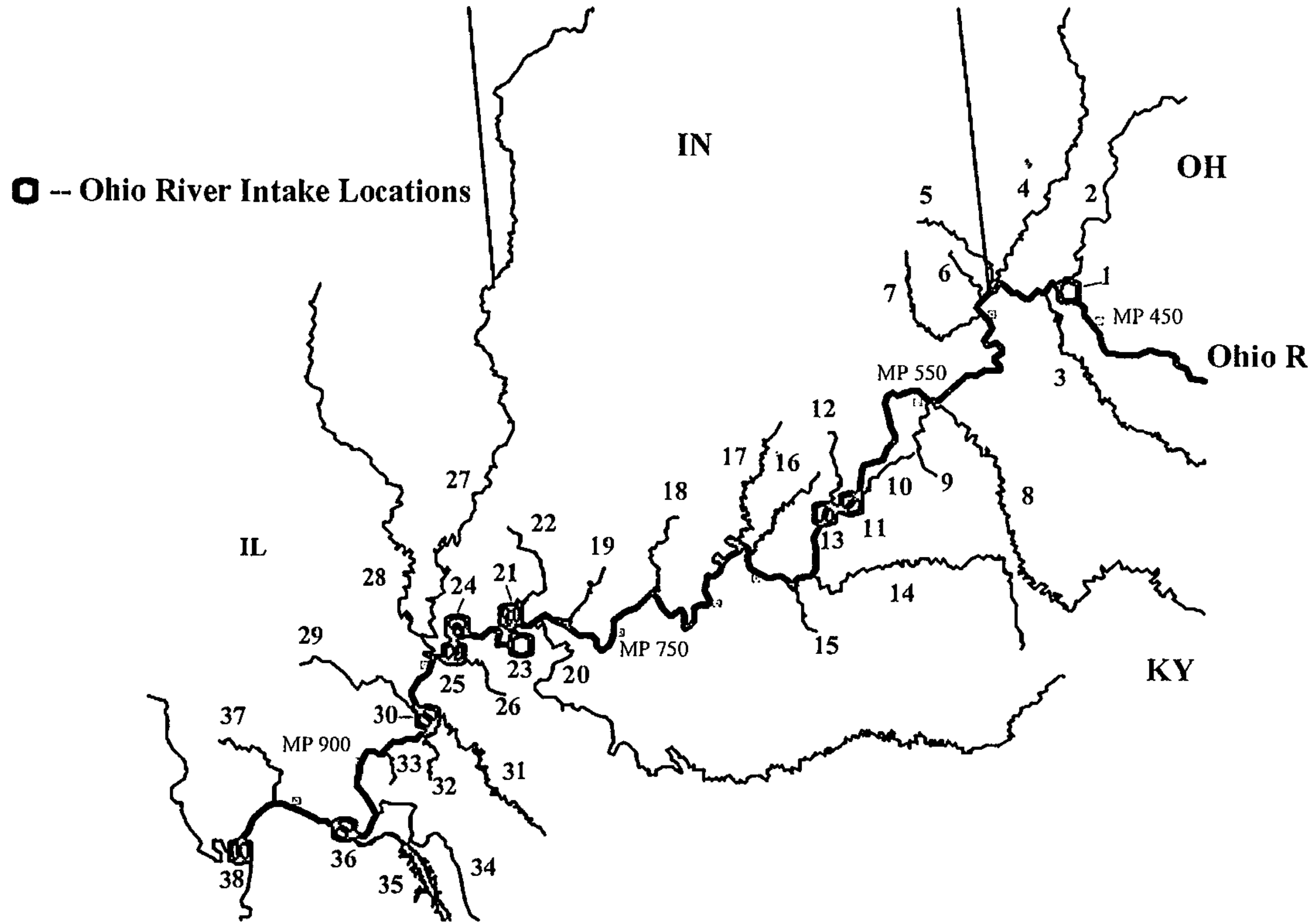

Figure 4. Tributary and Intake Sampling Locations
(Sampling locations are referenced by number in Table 3).

Site ID	Sampling Location	Ohio River Mile (Confluence if tributary)	State	Station Type	Sampling Frequency
1	Cincinnati WTP	462.8	OH	Ohio River	Weekly
2	Little Miami River	463.5	OH	Tributary	Biweekly
3	Licking River	470.3	KY	Tributary	Biweekly
4	Great Miami River	491.0	OH	Tributary	Biweekly
5	Whitewater River	491.0	IN	Tributary	Biweekly
6	Tanners Creek	494.8	IN	Tributary	Biweekly
7	Laughery Creek	498.7	IN	Tributary	Biweekly
8	Kentucky River	545.8	KY	Tributary	Biweekly
9	Little Kentucky River	546.6	KY	Tributary	Biweekly
10	Harrods Creek	595.9	KY	Tributary	Biweekly
11	Louisville CH WTP	600.6	KY	Ohio River	Weekly
12	Silver Creek	606.5	IN	Tributary	Biweekly
13	New Albany WTP	609.0	IN	Ohio River	Weekly
14	Salt River	629.9	KY	Tributary	Biweekly
15	Otter Creek	636.5	KY	Tributary	Biweekly
16	Indian Creek	657.0	IN	Tributary	Biweekly
17	Blue River	663.0	IN	Tributary	Biweekly
18	Anderson River	731.4	IN	Tributary	Biweekly
19	Little Pigeon Creek	772.9	IN	Tributary	Biweekly
20	Green River	784.2	KY	Tributary	Biweekly
21	Evansville WTP	791.7	IN	Ohio River	Weekly
22	Pigeon Creek	792.9	IN	Tributary	Biweekly
23	Henderson WTP	803.2	KY	Ohio River	Weekly
24	Mt. Vernon WTP	829.2	IN	Ohio River	Weekly
25	Morganfield WTP	839.9	KY	Ohio River	Weekly
26	Highland Creek	841.8	KY	Tributary	Biweekly
27	Wabash River	848.0	IL/IN	Tributary	Biweekly
28	Little Wabash River	848.0	IL	Tributary	Biweekly
29	Saline River	867.4	IL	Tributary	Biweekly
30	Sturgis WTP	871.3	KY	Ohio River	Weekly
31	Tradewater River	873.4	KY	Tributary	Biweekly
32	Crooked Creek	877.7	KY	Tributary	Biweekly
33	Deer Creek	893.0	KY	Tributary	Biweekly
34	Cumberland River	920.4	KY	Tributary	Biweekly
35	Tennessee River	934.5	KY	Tributary	Biweekly
36	Paducah WTP	935.5	KY	Ohio River	Weekly
37	Post Creek Cutoff	957.7	IL	Tributary	Biweekly
38	Cairo WTP	977.8	IL	Ohio River	Weekly

Table 3. Sampling Locations

of suppliers. The Ohmicron kits were selected to provide continuity between ORSANCO's results and data generated by Louisville and Evansville water utilities which also use Ohmicron products. These Ohio River water utili-ties conduct frequent atrazine analyses on the Ohio River, therefore, the use of compatible equipment was a distinct advantage. Data from these utilities are used in this report to provide a long-term perspective to intensive survey data collected by ORSANCO.

The analytical procedure for determining atrazine concentration in water is fairly simple, requiring little analytical expertise. First, a water sample is added to a test tube which has antibodies fixed to its inside walls. Enzymes and magnetic particles are then added to the test tube and a reaction occurs whereby the atrazine and magnetic particles attach to the test tube wall. The test tube is then inserted into a magnetic field such that the atrazine, along with the magnetic particles, are tightly bound to the inside wall of the test tube. The test tube is then rinsed to remove all other substances not of interest. A catalyst is then added to cause a color reaction, and a stopping agent then halts color development at the appropriate time. The amount of color is then measured with a spectrophotometer. This was performed simultaneously on water samples of unknown atrazine concentration, as well as on several samples of known atrazine concentration to build a standard curve. The color of the unknowns are then compared against the color of the known samples to determine actual concentrations. Approximately 50 unknown samples can be analyzed in one batch, taking approximately two hours by this method.

The linear working range of the immunoassay test is from 0.05 µg/L to 5.0 µg/L. This is established with a number of standards of known concentration which are analyzed with each batch. These knowns are used to establish a linear standard curve with color intensity versus concentration. Samples with concentrations above 5 µg/L are outside of the linear working range of the standard curve. These samples must be diluted to below 5 µg/L such that the standard curve with a known relationship of color intensity to atrazine concentration can be applied to determine the actual concentration.

The manufacturer has built its own quality assurance performance requirements into the test. Samples of known concentrations which are used to build the standard curve are analyzed in duplicate, and the test results must be within a certain tolerance for the batch run to be accepted. In addition to the manufacturer's quality assurance procedures, ORSANCO staff analyzed each sample in triplicate to minimize the effects of human error inherent to performing the test. Much pipetting is required, along with other test procedures, which affect test results. The manufacturer has indicated that consistent pipetting technique is important to achieve repeatable, accurate results. Therefore, samples were analyzed in triplicate, where each of the triplicates was contained in separate batches. Then, the median value of the three runs was assumed to be the most representative result, and this value is used in the results section of the report. It was believed that this procedure would minimize human error. Field blanks and duplicates were also analyzed.

Because the manufacturer indicates that "gross" suspended solids can interfere with test results, each sample was filtered in the laboratory prior to performing the test. Disposable 0.2 µm inorganic membrane filters, which attach to a syringe, were used to filter water samples. Several filtered and unfiltered samples were analyzed together, and no significant differences in results were found, even though samples were continually filtered throughout the analytical process. Early in the survey, samples were filtered in the field using Gelman 0.45 µm ground water capsules. Side by side analyses of filtered and unfiltered samples indicated that atrazine was being removed from the water sample by the Gelman filter. The use of these filters was immediately discontinued. No survey data was lost because an unfiltered sample was always collected to be analyzed along with the filtered sample. Had this procedure not been implemented, inaccurate results, lower than actual atrazine concentrations (a type 2 error), would have been reported.

Analytical results by the immunoassay technique generally produce atrazine concentrations which are higher than GC confirmation analyses by U.S. EPA Method 507. This is probably caused by cross-reactivity in the immunoassay technique. Cross-reactivity occurs when the immunoassay test measures other triazine compounds (cyanazine, simazine), or atrazine metabolites (degradation byproducts of atrazine) as atrazine itself. These compounds are almost always present in water samples along with atrazine. Another possible explanation of why immunoassay results are usually higher than GC results is that some atrazine is lost during the extraction process of the GC methods. Because the manufacturer of the immunoassay test recognizes inaccuracies due to cross-reactivity, and because other triazine compounds were measured in water samples collected in this survey, cross-reactivity is a viable explanation. Losses due to extraction in the GC methods may also contribute to differences between methods.

There are a number of advantages, and some disadvantages to the immunoassay technique. The primary disadvantage would be the accuracy of the test. If there is a need for results that are accurate to less than one part per billion, it might be advisable to utilize GC methodologies. Such inaccuracies can be reduced by analyzing each sample in triplicate, but this results in substantial additional costs and time requirements. Another disadvantage of the test is its upper range of 5.0 µg/L. Samples with concentrations above this upper limit must be diluted, thus introducing additional potential for error.

A major advantage of the test is its low cost, at least one-tenth of the cost to have a contract laboratory perform the analyses. In addition, little training is required to perform the test, results are available quickly, little sample preparation is required, and the test is highly sensitive. The low cost nature of this test enabled ORSANCO to conduct the survey, thus the benefits outweighed the disadvantages associated with this analytical technique. Another advantage of the immunoassay is its sensitivity with detection levels of 0.05 µg/L (according to the manufacturer). In actuality, quantifiable levels may be somewhat higher.

RESULTS

The quantitative results presented in this report were generated by the immunoassay analytical technique described in the previous section. The immunoassay technique generally produces results with higher concentrations than those produced by U.S. EPA approved GC Method 507. For samples where GC confirmations were performed, the mean atrazine concentration by the immunoassay method was 0.66 µg/L higher than the mean GC confirmation by U.S. EPA Method 507. The Quality Assurance section of this report provides more detail concerning the issue. Most of the results presented in this report were generated by the immunoassay method. Appendix A contains the survey data. Atrazine data presented in this section represent the median value of the immunoassay test run in triplicate on the same water sample in separate batches.

Data from several sources are used in this section, but are primarily from samples collected in conjunction with the ORSANCO survey and analyzed in triplicate by the immunoassay technique. Atrazine data from Louisville and Evansville water utilities on the Ohio River are used in this report. Both entities use the same immunoassay test that is used by ORSANCO, and results generally seem to be comparable. With the exception of those data which are presented to provide a long-term perspective on results of this survey, the data in this report were collected in the spring and early summer of 1995. Appendix A contains tables of all atrazine data generated by ORSANCO during this survey and also provides summary statistics. Results from each of three separate analyses are presented as maximum, median, and minimum atrazine concentration. The median value is used in the following assessment to minimize inaccuracies inherent to the test methodology.

Atrazine in the Main Stem

Figure 5 is a longitudinal representation of atrazine concentrations in the lower Ohio River, resulting from 13 weekly rounds of sampling at 10 water intakes from April through early July 1995. This graph shows the distribution of atrazine concentrations over the survey period. Atrazine concentrations fluctuated substantially over the 13 week period from a low of near zero to almost 4 µg/L at Cairo, IL. The average atrazine concentration over the period generally increased in a downstream direction from approximately 1 part per billion (ppb) at Cincinnati, OH to 2.5 ppb at Cairo. An anomaly in this downstream trend occurs at the Mt. Vernon, IN and Morganfield, KY intakes, located between Ohio River Mile Points 829 and 840. An explanation for this anomaly is not evident. There may be an atrazine sink in this segment of the River, or the sampling locations may not be representative of actual conditions. Most of the individual sampling rounds possess longitudinal curves of atrazine concentration that are the same shape as the average curve.

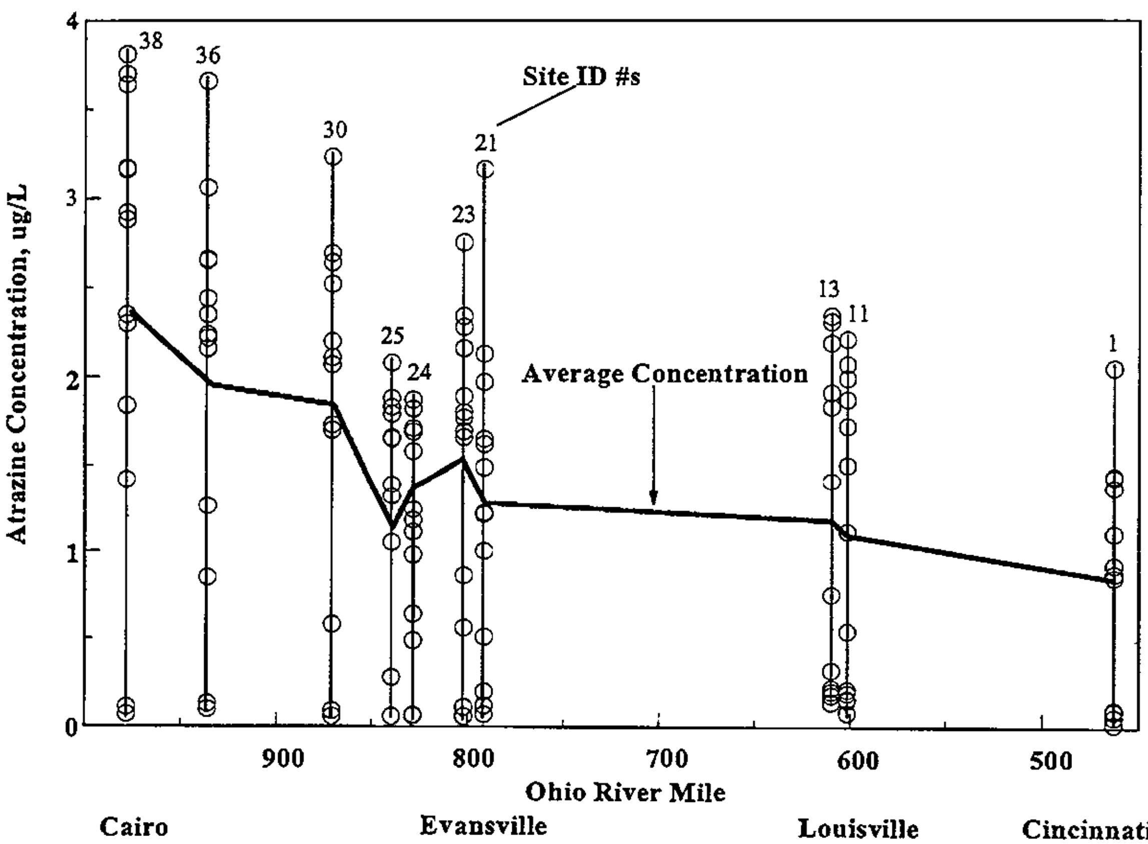

Figure 5. Atrazine Concentrations in the Ohio River (April - July, 1995) (Sampling locations are referenced by number in Table 3).

Figure 6 represents temporal changes in atrazine concentration, from April to early July, for each of 10 Ohio River intakes where weekly samples were collected. The three most upstream intakes exhibit virtually the same shape. Atrazine concentrations stay near zero until early May, increase steadily and peak at the beginning of June, tail off slightly through the end of June, and begin to increase in July. Based on immunoassay results, concentrations peak approximately one ppb below the MCL at all three of these most upstream intakes in the study.

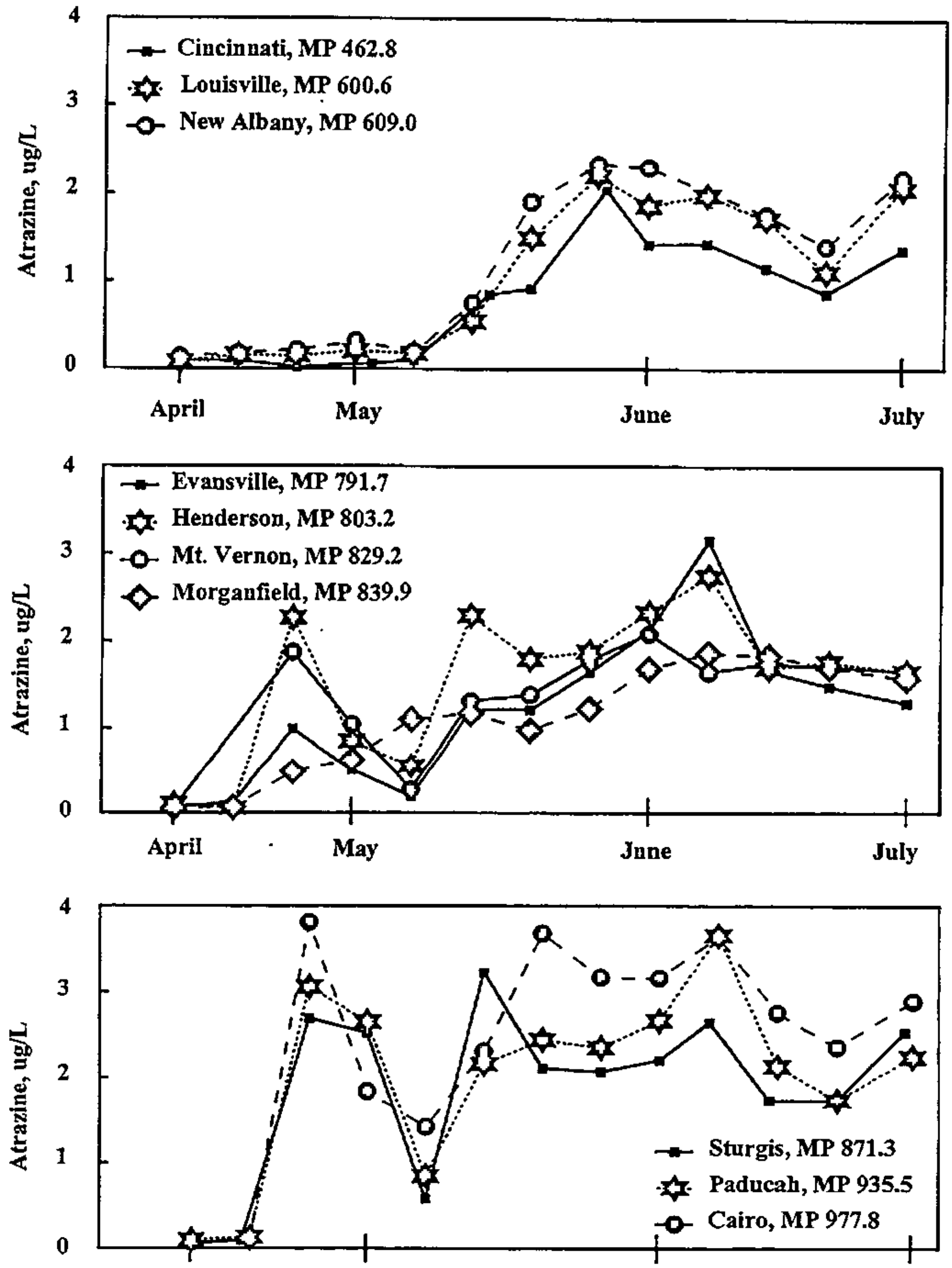

Figure 6. Temporal Change in Mainstem Atrazine Concentrations.

With the exception of Morganfield, and to a lesser extent Mt. Vernon, the other intakes possess a similar shape characterized by a spike in mid-April. A second sharp increase occurs during mid-May and these higher concentrations are generally sustained throughout the remainder of the survey. The three most downstream intakes exhibit almost identical characteristics. These in-takes are downstream of the Wabash River, a major source of atrazine to the Ohio River. Based on immunoassay results, atrazine concentrations remain above 3 µg/L at Cairo for extended periods of time, while concentrations at Paducah and Sturgis occasionally reach the MCL.

Atrazine concentrations in the Ohio River are not constant on a yearly basis. Peak concentrations in the spring of 1995, may not at all be indicative of peak concentrations during 1996. Figure 7 presents long-term, fixed station atrazine monitoring data from Louisville and Evansville water intakes on the Ohio River. ORSANCO monitoring data for 1995 is also overlayed on the graphs to place some perspective on 1995 results. It is immediately discernible that 1995 Ohio River atrazine concentrations, at both Louisville and Evansville, were moderate in comparison to concentrations which were lower in 1994 and higher in 1993. Peak atrazine concentrations occurred at quite different times

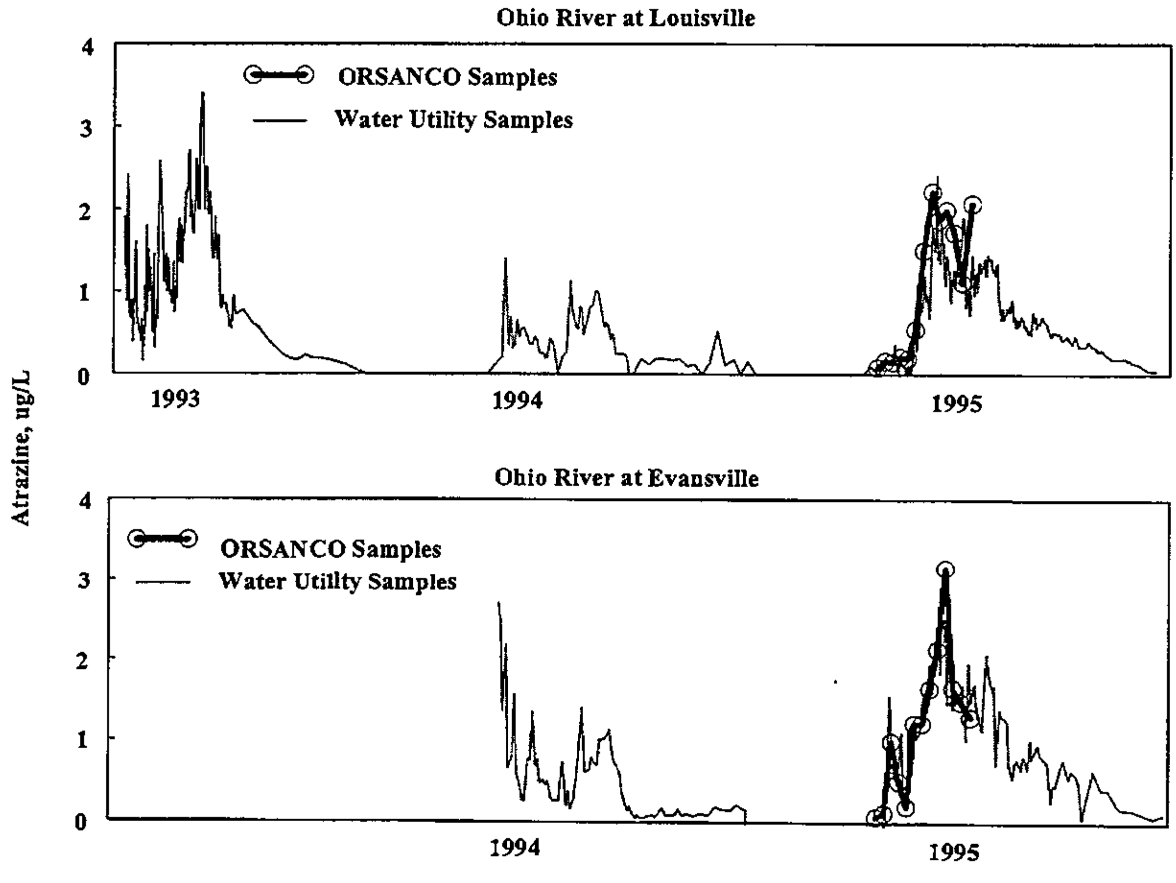

Figure 7. Temporal Changes in Atrazine from 1993 through 1995 at Louisville and Evansville

between the three years, from the end of July in 1993, to early May in 1994. Low-level atrazine detections begin to occur in mid to late April, and tail off toward the end of December. While peak concentrations tend to vary substantially, the beginning and ending points for atrazine detections in the annual cycle tend to be more consistent from year to year.

In terms of trend identification, three years of data is certainly not enough to ascertain any trend in peak concentration or amount of time atrazine is detected from one year to the next. However, it is evident that peak concentrations decreased between 1993 and 1994, then increased from 1994 to 1995. Continued long-term monitoring of atrazine in the Ohio River must occur in order to detect any long-term trends.

Tributary Sources of Atrazine

The 29 largest tributaries to the Ohio River were sampled every other week to determine the major sources of atrazine in the main stem. Figure 8 displays the range of concentrations found during seven rounds of sampling. While more than half of the tributaries had maximum atrazine concentrations below 5 µg/L, 25 percent of those sampled had maximum levels above 20 µg/L. The maximum concentration measured was approximately 60 µg/L in Highland Creek in Kentucky, which is 20 times higher than the drinking water MCL of 3 µg/L. Fortunately, this tributary is one of the lowest flow streams included in the survey, thus its impact on the Ohio River is not great. Tributaries entering the Ohio River on its north shore have noticeably higher atrazine concentrations than those entering from the south.

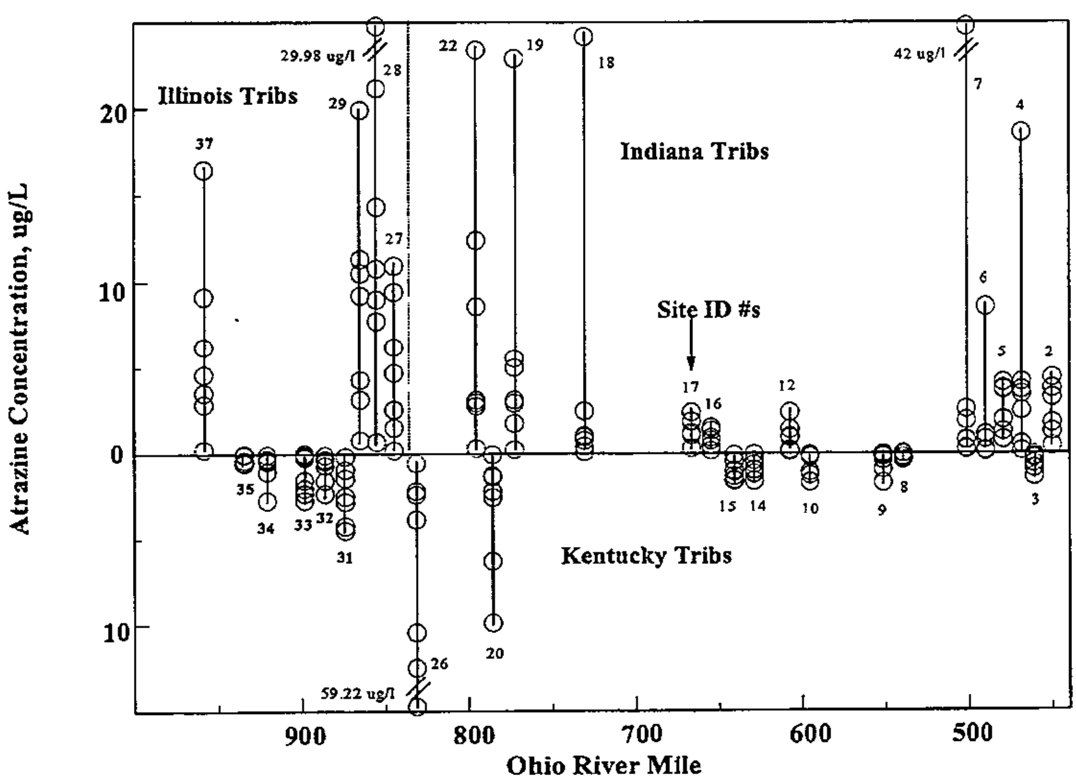

Figure 8. Atrazine Concentrations of Major Ohio River Tributaries (April - July, 1995) (Sampling locations are referenced by number in Table 3).

While concentrations are of concern on tributaries, especially in streams used as a source for public water supply, mass loading (i.e., lbs. per day) is used to evaluate the relative importance of tributaries as sources of atrazine to the Ohio River. Mass loading (or mass flux) considers both concentration and stream flow as these parameters determine the amount of atrazine influx per time to the Ohio River from tributaries. Figure 9 shows the *average* cumulative atrazine mass loading from seven rounds of tributary sampling along with the average atrazine mass flux in the Ohio River. The stacked bars represent the cumulative mass input from tributaries to the Ohio River and the line represents the flowing atrazine load in the Ohio River. The clear portion of the stacked bar represents the cumulative load to the Ohio from all upstream tributaries sampled, while the dark portion bar represents the atrazine mass influx from that tributary.

From Figure 9, it is evident that major atrazine sources to the Ohio River include the Great Miami River (Site ID #4), Green River (Site ID #20), Wabash River (Site ID #27), and the Little Wabash River (Site ID #28). This analysis also provides a mass balance accounting of atrazine in the system. In a perfect mass balance accounting, the tops of the stacked bars would be of equal height with the line. It is clear from the figure that the mass balance accounting is near perfect from Cincinnati to Evansville. This would suggest that the survey accurately characterized the system in terms of atrazine for that segment of the River. Then the only decrease in the main stem atrazine curve, occurring below Evansville, would suggest an atrazine sink. An alternative hypothesis is that the hydraulics of the system result in sampling sites which are not representative of the entire River at that point. Because the decrease occurs

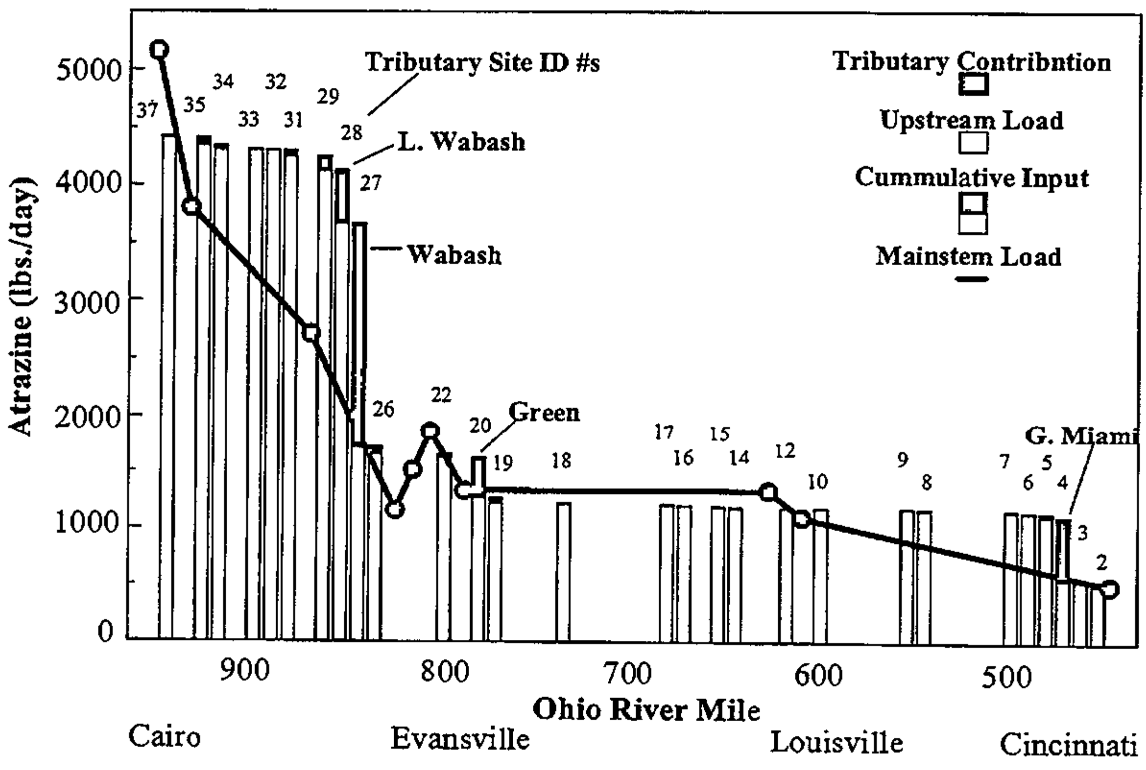

Figure 9. Average Cumulative Atrazine Loadings to the Ohio River (April - July, 1995) (Sampling locations are referenced by number in Table 3).

at two stations which are 10 miles apart, and because the decrease occurs consistently from one round of sampling to the next, the existence of an atrazine sink in the system is a possibility but remains unexplained. The mass balance accounting then remains reasonable for the last 150 miles of the River.

Figure 10 presents the relative contribution of atrazine by the major tributary sources. For each sampling event, the ratio of tributary atrazine loading to Ohio River loading at Cairo, IL is calculated. The average of these rounds is then presented in the figure. There are eight tributaries which contribute one percent or more of the total Ohio River atrazine loading, the Wabash River being by far the largest source contributing an average of 38 percent. The average contribution from all sources above Cincinnati, the upstream boundary of the study area, was almost 10 percent. The average mass of atrazine not accounted as tributary inputs to the system was 14 percent. This performance is quite good since not all flow influxes to the Ohio River were sampled for atrazine. In fact, a mass balance accounting of flow suggests that the average flow to the Ohio River (tributaries, direct runoff, etc.) not included in the survey was approximately five percent. The average contribution of the largest sources was as follows: Wabash River (38 percent), Great Miami River (11 percent), Little Wabash River (nine percent), and the Green River (seven percent).

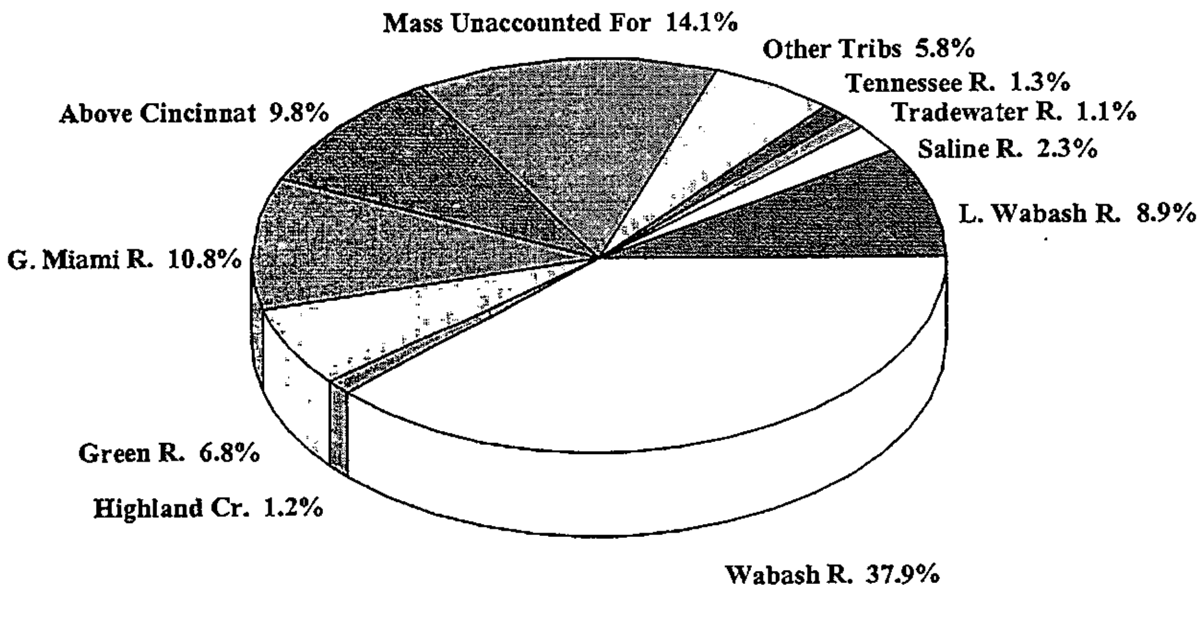

Figure 10. Average Tributary Contribution of Atrazine to the Ohio River (April - July, 1995)

Drinking Water Treatment for Atrazine

The Evansville water utility initiates powder activated carbon treatment when Ohio River source water reaches one half the maximum contaminant level (1.5 μg/L). Figure 11 presents raw and treated water atrazine concentrations at Evansville during 1994 and 1995. Addition of powder activated carbon is characterized by a downward spike in the treated water atrazine concentration. When carbon is not added, the finished water concentration generally mirrors the raw water atrazine level. This supports the conclusion that routine treatment scenarios are not effective in removing atrazine. For this reason, it would be beneficial to notify water utilities on the Ohio River when atrazine levels approach the drinking water MCL, particularly for those facilities that do not conduct routine monitoring.

Other Pesticides

Some of the most heavily used pesticides in the lower Ohio River Basin were discussed in a previous section on usage. In addition to atrazine, of which an estimated 11 million pounds were applied to corn crops in the lower Basin in 1994, the following other pesticides were commonly used: metolachlor (9 million lbs./yr.), alachlor (6 million lbs./yr.), cyanazine (3 million lbs./yr.), and simazine (<1 million lbs./yr.). As such, it might be expected that these herbicides too would be found in surface waters of the lower Basin, and in fact, such is the case.

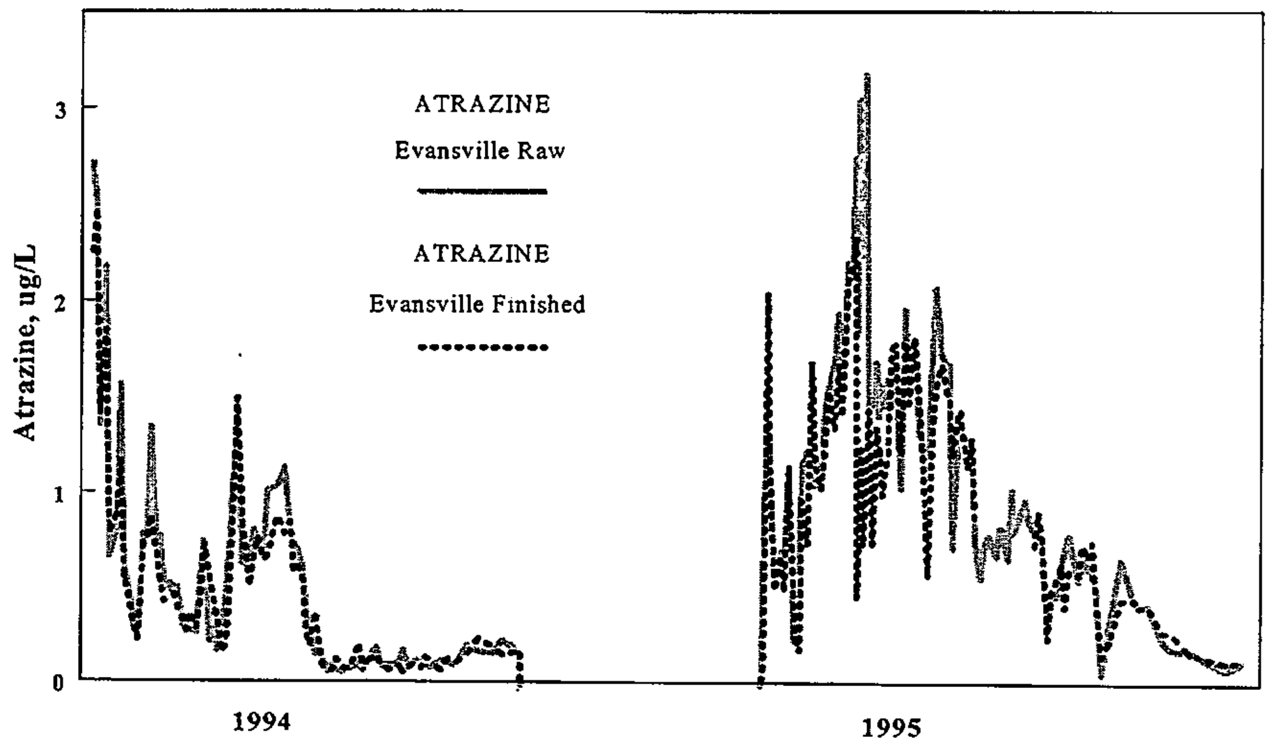

Figure 11. Effects of Drinking Water Treatment on Atrazine Levels

In addition to atrazine analyses by the immunoassay technique, approximately 10 percent of the samples were analyzed by gas chromatograph (GC). GC confirmation samples were analyzed for alachlor, metolachlor, cyanazine, and simazine, in addition to atrazine. Appendix B contains the data for these other herbicides. Figure 12 shows the relative composition of 49 confirmation analyses by gas chromatograph for the five herbicides. It can be seen that there is no constant relationship in the composition of herbicides in a sample. It can also be seen that the relative amount of metolachlor increases substantially in samples with total herbicide concentrations near or above 10 µg/L. Cyanazine is present in a large percentage of samples, 20 percent of which are greater than its MCL of 1 µg/L. Metolachlor was detected in approximately 50 percent of confirmation samples, but never at a level anywhere near its proposed MCL of 100 µg/L. Simazine was detected in three quarters of the confirmation samples, while the maximum concentration was only half its MCL of 4 µg/L. Alachlor was rarely detected in confirmation samples, while its MCL of 2 µg/L was not exceeded in any confirmation samples.

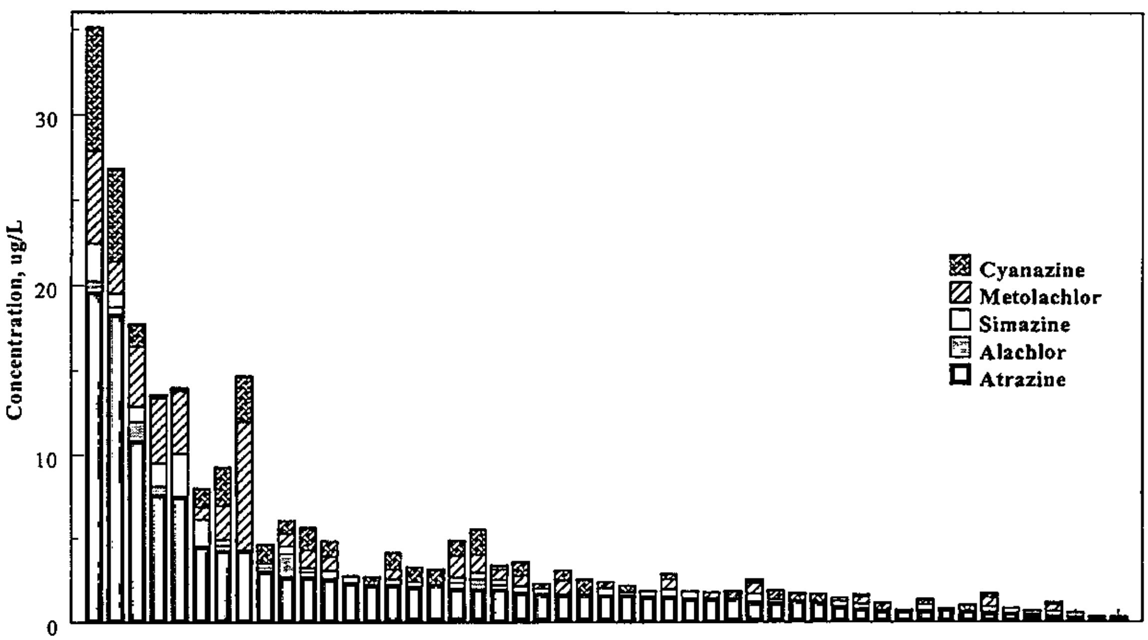

Figure 12. Composition of 49 Analyses by Gas Chromatography for 5 Herbicides

Figure 13 shows the average composition of the five pesticides based on analyses of 49 samples by gas chromatograph. The analysis shows that atrazine by far is the largest component of the five herbicides. Cyanazine is the second largest component at 15 percent on average. Metolachlor and simazine are each found in about 11 percent of samples, while alachlor is infrequently detected in only two percent of the samples. At Cairo, IL nine confirmation samples were collected over the 13 week survey. Figure 14 presents the results of these GC confirmation analyses for the five herbicides at Cairo, IL, where the highest atrazine concentrations generally occur. Except for atrazine, the other herbicides are generally below 1 µg/L, with the exception of one cyanazine sample. The other herbicides also do not exhibit the same shape as the atrazine curve. There is little or no temporal trend in these other herbicides.

Quality Assurance Performance Results

Two primary activities were conducted to assure that valid data were collected and generated for this study. First, analyses performed in-house by the immunoassay technique (described earlier) were completed in triplicate under separate runs. Each run had a standard curve developed with known standards. Secondly, 10 percent of samples collected were submitted to a contract laboratory for confirmation analyses by a U.S. EPA approved method utilizing gas chromatography. The following conclusions are supported later in this section, and are based on data contained in Appendix C which compares GC confirmation analyses by Method 507 to the median value of three runs performed by the immunoassay technique.

1. The immunoassay method performed in-house usually produced results which were higher than those generated by the contract laboratory applying U.S. EPA Method 507.

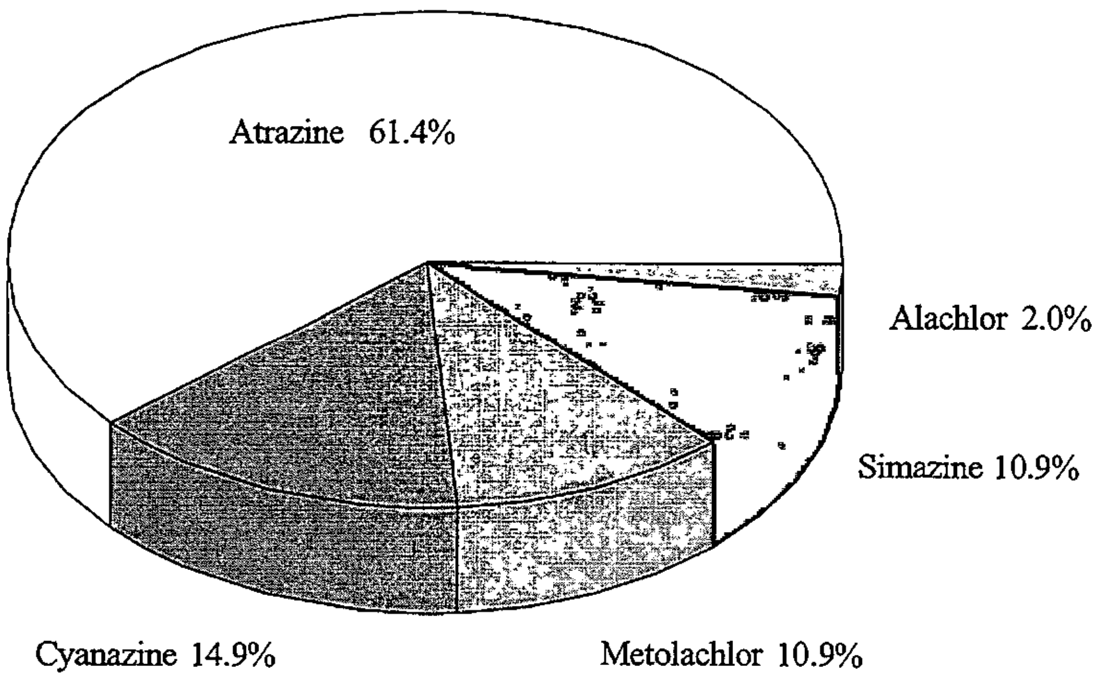

Figure 13. Average composition of 49 Samples Analyzed by GC.

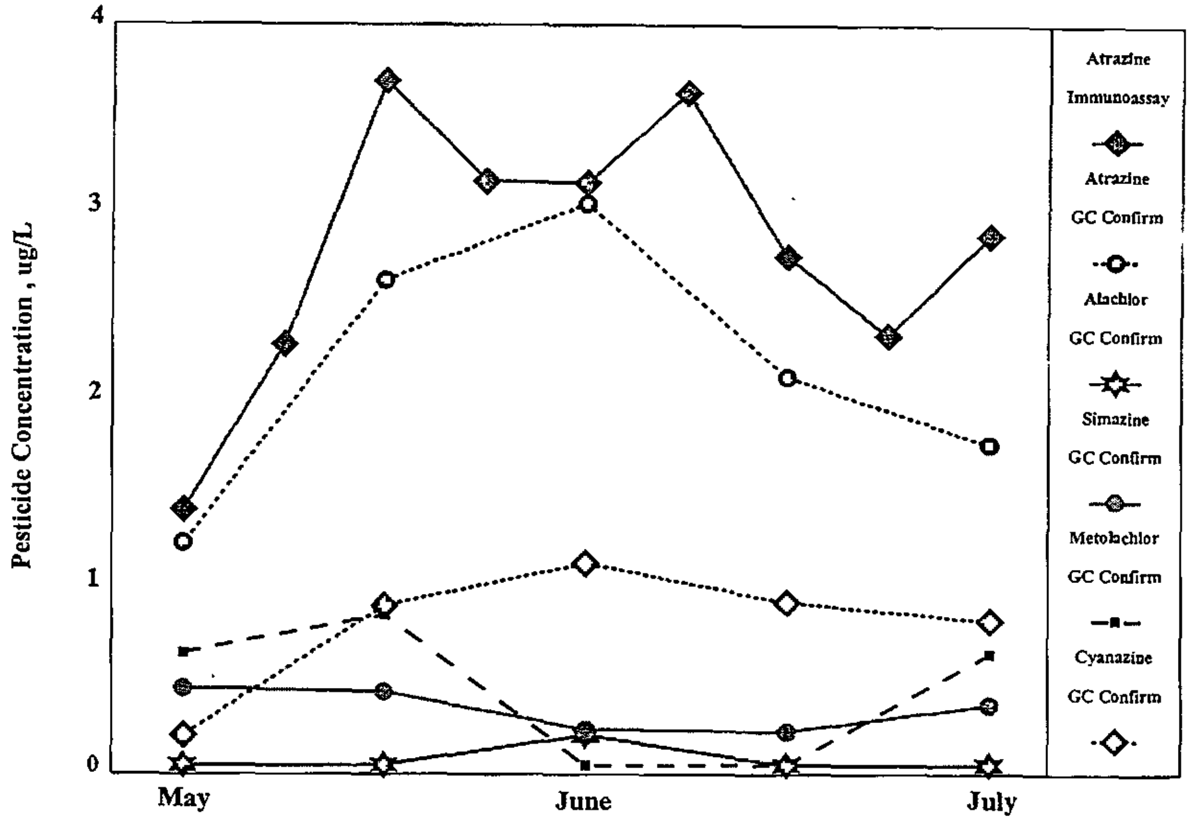

Figure 14. Comparison of Atrazine Concentrations at Cairo to Other Pesticides (1995).

2. Atrazine results produced in-house utilizing the immunoassay technique varied significantly between analytical runs in a number of cases.
3. Results by the immunoassay technique for samples above 5 µg/L were substantially less certain than those below 5 µg/L (samples above 5 µg/L required dilution).

Figure 15 presents the absolute difference between the median (of three runs) atrazine concentration produced in-house by the immunoassay technique and the GC confirmation result generated by U.S. EPA Method 507, for all samples below 5 µg/L. Samples below this concentration are within the linear working range of the immunoassay test and require no dilution. Samples above 5 µg/L must be diluted to fall within the linear range (0.05 µg/L to 5.0 µg/L) of a standard curve which is developed for each run of the immunoassay test. Of 43 observations below 5 µg/L, there were only four cases in which the atrazine concentration by GC was higher than by the immunoassay technique. These cases occurred at the lowest concentrations measured during the survey, and the difference between the two analytical techniques was very small. The reason that the immunoassay technique measured atrazine concentrations higher 90 percent of the time, than by GC, is explainable. In the immunoassay technique, cross-reactivity with other triazine herbicides results in the test measuring a certain portion of these closely related compounds as atrazine.

The average difference in atrazine concentration between the two methods, for 43 samples that were confirmed by GC and were not diluted in-house (causing additional error), was 0.68 µg/L with a standard deviation of 0.47 µg/L. Based on those 43 observations, there is a 90 percent probability that the difference in methods would be 1.5 µg/L or less, and a 95 percent probability that the difference would be 1.6 µg/L or less. There is a reasonably high degree of certainty then that the immunoassay technique is accurate to within 1.5 or 1.6 µg/L, and that the immuno-

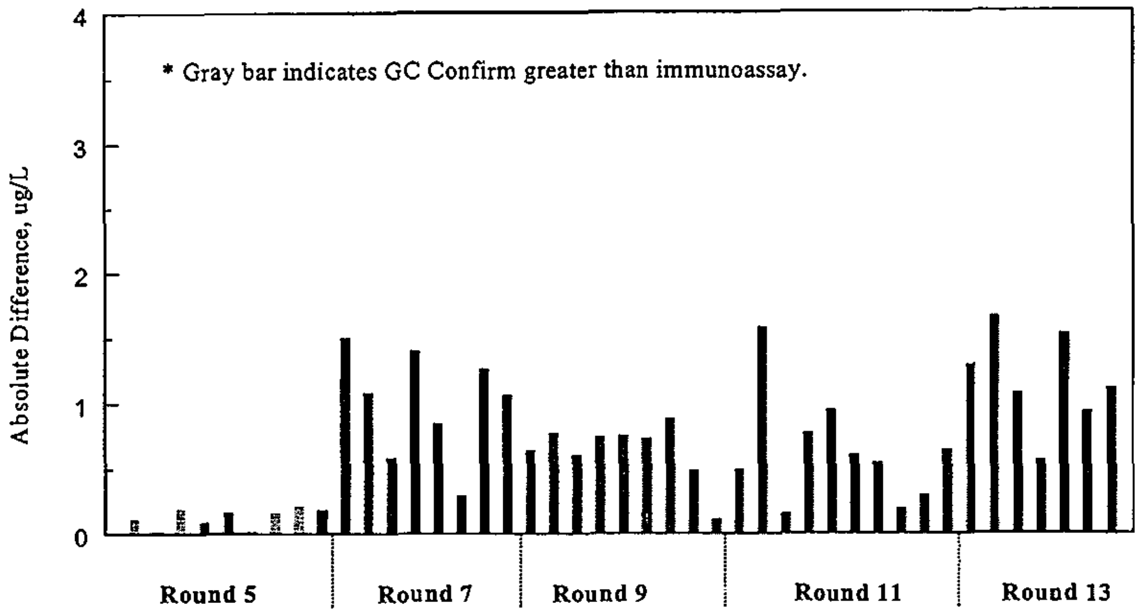

Figure 15. Absolute Difference Between Immunoassay and GC Methods

assay is higher than GC-measured concentrations. For seven samples greater than 5 µg/L with GC confirmation analyses, the average difference in results was 3.85 µg/L. All of these samples exhibited greater concentrations in the immunoassay method. A primary reason for larger differences between the two methodologies for samples greater than 5 µg/L is associated with sample dilution. A maximum concentration of 5 µg/L can be measured by the immunoassay technique, such that samples with higher concentrations were diluted without the use of highly accurate tools.

Each sample was analyzed in three separate analytical runs for the immunoassay technique. This procedure, while quite labor and time intensive, turned out to be invaluable. Instead of performing one analysis, three separate analyses were performed and the median atrazine concentration was selected to represent the true value. So instead of analyzing approximately 400 water samples by the immunoassay technique, over 1200 individual analyses were performed. While approximately tripling the analytical costs per sample, these costs were still quite low. The analytical cost, excluding confirmation samples which were $150 per sample, was approximately $20 per sample using the immunoassay technique.

For all samples analyzed by the immunoassay technique, the average range between the maximum and minimum result of three analyses performed on each water sample was 0.5 µg/L. The average range of results for data greater than 5 µg/L (atrazine) was 3.4 µg/L, while the average range for data less than 5 µg/L was 0.3 µg/L. By selecting the median (or middle) result of the three analyses to represent the true atrazine concentration, then both high and low outliers are eliminated from the data. These points would skew results if the mean of the three results were used to represent the actual concentrations.

Figure 16 shows the results of the median atrazine concentration by the immunoassay technique as compared with the GC confirmation result over a period of nine weeks at Cairo, IL.

It shows reasonably good agreement between the immunoassay and GC confirmation results. Figure 17 further supports this conclusion and illustrates the good correlation between the two methods. A linear correlation coefficient (r) of 0.85 between the median immunoassay atrazine concentration and the same result by GC Method 507 was achieved for 42 undiluted water samples.

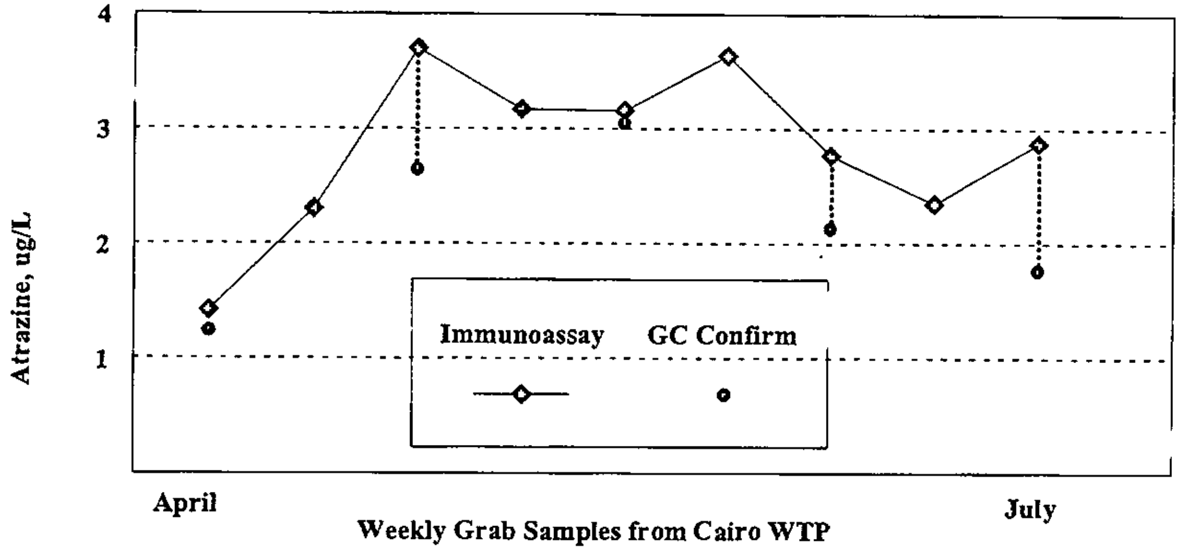

Figure 16. Atrazine by Immunoassay Technique VS. GC Confirmation Results at Cairo, IL.

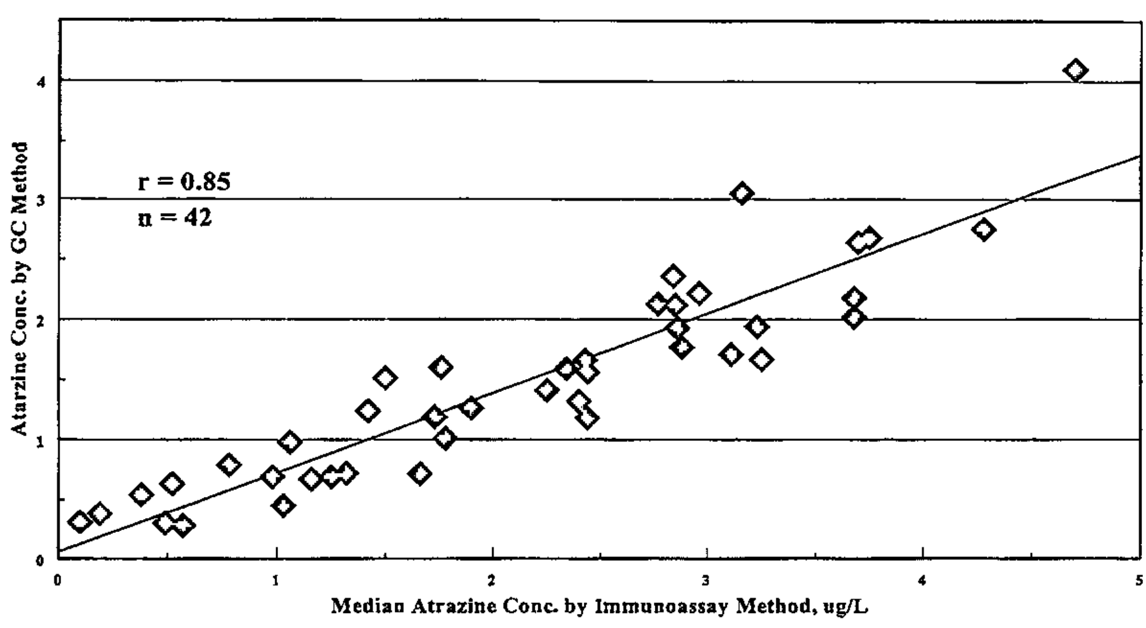

Figure 17. Correlation Between Immunoassay and GC Methods.

CONCLUSIONS

1) *Herbicide Use*

An estimated 70 million pounds of five herbicides (atrazine, cyanazine, simazine, metolachlor, and alachlor) were applied to corn and soybean crops in 1994 within the states which make up the lower Ohio River Basin (IL, IN, KY, and OH).

2) *Atrazine Use*

Atrazine is the most heavily used herbicide in the lower Ohio River Basin, with an estimated 23 million pounds applied to corn and soybean crops in 1994 within the lower Basin states. The heaviest use of atrazine within the lower Basin occurs in the Wabash River watershed.

3) *Trends in Herbicide Use*

While atrazine use has remained fairly constant over the past five years, alachlor usage has steadily decreased while metolachlor use shows an upward trend. It is important to recognize that use rates are not constant in terms of future concerns.

4) *Herbicide Characteristics*

The herbicides addressed in this report are persistent in the environment and soluble (except simazine) in water, making these substances quite mobile in the aquatic system.

5) *Human Health Concerns*

These herbicides have been classified as possible human carcinogens, while some have also been linked to birth defects and developmental abnormalities. They all are regulated or proposed for regulation under the federal Safe Drinking Water Act.

6) *Ohio River Atrazine Concentrations*

Atrazine concentrations in the Ohio River generally increase in a downstream direction to maximum concentrations at the Cairo, IL water intake. Concentrations occasionally exceeded the Safe Drinking Water Act Maximum Contaminant Level (MCL) based on immunoassay results (which have been shown to be higher than by GC). Some level of human health concern is warranted, given that routine treatment techniques (no carbon treatment) do not appear to remove atrazine. In addition, the synergistic effects of multiple pesticides on human health have not been defined, while almost all samples confirmed by GC in this study had more than one herbicide present.

7) *Concentrations of Other Pesticides*

Besides atrazine, cyanazine was the only other of the five herbicides to exceed its drinking water MCL (1 μg/L) in raw water samples analyzed by GC. Nine of 50 samples exceeded the MCL representing almost 20 percent of samples.

8) *Atrazine Sink (decrease in concentration/ loading)*

While Ohio River atrazine concentrations generally increase in a downstream direction, a sink appears to exist at Mt. Vernon, IN and Morganfield, KY monitoring sites as evidenced by decreases in concentrations and mass loading in a reasonably consistent fashion. An explanation for this is not evident, and it is possible that this apparent sink is a function of unrepresentative sample collection sites.

9) *Temporal Variations in Atrazine*

Atrazine concentrations vary on an annual basis, and from one year to the next depending on a variety of factors. Based on data from 1993 through 1995, atrazine generally begins to be detected in late March/early April, peaks sometime between early June and late July, and tails off to below detection by the year's end. Peak concentrations were highest in 1993 and lowest in 1994.

10) ***Tributary Atrazine Concentrations***

Atrazine concentrations in several tributaries were quite elevated. Concentrations as high as 60 µg/L were detected. Generally, tributaries on the north shore of the Ohio River had higher concentrations than those to the south, and this correlates with land use.

11) ***Major Tributary Sources of Atrazine***

Based on the average atrazine mass loading of seven rounds of tributary sampling distributed over 13 weeks as compared with the average loading at the downstream-most sampling location on the Ohio River (at Cairo, IL), the following tributaries were the major sources of atrazine with their relative contributions:

• Wabash River	38%
• Great Miami River	11%
• Little Wabash River	9%
• Green River	7%
• Saline River	2%
• Highland Creek	1%
• Tennessee River	1%
• Tradewater River	1%
• All Sources Combined Above Cincinnati	10%
• Mass Unaccounted For	14%

12) ***Composition of Herbicides in Water Samples***

Based on 49 samples analyzed by gas chromatograph for five herbicides, the average composition of these water samples from the Ohio River and selected tributaries is as follows:

• Atrazine	61%
• Cyanazine	15%
• Metolachlor	11%
• Simazine	11%
• Alachlor	2%

13) ***Cost-effective Aspects of Immunoassay Analytical Test***

Utilization of the immunoassay technique, in lieu of gas chromatography methods performed by a contract laboratory, reduced analytical costs from potentially $150 per sample to an actual $20 per sample cost. Analytical costs for this sampling program would have been $60,000 if contracted to a laboratory, as opposed to $8,000 actually paid for immunoassay test kits and equipment. This work could not have been completed without the cost-effective immunoassay procedure.

14) ***Low Detection Level with Immunoassay Technique***

The immunoassay technique for atrazine is very sensitive with a detection level of 0.05 µg/L. Detection levels for typical GC methods is 0.1 µg/L.

15) ***Inaccuracies Associated With Immunoassay Technique***

Based on comparisons with GC confirmation samples, 90 percent of samples (under 5 µg/L) by the immunoassay technique are accurate to within 1.5 µg/L atrazine (assuming GC concentration is 100 percent accurate). The average difference between techniques (samples under 5 µg/L) was 0.7 µg/L Based on immunoassay tests run in triplicate on all samples, results are repeatable to within 0.5 µg/L. Using the median atrazine concentration of analyses run in triplicate increases accuracy by removing the influences of high and low outliers.

16) ***Correlation of Immunoassay to GC Methods***

Atrazine concentration correlations between the immunoassay and GC methods are excellent, with a linear correlation coefficient (r) of 0.85. This implies a consistent relationship between the two methods (which does not imply equivalence).

RECOMMENDATIONS

1) *Monitor Trends in Pesticide Use*

Trends in pesticide use within the Basin must be monitored in order to identify emerging water quality issues. Special attention should be given to replacement products being developed or phased into use for the most heavily used pesticides in the Basin.

2) *Install Long-Term Atrazine Monitoring at Cairo, IL*

Because concentrations vary within a given year and from one year to the next, it is desirable to monitor atrazine at a worst case location on the Ohio River, which is at Cairo, IL. While Evansville and Louisville are conducting such monitoring, both of these sites are upstream of the Wabash River, which is the largest source to the Ohio.

3) *Provide Early Warning to Water Utilities*

All water utilities using the Ohio River as a source of drinking water should be notified when levels of atrazine exceed half the MCL (1.5 μg/L), based on monitoring from Louisville, Evansville and Cairo (if monitoring is installed) water utilities.

4) *Facilitate Exchange of Information on Treatment Techniques Between Water Utilities*

The Evansville Water and Sewer Utility has effectively reduced the level of atrazine in their finished water by modifying their treatment scheme. When atrazine levels exceed one half the MCL, Evansville treats with powder activated carbon. Specific information concerning this treatment technique should be made available to other utilities with similar problems.

5) *Priority Watersheds for State Nonpoint Source Control Programs*

Runoff from agricultural activities, and more specifically from corn production, is the primary means by which atrazine is present in the Ohio River Basin. This report outlines watersheds with the largest atrazine loads to the Ohio River. These watersheds should be appropriately prioritized by the affected states for implementation of non-point source control programs.

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Appendix A

ATRAZINE ANALYTICAL RESULTS BY IMMUNOASSAY: APRIL 10-12, 1995

Location	State	Ohio River * Mile Point	Sample ID	Collection Date	ATRAZINE CONC., ug/L Max	Median	Min	Range	Mean	Sample Std Dev	Stream Flow, cfs	Atrazine Mass Load, lbs/day
Cincinnati WTP	OH	462.8	1-1	04/10/95	0.15	0.09	0.01	0.14	0.08	0.07	57100	27.7
Little Miami R	OH	463.5	2-1	04/10/95	0.44	0.41	0.30	0.14	0.38	0.07	1100	2.4
Licking R	OH	470.3	3-1	04/10/95	0.18	0.11	0.04	0.14	0.11	0.07	1700	1.0
G. Miami R	OH	491.0	4-1	04/10/95	0.26	0.13	0.13	0.13	0.17	0.08	9200	6.4
Whitewater R	IN-OH	491.0	5-1	04/10/95	2.35	1.97	1.91	0.44	2.10	0.24	754	8.0
Tanners Cr	IN	494.8	6-1	04/10/95	0.22	0.17	0.14	0.08	0.18	0.04	82	0.1
Laughery Cr	IN	498.7	7-1	04/10/95	0.35	0.28	0.21	0.14	0.28	0.07	265	0.4
Kentucky R	KY	545.8	8-1	04/10/95	0.08	0.06	0.04	0.04	0.06	0.02	1700	0.5
L. Kentucky R	KY	546 6	9-1	04/10/95	0.18	0.12	0.09	0.09	0.13	0.05	203	0.1
Harrods Cr	KY	595.9	10-1	04/10/95	0.21	0.09	0.09	0.12	0.13	0.07	217	0.1
Louisville CH WT	KY	600.6	11-1	04/10/95	0.12	0.08	0.06	0.06	0.09	0.03	73200	31.6
Silver Cr	IN	606.5	12-1	04/10/95	0.11	0.10	0.10	0.01	0.10	0.01	30	0.0
New Albany WT	IN	609.0	13-1	04/10/95	0.14	0.14	0 07	0.07	0.12	0.04	73200	55.2
Salt R	KY	629.9	14-1	04/10/95	0.09	0.06	0.06	0.03	0.07	0.02	198	0.1
Otter Cr	KY	636.5	15-1	04/11/95	0.15	0.11	0.06	0.09	0.11	0.05	423	0.3
Indian Cr	IN	657.0	16-1	04/11/95	0.17	0.14	0 09	0.08	0.13	0.04	835	0.6
Blue R	IN	663.0	17-1	04/11/95	0.29	0.28	0.19	0.10	0.25	0.06	187	0.3
Anderson R	IN	731.4	18-1	04/11/95	0.10	0.07	0.06	0.04	0.08	0.02	179	0.1
Little Pigeon Cr	IN	772.9	19-1	04/11/95	0.25	0.22	0.15	0.10	0.21	0.05	717	0.9
Green R	KY	784.2	20-1	04/11/95	0.14	0.09	0.03	0.11	0.09	0 06	2400	1.2
Evansville WTP	IN	791.7	21-1	04/11/95	0.10	0.07	0.07	0.03	0.08	0.02	80000	30.2
Pigeon Cr	IN	792.9	22-1	04/11/95	0.36	0.28	0.25	0.11	0 30	0.06	341	0.5
Henderson WTP	KY	803.2	23-1	04/11/95	0.17	0.11	0.07	0.10	0.12	0.05	80000	47.4
Mt. Vernon WTP	IN	829.2	24-1	04/11/95	0.13	0.06	0.06	0.07	0.08	0.04	79300	25.6
Morganfield WTP	KY	839.9	25-1	04/11/95	0.08	0.06	0.06	0.02	0 07	0.01	79300	25.6
Highland Cr	KY	841.8	26-1	04/11/95	0.70	0.60	0.53	0.17	0.61	0.09	304	1.0
Wabash R	IL-IN	848.0	27-1	04/11/95	0.23	0.17	0.15	0.08	0.19	0.04	13500	12.4
L. Wabash R	IL	848.0	28-1	04/11/95	0.83	0.67	0.52	0.31	0.67	0.16	344	1.2
Saline R	IL	867.4	29-1	04/12/95	0.84	0.77	0.49	0.35	0.70	0.19	1032	4.3
Sturgis WTP	KY	871.3	30-1	04/12/95	0.08	0.06	0.04	0.04	0.06	0.02	117700	38 1
Tradewater R	KY	873.4	31-1	04/12/95	0.21	0.20	0.17	0.04	0.19	0.02	1682	1.8
Crooked Cr	KY	877.7	32-1	04/12/95	0.15	0.13	0.04	0.11	0.11	0.06	175	0.1
Deer Cr	KY	893.0	33-1	04/12/95	0.03	0.01	0.00	0.03	0.01	0.02	175	0.0
Cumberland R	KY	920.4	34-1	04/12/95	0.09	0.09	0.07	0.02	0.08	0.01	6000	2.9
Tennessee R	KY	934.5	35-1	04/12/95	0.03	0.02	0.02	0.01	0.03	0.01	15000	1.6
Paducah WTP	KY	935.5	36-1	04/12/95	0.10	0.10	0.06	0.04	0.09	0.02	129300	69.7
Post Cr Cutoff	IL	957.7	37-1	04/12/95	0.32	0.22	0.16	0.16	0.23	0.08	147	0.2
Cairo WTP	IL	977.8	38-1	04/12/95	0.12	0.07	0.06	0.06	0.08	0.03	129300	48.8

* For tributaries, Ohio River Mile Points are at the confluence with the tributary.

** Each water sample was analyzed by immunoassay in three separate batches.

ATRAZINE ANALYTICAL RESULTS BY IMMUNOASSAY: APRIL 17-19, 1995

Location	State	Ohio River * Mile Point	Sample ID	Collection Date	ATRAZINE CONC., ug/L Max	Median	Min	Range	Mean	Sample Std Dev	Stream Flow, cfs	Atrazine Mass Load, lbs/day
Cincinnati WTP	OH	462.8	1-2	04/17/95	0.13	0.09	0.07	0.06	0.10	0.03	87500	42.4
Louisville CH WTP	KY	600.6	11-2	04/17/95	0.29	0.16	0.13	0.16	0.19	0.09	108600	93.7
New Albany WTP	IN	609.0	13-2	04/17/95	0.24	0.18	0.17	0.07	0.20	0.04	108600	105.4
Evansville WTP	IN	791.7	21-2	04/18/95	0.16	0.12	0.08	0.08	0.12	0.04	114600	74.1
Henderson WTP	KY	803.2	23-2	04/18/95	0.06	0.06	0.05	0.01	0.06	0.01	114600	37.1
Mt. Vernon WTP	IN	829.2	24-2		NO SAMPLE COLLECTED						116700	
Morganfield WTP	KY	839.9	25-2	04/18/95	0.08	0.07	0.04	0.04	0.06	0.02	116700	44.0
Sturgis WTP	KY	871.3	30-2	04/18/95	0.10	0.09	0.07	0.03	0.09	0.02	156400	75.9
Paducah WTP	KY	935.5	36-2	04/19/95	0.20	0.13	0.13	0.07	0.15	0.04	179900	126.1
Cairo WTP	IL	977.8	38-2	04/19/95	0.11	0.11	0.07	0.04	0.10	0.02	179900	106.7

* For tributaries, Ohio River Mile Points are at the confluence with the tributary.

** Each water sample was analyzed by immunoassay in three separate batches.

ATRAZINE ANALYTICAL RESULTS BY IMMUNOASSAY: APRIL 24-26, 1995

					ATRAZINE CONC., ug/L							
Location	State	Ohio River * Mile Point	Sample ID	Collection Data	Max	Median	Min	Range	Mean	Sample Std Dev	Stream Flow, cfs	Atrazine Mass Load, lbs/day
Cincinnati WTP	OH	462.8	1-3	04/24/95	0.08	0.05	0.03	0.05	0.05	0.03	94600	10.2
Little Miami R	OH	463.5	2-3	04/24/95	1.78	1.75	1.62	0.16	1.72	0.09	3500	33.0
Licking R	OH	470.3	3-3	04/24/95	0.88	0.63	0.62	0.26	0.71	0.15	7300	24.8
G. Miami R	OH	491.0	4-3	04/24/95	2.57	2.46	2.39	0.18	2.47	0.09	21600	286.4
Whitewater R	IN-OH	491.0	5-3	04/24/95	2.02	1.93	1.92	0.10	1.96	0.06	4300	44.7
Tanners Cr	IN	494.8	6-3	04/24/95	0.18	0.09	0.05	0.13	0.11	0.07	141	0.1
Laughery Cr	IN	498.7	7-3	04/24/95	0.36	0.20	0.19	0.17	0.25	0.10	456	0.5
Kentucky R	KY	545.8	8-3	04/24/95	0.04	0.02	0.00	0.04	0.02	0.02	17000	1.8
L. Kentucky R	KY	546.6	9-3	04/24/95	0.07	0.05	0.04	0.03	0.05	0.02	374	0.1
Harrods Cr	KY	595.9	10-3	04/24/95	0.19	0.18	0.13	0.06	0.16	0.03	423	0.4
Louisville CH WT	KY	600.8	11-3	04/24/95	0.33	0.15	0.12	0.21	0.20	0.11	142600	115.3
Silver Cr	IN	606.5	12-3	04/24/95	0.12	0.11	0.05	0.07	0.09	0.04	420	0.2
New Albany WT	IN	609.0	13-3	04/24/95	0.31	0.22	0.20	0.11	0.24	0.06	142600	169.1
Salt R	KY	629.9	14-3	04/24/95	1.22	0.66	0.52	0.70	0.80	0.37	3840	13.7
Otter Cr	KY	636.5	15-3	04/24/95	1.53	1.11	1.08	0.45	1.24	0.25	717	4.3
Indian Cr	IN	657.0	16-3	04/24/95	0.63	0.43	0.40	0.23	0.49	0.13	1414	3.3
Blue R	IN	663.0	17-3	04/25/95	1.43	1.19	1.02	0.41	1.21	0.21	1500	9.6
Anderson R	IN	731.4	18-3	04/25/95	0.57	0.41	0.28	0.29	0.42	0.15	397	0.9
Little Pigeon Cr	IN	772.9	19-3	04/25/95	6.52	5.56	5.39	1.13	5.82	0.61	1766	52.9
Green R	KY	784.2	20-3	04/25/95	6.82	6.31	5.41	1.41	6.18	0.71	22000	748.2
Evansville WTP	IN	791.7	21-3	04/25/95	1.08	1.00	0.80	0.28	0.96	0.14	199900	1077.5
Pigeon Cr	IN	792.9	22-3	04/25/95	23.38	23.38	21.08	2.30	22.61	1.33	678	85.4
Henderson WTP	KY	803.2	23-3	04/25/95	2.40	2.28	2.08	0.32	2.25	0.16	199900	2456.6
Mt. Vernon WTP	IN	829.2	24-3	04/25/95	2.12	1.88	1.72	0.40	1.91	0.20	199100	2017.5
Morganfield WTP	KY	839.9	25-3	04/25/95	0.57	0.49	0.43	0.14	0.50	0.07	199100	525.8
Highland Cr	KY	841.8	26-3	04/25/95	64.05	59.22	47.46	16.59	56.91	8.53	747	238.4
Wabash R	IL-IN	848.0	27-3	04/25/95	2.84	2.56	2.21	0.63	2.51	0.24	58900	812.7
L. Wabash R	IL	848.0	28-3	04/25/95	21.93	21.16	20.57	1.36	21.22	0.68	4130	471.0
Saline R	IL	867.4	29-3	04/25/95	20.06	19.89	19.04	1.02	19.66	0.55	2289	245.4
Sturgis WTP	KY	871.3	30-3	04/26/95	2.80	2.69	2.54	0.26	2.68	0.13	261000	3784.3
Tradewater R	KY	873.4	31-3	04/26/95	4.41	4.26	3.85	0.56	4.17	0.29	3782	86.8
Crooked Cr	KY	877.7	32-3	04/26/95	0.85	0.72	0.59	0.26	0.72	0.13	393	1.5
Deer Cr	KY	893.0	33-3	04/26/95	0.42	0.26	0.21	0.21	0.30	0.11	414	0.6
Cumberland R	KY	920.4	34-3	04/26/95	0.34	0.26	0.15	0.19	0.24	0.08	15000	21.0
Tennessee R	KY	934.5	35-3	04/26/95	0.19	0.10	0.02	0.17	0.10	0.07	42000	22.6
Paducah WTP	KY	935.5	36-3	04/26/95	3.32	3.06	2.71	0.61	3.03	0.31	317900	5243.3
Post Cr Cutoff	IL	957.7	37-3	04/26/95	10.37	9.18	9.01	1.36	9.52	0.74	363	18.0
Cairo WTP	IL	977.8	38-3	04/26/95	5.14	3.81	3.30	1.84	3.99	0.65	317900	6528.4

* For tributaries, Ohio River Mile Points are at the confluence with the tributary.

** Each water sample was analyzed by immunoassay in three separate batches.

ATRAZINE ANALYTICAL RESULTS BY IMMUNOASSAY: May 1 - 3, 1995

				ATRAZINE CONC., ug/L							
Location	State	Ohio River Mile Point	Collection Date	Max	Median	Min	Range	Mean	Sample Std Dev	Stream Flow, cfs	Atrazine Mass Load, lbs/day
Cincinnati WTP	OH	462.8	05/03/95	0.11	0.06	0.04	0.07	0.07	0.04	140100	45.3
Louisville CH WT	KY	600.6	05/01/95	0.24	0.21	0.21	0.03	0.22	0.02	90400	102.3
New Albany WTP	IN	609.0	05/01/95	0.35	0.32	0.29	0.06	0.32	0.03	90400	155.9
Evansville WTP	IN	791.7	05/02/95	0.54	0.51	0.48	0.06	0.51	0.03	126500	347.7
Henderson WTP	KY	803.2	05/02/95	0.96	0.86	0.79	0.17	0.87	0.09	126500	586.4
Mt. Vernon WTP	IN	829.2	05/02/95	1.09	1.05	0.90	0.19	1.01	0.10	125100	708.0
Morganfield WTP	KY	839.9	05/02/95	0.65	0.64	0.57	0.08	0.62	0.04	125100	431.5
Sturgis WTP	KY	871.3	05/03/95	2.65	2.62	2.40	0.25	2.52	0.13	195400	2654.1
Paducah WTP	KY	935.5	05/03/95	2.67	2.65	2.17	0.50	2.50	0.28	260100	3715.1
Cairo WTP	IL	977.8	05/03/95	2.10	1.84	1.73	0.37	1.89	0.19	260100	2579.6

* For tributaries, Ohio River Mile Points are at the confluence with the tributary.

** Each water sample was analyzed by immunoassay in three separate batches.

ATRAZINE ANALYTICAL RESULTS BY IMMUNOASSAY: May 8 - 10, 1995

Location	State	Ohio River * Mile Point	Sample ID	Collection Date	ATRAZINE CONC., ug/L Max	Median	Min	Range	Mean	Sample Std Dev	Stream Flow, cfs	Atrazine Mass Load, lbs/day
Cincinnati WTP	OH	462.8	1-5	05/08/95	0.13	0.10	0.08	0.05	0.10	0.03	104300	56.2
Little Miami R	OH	463.5	2-5	05/08/95	1.35	1.26	0.96	0.39	1.19	0.20	1300	8.8
Licking R	OH	470.3	3-5	05/08/95	0.24	0.23	0.20	0.04	0.22	0.02	6900	8.6
G. Miami R	OH	491.0	4-5	05/08/95	0.67	0.52	0.47	0.20	0.55	0.10	5100	14.3
Whitewater R	IN-OH	491.0	5-5	05/08/95	0.83	0.78	0.77	0.06	0.79	0.03	1340	5.6
Tanners Cr	IN	494.8	6-5	05/08/95	0.17	0.17	0.13	0.04	0.16	0.02	160	0.1
Laughery Cr	IN	498.7	7-5	05/08/95	0.79	0.77	0.64	0.15	0.73	0.08	517	2.1
Kentucky R	KY	545.8	8-5	05/08/95	0.08	0.04	0.03	0.05	0 05	0.03	7000	1.5
L. Kentucky R	KY	546.6	9-5	05/08/95	0.30	0.17	0.14	0.16	0.20	0.09	387	0.4
Harrods Cr	KY	595.9	10-5	05/08/95	0.27	0.23	0.17	0.10	0.22	0.05	411	0.5
Louisville CH WT	KY	600.6	11-5	05/08/95	0.21	0.18	0.12	0.09	0.17	0.03	138900	134.8
Silver Cr	IN	606.5	12-5	05/08/95	0.20	0.19	0.17	0.03	0.19	0.02	76	0.1
New Albany WT	IN	609.0	13-5	05/08/95	0.30	0.20	0.15	0.15	0.22	0.08	138900	149.7
Salt R	KY	629.9	14-5	05/08/95	0.72	0.44	0.38	0.34	0.51	0.18	577	1.4
Otter Cr	KY	636.5	15-5	05/08/95	0.83	0.49	0.46	0.37	0.59	0.21	698	1.8
Indian Cr	IN	657.0	16-5	05/09/95	1.18	0.90	0.66	0.52	0.91	0.26	1220	5.9
Blue R	IN	663.0	17-5	05/09/95	1.48	1.06	1.02	0.46	1.19	0.25	1410	8.1
Anderson R	IN	731.4	18-5	05/09/95	2.89	2.47	2.24	0.65	2.53	0.33	314	4.2
Little Pigeon Cr	IN	772.9	19-5	05/09/95	1.85	1.76	1.57	0.28	1.73	0.14	1354	12.8
Green R	KY	784.2	20-5	05/09/95	10.01	N/A	9.79	0.22	9.90	N/A	8900	0.0
Evansville WTP	IN	791.7	21-5	05/09/95	0.27	0.20	0.19	0.08	0.22	0.04	153200	165.1
Pigeon Cr	IN	792.9	22-5	05/09/95	2.87	2.76	2.61	0.26	2.75	0.13	520	7.7
Henderson WTP	KY	803.2	23-5	05/09/95	0.72	0.56	0.53	0.19	0.60	0.10	153200	462.4
Mt. Vernon WTP	IN	829.2	24-5	05/09/95	0.33	0.28	0.27	0.06	0.29	0.03	156800	236.6
Morganfield WTP	KY	839.9	25-5	05/09/95	1.16	1.11	0.99	0.17	1.09	0.09	156800	938.1
Highland Cr	KY	841.8	26-5	05/09/95	10.78	N/A	10.12	0.66	10.45	N/A	588	0.0
Wabash R	IL-IN	848.0	27-5	05/09/95	1.53	1.50	1.46	0.07	1.50	0.04	28100	227.2
L. Wabash R	IL	848.0	28-5	05/09/95	14.85	N/A	13.75	1.10	14.30	N/A	1330	0.0
Saline R	IL	867.4	29-5	05/09/95	11.77	N/A	10.89	0.88	11.33	N/A	1747	0.0
Sturgis WTP	KY	871.3	30-5	05/10/95	0.66	0.58	0.51	0.15	0.58	0.08	195500	611.2
Tradewater R	KY	873.4	31-5	05/10/95	4.86	4.51	4.08	0.78	4.48	0.39	2794	67.9
Crooked Cr	KY	877.7	32-5	05/10/95	0.53	0.49	0.43	0.10	0.48	0.05	290	0.8
Deer Cr	KY	893.0	33-5	05/10/95	0.16	0.15	0.12	0.04	0.14	0.02	312	0 3
Cumberland R	KY	920.4	34-5	05/10/95	0.45	0.38	0.35	0.10	0.39	0 05	12000	24.6
Tennessee R	KY	934.5	35-5	05/10/95	0.18	0.10	0.06	0.12	0.11	0.04	32000	17.2
Paducah WTP	KY	935.5	36-5	05/10/95	0.89	0.85	0.73	0.16	0.82	0.08	255600	1171.0
Post Cr Cutoff	IL	957.7	37-5	05/10/95	16.72	N/A	16.17	0.55	16.45	N/A	290	0.0
Cairo WTP	IL	977.8	38-5	05/10/95	1.55	1.42	1.36	0.19	1.44	0.07	255600	1956.3

* For tributaries, Ohio River Mile Points are at the confluence with the tributary.
** Each water sample was analyzed by immunoassay in three separate batches.

ATRAZINE ANALYTICAL RESULTS BY IMMUNOASSAY: May 15-17, 1995

					ATRAZINE CONC., ug/L							
Location	State	Ohio River * Mile Point	Sample ID	Collection Date	Max	Median	Min	Range	Mean	Sample Std Dev	Stream Flow, cfs	Atrazine Mas Load, lbs/day
Cincinnati WTP	OH	462.8	1-6	05/17/95	0.92	0.85	0.63	0.29	0.80	0.15	274200	1256.2
Louisville CH WT	KY	600.6	11-6	05/15/95	0.69	0.54	0.43	0.26	0.55	0.13	237100	690.1
New Albany WT	IN	609.0	13-6	05/15/95	0.84	0.75	0.61	0.23	0.73	0.12	237100	958.5
Evansville WTP	IN	791.7	21-6	05/16/95	1.36	1.22	1.09	0.27	1.22	0.14	310900	2044.4
Henderson WTP	KY	803.2	23-6	05/16/95	2.50	2.30	2.13	0.47	2.30	0.26	310900	3854.2
Mt. Vernon WTP	IN	829.2	24-6	05/16/95	1.46	1.32	1.27	0.19	1.35	0.10	297900	2119.5
Morganfield WTP	KY	839.9	25-6	05/16/95	1.40	1.18	1.06	0.34	1.21	0.17	297900	1894.7
Sturgis WTP	KY	871.3	30-6	05/17/95	3.50	3.23	2.91	0.59	3.21	0.30	362700	6314.5
Paducah WTP	KY	936.6	36-6	05/17/95	2.57	2.16	1.80	0.77	2.18	0.39	445100	5182.0
Cairo WTP	IL	977.8	38-6	05/17/95	2.62	2.30	1.84	0.78	2.25	0.39	445100	5517.9

* For tributaries, Ohio River Mile Points are at the confluence with the tributary.

** Each water sample was analyzed by immunoassay under three separate runs.

ATRAZINE ANALYTICAL RESULTS BY IMMUNOASSAY: May 22-24, 1995

Location	State	Ohio River * Mile Point	Sample ID	Collection Date	ATRAZINE CONC., ug/L Max	Median	Min	Range	Mean	Sample Std Dev	Stream Flow, cfs	Atrazine Mass Load, lbs/day
Cincinnati WTP	OH	462.8	1-7	05/22/95	1.14	0.92	0.79	0.35	0.95	0.18	349000	1730.6
Little Miami R	OH	463.5	2-7	05/22/95	3.97	3.75	3.46	0.51	3.73	0.26	5100	103.1
Licking R	OH	470.3	3-7	05/22/95	0.39	0.32	0.29	0.10	0.33	0.05	20500	35.4
G. Miami R	OH	491.0	4-7	05/22/95	20.18	N/A	17.01	3.15	18.59	N/A	30800	0.0
Whitewater R	IN-OH	491.0	5-7	05/22/95	3.86	3.68	3.03	0.83	3.53	0.34	6130	121.6
Tanners Cr	IN	494.8	6-7	05/22/95	1.21	1.05	0.89	0.32	1.05	0.16	539	3.1
Laughery Cr	IN	498.7	7-7	05/22/95	0.86	0.71	0.59	0.27	0.72	0.14	1739	6.7
Kentucky R	KY	545.8	8-7	05/22/95	0.56	0.20	0.17	0.39	0.31	0.22	59800	64.5
Little Kentucky R	KY	546.6	9-7	05/22/95	1.27	0.97	0.86	0.41	1.03	0.21	1383	7.2
Harrods Cr	KY	595.9	10-7	05/22/95	1.62	1.30	1.29	0.33	1.40	0.19	1577	11.1
Louisville CH WT	KY	600.6	11-7	05/22/95	1.70	1.50	1.42	0.28	1.54	0.14	532100	4302.0
Silver Cr	IN	606.5	12-7	05/22/95	1.08	0.90	0.83	0.25	0.94	0.13	350	1.7
New Albany WT	IN	609.0	13-7	05/22/95	2.16	1.91	1.81	0.35	1.94	0.13	532100	5477.9
Salt R	KY	629.9	14-7	05/22/95	1.03	1.02	0.90	0.13	0.98	0.07	4100	22.5
Otter Cr	KY	636.5	15-7	05/22/95	1.76	1.65	1.50	0.26	1.64	0.13	2675	23.8
Indian Cr	IN	657.0	16-7	05/22/95	1.70	1.49	1.48	0.22	1.56	0.12	5277	42.4
Blue R	IN	663.0	17-7	05/22/95	2.42	2.40	2.32	0.10	2.38	0.05	1650	21.3
Anderson R	IN	731.4	18-7	05/23/95	1.10	1.03	0.88	0.22	1.00	0.11	1302	7.2
Little Pigeon Cr	IN	772.9	19-7	05/23/95	3.13	3.11	2.97	0.16	3.07	0.09	5446	91.3
Green R	KY	784.2	20-7	05/23/95	3.22	2.25	2.25	0.97	2.60	0.54	60700	736.1
Evansville WTP	IN	791.7	21-7	05/23/95	1.31	1.22	1.06	0.25	1.20	0.13	616200	4052.0
Pigeon Cr	IN	792.9	22-7	05/23/95	9.66	8.61	8.19	1.47	8.82	0.76	2091	97.0
Henderson WTP	KY	803.2	23-7	05/23/95	2.10	1.80	1.54	0.56	1.81	0.28	616200	5978.4
Mt. Vernon WTP	IN	829.2	24-7	05/23/95	1.44	1.39	1.11	0.33	1.31	0.18	587500	4401.6
Morganfield WTP	KY	839.9	25-7	05/23/95	1.18	0.98	0.60	0.58	0.91	0.22	587500	3103.3
Highland Cr	KY	841.8	26-7	05/23/95	12.81	12.50	11.13	1.68	12.23	0.76	2204	148.5
Wabash R	IL-IN	848.0	27-7	05/23/95	10.29	9.45	8.82	1.47	9.52	0.74	126300	6433.2
L. Wabash R	IL	848.0	28-7	05/23/95	8.40	7.77	7.35	1.05	7.84	0.53	30400	1273.2
Saline R	IL	867.4	29-7	05/23/95	11.55	9.24	9.03	2.52	9.94	1.40	5779	287.8
Sturgis WTP	KY	871.3	30-7	05/24/95	2.67	2.11	2.03	0.64	2.27	0.35	709500	8069.1
Tradewater R	KY	873.4	31-7	05/24/95	3.23	2.54	2.54	0.69	2.79	0.38	10141	138.8
Crooked Cr	KY	877.7	32-7	05/24/95	0.55	0.45	0.42	0.13	0.47	0.07	1052	2.6
Deer Cr	KY	893.0	33-7	05/24/95	2.85	2.36	2.28	0.57	2.50	0.31	1064	13.5
Cumberland R	KY	920.4	34-7	05/24/95	1.12	1.08	0.97	0.15	1.07	0.05	6000	34.9
Tennessee R	KY	934.5	35-7	05/24/95	0.41	0.40	0.17	0.24	0.35	0.09	15000	32.3
Paducah WTP	KY	935.5	36-7	05/24/95	2.46	2.44	2.43	0.03	2.44	0.02	723200	9511.2
Post Cr Cutoff	IL	957.7	37-7	05/24/95	4.28	3.53	3.07	1.21	3.63	0.61	800	15.2
Cairo WTP	IL	977.8	38-7	05/24/95	4.70	3.68	3.12	1.58	3.76	0.62	723200	14344.8

* For tributaries, Ohio River Mile Points are at the confluence with the tributary.

** Each water sample was analyzed by immunoassay under three separate runs.

ATRAZINE ANALYTICAL RESULTS BY IMMUNOASSAY: May 30 - May 31, 1995

Location	State	Ohio River * Mile Point	Sample ID	Collection Date	ATRAZINE CONC., ug/L Max	Median	Min	Range	Mean	Sample Std Dev	Stream Flow, cfs	Atrazine Mas Load, lbs/day
Cincinnati WTP	OH	462.8	1-8	05/31/95	2.21	2.05	1.96	0.25	2.07	0.13	102100	1128.2
Louisville CH WT	KY	600.6	11-8	05/30/95	2.34	2.21	2.06	0.28	2.20	0.14	143800	1712.9
New Albany WT	IN	609.0	13-8	05/30/95	2.37	2.34	2.21	0 16	2.31	0.09	143800	1813.7
Evansville WTP	IN	791.7	21-8	05/30/95	1.79	1.65	1.56	0.23	1.67	0.12	331100	2944.6
Henderson WTP	KY	803 2	23-8	05/30/95	2.09	1.89	1.48	0.61	1.82	0.31	331100	3372.9
Mt. Vernon WTP	IN	829.2	24-8	05/30/95	1.99	1.79	1.69	0.30	1.82	0.15	367900	3549.5
Morganfield WTP	KY	839.9	25-8	05/30/95	1.40	1.24	1.19	0.21	1.28	0.11	367900	2458.9
Sturgis WTP	KY	871.3	30-8	05/31/95	2.10	2.07	1.73	0.37	1.97	0.21	551500	6153.3
Paducah WTP	KY	935.5	36-8	05/31/95	2.49	2.35	2.24	0.25	2.36	0.13	699900	8865.3
Cairo WTP	IL	977.8	38-8	05/31/95	3.58	3.17	3.04	0.54	3.26	0.28	699900	11958.7

* For tributaries, Ohio River Mile Points are at the confluence with the tributary.

** Each water sample was analyzed by immunoassay under three separate runs.

ATRAZINE ANALYTICAL RESULTS BY IMMUNOASSAY: June 5 - June 7, 1995

Location	State	Ohio River * Mile Point	Sample ID	Collection Date	ATRAZINE CONC., ug/L Max	Median	Min	Range	Mean	Sample Std Dev	Stream Flow, cfs	Atrazine Mass Load, lbs/day
Cincinnati WTP	OH	462.8	1-9	06/05/95	1.49	1.43	1.33	0.16	1.42	0.08	124600	960.4
Little Miami R	OH	463.5	2-9	06/05/95	4.40	4.39	4.23	0.17	4.34	0.10	4400	104.1
Licking R	OH	470.3	3-9	06/05/95	0.34	0.31	0.28	0.06	0.31	0.03	6100	10.2
G. Miami R	OH	491.0	4-9	06/05/95	4.34	4.14	4.05	0.29	4.24	0.15	12100	270.0
Whitewater R	IN-OH	491.0	5-9	06/05/95	4.57	4.11	3.97	0.60	4.22	0.31	1970	43.6
Tanners Cr	IN	494.8	6-9	06/05/95	0.87	0.80	0.70	0.17	0.79	0.09	185	0.8
Laughery Cr	IN	498.7	7-9	06/05/95	2.03	1.90	1.78	0.25	1.90	0.11	595	6.1
Kentucky R	KY	545.8	8-9	06/05/95	0.33	0.30	0.25	0.08	0.29	0.04	6100	9.9
L. Kentucky R	KY	546.6	9-9	06/05/95	1.86	1.76	1.62	0.24	1.75	0.12	433	4.1
Harrods Cr	KY	595.9	10-9	06/05/95	1.16	1.12	1.01	0.15	1.10	0.08	426	2.6
Louisville CH WT	KY	600.6	11-9	06/05/95	1 92	1.87	1.76	0.16	1.85	0.08	143900	1450.4
Silver Cr	IN	606.5	12-9	06/05/95	1.00	0.99	0.91	0.09	0.97	0.05	362	1.9
New Albany WTP	IN	609.0	13-9	06/05/95	2.66	2.31	2.11	0.55	2.33	0.20	143900	1787.8
Salt R	KY	629.9	14-9	06/05/95	1.09	0.97	0.88	0 21	0.98	0.08	3050	15.9
Otter Cr	KY	636.5	15-9	06/05/95	1.46	1.37	1.26	0.20	1.36	0.10	723	5.3
Indian Cr	IN	657.0	16-9	06/06/95	1.45	1.32	1.01	0.44	1.27	0.16	1471	10.5
Blue R	IN	663.0	17-9	06/06/95	2.07	1.89	1.34	0.73	1.77	0.38	1170	11.9
Anderson R	IN	731.4	18-9	06/06/95	0.80	0.75	0.63	0.17	0.73	0.09	355	1.4
Little Pigeon Cr	IN	772.9	19-9	06/06/95	5.09	5.00	4.90	0.19	5.00	0.10	1626	43.8
Green R	KY	784.2	20-9	06/06/95	2.75	2.60	2.57	0.18	2.64	0.10	23800	333.5
Evansville WTP	IN	791.7	21-9	06/06/95	2.45	2.13	2.07	0.38	2.22	0.20	184000	2112.4
Pigeon Cr	IN	792.9	22-9	06/06/95	3.19	2.96	2.50	0.69	2.91	0.26	624	10.0
Henderson WTP	KY	803.2	23-9	06/06/95	2.67	2.34	2.08	0.59	2.34	0.20	184000	2320.7
Mt. Vernon WTP	IN	829.2	24-9	06/06/95	2.19	2.09	1.93	0.26	2.08	0.09	185500	2084.7
Morganfield WTP	KY	839.9	25-9	06/06/95	1.73	1.69	1.54	0.19	1.65	0.10	185500	1689.7
Highland Cr	KY	841.8	26-9	06/06/95	2.70	2.44	2.35	0.35	2.50	0.14	696	9.2
Wabash R	IL-IN	848.0	27-9	06/06/95	11.00	N/A	10.89	0.11	10.95	N/A	76400	0.0
L. Wabash R	IL	848.0	26-9	06/06/95	9.02	N/A	9.02	0.00	9.02	N/A	18200	0.0
Saline R	IL	667.4	29-9	06/06/95	13.84	10.51	8.58	5.06	11.06	1.87	2666	151.0
Sturgis WTP	KY	871.3	30-9	06/07/95	2.43	2.20	1.66	0.77	2.10	0.40	283600	3362.9
Tradewater R	KY	873.4	31-9	06/07/95	3.50	2.84	2.41	1.09	2.86	0.40	4053	62.0
Crooked Cr	KY	677.7	32-9	06/07/95	0.42	0.35	0.21	0.21	0.33	0.11	420	0.8
Deer Cr	KY	693.0	33-9	06/07/95	2.37	2.07	1.81	0.56	2.08	0.28	478	5.3
Cumberland R	KY	920.4	34-9	06/07/95	0.60	0.47	0.30	0.30	0.46	0.15	30000	76.0
Tennessee R	KY	934.5	35-9	06/07/95	0.60	0.59	0.39	0.21	0.53	0.12	50000	159.0
Paducah WTP	KY	935.5	36-9	06/07/95	2.93	2.66	2.40	0.53	2.66	0.27	417200	5981.6
Post Cr Cutoff	IL	957.7	37-9	06/07/95	7.26	8.27	5.28	1.98	8.27	0.99	473	18.0
Cairo WTP	IL	977.8	38-9	06/07/95	4.15	3.16	2.94	1.21	3.42	0.64	417200	7105.9

* For tributaries, Ohio River Mile Points are at the confluence with the tributary.

** Each water sample was analyzed by immunoassay under three separate runs.

ATRAZINE ANALYTICAL RESULTS BY IMMUNOASSAY: June 12-14, 1995

Location	State	Ohio River * Mile Point	Sample ID	Collection Date	ATRAZINE CONC., ug/L						Stream Flow, cfs	Atrazine Mas Load, lbs/day
					Max	Median	Min	Range	Mean	Sample Std Dev		
Cincinnati WTP	OH	462.8	1-10	06/12/96	1.57	1.44	1.40	0.17	1.47	0.09	94100	730.4
Louisville CH WT	KY	600.6	11-10	06/12/95	2.00	1.99	1.90	0.10	1.96	0.06	104500	1120.9
New Albany WT	IN	609.0	13-10	NO SAMPLE COLLECTED								
Evansville WTP	IN	791.7	21-10	06/13/95	3.31	3.16	3.10	0.21	3.19	0.11	155200	2643.4
Henderson WTP	KY	803.2	23-10	06/13/95	2.78	2.75	2.61	0.17	2.71	0.09	155200	2300.5
Mt. Vernon WTP	IN	829.2	24-10	06/13/95	1.79	1.65	1.54	0.25	1.66	0.13	151000	1342.9
Morganfield WTP	KY	839.9	25-10	06/13/95	2.02	1.87	1.77	0.25	1.89	0.13	151000	1522.0
Sturgis WTP	KY	871.3	30-10	06/13/95	2.74	2.64	2.55	0.19	2.64	0.10	197000	2803.2
Paducah WTP	KY	935.5	36-10	06/14/95	3.74	3.66	3.45	0.29	3.62	0.15	256000	5050.2
Cairo WTP	IL	977.8	38-10	06/14/95	3.66	3.64	3.38	0.28	3.56	0.16	256000	5022.6

* For tributaries, Ohio River Mile Points are at the confluence with the tributary.
** Each water sample was analyzed by Immunoassay under three separate runs.

ATRAZINE ANALYTICAL RESULTS BY IMMUNOASSAY: June 19-21, 1995

Location	State	Ohio River * Mile Point	Sample ID	Collection Date	ATRAZINE CONC., ug/L Max	Median	Min	Range	Mean	Sample Std Dev	Stream Flow, cfs	Atrazine Mass Load, lbs/day
Cincinnati WTP	OH	462.8	1-11	06/19/95	1.26	1.16	0.95	0.31	1.12	0.12	55200	345.1
Little Miami R	OH	463.5	2-11	06/19/95	3.54	3.25	2.83	0.71	3.24	0.27	900	15.8
Licking R	OH	470 3	3-11	06/19/95	1.06	0.92	0.79	0.27	0.92	0.14	2000	10.0
G Miami R	OH	491.0	4-11	06/19/95	3.64	3.43	2.84	0.80	3.30	0.41	3800	70.3
Whitewater R	IN-OH	491.0	5-11	06/19/95	1.51	1.32	1.20	0.31	1.32	0.16	593	4 2
Tanners Cr	IN	494.8	6-11	06/19/95	1.26	1.12	1.01	0.25	1.12	0.13	82	0.5
Laughery Cr	IN	498.7	7-11	06/19/95	2.79	2.59	2.42	0.37	2.59	0.19	263	3.7
Kentucky R	KY	545.8	8-11	06/19/95	0.26	0.20	0.16	0.10	0.21	0.04	2500	2.7
L. Kentucky R	KY	546.6	9-11	06/19/95	0.32	0.25	0.18	0.14	0.25	0.07	202	0.3
Harrods Cr	KY	595.9	10-11	06/19/95	1.16	1.11	1.05	0.11	1.11	0.06	214	1.3
Louisville CH WT	KY	600.6	11-11	06/19/95	2.00	1.72	1.61	0.39	1.75	0.16	72300	670.3
Silver Cr	IN	606.5	12-11	06/19/95	1.55	1.39	1.27	0.28	1.40	0.14	14	0.1
New Albany WT	IN	609.0	13-11	06/19/95	2.14	1.77	1.57	0.57	1.83	0.29	72300	689.8
Salt R	KY	629.9	14-11	06/19/95	1.89	1.65	1.53	0.36	1.68	0.16	206	1.8
Otter Cr	KY	636.5	15-11	06/19/95	1.05	1.04	0.96	0.09	1.02	0.05	363	2.0
Indian Cr	IN	657.0	16-11	06/19/95	0.96	0.75	0.67	0.29	0.79	0.15	717	2.9
Blue R	IN	663.0	17-11	06/19/95	2.67	2.39	2.22	0.45	2.43	0.23	297	3.8
Anderson R	IN	731.4	18-11	06/19/95	1.01	0.94	0.72	0.29	0.89	0.15	184	0.9
Little Pigeon Cr	IN	772.9	19-11	06/20/95	3.41	2.94	2.80	0.61	3.05	0.32	758	12.0
Green R	KY	784 2	20-11	06/20/95	1.45	1.41	1.33	0.12	1.40	0.06	12400	94.2
Evansville WTP	IN	791.7	21-11	06/20/95	1.77	1.66	1.54	0.23	1.66	0.08	85700	766.8
Pigeon Cr	IN	792.9	22-11	06/20/95	3.12	3.10	2.51	0.61	2.91	0.35	291	4.9
Henderson WTP	KY	803.2	23-11	06/20/95	1.88	1.70	1.49	0.39	1.69	0.20	85700	785.3
Mt. Vernon WTP	IN	829.2	24-11	06/20/95	2.02	1.75	1.71	0.31	1.83	0.17	88400	833.8
Morganfield WTP	KY	839.9	25-11	06/20/95	1.87	1.84	1.75	0.12	1.82	0.06	88400	876.7
Highland Cr	KY	841.8	26-11	06/20/95	2.23	2.23	2.00	0.23	2.15	0.13	332	4.0
Wabash R	IL-IN	848.0	27-11	06/20/95	5.54	4.70	4.33	1.21	4.74	0.43	22600	572.5
L. Wabash R	IL	848.0	28-11	06/20/95	15.07	10.78	10.34	4.73	12.06	2.61	4060	235.9
Saline R	IL	867 4	29-11	06/20/95	3.19	3.14	2.83	0.36	3.05	0.20	1042	17.6
Sturgis WTP	KY	871.3	30-11	06/20/95	2.06	1.73	1.55	0.51	1.76	0.19	118000	1100.3
Tradewater R	KY	873.4	31-11	06/20/95	1.67	1.48	0.99	0.68	1.38	0.35	1698	13.5
Crooked Cr	KY	877.7	32-11	06/20/95	1.89	1.62	1.51	0.38	1.67	0.20	176	1.5
Deer Cr	KY	893.0	33-11	06/20/95	1.88	1.59	1.52	0.36	1.66	0.19	205	1.8
Cumberland R	KY	920.4	34-11	06/20/95	0.59	0.50	0.30	0.29	0.46	0.12	10000	27.0
Tennessee R	KY	934.5	35-11	06/20/95	0.66	0.55	0.42	0.24	0.54	0.09	25000	74.1
Paducah WTP	KY	935.5	36-11	06/21/95	2.50	2.13	1.57	1.44	1.40	0.25	160600	1843.8
Post Cr Cutoff	IL	957.7	37-11	06/21/95	5.09	4.60	2 00	1 99	1.90	0.53	182	4.5
Cairo WTP	IL	977.8	38-11	06/21/95	3 30	2.75	2.70	0.60	2.92	0.33	160600	2380.5

* For tributaries, Ohio River Mile Points are at the confluence with the tributary.

** Each water sample was analyzed by immunoassay under three separate runs.

ATRAZINE ANALYTICAL RESULTS BY IMMUNOASSAY: June 26- June 28, 1995

Location	State	Ohio River * Mile Point	Sample ID	Collection Date	ATRAZINE CONC., ug/L Max	Median	Min	Range	Mean	Sample Std Dev	Stream Flow, cfs	Atrazine Mas Load, lbs/day
Cincinnati WTP	OH	462.8	1-12	06/26/95	0.99	0.87	0.83	0.16	0.90	0.08	64900	304.3
Louisville CH WT	KY	600.6	11-12	06/26/95	1.21	1.11	0.93	0.28	1.08	0.14	73900	442.1
New Albany WT	IN	609.0	13-12	06/26/95	1.43	1.41	1.3	0.13		0.07	73900	561.6
Evansville WTP	IN	791.7	21-12	06/27/95	1.54	1.49	1.44	0.1	1.49	0.05	86700	696.3
Henderson WTP	KY	803.2	23-12	06/27/95	1.82	1.77	1.62	0.2	1.74	0.10	86700	827.1
Mt. Vernon WTP	IN	829.2	24-12	06/27/95	NO SAMPLE COLLECTED							
Morganfield WTP	KY	839.9	25-12	06/27/95	1.73	1.71	1.68	0.05	1.71	0.03	87100	802.8
Sturgis WTP	KY	871.3	30-12	06/28/95	1.78	1.73	1.43	0.35	1.65	0.19	122100	1138.5
Paducah WTP	KY	935.5	36-12	06/28/95	1.29	1.26	1.04	0.25	1.20	0.14	170600	1158.6
Cairo WTP	IL	977.8	38-12	06/28/95	2.52	2.35	1.96	0.56	2.28	0.29	170600	2160.9

* For tributaries, Ohio River Mile Points are at the confluence with the tributary.

** Each water sample was analyzed by Immunoassay under three separate runs.

ATRAZINE ANALYTICAL RESULTS BY IMMUNOASSAY: July 5 - July 7, 1995

Location	State	Ohio River * Mile Point	Sample ID	Collection Date	ATRAZINE CONC., ug/L Max	Median	Min	Range	Mean	Std Dev	Stream Flow, cfs	Atrazine Mass Load, lbs/day
Cincinnati WTP	OH	462.8	1-13	07/05/95	1.47	1.37	1.18	0.29	1.34	0.15	52300	388.2
Little Miami R	OH	463 5	2-13	07/05/95	3.53	3.23	2.75	0.78	3.22	0.27	1200	20.9
Licking R	OH	470.3	3-13	07/05/95	1.4	1.39	1.35	0.05	1.37	0.03	1100	8.2
G. Miami R	OH	491.0	4-13	07/05/95	3.86	3.68	3.42	0.54	3.69	0.22	7300	144.8
Whitewater R	IN-OH	491.0	5-13	07/05/95	3.9	3.76	3.36	0.54	3.73	0.20	1050	21.3
Tanners Cr	IN	494.8	6-13	07/05/95	10.78	8.58	6.71	4.07	8.69	2.04	78	3.6
Laughery Cr	IN	498.7	7-13	07/05/95	43.26	42.00	38.22	5.04	41.16	2.62	251	56.8
Kentucky R	KY	545.8	8-13	07/05/95	0.45	0.41	0.38	0.07	0.41	0.04	2600	5.7
L. Kentucky R	KY	546.6	9-13	07/05/95	0.48	0.43	0.35	0.13	0.42	0.07	208	0.5
Harrods Cr	KY	595.9	10-13	07/05/95	1.74	1.72	1.44	0.3	1.63	0.17	244	2.3
Louisville CH WT	KY	600.6	11-13	07/05/95	2 24	2.07	2.05	0.19	2.12	0.10	82400	919.4
Silver Cr	IN	606.5	12-13	07/05/95	2.46	2.39	2.2	0.26	2.35	0.13	207	2.7
New Albany WT	IN	609.0	13-13	07/05/95	2.2	2.19	2.05	0.15	2.15	0.08	82400	972.7
Salt R	KY	629.9	14-13	07/05/95	1.35	1.20	0.96	0.39	1.17	0.20	2130	13.8
Otter Cr	KY	636.5	15-13	07/05/95	1.58	1.56	1.43	0.15	1.52	0.08	414	3.5
Indian Cr	IN	657.0	16-13	07/05/95	1.73	1.52	1.5	0.23	1.58	0.13	817	6.7
Blue R	IN	663.0	17-13	07/05/95	2.21	1.83	1.81	0.4	1.95	0.23	419	4.1
Anderson R	IN	731.4	18-13	07/05/95	26.04	24.15	20.79	5.25	23.66	2.66	218	28.4
Little Pigeon Cr	IN	772.9	19-13	07/05/95	31.92	22.89	22.68	9.24	25.83	5.28	1069	131.9
Green R	KY	784.2	20-13	07/06/95	1.31	1.25	0.99	0.32	1.20	0.15	4900	33.0
Evansville WTP	IN	791.7	21-13	07/06/95	2.11	1.30	1.84	0.27	1.97	0.14	103700	728.6
Pigeon Cr	IN	792.9	22-13	07/06/95	13.65	12.39	12.39	1.26	12.81	0.73	351	23.4
Henderson WTP	KY	803.2	23-13	07/06/95	1.7	1.66	1.43	0.27	1.60	0.15	103700	927.8
Mt. Vernon WTP	IN	829.2	24-13	07/06/95	1.89	1.66	1.52	0.37	1.69	0.19	107500	961.8
Morganfield WTP	KY	839 9	25-13	07/06/95	1.81	1.58	1.5	0.31	1.63	0.16	107500	915.5
Highland Cr	KY	841.8	26-13	07/06/95	4.76	3.88	3.79	0.97	4.14	0.54	403	8.4
Wabash R	IL-IN	848.0	27-13	07/06/95	7.48	6.27	4.97	2.51	6.24	1.26	32400	1095.0
L. Wabash R	IL	848.0	28-13	07/06/95	28.98	28.98	24.15	4.83	26.57	2.79	1600	249.9
Saline R	IL	867.4	29-13	07/06/95	4.43	4.356	4.12	0.31	4.30	0.46	1275	29.9
Sturgis WTP	KY	871.3	30-13	07/06/95	3.01	2.52	2.46	0.55	2.66	0.30	145400	1974.9
Tradewater R	KY	873.4	31-13	07/06/95	1.09	0.97	0.94	0.15	1.00	0.08	2078	10.9
Crooked Cr	KY	877.7	32-13	07/08/95	2.45	2.37	2.32	0.13	2.38	0.07	216	2.8
Deer Cr	KY	893.0	33-13	07/06/95	3.46	2.76	2.75	0.71	2.99	0.41	247	3.7
Cumberland R	KY	920.4	34-13	07/06/95	0.57	2.76	0.36	0.21	0.47	0.11	29000	431.4
Tennessee R	KY	934.5	35-13	07/06/95	0.66	0.58	0.55	0.11	0.60	0.06	52000	162.6
Paducah WTP	KY	935.5	36-13	07/07/95	2.28	2.24	1.85	0.41	2.12	0.23	231800	2798.7
Post Cr Cutoff (	IL	957.7	37-13	07/07/95	3.61	2.86	2.78	0.85	3.02	0.40	230	3.5
Cairo WTP	IL	977.8	38-13	07/07/95	3.35	2.88	2.76	0.59	2.97	0.26	231800	3598.3

* For tributaries, Ohio River Mile Points are at the confluence with the tributary.

** Each water sample was analyzed by immunoassay under three separate runs.

Appendix B

Results of Confirmation Analyses for Other Herbicides

Location	Sample ID	Immunoassay Atrazine Median	Atrazine GC Confirm, ug/L	Alachlor GC Confirm, ug/L	Simazine GC Confirm, ug/L	Metolachlor GC Confirm, ug/L	Cyanazine GC Confirm, ug/L
L. Wabash R	28-13	28.98	19.60	0.64	2.24	5.41	7.22
Little Pigeon Cr	19-13	22.89	18.30	0.45	0.77	1.90	5.45
Highland Cr	26-7	12.50	7.51	<0.20	2.56	3.75	0.19
Saline R	29-9	10.51	10 90	1.10	0.90	3.53	1.33
Green R	20-5	9.90	7.58	0.53	1.38	3.92	0.2
L. Wabash R	28-7	7.77	4.52	<0.20	1.63	0.75	1.10
Wabash R	27-13	6.27	4.27	0.30	0.37	2.02	2.29
Wabash R	27-11	4.70	4 10	<0.20	0.18	7.75	2.68
Saline R	29-13	4.28	2.75	1.35	0.43	0.80	0.75
Whitewater R	5-13	3.75	2 68	0.33	0.23	1.09	1.33
Cairo WTP	38-7	3.70	2.64	<0.20	0.44	0.85	0.90
G. Miami R	4-13	3.68	2.02	0.33	0.30	1.31	0.92
Whitewater R	5-7	3.68	2.18	0.37	<0.07	0.60	0.99
Little Miami R	2-11	3.25	1.67	<0.20	<0.07	0.82	0.60
Little Miami R	2-13	3.23	1.94	0.63	0.39	1.07	1.51
Cairo WTP	38-9	3.16	3.05	0.21	0.24	<0.20	1.13
Little Pigeon Cr	19-7	3.11	1 71	<0.20	0.28	<0.20	0.30
Pigeon Cr	22-9	2.96	2.22	<0.20	<0.07	<0.20	0.47
Cairo WTP	38-13	2.88	1.77	<0.20	0.37	0.64	0.82
Post Cr Cutoff (Cache	37-13	2.86	1.93	0.30	0.31	0.60	0.25
Tradewater R	31-9	2.84	2.36	<0.20	0.40	<0.20	<0.10
Cairo WTP	38-11	2.77	2.13	<0.20	0.23	<0.20	0.92
Paducah WTP	36-7	2.44	1.18	<0.20	0.15	<0.20	0.41
Highland Cr	26-9	2.44	1.56	<0.20	0.28	<0.20	<0.10
New Albany WTP	13-9	2.43	1.66	<0.20	<0.07	<0.20	0.91
Blue R	17-7	2.40	1.32	<0.20	0.11	0.35	<0.10
Henderson WTP	23-9	2.34	1.59	<0.20	0.19	<0.20	0.40
Green R	20-7	2.25	1.41	<0.20	0.42	<0.20	<0.10
Laughery Cr	7-9	1.90	1.26	<0.20	0.13	<0.20	0.45
Louisville CH WTP	11-11	1.78	1.01	<0.20	0.13	<0.20	0.54
Little Pigeon Cr	19-5	1.76	1.6	<0.20	0.43	<0.20	0.37
Sturgis WTP	30-11	1.73	1 19	<0.20	0.17	<0 20	0.53
Evansville WTP	21-11	1.66	0.72	<0.20	<0.07	<0.20	0.44
Wabash R	27-5	1.50	1.51	<0.20	0.46	0.63	0.28
Cairo WTP	38-5	1.42	1.24	<0.20	0.46	0.65	0.21
Indian Cr	16-9	1.32	0.72	<0.20	<0.07	<0.20	<0.10
Green R	20-13	1.25	0.69	<0.20	0.36	<0.20	0.31
Cincinnati WTP	1-11	1.16	0.67	<0.20	<0.07	<0.20	0.34
Blue R	17-5	1.06	0.98	<0.20	0.27	0.2	<0.10
Anderson R	18-7	1.03	0.45	<0.20	0.22	<0.20	<0.10
Morganfield WTP	25-7	0.98	0.69	<0.20	<0.07	<0.20	0.11
Whitewater R	5-5	0.78	0.79	<0.20	0.29	0.42	0.16
Tennessee R	35-11	0.57	0.28	<0.20	<0.07	<0.20	<0.10
G. Miami R	4-5	0.52	0.63	<0.20	0.29	0.54	0.22
Cumberland R	34-11	0.49	0 30	<0.20	<0.07	<0.20	<0.10
Cumberland R	34-5	0.38	0.54	<0.20	0.27	<0.20	<0.10
Kentucky R	8-11	0.20	<0.1	<0.20	<0.07	<0.20	<0.10
Louisville CH WTP	11-5	0.19	0.38	<0.20	0.26	0.42	0.13
Tennessee R	35-5	0.10	0.31	<0.20	0.25	<0.20	<0.10
Mt. Vernon WTP	24-9		2.12	<0.20	0.15	<0.20	0.86

Appendix C

Atrazine Survey QA Performance Data

Location	Sample ID	Immunoassay Median	Atrazine GC Confirm. ug/L	% Recovery	Absolute Difference
L. Wabash R	26-13	28.98	19.60	148	9.38
Little Pigeon Cr	19-13	22.89	18.30	126	4.59
Highland Cr	26-7	12.50	7.61	166	4.89
Saline R	29-9	10.51	10.90	96	0.39
Green R	20-5	9.90	7.58	31	2.32
L. Wabash R	28-7	7.77	4.62	172	3.25
Wabash R	27-13	6.27	4.27	147	2.00
Wabash R	27-11	4.70	4.10	116	0.6
Saline R	29-13	4.28	2.75	156	1.53
Whitewater R	5-13	3.76	2.68	140	1.07
Cairo WTP	36-7	3.70	2.64	140	1.06
Whitewater R	5-7	3.68	2.18	169	1.6
G. Miami R	4-13	3.68	2.02	182	1.66
Little Miami R	2-11	3.25	1.67	196	1.58
Little Miami R	2-13	3.23	1.94	166	1.29
Cairo WTP	38-9	3.16	3.05	104	0.11
Little Pigeon Cr	19-7	3.11	1.71	182	1.4
Pigeon Cr	22-9	2.96	2.22	133	0.74
Cairo WTP	38-13	2.88	1.77	163	1.11
Post Cr Cutoff	37-13	2.86	1.93	148	0.93
Mt. Vernon WTP	24-8	2.85	2.12	134	0.73
Tradewater R	31-9	2.84	2.36	120	0.48
Cairo WTP	38-11	2.77	2.13	130	0.64
Paducah WTP	36-7	2.44	1.18	207	1.26
Highland Cr	26-9	2.44	1.56	156	0.88
New Albany WTP	13-9	2.43	1.66	146	0.77
Blue R	17-7	2.40	1.32	182	1.08
Henderson WTP	23-9	2.34	1.59	147	0.75
Green R	20-7	2.25	1.41	160	0.84
Laughery Cr	7-9	1.90	1.26	151	0.64
Louisville CH WTP	11-11	1.78	1.01	176	0.77
Little Pigeon Cr	19-6	1.76	1.60	110	0.16
Sturgis WTP	30-11	1.73	1.19	145	0.54
Evansville WTP	21-11	1.66	0.72	231	0.94
Wabash R	27-5	1.50	1.51	98	0.01
Cairo WTP	38-5	1.42	1.24	116	0.18
Indian Cr	16-9	1.32	0.72	183	0.6
Green R	20-13	1.25	0.69	181	0.56
Cincinnati WTP	1-11	1.16	0.87	173	0.49
Blue R	17-5	1.06	0.98	108	0.08
Andersen R	18-7	1.03	0.45	229	0.58
Morganfield WTP	26-7	0.98	0.69	142	0.29
Whitewater R	5-5	0.78	0.79	99	0.01
Tennessee R	35-11	0.57	0.28	204	0.29
G. Miami R	4-5	0.52	0.63	83	0.11
Cumberland R	34-11	0.49	0.30	163	0.19
Cumberland R	34-5	0.38	0.54	70	0.16
Kentucky R	8-11	0.20	<0.10	393	0.15
Louisville CH WTP	11-5	0.19	0.38	50	0.19
Tennessee R	35-5	0.10	0.31	32	0.21

ALL DATA INCLUDED, N = 50	% Recovery	Absolute Difference
MAX VALUE, ug/L	393	9.38
MEDIAN VALUE, ug/L	148	0.74
MIN VALUE, ug/L	31	0.01
RANGE, ug/L	362	9.37
MEAN VALUE, ug/L	148	1.12
SAMPLE STD DEV, ug/L	56	1.567

ATRAZINE DATA GREATER THAN 5 ug/L, N = 7	% Recovery	Absolute Difference
MAX VALUE, ug/L	172	9.38
MEDIAN VALUE, ug/L	147	3.25
MIN VALUE, ug/L	31	0.39
RANGE, ug/L	141	9.99
MEAN VALUE, ug/L	126.6	3.86
SAMPLE STD DEV, ug/L	49.4	2.902

ATRAZINE DATA LESS THAN 5 ug/L, N = 43	% Recovery	Absolute Difference
MAX VALUE, ug/L	393	1.66
MEDIAN VALUE, ug/L	145	0.60
MIN VALUE, ug/L	32	0.01
RANGE, ug/L	361	1.65
MEAN VALUE, ug/L	151	0.68
SAMPLE STD DEV, ug/L	57	0.472

ATRAZINE DATA LESS THAN 3 ug/L, N = 33	% Recovery	Absolute Difference
MAX VALUE, ug/L	393	1.26
MEDIAN VALUE, ug/L	134	0.54
MIN VALUE, ug/L	32	0.01
RANGE, ug/L	361	1.25
MEAN VALUE, ug/L	160	0.53
SAMPLE STD DEV, ug/L	64	0.350

ATRAZINE DATA LESS THAN 1 ug/L, N = 9	% Recovery	Absolute Difference
MAX VALUE, ug/L	393	0.29
MEDIAN VALUE, ug/L	83	0.11
MIN VALUE, ug/L	32	0.01
RANGE, ug/L	361	0.28
MEAN VALUE, ug/L	137	0.18
SAMPLE STD DEV, ug/L	111	0.087

** Values below the detection level were assumed to be half the detection level.