

**PESTICIDE DISTRIBUTION IN WATER, SEDIMENT, AND FISH
OF THE OCCOQUAN WATERSHED**

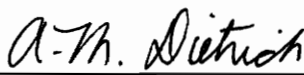
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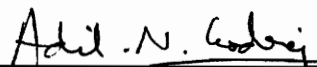
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by

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Environmental Engineering

(ABSTRACT)

About 50 synthetic organic chemicals (SOCs), including pesticides and polyaromatic hydrocarbons (PAHs), have been identified as possible contaminants in the Occoquan Watershed. Since 1982, water, sediment, and fish samples have been collected from the streams and reservoirs of the watershed 2-4 times per year. The Occoquan Watershed Monitoring Laboratory (OWML) collected samples and analyzed for a targeted set of compounds. Beginning in 1993, new SOC screening methods consisting of solid-phase extraction (SPE) followed by gas chromatography with mass spectrometric detection (GC/MS) were developed for water and sediment samples. A similar method for fish tissue was developed in this study using methanol extraction with C-18 and alumina SPE cleanup. Method detection limits (MDLs) ranged from 0.03-0.37 mg/kg wet weight and recoveries in matrix spikes ranged from 15-92%.

Very few SOC's in OWML's database were found at levels above method detection limits. In water, atrazine was the most commonly detected compound (87 detections out of 610 samples analyzed). It was also found in 8 sediment samples and 1 fish organ sample. Atrazine concentrations were highest in the spring; summer provided the most frequent detections. Detections occurred at multiple locations during the same sampling period; stations furthest west (nearest to agricultural areas)

tended to show the highest values. Rainfall events were associated with 23% of atrazine detections. The raw and finished water samples from the two water treatment plants in the basin showed that the average atrazine removal by conventional treatment was 37%.

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I. INTRODUCTION

The use of synthetic organic chemicals (SOCs) as pesticides began in earnest following the development of toxic SOCs for military purposes during the 1940s. Interest in controlling pesticide use and measuring residues in the U.S. began in the 1960s as the serious environmental consequences of using highly toxic and persistent chlorinated pesticides became known. While many chlorinated pesticides have been banned in the U.S., persistent residues remain widespread and other less persistent compounds with known health effects are still commonly used. Information on the toxicity of these compounds has led the U.S. Environmental Protection Agency (USEPA) to promulgate drinking water maximum contaminant levels (MCLs) for a growing number of SOCs.

About 50 SOCs, including polyaromatic hydrocarbons (PAHs) as well as pesticides, have been identified as possible anthropogenic contaminants in the Occoquan Watershed. The Occoquan Watershed provides drinking water to a large portion of heavily developed Northern Virginia; consequently, monitoring of this watershed has been supported by the local governments and water authorities. From 1982 through 1994, water, sediment, and fish samples were collected by the Occoquan Watershed Monitoring Laboratory (OWML) in Manassas, Va. Initially, the Virginia Tech Pesticide Residue Laboratory in Blacksburg, Va. analyzed these samples for a targeted set of SOCs using traditional extraction techniques such as liquid-liquid and Soxhlet extraction. Beginning in 1993, a new method consisting of solid-phase extraction (SPE) followed by gas chromatography with mass spectrometric detection (GC/MS) was developed and implemented at OWML to determine SOC concentrations in water and sediment samples. During 1993-94, fish samples were frozen and stored

pending development of a similar new method for fish tissue analysis.

Thus, two tasks dealing with OWML's SOC monitoring program became objectives for this work: 1) to investigate trends in concentrations of SOC's detected in water, sediment, and fish throughout the period of record of OWML's SOC database for the Occoquan Watershed (1982-1994), and 2) to develop an extraction and cleanup method for fish tissue to meet OWML's analytical needs.

II. LITERATURE REVIEW

When pesticide use escalated following World War II, many chemicals were synthesized and applied with very little preliminary research to determine potential side effects. Since then, a large, but by no means complete, body of information has been collected on every aspect of SOC's from toxicity to transport in groundwater. This review focuses on three elements of the SOC story specific to the work at OWML: the history of watershed monitoring in the Occoquan and other watersheds, the characteristics of the different classes of compounds monitored in the Occoquan program, and the methods for pesticide residue analysis in fish tissue found in the literature.

A. Watershed Monitoring

The fate of contaminants in specific situations, such as chemical or biological degradation under one set of conditions or seepage distance in a particular soil, have been studied extensively in small scale experiments. However, the broader picture of fate in a large watershed is difficult to obtain from such work. Watershed monitoring steps in where more specific work leaves off. It provides a comprehensive view of the impacts of both point source and nonpoint source pollution. A watershed monitoring system produces measurements of environmental parameters over time and space which can then be used to evaluate the condition of the area, determine trends over time, isolate sources of contamination, or study the effects of pollution control measures.

1. The Occoquan Watershed

The Occoquan Watershed encompasses approximately 570 sq. mi. (OWML 1994) and is located southwest of Washington, D.C. (see Figure 1). Two of its surface water impoundments, the Occoquan Reservoir and

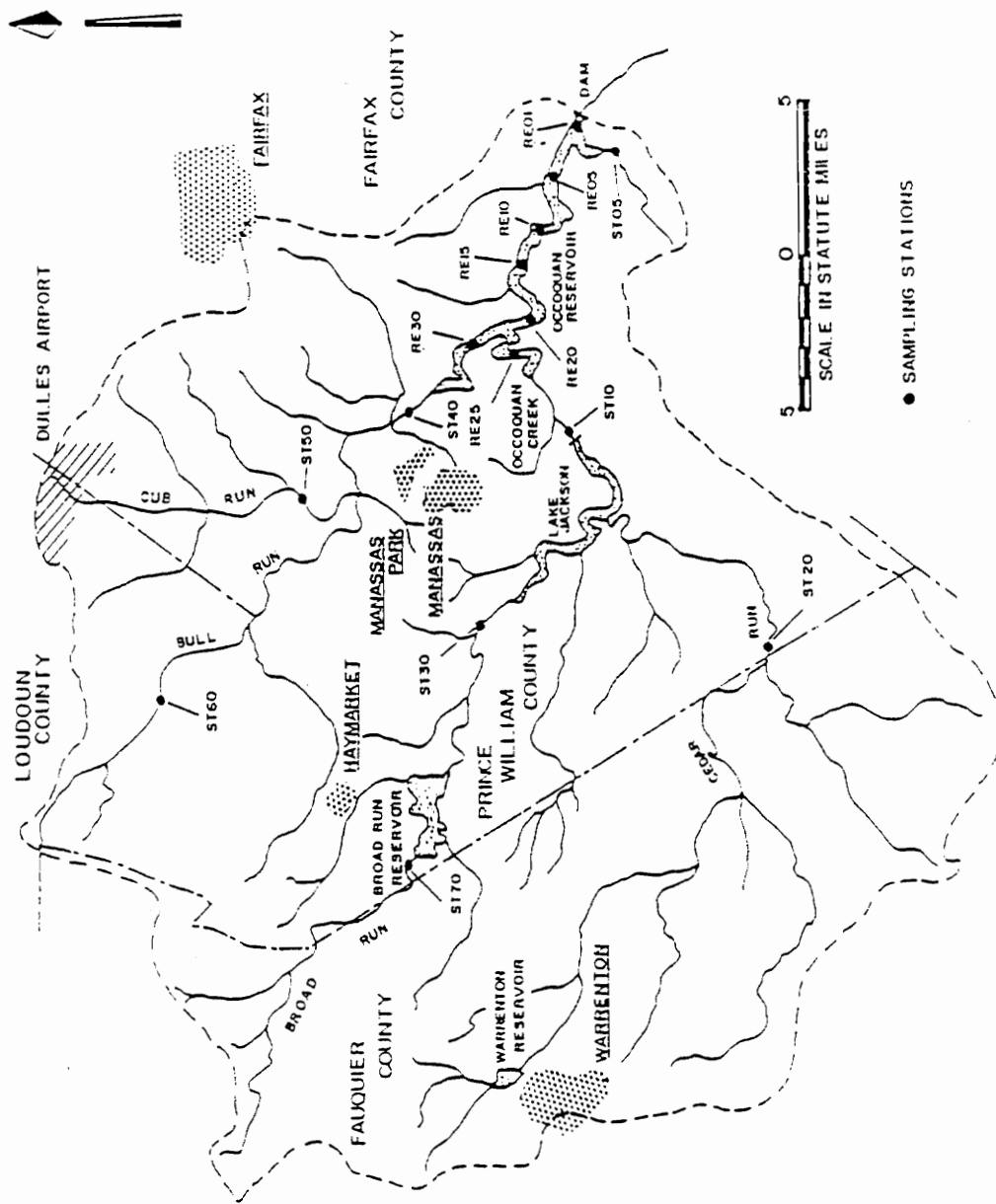


Figure 1. The Occoquan Watershed with Boundaries and Station Locations Shown, after OWML (1992).

Lake Manassas, supply drinking water to a total of over 800,000 Northern Virginia residents. The Occoquan Reservoir begins at the confluence of Bull Run and Occoquan Creek in Prince William County, Va. Its storage capacity is 11.2 billion gallons. The Fairfax County Water Authority's Lorton Water Treatment Plant is located adjacent to the high dam at Occoquan, Va. and produces roughly 100 million gallons per day (mgd). It is a conventional water treatment plant with alum coagulation and polyaluminum chloride as a coagulant aid, dual media rapid filtration, and chlorine disinfection. The plant employs a mixture of combined rapid mix/flocculation/settling units and traditional basins. Powdered activated carbon (PAC) was sporadically added to the raw water to control taste-and-odor until February 1995; since then, potassium permanganate has been used for taste-and-odor control. The reservoir is about 16 mi. long with a maximum width of about 1000 ft., making it almost a plug flow system (OWML 1994). Hydraulic detention times reported in a 1970 study ranged from less than 1 month (in March) to 4 months (in summer) (Mastran 1992 citing Metcalf and Eddy, Inc. 1970). Immediately surrounding the reservoir are park lands to the north and residential developments to the south.

Lake Manassas is an artificial impoundment on Broad Run (see Figure 2), which later joins Cedar Run to become Occoquan Creek. It is the primary drinking water supply for the City of Manassas. The Manassas Water Treatment Plant is a conventional plant with alum coagulation producing about 8 mgd. Lake Manassas is generally bordered by residential and farmland areas, along with the more developed area of Gainesville to the northeast, and a golf course and a military reservation to the south.

Land uses beyond the immediate surroundings of the reservoirs are also quite varied. Of the two branches that become the Occoquan Reservoir, Bull Run drains 185 sq. mi. (OWML 1994) and is the more urban

of the two, with runoff from Dulles Airport and the Cities of Manassas and Manassas Park. Occoquan Creek drains 343 sq. mi. (OWML 1994), and this area is generally more rural. The remaining 42 sq. mi. of the basin are drained by small tributaries to the Occoquan Reservoir (OWML 1994).

Table 1 summarizes available land use data for the basin. Note that while the more urban use categories have seen increases over time, the majority of the watershed (70.9%) is still rural (agricultural, pasture, or forest/idle), and the agricultural percentage seems to have stabilized at about 10%.

Table 1. Land Use in the Occoquan Watershed¹

<u>Land Use Category</u>	<u>Percent of Watershed Area in Study Year</u>			
	<u>1977</u>	<u>1979</u>	<u>1984</u>	<u>1989</u>
Low Density Residential	3.2	5.1	11.4	18.2
Medium Density Residential	1.7	1.6	2.7	4.5
Townhouse/Garden Apt.	0.4	0.3	0.7	1.6
Commercial	0.4	0.5	0.7	1.1
Industrial	1.0	1.0	1.3	2.3
Institutional	0.6	1.0	0.9	1.3
Agricultural	15.9	10.8	10.8	10.1
Pasture	20.5	24.5	24.5	21.8
Forest/Idle	56.4	55.3	47.0	39.0
Total	100	100	100	100

¹ after OWML 1994 citing the Northern Virginia Planning District Commission 1991.

This mixture of urban and rural areas gives the Occoquan Watershed the potential to be contaminated by a variety of different pollutants. Prior to the start of operations at the Upper Occoquan Sewage Authority (UOSA) in the summer of 1978, the most obvious water quality problem in the basin was nutrient loading from wastewater inputs. The population increase in the basin had led to increased municipal wastewater flows, and the resulting excess nutrients fed heavy algal blooms, causing taste-and-odor problems and even fish kills in the Occoquan Reservoir (OWML 1994).

Increased agricultural activity and accompanying use of fertilizer in the western part of the watershed added to the nutrient problem (OWML 1994). The effluent limitations at UOSA are extraordinarily strict, including a COD limit of 10 mg/L, a TSS limit of 1 mg/L, a total Kjeldahl nitrogen limit of 1 mg/L, and a total phosphorus limit of 0.1 mg/L (OWML 1994). UOSA also has one more very unusual limit, a nitrate limit of 5 mg/L as nitrogen, measured not at UOSA but at the Lorton Water Treatment Plant intake (OWML 1994). The processes used to meet these limits at UOSA include activated sludge with a selector basin, chemical phosphorus removal, rapid filtration, and granular activated carbon (GAC) adsorption. The advanced wastewater treatment accomplished at UOSA has greatly diminished the Occoquan Reservoir's eutrophication problems and served to help protect the public water supply.

Synthetic organic chemicals are another threat to the environmental quality of the basin. Various pesticides may be used in agricultural and residential settings. In OWML's 1992 report on the SOC monitoring program, it was found that atrazine was the most commonly detected SOC in water. Atrazine is a non-selective herbicide often used with corn crops (Meister 1995) and in the practice of no-till farming. Table 2 indicates corn plantings in the counties that are partially included in the watershed area; it can be seen that even during the period of urban expansion in the basin, corn planting increased.

Table 2. Corn plantings in Northern Virginia Counties

<u>County</u>	<u>Square miles planted in the Year</u>			
	<u>1978¹</u>	<u>1979¹</u>	<u>1980²</u>	<u>1981²</u>
Fairfax	3.4	3.4	3.0	3.3
Fauquier	39.7	41.7	48.8	49.7
Loudoun	62.5	68.8	75.6	77.3
Prince William	12.5	12.8	15.5	16.1

¹after Virginia Crop Reporting Service 1980

²after Virginia Crop Reporting Service 1982.

Combustion products such as PAHs would be expected contaminants given the heavy traffic in the urban areas. In a 1992 study of PAHs in water and sediment of the Occoquan Reservoir, few PAHs were found above detection limits. Their presence was found to partially coincide with increased boating activity; urban runoff and atmospheric deposition were other major sources of PAH input to the reservoir (Mastran 1992). Atrazine was also identified in the water in that study. A study of fish from the waters of the nearby District of Columbia found multiple PAHs, phthalates, and organochlorine pesticides present in fish tissues (Velinsky and Cummins 1994).

2. Monitoring in other watersheds

As interest has turned from point source to nonpoint source pollution, whole watershed management approaches to pollution control have become more popular. Programs designed to protect and monitor bodies of water such as the Chesapeake Bay, the Great Lakes, and the Gulf of Mexico are well known (Rubin *et al.* 1993). Other areas where watershed management approaches have been used include North Carolina, which has split the entire state into watersheds for discharge permitting purposes, and the USEPA's Pacific Northwest region, which has done the same with its jurisdiction (Rubin *et al.* 1993).

Point source pollution is relatively easy to isolate and treat as compared to nonpoint source pollution. A point source is basically any sort of discernable conveyance from which pollution might be discharged (Novotny and Olem 1994). Nonpoint source pollution is harder to define. Generally it includes agricultural runoff, urban runoff from small communities (population < 100,000) or those with no storm sewers, wet and dry atmospheric deposition, runoff from construction sites, and abandoned mine runoff, to name a few (Novotny and Olem 1994). The

occurrence of nonpoint source pollution is largely dependent on the weather and geographic conditions. Since variables like the weather cannot be controlled and years of data may be needed to detect changes, monitoring is one of the best ways to quantify nonpoint source pollution (Menzel 1993). Monitoring has become an important part of pollution control on a watershed level.

As one of the most commonly used herbicides in the U.S., atrazine has received a fair amount of attention in agricultural nonpoint source pollution monitoring. In a study of the tributaries to Lake Erie, atrazine was present at concentrations above detection limits for much of the year (averaging about $1.9 \mu\text{g/L}$) (USEPA 1988). Peak herbicide concentrations ($20\text{-}30 \mu\text{g/L}$) for atrazine, alachlor metolachlor, and cyanazine occurred in late May, June, or July. Multiple storms of sufficient intensity produced multiple peak concentrations in the same year. A sufficiently intense rainfall event could cause a peak concentration in July even though the pesticides had been on the field for several months. Studying the Platte River in Nebraska, Stamer (1996) found that spring and summer concentrations were higher than those in fall and winter, and the highest values were found during the growing season following intense rains. Atrazine concentrations in the month of May ranged from $0.17 \mu\text{g/L}$ to as high as $30 \mu\text{g/L}$, while February values stayed in the $0.08\text{-}0.1 \mu\text{g/L}$ range. Pereira and Hostettler in a study of the Mississippi River (1993) found that atrazine concentrations were highest following spring application. They sampled at three periods of the year, April-May, July-August, and October-November. The spring and summer concentrations were similar to each other (around $1 \mu\text{g/L}$) and significantly higher than the fall values (about $0.2 \mu\text{g/L}$). The ratio of deethylatrazine (a soil bacteria metabolite of atrazine) to atrazine was used as an indicator of groundwater contribution to herbicide

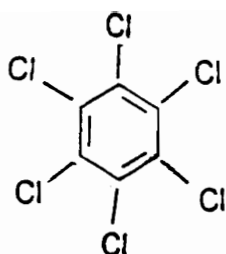
transport. In summer, the ratio was about 0.2. In fall, when the river was at or near base flow, the ratio increased to about 0.6, indicating the greater percentage of herbicide loading from groundwater. In another river study, Schottler *et al.* (1994) found that application of atrazine tended to occur in May and atrazine flux into the river peaked in June. Atrazine, alachlor, and cyanazine concentrations ranged from 500-6500 ng/L during the first significant storm event following application, as opposed to atrazine concentrations in base flow of 20-65 ng/L. Herbicide loading to surface waters has been estimated at 1% (USEPA 1988) to 1.5% (Schottler *et al.* 1994) of the total amount applied.

B. Semi-volatile Synthetic Organic Chemicals

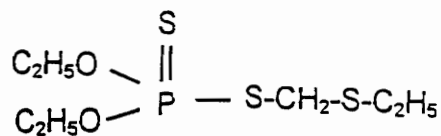
The 50 SOC's monitored at OWML represent several different classes of compounds, including organochlorine, organophosphorus and carbamate insecticides, herbicides, polycyclic aromatic hydrocarbons (PAHs), and phthalate esters (See Tables 4 and 5 for the entire list). Example structures of some of these compounds are shown in Figure 3. This section discusses the characteristics of different classes of compounds.

1. Organochlorine pesticides

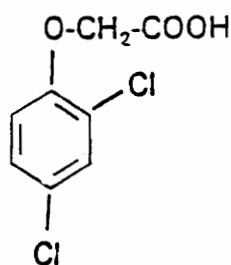
The organochlorine class of compounds includes dieldrin, heptachlor, lindane, hexachlorobenzene (HCB) and DDT to name a few. The structures of these compounds are characterized by 5-6 membered rings and multiple chlorine atoms. HCB is shown as an example in Figure 3. Changing orientations of the chlorine atoms results in the production of isomers with varying toxicities. For example, lindane is the only BHC isomer that is really useful as an insecticide; this is because it is the most toxic of the four BHC isomers monitored at OWML. Dieldrin has an acute oral LD₅₀ for rats of about 38 mg/kg and has shown carcinogenicity at 1-2.5 ppm in mice (USEPA 1989). Due to their high toxicity, environmental persistence,



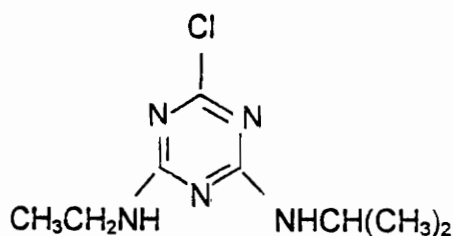
Organochlorine Pesticide
Example: HCB (Hexachlorobenzene)



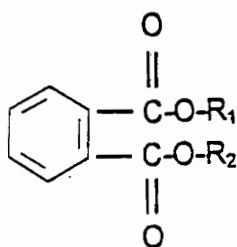
Organophosphorus Pesticide
Example: Phorate



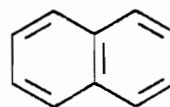
Acid Herbicide
Example: 2,4-D
(2,4-Dichlorophenoxyacetic acid)



Triazine herbicide
Example: Atrazine



General phthalate ester



PAH (polyaromatic hydrocarbon)
Example: Naphthalene

Figure 3. General Structures and Examples of some Semi-volatile SOC's.

and tendency to bioaccumulate, these compounds are now banned in the U.S. (Heath 1987, Grover 1988, USEPA 1988). However, these were heavily used in the 1940-60s in the form of mass spraying intended to eradicate undesirable insects such as gypsy moths and fire ants (Carson 1962) and mosquitos which had the potential to be malaria vectors (Novotny and Olem 1994). Since these were often applied by aerial spraying, winds were able to carry the pesticides far from the original spraying site. They have become a component of global atmospheric pollution and are still detected even in remote locations where no direct spraying was done (Novotny and Olem 1994).

In fish, these compounds tend to bind to lipids and bioconcentrate. The amount of bioconcentration tends to increase with octanol/water partition coefficient (this can be considered an indirect measure of the lipid solubility of a molecule) (Heath 1987). A larger organochlorine molecule such as heptachlor is less likely to be excreted and thus will have a higher bioconcentration factor than a smaller molecule such as lindane (Heath 1987). A study of fish in Australia suggested that exposure to dieldrin and DDT contaminated waters led to increased accumulated with age (Cullen and Connell 1992).

2. Organophosphorus pesticides

Early organophosphorus pesticides were developed during the same period as the organochlorine compounds. The structure of an organophosphorus pesticide usually consists of a P atom bonded to four radicals (one bond is a double bond). Phorate is pictured as an example in Figure 3. Organophosphorus compounds included in OWML's target list include Diazinon, Fensulfothion, Mevinphos, Mocap, Phorate, Ronnel, Terbufos, Vapona, and Parathion. Less toxic and shorter-lived than the organochlorine compounds, organophosphorus and carbamate compounds

took the place of the banned chlorinated pesticides (Domagalski and Kuivila 1993). They are used as insecticides in a variety of different settings (Smith 1993, Meister 1995). One common application aside from agricultural use is mosquito control (Smith 1993). Some example LD₅₀ values for male rats include 3.7 mg/kg for Phorate, 250 mg/kg for Diazinon, and 1250 mg/kg for Ronnel (Smith 1993).

3. Acid herbicides

The acid herbicides include 2,4-D, 2,4,5-T, and Silvex (2,4,5-TP). These are polychlorinated organic acids (2,4-D is shown as an example in Figure 3). They are broad-leaf weed killers and have been used most often on rangeland, pastures, and rights-of-way (Bovey and Young 1980). They were also sprayed over Vietnam in the 1960s for tactical reasons; defoliating the countryside made it easier for U.S. troops to spot attacks (Bovey and Young 1980). Different formulations of these compounds may contain esters or amine salts rather than the parent acids (Bovey and Young 1980). The greatest health concern associated with these herbicides is that the formulations often contained a small amount of dioxins (Bovey and Young 1980, USEPA 1989). Dioxins are so toxic that their LC in toxicity studies is essentially 0; no safe level seems to exist. The use of 2,4,5-T in the U.S. was canceled in 1985 (USEPA 1989).

4. Triazine herbicides

The triazine herbicides include atrazine, simazine, cyanazine, propazine, prometryn, prometon, and metribuzin (Grover 1988). Atrazine and propazine are target compounds at OWML. All are variations based on the triazine ring structure (see Figure 4 for an example). Atrazine is the most popular of this group. Atrazine is a herbicide used for season-long weed control in corn, soybeans, and other crops (Meister 1995). It is widely used, particularly in the Midwestern U.S., where 75% of the

nation's corn and 60% of soybeans are grown (Pereira and Hostettler 1993); consequently, it has often been detected in water supplies there (USEPA 1989, Pereira and Hostettler 1993, Schottler *et al.* 1994, Stamer 1996). It is sometimes employed to remove vegetation from an untilled field in no-till farming, a soil conservation practice where fields are not tilled between harvests. It can be applied as a dry powder or as a water solution (Meister 1995). Mixing it with other herbicides is often done to improve weed control (Stamer 1996). In 1993, the Ciba-Giegy label for the compound was revised to require buffer zones between application areas and surface waters (Meister 1995). Atrazine is degraded by soil bacteria into deethyl- and deisopropylatrazine, among other products (Pereira and Hostettler 1993). The soil half-life of atrazine is 60 days (Pereira and Hostettler 1993).

5. Phthalate esters

Phthalate esters are a family of compounds consisting of a benzene ring with ester linkages to two alkyl groups on two adjacent carbons atoms (see Figure 4). They are most commonly used as plasticizers, compounds which interact with polymers to give plastics their flexibility. Thus, they may leach from any flexible plastic. Dimethylphthalate and dibutylphthalate have also been used in insect repellants (Meister 1995). Since flexible plastics are everywhere, phthalates are often detected in SOC monitoring. Laboratory contamination is difficult to prevent. They can be considered general indicators of anthropogenic contamination.

6. Semi-volatile SOCs regulated in drinking water

The USEPA has added several sets of compounds from different categories to its list of contaminants regulated in drinking water (Pontius 1993). Those included in this study are shown in Table 3.

Table 3. Semi-volatile SOC_s Regulated in U.S. Drinking Water¹

Compound	MCLG (mg/L)	MCL (mg/L)
Atrazine	0.003	0.003
Benzo(a)pyrene	0	0.0002
Di(2-ethylhexyl) phthalate	0	0.006
Heptachlor	0	0.0004
Heptachlor epoxide	0	0.0002
Hexachlorobenzene	0	0.001
Lindane	0.0002	0.0002
2,4,5-TP (Silvex)	0.05	0.05
Carbaryl ²	-	-
Dieldrin ²	-	-
Metolachlor ²	-	-

¹After Pontius 1993

²Monitoring only

Each of these regulated compounds has a story behind the regulation. Atrazine is a skin irritant and was shown to cause an increased incidence of mammary cancer in female rats (USEPA 1989, citing Ciba-Giegy 1986). Based on this rat study as well as a dog study, a lifetime health advisory of 0.003 mg/L was calculated (USEPA 1989), and this number became the drinking water maximum contaminant level (MCL) for atrazine in 1991 as part of the Phase II SOC list (Pontius 1993). Recently, the USEPA has been required by the Court of Appeals to reconsider this MCL (Pontius 1996). Benzo(a)pyrene is a confirmed carcinogen. Di(2-ethylhexyl) phthalate is a common plasticizer, so it is a good general indicator of anthropogenic pollution (unfortunately, it is also a common laboratory contaminant, so it is difficult to measure accurately). Heptachlor and its oxidation product heptachlor epoxide, lindane, dieldrin, and HCB are organochlorine pesticides. They were used in the U.S. in the 1940-60s, and since organochlorine compounds are essentially conservative, they may still be detected. Note that the MCLs for these compounds are generally a power of ten lower than the those for others listed; this reflects the

compounds' high toxicity.

For water treatment plants, GAC is the best available technology (BAT) set forth by the USEPA for removal of every one of the contaminants with MCLs (Pontius 1996). Conventional treatment has been found ineffective for atrazine removal (USEPA 1989 citing ESE 1984 and Miltner and Fronk 1985). Randke (1988) concluded in his review that coagulation can remove some SOC's in cases where they adsorb to floc particles, and the degree of removal may be influenced by coagulant dose, pH, and presence of other particles and natural organic matter in the raw water. Other processes that can remove atrazine from water are powdered activated carbon (PAC) adsorption, ion exchange, reverse osmosis, and UV and ozone oxidation (USEPA 1989).

C. Extraction and Cleanup Methods for Semi-volatile SOC's in Solid Matrices

Different solid matrices pose unique challenges in analysis for semi-volatile SOC's. Matrix interference in soil and sediment samples may be caused by organic matter or other inert components (Taylor 1991), and organic contaminants are likely to be adsorbed to the soil organic matter. In fish tissue, organic contaminants adsorb to lipids, and these biogenic compounds may become interferences in detection. Some interfering compounds will almost inevitably be extracted along with the organic analytes of interest no matter what extraction procedure is used. This necessitates a cleanup step following extraction to remove interferences from the analytes of interest.

Soxhlet extraction, supercritical fluid extraction (SFE), blending/shaking/sonication, and accelerated solvent extraction (ASE) are some extraction techniques found in the literature. Cleanup methods include gel permeation chromatography (GPC) and solid phase extraction

(SPE) using Florisil, C-18, or Alumina columns. Table 4 gives an overview of extraction, cleanup, and detection methods found in the literature for various organic analytes and solid matrices.

1. Extraction

Soxhlet extraction is an old and still common extraction method found in the literature for analysis of pesticides. In this method, the sample (typically 5-30 g) is ground with sodium sulfate or vacuum dried (Kingston *et al.* 1994) to remove water, then placed in a soxhlet apparatus, in which a solvent is boiled, then condensed and poured over the sample repeatedly for 12-24 hrs. Solvents used for various compounds include petroleum ether (Kingston *et al.* 1994, USEPA 1981), 90:10 (v/v) petroleum ether/ethyl acetate (Schmidt and Hesselberg 1992), methylene chloride (Rahman *et al.* 1993), 1:1 hexane/methylene chloride (Marquis *et al.* 1994), 1:1 acetone/hexane (USEPA 1979, NIST 1991) and hexane (Grob and Kalin 1991). This method is time consuming, requires a fairly elaborate setup of specialized glassware, and uses a large volume of organic solvent (usually 200-1000 mL) per sample. Automated soxhlet systems which reduce solvent usage to 50-100 mL exist but they may be no less time and labor intensive than manual ones (Ezzell 1995). The sodium sulfate that typically is used for dehydrating wet samples may also adsorb analytes (Kingston *et al.* 1994). Heating the sample to the boiling point of the solvent helps dissolve contaminants and fish lipids into the solvent but may also result in loss of the lightest semi-volatiles, such as naphthalene and Vapona. Soxhlet extraction has its drawbacks, but it is a time-honored method that works well for a variety of matrices.

SFE is a technique which utilizes supercritical carbon dioxide (CO₂) as the extracting solvent. It has been demonstrated in analysis of carbamate pesticides (Murugaverl *et al.* 1993) and polychlorinated

Table 4. Fish and Sediment Analysis Methods from the Literature

<u>Extraction</u>		<u>Solvent</u>	<u>Cleanup</u>	<u>Analytes</u>	<u>Detector</u>	<u>Reference</u>
<u>Matrix</u>	<u>Method</u>					
Sediment & Fish	Shaking (12 hr., 45 cycles/min)	Acetonitrile	C-18	Organochlorine Pesticides	GC/ECD	Marble and Delfino 1988
Soil & Fish	Blending	1:2 Water:Acetonitrile or Water:Acetone	GPC or Silica	Organochlorine, Organophosphorus pesticides, PCBs	GC or LC	Steinwandter 1985
Fish (carp)	Solid phase dispersion (mix w/ C-18)	N/A	C-18 (solid phase dispersion, then acidic silica)	PCBs	GC/MS	Ling et al. 1994
Soil	Shaking 1 hr.	4:1 Methanol:Water	Phenyl SPE	Triazine herbicides, Organophosphorus pesticides	GC/N-P	Turin and Bowman 1993
Whale Blubber	Soxhlet 18 hr.	1:1 Acetone:Hexane	Sulfuric acid, Silica SPE	PCBs	GC/MS	NIST (1994) (Standard Reference Material 1945)
		Methylene chloride	GPC, then SPE w/ divinylbenzene polystyrene, aminopropylsilane	PCBs	GC/ECD	
Mussels	Soxhlet 18 hr.	Methylene chloride	GPC as above, then silica SPE	PAHs	GC/MS	NIST (1991) (Standard Reference Material 1974)
		1:1 Acetone:Hexane	Amino silane SPE	PAHs	LC/FL (fluorescence)	
Sediment	Homogenization	1:1 Acetone:Hexane	Silica gel	general (none specified)	GC/MS	USEPA 1979
Fish	Soxhlet 8 hr.	1:1 Acetone:Hexane	GPC	general (none specified)	GC/MS	USEPA 1979

Table 4, Continued

<u>Matrix</u>	<u>Extraction Method</u>	<u>Solvent</u>	<u>Cleanup</u>	<u>Analytes</u>	<u>Detector</u>	<u>Reference</u>
Fish	Soxhlet	Petroleum ether	Florisil	Organochlorine, Organophosphorus pesticides	GC/ECD	USEPA 1981
Fish	Soxhlet 12 hr.	1:1 Hexane: Methylene chloride	GPC, silica gel w/ autosampler, computer control	Organochlorine pesticides, PCBs	GC/MS	Marquis <i>et al.</i> 1994
Fish	Soxhlet 16 hr.	Methylene chloride	GPC, florisil	Organochlorine pesticides, PCBs	GC/ECD	Rahman <i>et al.</i> 1993
Fish	Chromatographic column	90:10 Petroleum ether: Ethyl Acetate	Automated GPC	Organochlorine pesticides, PCBs	GC/MS, NCI (Negative Chemical	Schmidt and Hesselberg 1992
Soil & Sediments	30 min. at 75 degrees C	15:5 Methanol:Water	C-18, anion exchange for humics	Triazine herbicides	GC/MS	Mills and Thurman 1994
Fish	Soxhlet	Hexane	Automated GPC	Organochlorine pesticides	GC/ECD	Grob and Kalin 1991
Soil	Sonication 2 hr.	Methanol:Acetone	none	Organochlorine, Organophosphorus pesticides	GC/FTIR and MS LC-diode array	Taylor 1991
Fish	Homogenization	Petroleum ether	Florisil and/or automated GPC, derivitization for acid herbicides	Organophosphorus pesticides, Acid herbicides	GC/ECD	USFDA 1994
Fish	SFE at 90 degrees C 219 atm., 30 min.	Carbon dioxide	7:93 Diol:C-18 column	Carbamate pesticides	SFC/MS	Murugaverl <i>et al.</i> 1993

Table 4, Continued

<u>Matrix</u>	<u>Extraction Method</u>	<u>Solvent</u>	<u>Cleanup</u>	<u>Analytes</u>	<u>Detector</u>	<u>Reference</u>
Plant/ Animal Tissue	Homogenization	Methanol	C-18	Organochlorine pesticides	-	J.T. Baker 1989
Solid Waste	Sonication (probe, few minutes)	Hexane, Methylene chloride, or 1:1 Methylene chloride: Acetone	GPC, alumina, florisil, silica gel	Organochlorine, Organophosphorus pesticides, phthalate esters, PCB	GC/ECD or MS	USEPA 1986
Fish and Seafood	Homogenization	Acetonitrile	C-18, then florisil	Organochlorine pesticides	GC/ECD	Schenck <i>et al.</i> 1994
Soil	Sonication (water bath, 30 min.)	Water (10 min.), then 70:30 methanol/ water (20 min.)	C-18	Triazine herbicides, Organophosphorus pesticides	GC/N-P	Watts <i>et al.</i> 1994
Fish	Soxhlet 8 hr.	Petroleum ether	Florisil or C-18	Organochlorine, Organophosphorus pesticides, PCBs, Phthalate esters	GC/ECD	Virginia Tech Pesticide Residue Laboratory 1989

biphenyls (PCB's) (Bowadt *et al.* 1994) in fish tissue. The advantages of SFE include the less toxic, less expensive solvent as compared to organic solvents and the reduced time (1-2 hrs. as opposed to 12-24 hrs. for the Soxhlet method). Also, since these are typically closed systems, there is less potential for analyte loss. In some cases, SFE may be immediately followed by determinative chromatography; however, in the case of fish tissue, CO₂ can solubilize fish lipids and a cleanup step following SFE is usually needed to remove them (Murugaverl *et al.* 1993). The greatest difficulty with this method is the high cost of the SFE apparatus.

Obtaining contact with solvent through blending, shaking, or sonication is another common extraction method. Blending for 5-10 min. with acetonitrile followed by 12 hrs. of shaking has been shown to be as effective as a 12 hr. Soxhlet extraction (Marble and Delfino 1988). Homogenizing with acetonitrile has also been used (Schenck *et al.* 1994), as well as blending in water for 3 min., then adding acetonitrile and blending for another 1-2 min. (Steinwandter 1985). In both blending procedures, salt (NaCl) was added to "salt out" the analytes into the organic phase. The United States Food and Drug Administration (USFDA) prescribed blending or homogenizing with petroleum ether and sodium sulfate for extracting pesticides from fatty (> 2% fat by weight) meat and fish (the fish usually sampled in the Occoquan Reservoir are in this category, with largemouth bass at about 3% fat and catfish at 5%) (USFDA 1994). Advantages of these physical methods include speed, simplicity, and possibly decreased solvent use as compared with Soxhlet methods. Analyte losses due to volatilization may be less likely, but these methods may not provide as thorough an extraction or, for fish, as much solubilization of lipids.

Accelerated solvent extraction or ASE is a relatively new method that

may be the best replacement for Soxhlet extraction. In this method, a pressure vessel containing the sample and solvent (about 15 mL of organic solvent per 10 g sample) is heated to 50-200°C and pressurized to 1500-2000 psi for 5-10 min. (Ezzell 1995). During extraction, the expanding solvent is vented and collected, and afterward, remaining solvent is purged with nitrogen and collected as well (Ezzell 1995). This technique has been shown to give comparable results as compared to Soxhlet for PAHs (Dionex 1995) and organophosphorus pesticides and shaking for acid herbicides (Ezzell 1995).

2. Cleanup

The goal of the cleanup step is to separate the organic analytes from compounds extracted with them that might prevent detection. This separation may be accomplished by physical or chemical means.

GPC is a form of size exclusion chromatography (SEC), whereby molecules of different sizes can be separated. Lipids in fish tissue are, for the most part, considerably larger molecules (20-20000 amu) (Turnham 1994) than the analytes of interest here (approx. 100-400 amu), so GPC can be used to separate the larger lipids from the analytes. Given these size ranges, it is clear that lower molecular weight lipids may remain with the analytes, necessitating a second cleanup step following GPC. One would need to find out by experimentation which compounds elute in which fraction(s) and if a compound eluted in more than one fraction, amounts in each would have to be added up later to find the total mass present. Automated GPC systems are available, and the USFDA recommends them over manual systems (1994).

Another cleanup method is solid phase extraction using a Florisil, Alumina, or C-18 column. Florisil and Alumina are normal phase chromatography methods in which a nonpolar solvent containing the

analytes and impurities is passed through a polar column, and polar impurities may be retained. Florisil columns are typically eluted in successively more polar fractions, for example, petroleum ether, ethyl ether/petroleum ether, methylene chloride, 47:3:50 acetonitrile methylene chloride (USFDA 1994). As in GPC, a compound may elute in multiple fractions. Alumina (aluminum hydroxide) is another adsorbent that can be used to remove interferences such as excess fat in fish tissue (USFDA 1994). A reverse phase chromatography method, C-18 has become a popular choice for separating a wide variety of organic compounds from a polar solvent. The decreased solvent use with a C-18 extraction as compared to liquid-liquid methods has been a great improvement in water extractions. A C-18 cleanup has also been used for soil (Marble and Delfino 1988, Mills and Thurman 1994, Watts *et al.* 1994) and fish cleanup (Marble and Delfino 1988, Ling *et al.* 1994, Schenck *et al.* 1994).

3. Detection

Gas chromatography is almost the universal analysis technique for a wide range of SOCs. A few compounds, notably the carbamate pesticides and the acid herbicides, cannot be detected reliably with gas chromatography and high performance liquid chromatography (HPLC) or a derivitization procedure must be used.

The detectors usually used in gas chromatography of pesticides include the electron capture detector (ECD), the nitrogen-phosphorus detector (N-P), and the mass spectrometer (MS). The ECD is very sensitive for compounds with high electron densities. Chlorinated compounds are in this category, so the ECD has been used to obtain low detection limits for polychlorinated biphenyls (PCBs) and organochlorine pesticides (to as low as 5-10 $\mu\text{g/kg}$ wet weight in whale blubber [NIST 1994], for example). The N-P detector is selective for compounds containing N and/or P. Thus, it

has been used for triazine and organophosphorus compounds (Turin and Bowman 1993, Watts *et al.* 1994). While the ECD and N-P detectors may be more sensitive than the MS for certain compounds, the MS is more of an all purpose detector. It can detect virtually anything that can be brought through a GC column. The spectrum of a compound is a unique fingerprint that can be used to identify the molecular structure. Quantitating selected ions rather than the total signal in the total ion chromatogram minimizes some interferences. Operating the MS in selected ion monitoring (SIM) mode, where the MS only scans for ions of certain masses, can improve sensitivity. Results comparable to those from the ECD for PCBs and organochlorine compounds in whale blubber have been obtained using SIM mode (NIST 1994). The GC/MS system at OWML was a good choice given the wide variety of target compounds in their monitoring program.

III. MATERIALS AND METHODS

The analysis of organic chemicals in environmental matrices is one of the most complex operations in environmental chemistry. This section describes the methods of SOC analysis used at OWML for water and sediment, as well as the fish tissue analysis method developed during this study.

A. Experimental Design

The research was divided into two distinct parts: the database analysis and the fish extraction method development. In the analysis portion, trends throughout the entire eleven year database of water, sediment, and fish concentrations were investigated. Atrazine was selected as the one compound that was consistently detected and for which trends could be evaluated. Bar graphs showing atrazine concentration plotted against time were constructed for the entire period of record at each sampling station. Graphs of concentration at each sampling station on sampling dates that showed a series of concurrent detections were also made. Mean and median concentrations and frequency of detections were calculated; spatial and seasonal variations were considered. The relationship between concentrations and rainfall was investigated. The removal efficiencies for atrazine in the water treatment plants were also considered.

In the method development phase, fish extraction and cleanup methods in the literature were investigated and various methods were considered. Some options that involved materials and equipment already available at OWML were tested by performing matrix spikes using practice fish samples and the full suite of compounds. A method using methanol extraction and C-18 and alumina SPE cleanup was selected. Using this

method, stored 1993-94 fish samples and QA/QC samples were analyzed, and MDLs for the method were determined.

B. Reagents, Standards, and Glassware

Solvents used in this study were Fisher Scientific Optima Grade hexane, acetone, methanol, acetonitrile, methylene chloride, and ethyl acetate (Pittsburgh, PA) and water treated by a Milli-Q® system (Millipore Corp., Milford, MA). Anhydrous sodium sulfate from Fisher Scientific (Pittsburgh, PA) was ignited in a muffle furnace at 400°C for 4 hrs. to remove moisture and kept in a desiccator until use. Burdick and Jackson 3000 mg Neutral Alumina and 1000 mg C-18 SPE cartridges were obtained from Scientific Products (McGaw Park, IL). Zero grade Nitrogen and ultra high purity Helium gases were obtained from Potomac Airgas (Baltimore, MD).

Standard solutions of the SOC_s, internal standards, and surrogates were obtained from Absolute Standards, Inc. (Hamden, CT) in concentrations of 100-1000 mg/L in acetone. They were stored in the original one milliliter amber glass ampules in a freezer at approximately -18°C until use, when they were transferred to two milliliter amber glass vials (crimp-top, autosampler type). Dilutions were made using acetone and diluted stock solutions were stored in the same freezer in amber glass vials with Teflon-lined screw caps. The contents of the stock solutions are shown in Tables 5, 6, and 7. The secondary solutions for calibration and matrix spikes were prepared in two mixed solutions (Sets 1 and 2, as shown in Tables 5 and 6) at 10 mg/L. Internal standards were not diluted, and a combined surrogate solution was prepared at 10 mg/L (see Table 7).

Glassware was subjected to a soap wash, followed by a 15 min. Chromerge soak (chromium trioxide, Fisher Scientific, Pittsburgh, PA), three

rinses with reverse osmosis (RO) treated water followed by two with Milli-Q, and a final acetone rinse (OWML SOP 1994). Pipettes were soap washed, chromerged for 15 min., rinsed with RO water for 15 min., and oven dried (OWML SOP 1994). Stored glassware was covered with aluminum foil.

Table 5. Set 1 - Calibration/Matrix Spike Solution (prepared in 50 mL volumetric flask).

Absolute Standards, Inc. Stock #	Conc. (mg/L)	Compounds in mix	Volume added (mL)	Conc. in Spike Std. (mg/L)
10007	2000 ± 10	All compounds Acenaphthene Acenaphthylene Anthracene Benzo(a)anthracene Benzo(a)pyrene Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(g,h,i)perylene Carbazole Chrysene Dibenzo(a,h)anthracene Fluoranthene Fluorene Indeno(1,2,3-cd)pyrene Naphthalene Phenanthrene Pyrene	0.25	10
70383	1000 ± 5	Parathion	0.5	10

Table 6. Set 2 - Calibration/Matrix Spike Solution (prepared in 10 mL volumetric flask)

Absolute Standards, Inc. Stock #	Conc. (mg/L)	Compounds in mix	Volume added (mL)	Conc. in Spike Std. (mg/L)
19102	200 ± 1	All compounds Benzyl butyl phthalate Bis(2-ethylhexyl) phthalate Di-n-butyl phthalate Di-n-octyl phthalate Diethyl phthalate Dimethyl phthalate	0.5	10
90150	100 ± .5	All compounds Aldicarb αBHC βBHC γBHC (Lindane) δBHC Dacthal Dieldrin Hexachlorobenzene Heptachlor epoxide Methomyl Mevinphos Diazinon	1	10
90151	100 ± .5	All compounds Mocap Pendimethalin Phorate Ronnel Terbufos Vapona Silvex 2,4,5-T	1	10

Table 6, Continued

Absolute Standards, Inc. Stock #	Conc. (mg/L)	Compounds in mix	Volume added (mL)	Conc. in Spike Std. (mg/L)
90186	100 ± .5	All compounds Atrazine Carbaryl Carbofuran Dual (Metolachlor) Fensulfothion Heptachlor γBHC (Lindane) Propazine	1	10

Table 7. Internal and Surrogate Standards

Absolute Standards, Inc. Stock #	Conc. (mg/L)	Compounds in mix	Volume added (mL)	Conc. in Spike Std. (mg/L)
Internal Standards				
30031	500 ± 2.5	Acenaphthene d ₁₀ Chrysene d ₁₂ Perylene d ₁₂ Phenanthrene d ₁₀	All compounds pipetted directly from standards	
90272	1000 ± 5	Benzo(g,h,i)perylene d ₁₂ Naphthalene d ₈		
Surrogates (prep'd in 50 mL volumetric)				
30032	500 ± 2.5	Terphenyl d ₁₄	1	10
90271	500 ± 2.5	Fluoranthene d ₁₀ Bis(2-ethylhexyl) phthalate d ₄	1	10

C. Equipment and Analytical Instrumentation

Sediment samples were collected using an Eckman dredge (Wildco Wildlife Supply Co., Saginaw, MI). Fish samples were homogenized using an Ultra Turax® model TP 18/10 homogenizer (IKA Works Inc., Wilmington, NC) or a Waring Commercial blender, model 34BL97 (New Hartford, CT). Water samples were extracted using an Autotrace® automatic SPE extraction system (Zymark Corp., Hopkington, MA), sediment samples were extracted using a Burrell wrist-action shaker (Pittsburgh, PA), and fish samples were extracted in a Branson model 2500 ultrasonic cleaner (Shelton, CT). Concentration was accomplished in a Zymark TurboVap® (Hopkington, MA). Internal standard was added to samples using a 25 µL Drummond Digital Microdispenser (Bloomall, PA).

A Hewlett Packard model 5890 Series II Gas Chromatograph with a 30 m x .25 mm HP-5 M.S. column, a model 5871A Mass Selective Detector, and a model 7673 Autoinjector was used (Palo Alto, CA). These were controlled using HP G1034C MS ChemStation software.

D. Sampling

SOC sampling was done quarterly at stations on Lake Manassas and the Occoquan Reservoir, and tributaries to these. Stations are shown in Figures 1 and 2. Water samples are taken at 26 stations, designated BR for tributaries to Lake Manassas, LM for Lake Manassas itself, RE for the Occoquan Reservoir, and ST for other streams in the watershed. Sediment is taken only from the LM and RE stations and fish are taken only at the RE stations.

Water samples were grab samples collected in two liter glass jars with foil lined caps. They were preserved at pH<2 with 6N hydrochloric acid to inhibit microbial degradation of analytes, and stored at 0-4°C until extraction (OWML SOP 1994). Sediment samples were collected using a

clean Eckman dredge, placed in 125 mL amber jars with teflon lined caps and stored at 0-4°C.

Fish were caught 2-4 times per year, and an effort was made to collect both a surface feeder (largemouth bass, Micropterus salmoides) and a bottom feeder (channel catfish, Ictalurus punctatus) at each sampling time. The fish were caught with hook and line with artificial lures. They were kept in coolers until they could be brought into the laboratory, where each fish was then placed on a glass cutting board, rinsed with Milli-Q water, and gutted using a stainless steel knife. The head and tail were removed, the internal organs and body were wrapped in separate aluminum foil packets, and the packets were frozen and stored at approximately -18°C until analysis. Each packet was labeled with a sample identification number, the station designation, the date and time of capture, the type of fish, and the length and gross weight of the fish.

E. Extractions

Water, sediment, and fish were extracted using methods appropriate to each matrix.

1. Water samples

One liter water samples were aspirated through 1000 mg C-18 cartridges using the Autotrace® automated SPE apparatus at a rate of 15 mL/min. The eluting solvents, methylene chloride (15 mL), followed by 60:40 methylene chloride/ethyl acetate (15 mL), were drawn through the cartridges using the Autotrace®. The combined eluent was decanted through a sodium sulfate column (approximately 10 g), concentrated to < 1 mL in a TurboVap®, transferred to an autosampler vial, and stored at ~4°C until analysis.

2. Sediment samples

Sediments were air-dried at room temperature for at least one month

in ceramic dishes covered with teflon mesh. A sample of approximately 5 g was then weighed out and extracted with 50 mL of acetonitrile by shaking for 1.5 hrs. on a wrist-action shaker. The acetonitrile was decanted through approximately 10 g sodium sulfate over a Whatman #42 filter and the filtered extract was concentrated to 5 mL in a TurboVap®. A 1 mL aliquot was combined with 2 mL Milli-Q water and aspirated through a C-18 cartridge using a sidearm flask and vacuum pump assembly. The C-18 cartridge was eluted with x mL 50:3:47 methylene chloride/ acetonitrile/hexane, the eluent was again concentrated to < 1 mL in a TurboVap®, and the extract was stored at ~4°C until analysis.

3. Fish samples

Fish samples were thawed in their foil wrap for 1-4 hours, depending on the size of the fish. Flesh was cut from the body, placed in a stainless steel cup, and homogenized at 20,000 rpm using the Ultra Turrax® homogenizer until the sample appeared uniform (about 5 min.). A few large fish were homogenized in the Waring blender with a stainless steel blender jar; the speed was varied and the sides were scraped down with a teflon spatula several times during blending. Organs were blended together using the homogenizer as above; these included the entire contents of the body cavity including any fatty tissue present and excluding the brain. A 10 g sample of either homogenized flesh or organs was placed in a 125 mL Erlenmeyer flask. To this, 0.25 mL of 10 mg/L surrogate solution were added and allowed to equilibrate for 10-15 min. The final concentration of the surrogates was approximately 0.25 mg/kg wet fish tissue.

A graduated cylinder was used to measure 40 mL of methanol, which was then added to the Erlenmeyer flask. The flask was capped with a ground glass stopper. Samples were sonicated four at a time for 1 hr. in the Branson 2500 water bath sonicator at a frequency of 50-60 Hz. During

sonication, the sample reached a temperature of $\sim 40^{\circ}\text{C}$, comparable to the temperature reached when boiling methylene chloride in a Soxhlet. After sonication, the methanol was decanted through Whatman #41 filter paper into a 250 mL beaker, the remaining fish tissue was rinsed twice with methanol, and the rinsings were added to the filter. The filter was then rinsed with ~ 2 mL of methanol and discarded. A graduated cylinder was used to measure 120 mL of Milli-Q[®] water and add it to the methanol in the beaker (giving a methanol/water ratio of $\sim 1:4$).

For cleanup of the fish tissue to remove fats and other compounds which could cause chromatographic interference, a C-18 cartridge was placed in a cored stopper above a sidearm flask attached to a vacuum pump (see Figure 4). The C-18 was conditioned with 2 X 3 mL methanol and rinsed with 2 X 3 mL Milli-Q[®] water. Teflon tubing fitted into an adapter atop the C-18 cartridge formed a siphon through which sample was drawn into the cartridge and aspirated at a rate of ~ 10 mL/min. The C-18 cartridge was dried under full vacuum for 10 min., then eluted with 4 mL of 50:3:47 methylene chloride/acetonitrile/ hexane at a rate of about 5 mL/min. The eluent was collected in a graduated 25 mL concentration tube. A 3000 mg neutral alumina cartridge was placed in the vacuum assembly, about 1 mL of sodium sulfate was added on top of the alumina, and the sample was transferred to the cartridge using a Pasteur pipette and aspirated. The concentration tube rinsings, plus 2 mL of 50:3:47 elution solvent, were applied to rinse the alumina. The sample was again collected in a 25 mL tube. If the amount of sample was > 2 mL, it was concentrated for a few minutes in the TurboVap[®] until it was just below 2 mL. The volume was then brought up to 2 mL with elution solvent, and the sample was transferred using a Pasteur pipette to an autosampler vial and stored at 4°C .

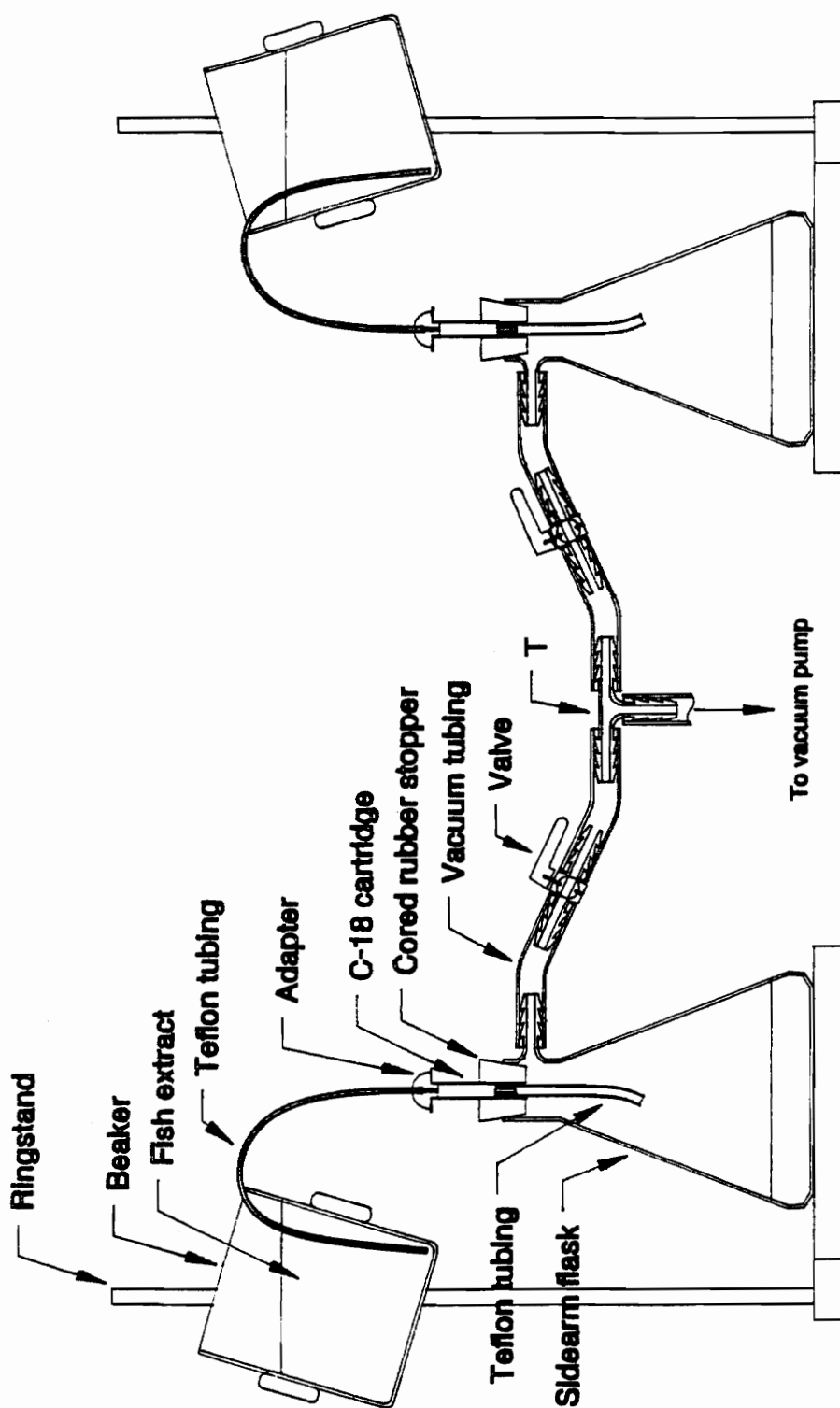


Figure 4. Vacuum Assembly used in Fish Extraction Method.

F. Chromatographic Analysis

Chromatography using GC/MS was used to determine individual organic compounds in extracts of water, sediment, and fish tissue.

1. Internal standards

Volumes of internal standards were pipetted directly from the two stocks into the autosampler vials containing sample extracts immediately following the extraction process. A 25 μL Drummond Digital Microdispenser was used to dispense amounts of 5 (#90272) and 10 (#30031) μL for the water and sediment and 10 and 20 μL for the fish to give a final concentration of 5 mg/L of each standard in every sample.

2. GC/MS conditions

The conditions employed with the HP GC/MS (model 5890 GC with model 5871A MS) were as follows:

- 30 m x .25 mm HP-5 M.S. column (5% methyl/phenyl, 0.25 μm film thickness)
- 1 μL volume of sample injected by the autoinjector
- temperature program slightly modified from the multi-ramp program suggested in EPA Method 525.1:
 - initial oven temperature of 45°F, held for 2 min.
 - first ramp rate of 35°C/min. up to 130°C
 - second ramp rate of 12°/min. up to 180°C
 - final ramp rate of 9°C/min. up to 300°C
 - held at 300°C for 17 min., giving a total time of 38.9 min.
- injector temperature of 250°C
- detector temperature of 165°C
- MS transfer line temperature of 285°C
- 5 min. solvent delay
- carrier gas was Helium flowing at 1 mL/min.

3. Calibration

A calibration curve was compiled for each analyte by injecting solutions of Set 1 and Set 2 prepared in concentrations of 10, 5, 2, 1, .5, and .1 mg/L. Internal standard was added to each calibration standard at the same concentration (5 mg/L) used in samples. A target ion to use for quantitation of each compound was specified in a method created using the HP Chemstation software. Qualifier ions, prominent ions other than the target ion, were added to the method along with an estimate of the relative abundance of the qualifier as compared with the target and a margin of error for that relative abundance. Qualifier ion responses outside that margin of error were noted on the quantitation report. The qualifiers were chosen based on EPA Method 525.1 and OWML's reference spectra for each compound and are shown along with the target ions in Table 8.

The software stored the calibration responses for the target ions and generated a response ratio vs. concentration ratio curve:

$$Ax/Ais = a(Cx/Cis) + b$$

where: Ax = response area of analyte

Ais = response area of the internal standard immediately preceding the analyte in retention time

Cx = concentration of analyte in extract (mg/L)

Cis = concentration of internal standard in extract (5 mg/L)

a, b = linear regression constants

Unique regression constants (a and b) were calculated for each compound using the calibration data. The value of a ranged from 0.058 to 1.98 and the value of b ranged from 0.001 to 0.396. The program found unknown concentrations by substituting in the known a and b values and the Ax , Ais , and Cis values found in a sample and solving the previous equation for Cx .

Table 8. Target and Qualifier Ions for Analytes

Compound	Target Ion	Qualifier Ion(s)
Acenaphthene	153	154
Acenaphthylene	152	76, 151
Anthracene	178	176
Benzo(a)anthracene	228	226
Benzo(a)pyrene	252	126
Benzo(b)fluoranthene	252	-
Benzo(k)fluoranthene	252	126
Benzo(g,h,i)perylene	276	138
Carbazole	167	139
Chrysene	228	-
Fluoranthene	202	101
Fluorene	166	165
Naphthalene	128	127
Phenanthrene	178	152
Pyrene	202	200
Parathion	97	291, 109
Benzyl butyl phthalate	149	206
Bis(2-ethylhexyl) phthalate	149	167
Di-n-butyl phthalate	149	150
Di-n-octyl phthalate	149	279
Diethyl phthalate	149	177
Dimethyl phthalate	163	77
α BHC	181	183
β BHC	181	109
γ BHC (Lindane)	183	219
δ BHC	219	181
Dacthal	300	299
Dieldrin	79	263
Hexachlorobenzene	284	286
Heptachlor epoxide	353	355
Mevinphos	127	192
Diazinon	137	179, 152, 304
Mocap	158	200
Pendimethalin	252	281
Phorate	75	121
Ronnel	285	125
Terbufos	231	186
Vapona	109	185
Silvex	196	198

Table 8, Continued

<u>Compound</u>	<u>Target Ion</u>	<u>Qualifier Ion(s)</u>
2,4,5-T	233	235
Atrazine	200	215
Carbaryl	144	115
Dual (Metolachlor)	162	238
Fensulfothion	156	292, 140
Heptachlor	100	272
Propazine	214	231
Acenaphthene d ₁₀	164	162
Chrysene d ₁₂	240	236
Perylene d ₁₂	264	265
Phenanthrene d ₁₀	188	189
Naphthalene d ₈	136	-
Terphenyl d ₁₄	244	-
Fluoranthene d ₁₀	212	-

The concentrations in each sample were then found by:

Water: $C = Cx/1000 \mu\text{g/L}$

Sediment: $C = Cx \cdot V_{\text{ext}} \cdot 5/W \text{ mg/kg}$

Fish: $C = Cx \cdot V_{\text{ext}}/W \text{ mg/kg}$

where: V_{ext} = volume of final extract

W = weight of sample analyzed

Up to 100 samples could be placed in the autosampler; however, samples were typically analyzed 4-20 at a time as the extracts were produced. Sequences which specified the method to be used, the vial number, and the data file name for each were created in the software.

G. Quality Assurance/Quality Control

Several measures were taken to monitor quality of the SOC results in water, sediment, and fish.

1. Surrogates

Surrogate standards were added to every water, sediment, and fish sample prior to extraction to assess the reliability of the extraction/cleanup

procedure. Surrogate concentrations were 2.5 or 5.0 $\mu\text{g/L}$ in water, 5 mg/kg in sediment, and 0.25 mg/kg in fish.

2. Blanks

Laboratory blanks using reagent water (water samples), teflon chips (sediment), and solvent (fish) were analyzed to evaluate contamination. If contaminants were detected in the laboratory blanks, the amount present was quantified and subtracted from the sample results. Water, sediment and fish samples following a blank were adjusted based on the blank immediately prior to those samples. The blank done with the MDL samples for fish was applied only to the MDL results.

3. Matrix spikes

Full matrix spikes (containing all analytes - both Sets 1 and 2) were prepared using duplicates of actual samples to determine analyte recoveries. For water, matrix spikes were performed approximately every ten samples. In sediment and fish, seven matrix spikes were performed in order to determine MDLs. The matrix spikes used to determine average recoveries included the MDL analyses and 1-2 other matrix spikes performed near the beginning and end of the 1993-94 sample analysis process.

4. Method detection limits

Precision-based MDLs were found by preparing seven replicates of one full matrix spike concentration level to find a standard deviation and multiplying this value by the 99.0% t distribution quantile for $7-1 = 6$ degrees of freedom. The concentration used for all matrices was designed to produce a 2 mg/L concentration in the sample extract (this is equivalent to 2 $\mu\text{g/L}$ in water, 2 mg/kg in sediment, and 0.4 mg/kg in fish). This was the calibration level at which all compounds were reliably detected; at the 1, 0.5, and 0.1 mg/L levels, some compounds in the two sets were still

detected, while others were not. Reagent water was used to determine the water MDL, while teflon chips were used for sediment and the remainder of an actual fish flesh sample in which no contaminants were detected was used for the fish MDL.

5. GC/MS tuning

GC/MS instrument performance was adjusted using a perfluorotributylamine (PFTBA) autotune at least once per week, often before each sequence. Decafluorotriphenyl phosphate (DFTPP) tunes were analyzed at the beginning of each sample sequence to gauge GC/MS instrument performance. If the DFTPP tune results showed more than a few slight failures in relative ion abundance, the sequence was stopped, the problem was investigated, and an autotune was performed prior to restarting the sequence.

6. Quantitation

The HP Chemstation software method was adjusted with respect to target and qualifier ions and their relative ratios and retention times to the point where the software was able to correctly identify compounds in spiked samples. In regular samples, however, there are cases where interferences produce a target ion and thus a detected value; the qualifier ion(s) may not be present, or there is no true chromatographic peak but simply noise that includes the target ion. Also, the software occasionally does not integrate the whole peak or misidentifies closely related compounds, such as phenanthrene and anthracene, benzo(b) and benzo(k)pyrene, or β and γ BHC. Thus, each sample chromatogram was manually checked to find and eliminate errors in the computer generated quantitation report.

IV. RESULTS

The Occoquan Laboratory's SOC monitoring database is quite extensive, with over 10 years of record at some stations (1982-1994), data from 3 environmental matrices, and over 60 compounds monitored at one time or another. In all this, however, very few compounds were ever found at levels above the MDLs. The Virginia Tech Pesticide Residue Laboratory did not perform MDL studies until 1991-92, so some values recorded in the database were later found to be below the calculated MDLs. Atrazine was the most commonly detected compound in water (OWML 1992). Other compounds found with some frequency included metolachlor, aldicarb, and various phthalate esters (OWML 1992). When the 1991-92 MDLs were applied to the entire database, atrazine was the only analyte with several measured concentrations above the detection limit ($1.11 \mu\text{g/L}$ for 1982-92 and $1.4 \mu\text{g/L}$ for 1993-94). Atrazine is also of particular interest because of its MCL in drinking water. Thus, for this research, trend analysis of OWML's SOC database focused on atrazine.

A. Atrazine in Water, Sediment, and Fish

Atrazine concentrations were plotted against time for each station and matrix. Figures 1 and 2 showed the locations of the monitoring stations. Total and seasonal statistics were also compiled. Throughout this results section, concentrations referred to as detections are those greater than the MDL values. All concentrations less than the MDLs, whether they were recorded as NDs or as estimated values, were plotted as one-half of the appropriate MDL.

1. Water

Figures 5-14 show atrazine concentrations in water at each station over time. Horizontal lines delineate the MDL (1.11 for points through

1992 and 1.40 for 1993-94) and MCL (3 µg/L). In all graphs, values below the MDL are shown as one-half of the MDL.

Average water concentrations were calculated by two methods: 1) values greater than the MDL only; and 2) values less than the MDL included as one-half of the MDL. The results are shown in Table 9. The frequency at which atrazine was detected is also indicated. Seasonal averages of atrazine values are shown in Table 10, along with the seasonal and total number of detections relative to the number of samples analyzed.

Table 9. Mean and Median Atrazine Concentrations in Water at Sampling Sites in the Occoquan Watershed (1982-1994)

Station Group ¹	Mean		Median		Detects/Samples Analyzed
	Detects ²	All ³	Detects	All	
BR02-BR07, ST70	3.05	0.75	2.25	0.56	12/134 (9%)
LM01-LM08, MANRAW	3.32	1.10	1.98	0.56	38/206 (18%)
MANFIN	1.95	0.80	1.83	0.56	5/32 (16%)
RE02-RE30, OCCRAW	2.53	0.93	1.74	0.56	12/71 (17%)
OCCFIN	1.51	0.67	1.35	0.56	3/32 (9%)
ST10-ST40	1.92	0.77	1.70	0.56	17/135 (13%)
All Stations	2.69	0.89	1.77	0.56	87/610 (14%)

¹Stations are grouped according to location.

²Mean calculated based on data when atrazine was detected above the MDL.

³Mean calculated based on all samples; when atrazine concentration was < MDL or ND, the concentration was estimated at one-half the MDL.

Table 10. Seasonal Mean Atrazine Concentrations in Water at Sampling Sites in the Occoquan Watershed (1982-1994)

Season	Seasonal Ave. of Detects ¹	Detects/Samples Analyzed
Winter (Dec.-Feb.)	2.24	12/131 (9%)
Spring (March-May)	7.20	10/160 (6%)
Summer (June-Aug.)	1.98	49/208 (24%)
Fall (Sept.-Nov.)	2.41	16/111 (14%)
Total	-	87/610 (14%)

¹Mean calculated based on data when atrazine was detected above the MDL.

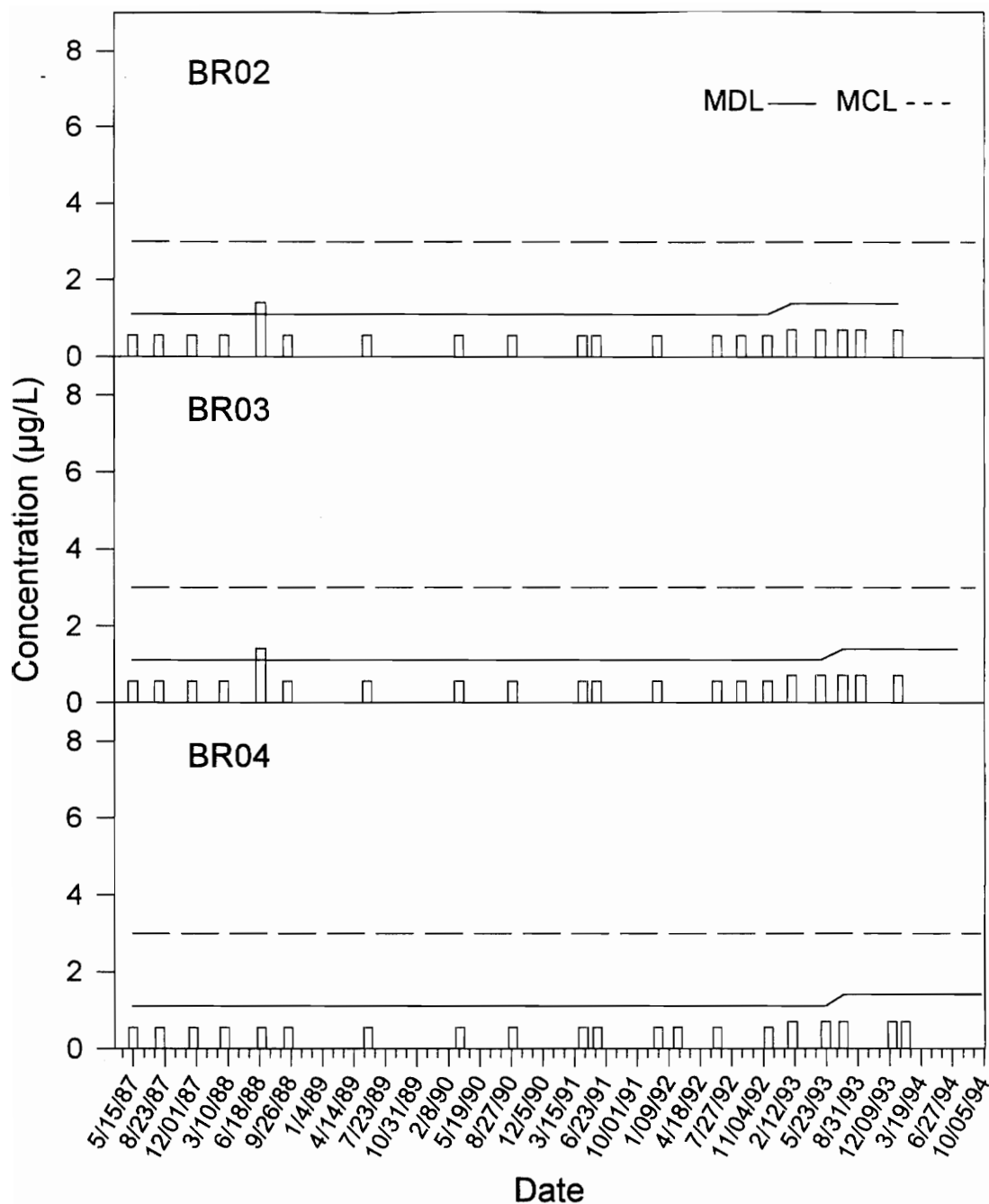


Figure 5. Aqueous Atrazine Concentrations at BR02, BR03, and BR04, stations on tributaries to Lake Manassas. MDL denotes the method detection limit (1.11 and 1.4 µg/L). MCL denotes the Maximum Contaminant Level for drinking water (3 µg/L). All values below the MDL are shown as one-half the MDL.

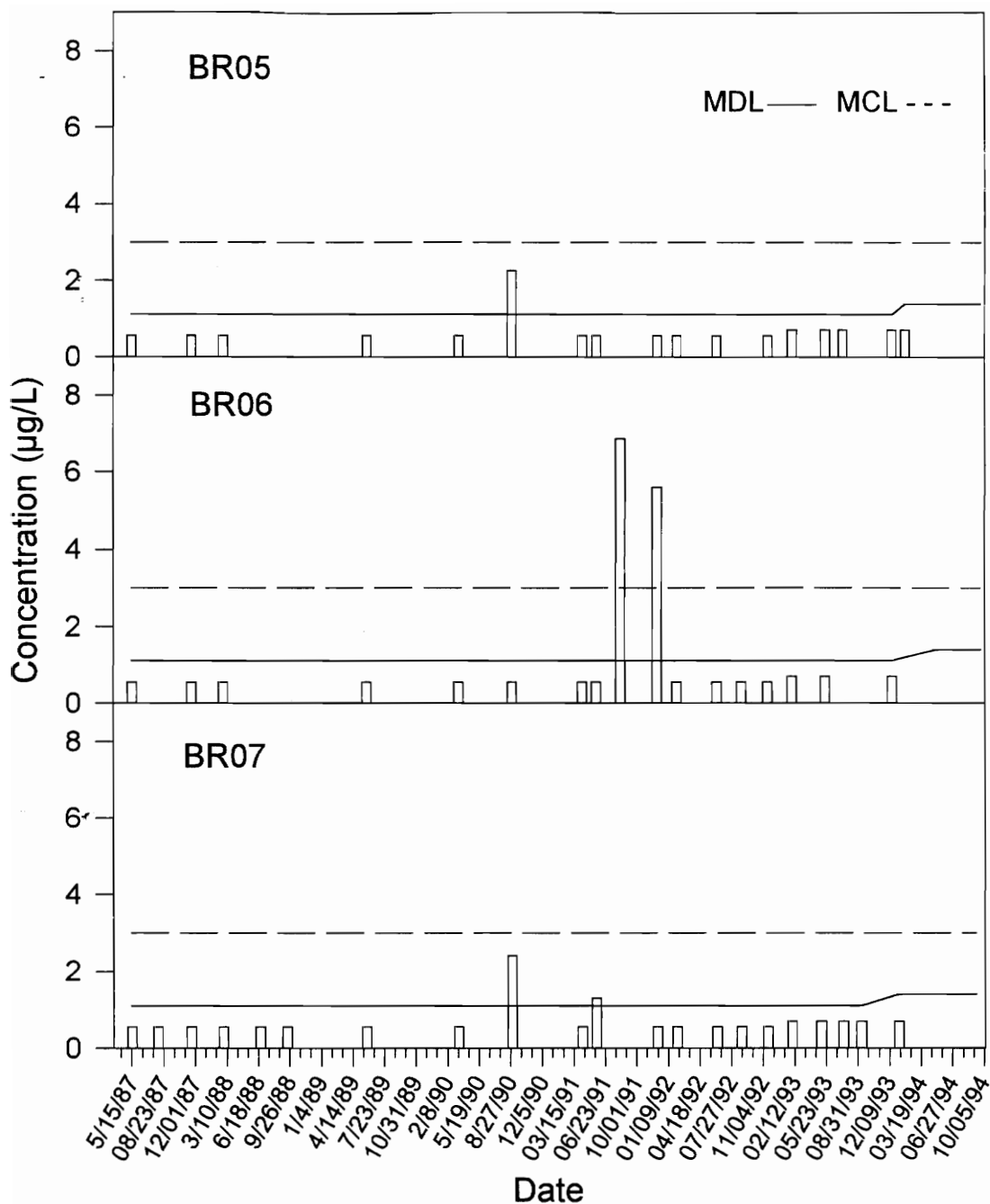


Figure 6. Aqueous Atrazine Concentrations at BR05, BR06, and BR07, stations on tributaries to Lake Manassas. MDL denotes the method detection limit (1.11 and 1.4 µg/L). MCL denotes the Maximum Contaminant Level for drinking water (3 µg/L). All values below the MDL are shown as one-half the MDL.

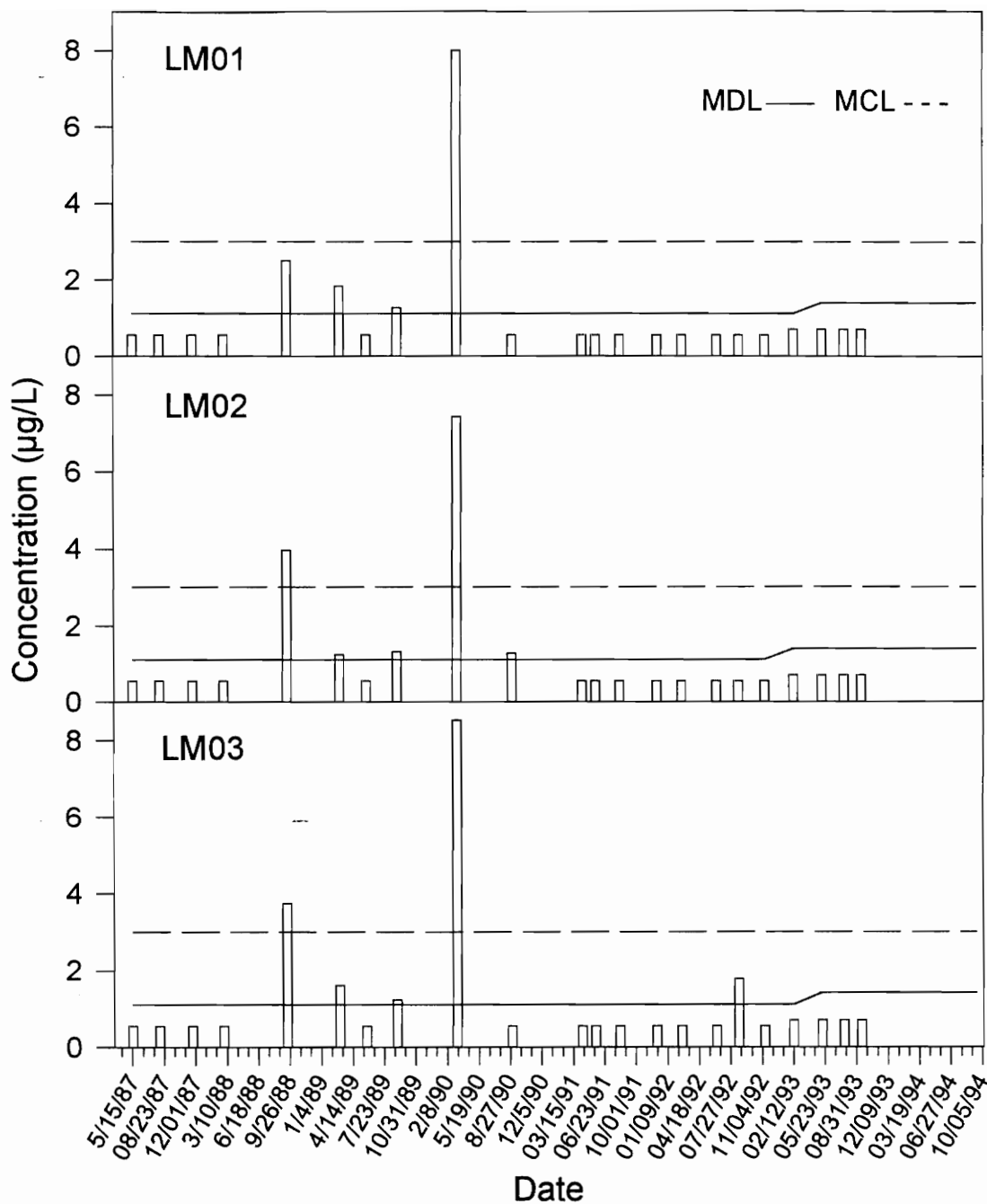


Figure 7. Aqueous Atrazine Concentrations at LM01, LM02, and LM03, stations on Lake Manassas. MDL denotes the method detection limit (1.11 and 1.4 µg/L). MCL denotes the Maximum Contaminant Level for drinking water (3 µg/L). All values below the MDL are shown as one-half the MDL.

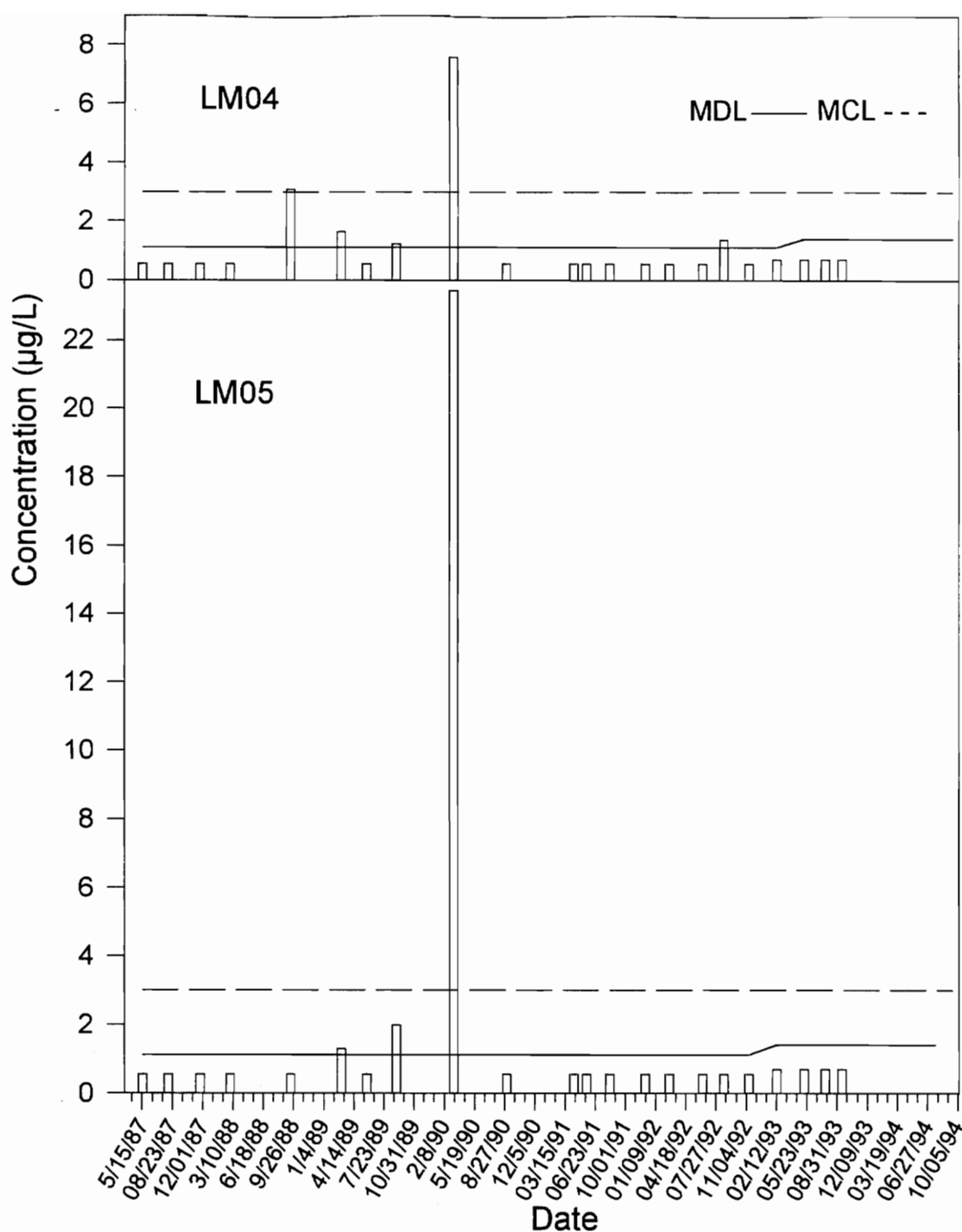


Figure 8. Aqueous Atrazine Concentrations at LM04 and LM05, stations on Lake Manassas. MDL denotes the method detection limit (1.11 and 1.4 $\mu\text{g/L}$). MCL denotes the Maximum Contaminant Level for drinking water (3 $\mu\text{g/L}$). All values below the MDL are shown as one-half the MDL.

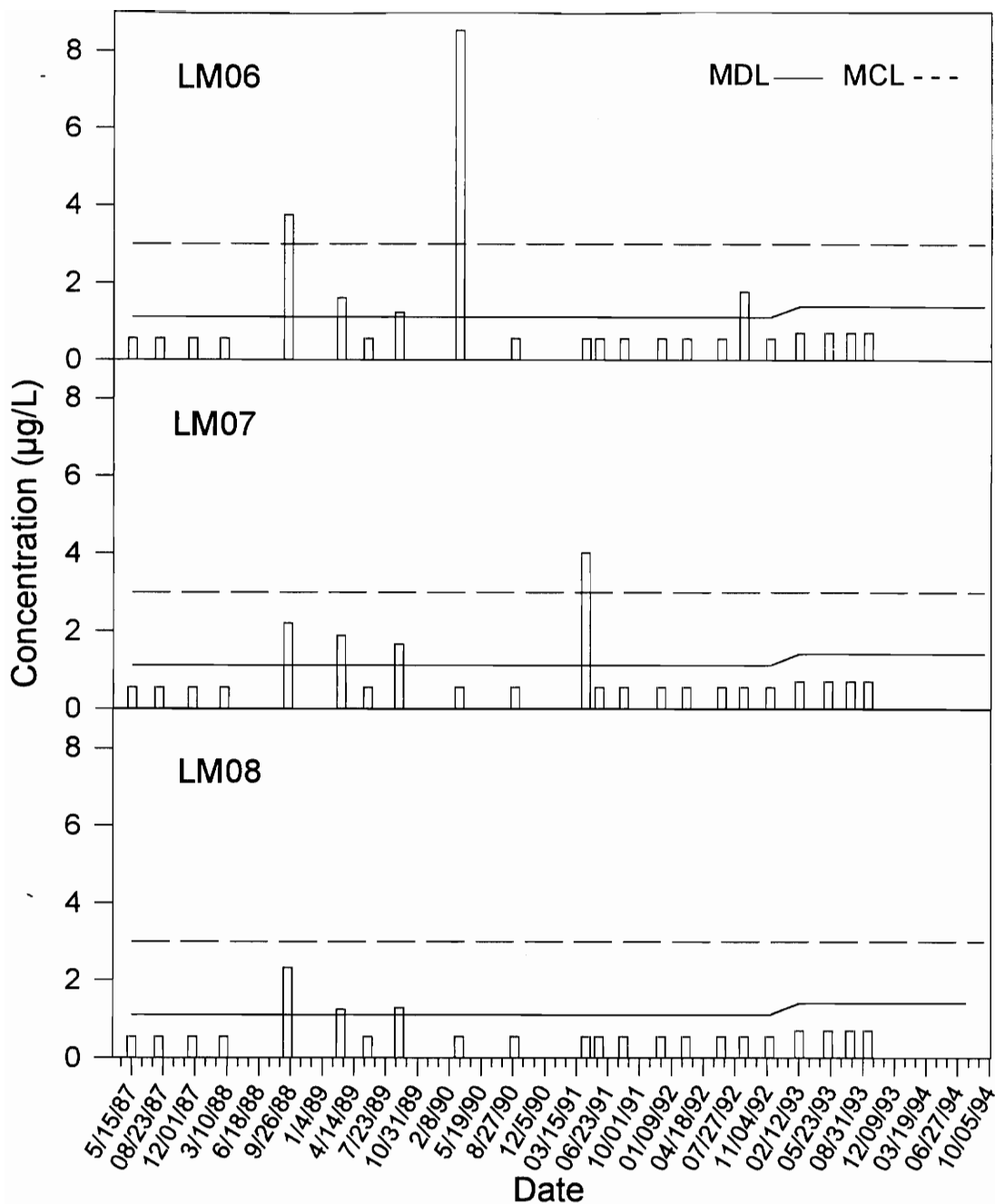


Figure 9. Aqueous Atrazine Concentrations at LM06, LM07, and LM08, stations on Lake Manassas. MDL denotes the method detection limit (1.11 and 1.4 µg/L). MCL denotes the Maximum Contaminant Level for drinking water (3 µg/L). All values below the MDL are shown as one-half the MDL.

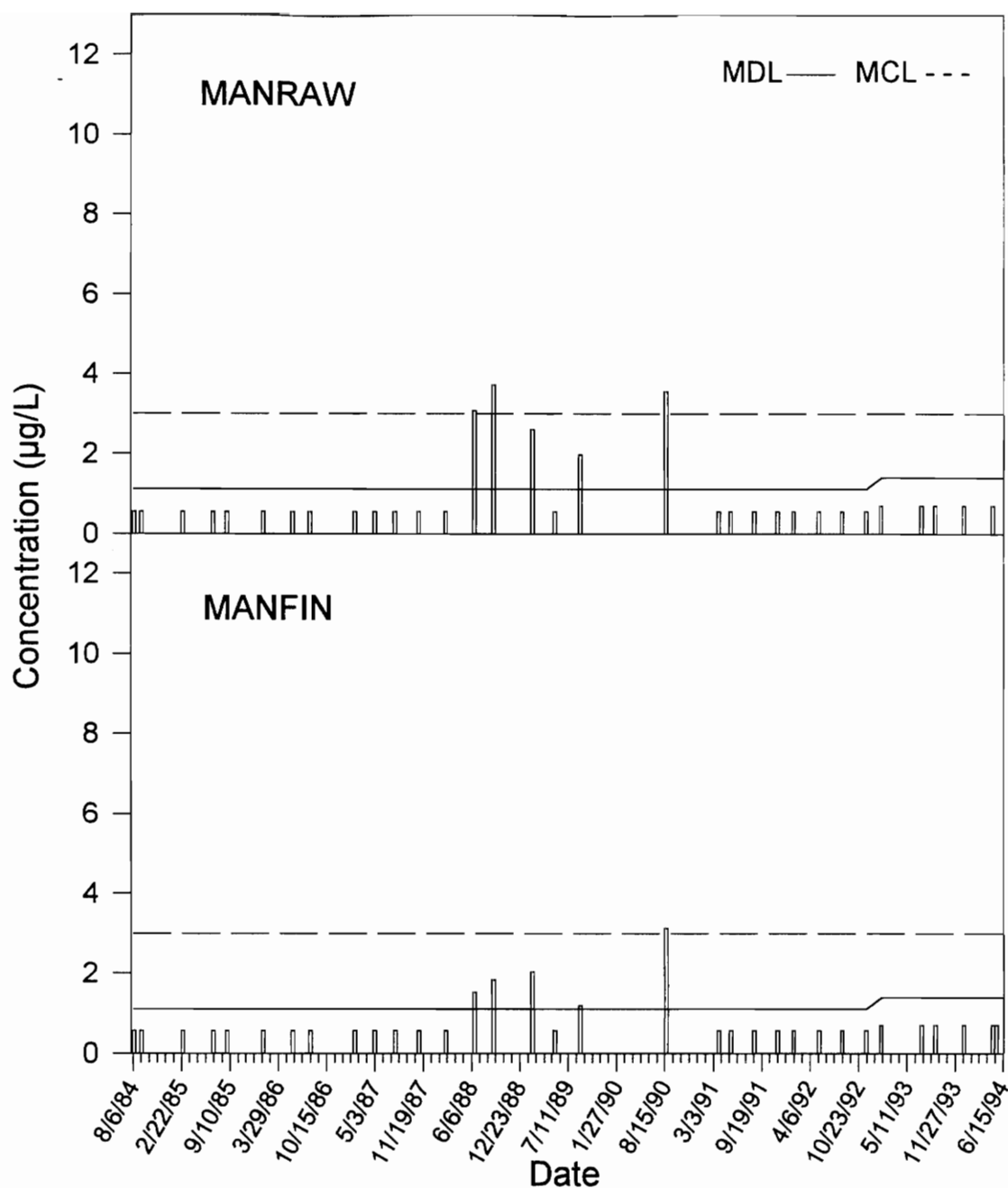


Figure 10. Aqueous Atrazine Concentrations at MANRAW and MANFIN, stations at the intake (MANRAW) and outlet (MANFIN) of the Lake Manassas Water Treatment Plant. MDL denotes the method detection limit (1.11 and 1.4 µg/L). MCL denotes the Maximum Contaminant Level for drinking water (3 µg/L). All values below the MDL are shown as one-half the MDL.

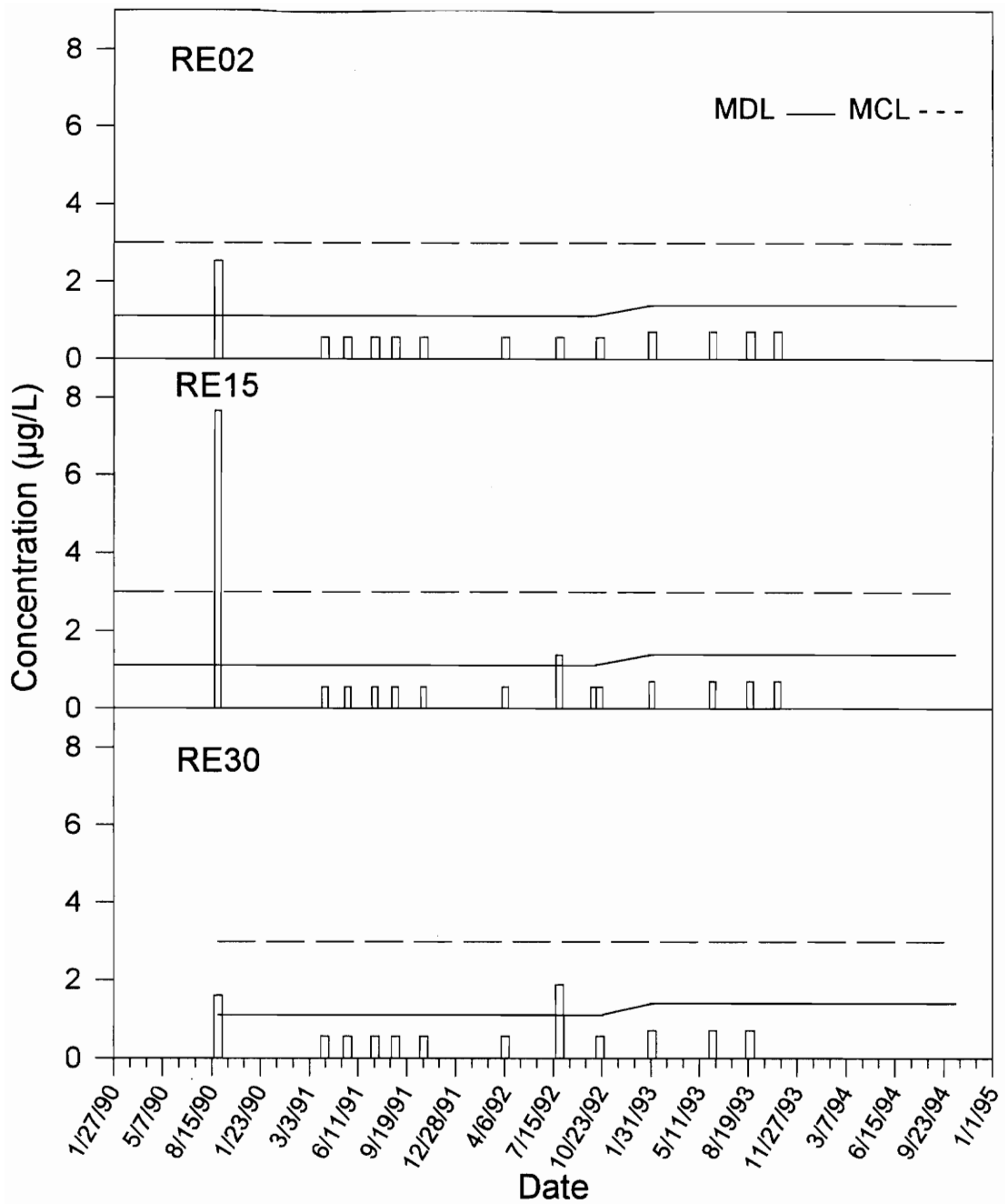


Figure 11. Aqueous Atrazine Concentrations at RE02, RE15, and RE30, stations on the Occoquan Reservoir. MDL denotes the method detection limit (1.11 and 1.4 µg/L). MCL denotes the Maximum Contaminant Level for drinking water (3 µg/L). All values below the MDL are shown as one-half the MDL.

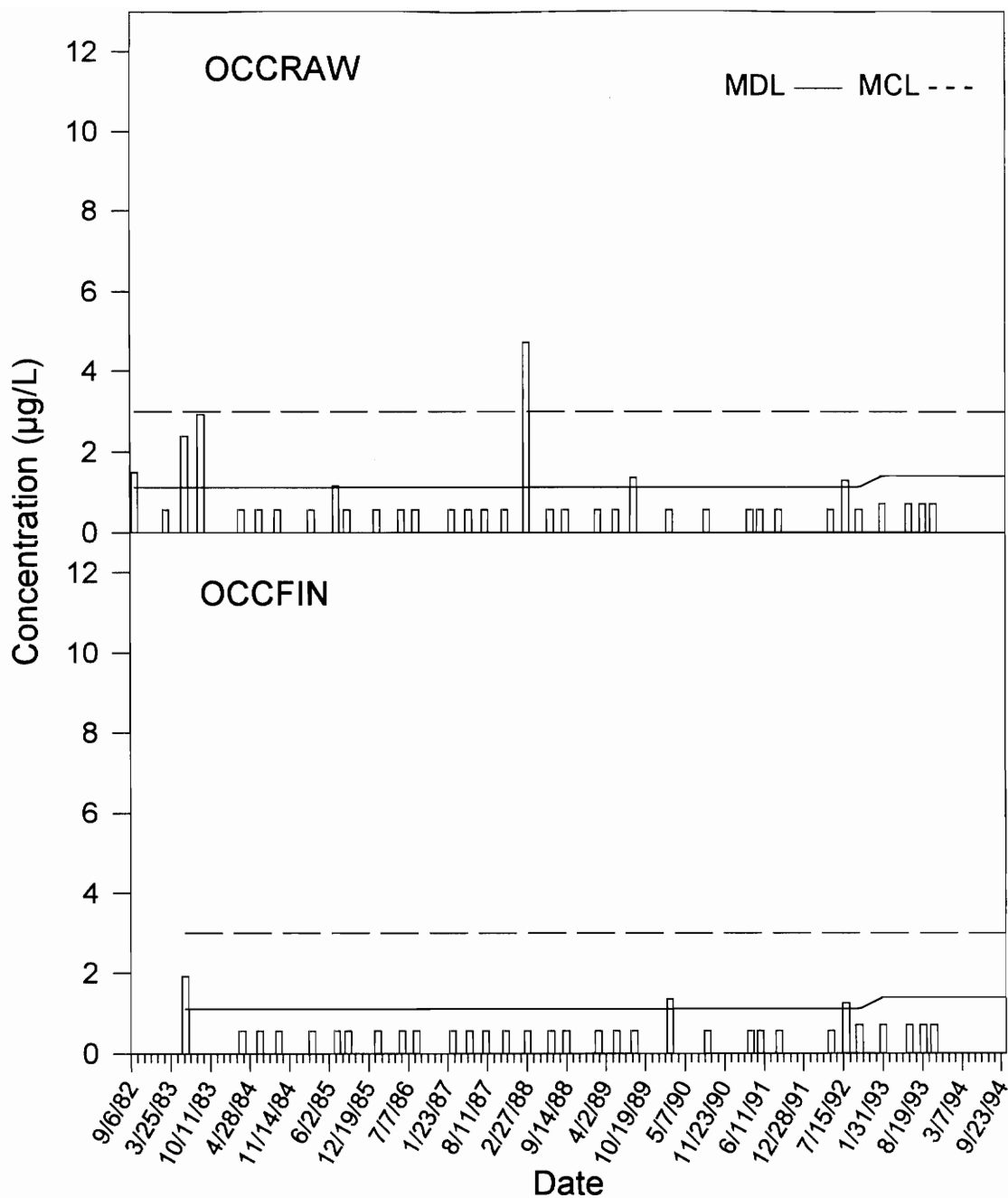


Figure 12. Aqueous Atrazine Concentrations at OCCRAW and OCCFIN, stations at the intake (OCCRAW) and outlet (OCCFIN) of the Lorton Water Treatment Plant. MDL denotes the method detection limit (1.11 and 1.4 µg/L). MCL denotes the Maximum Contaminant Level for drinking water (3 µg/L). All values below the MDL are shown as one-half the MDL.

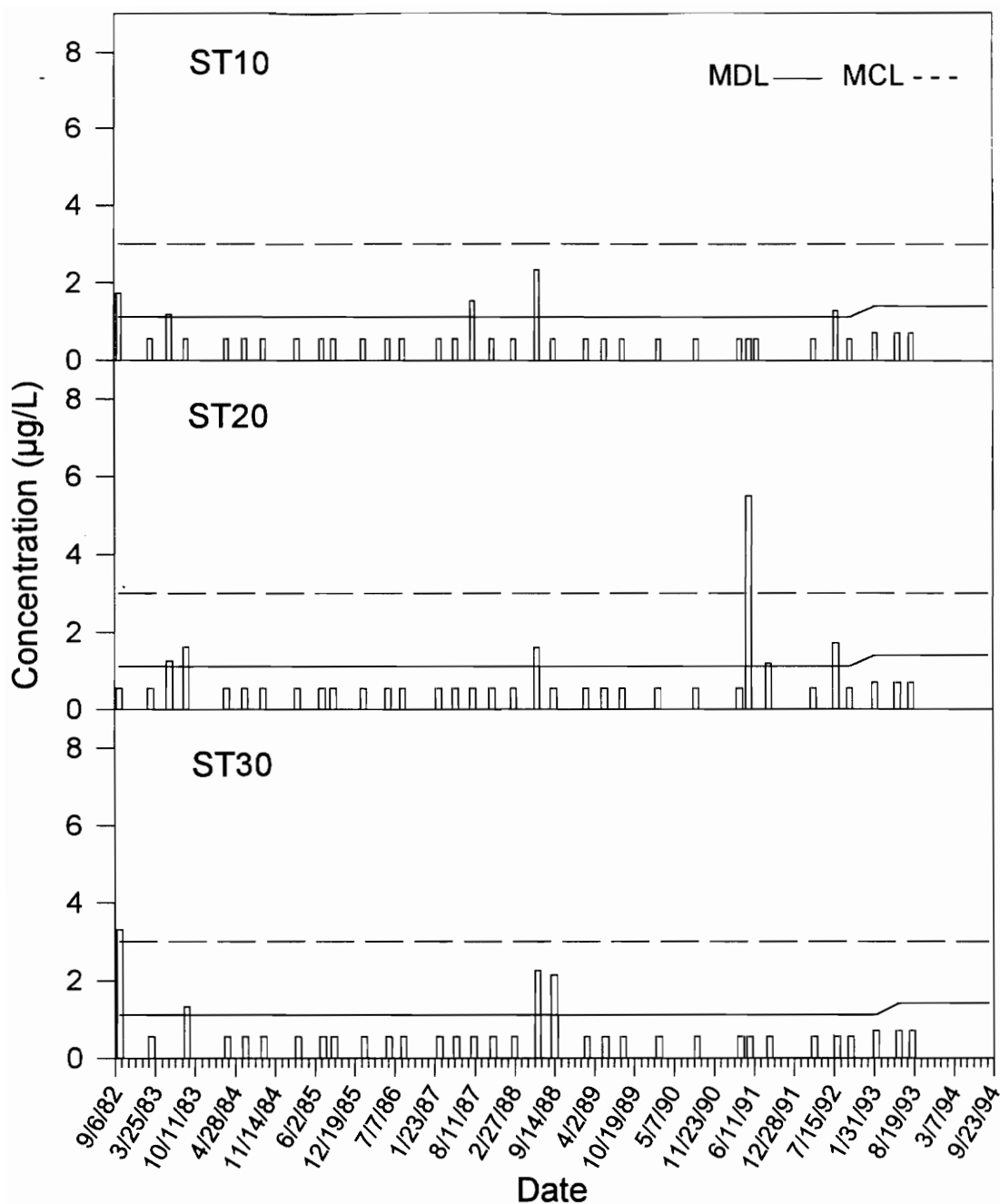


Figure 13. Aqueous Atrazine Concentrations at ST10, ST20, and ST30, stations on tributaries to the Occoquan Reservoir. MDL denotes the method detection limit (1.11 and 1.4 µg/L). MCL denotes the Maximum Contaminant Level for drinking water (3 µg/L). All values below the MDL are shown as one-half the MDL.

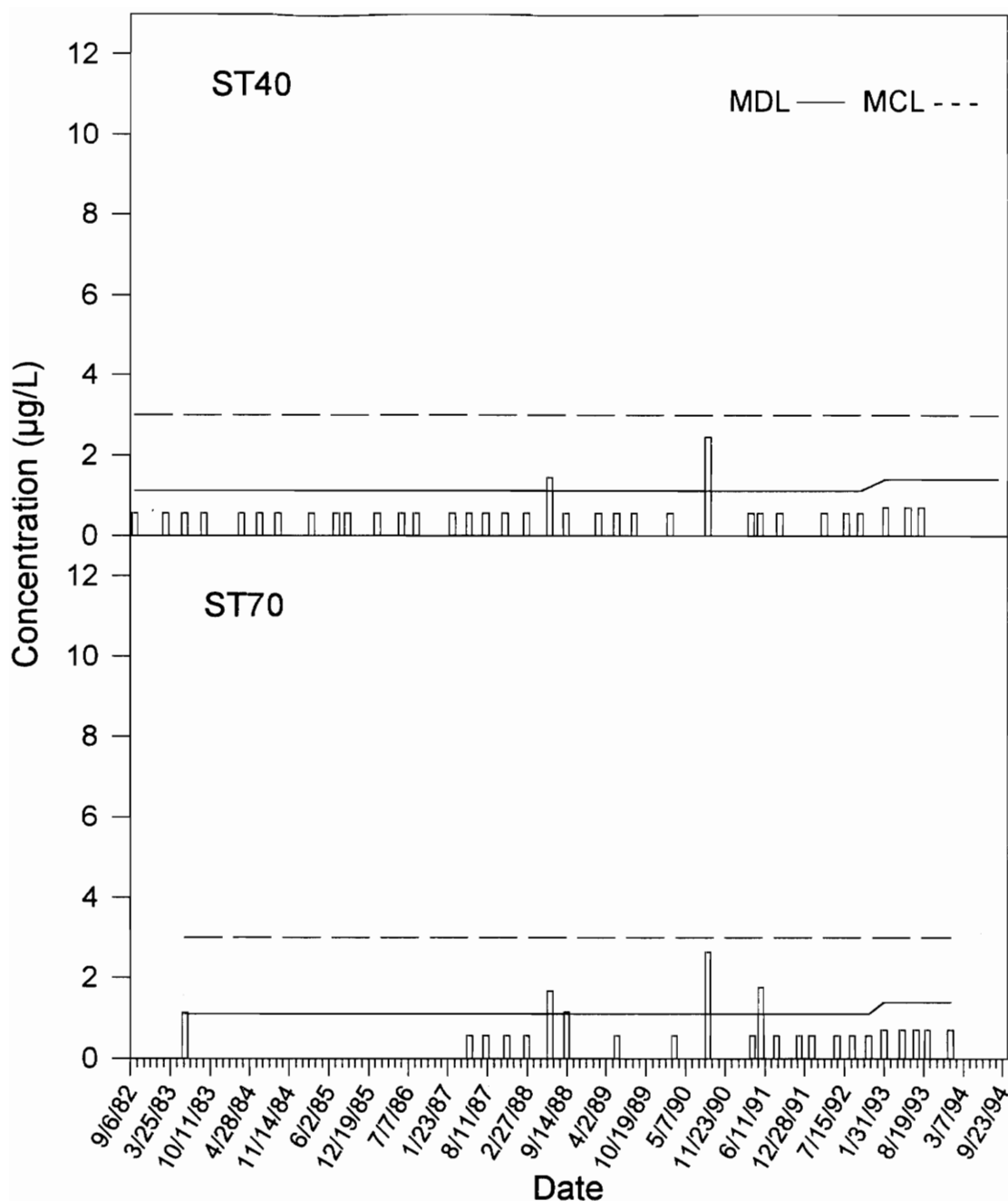


Figure 14. Aqueous Atrazine Concentrations at ST40 and ST70, stations on tributaries to the Occoquan Reservoir. MDL denotes the method detection limit (1.11 and 1.4 µg/L). MCL denotes the Maximum Contaminant Level for drinking water (3 µg/L). All values below the MDL are shown as one-half the MDL.

2. Sediment

Atrazine concentrations in sediment are shown in Figures 15-18. The MDL (0.8 mg/kg) is represented by a line, and all values below this line are shown as one-half of the MDL.

Eight detections occurred, all but one of which were during the spring samplings of 1990 and 1991 in Lake Manassas. The one exception was a sample from RE02, near the Occoquan Dam, taken in the Fall of 1992. The basinwide mean concentration for samples containing atrazine above the MDL was 8.81 mg/kg, and the median was 8.02 mg/kg. When <MDL and ND values were included as one-half of the MDL, the mean became 0.81 mg/kg and the median became 0.40 mg/kg.

3. Fish

Atrazine was only detected once in fish, in the organs of a largemouth bass, as shown in Figure 19. All other atrazine concentrations in fish were below the MDL.

B. Aqueous Atrazine Concentrations and Rainfall

The relationship between rainfall and aqueous atrazine concentrations was investigated. Daily rainfall was recorded at the Occoquan Laboratory and at the Lorton Water Treatment Plant. Table 11 shows detections which corresponded with rainfall amounts of above 0.1 in. The rainfall amounts shown are the sum of the amount recorded on the day the sample was collected and the amounts from the two days prior to the sample collection date. Rainfall data from the gage closest to each station was used. Concentrations in the table are from various stations. These detections accounted for 20 out of the 87 detections (23%).

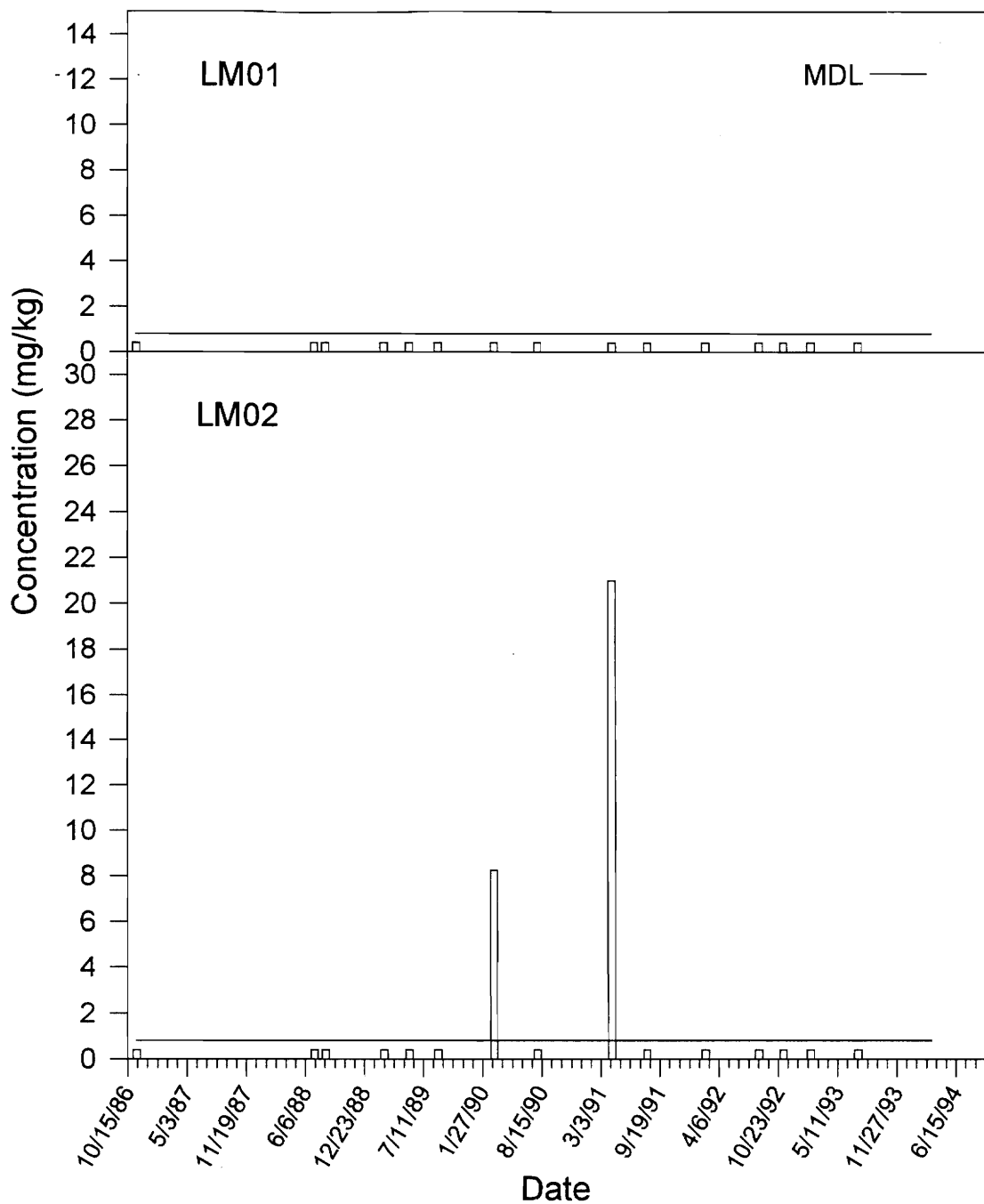


Figure 15. Atrazine Concentrations in Sediment obtained from LM01 and LM02, stations on Lake Manassas. MDL denotes the method detection limit (0.8 mg/kg). All values below the MDL are shown as one-half the MDL.

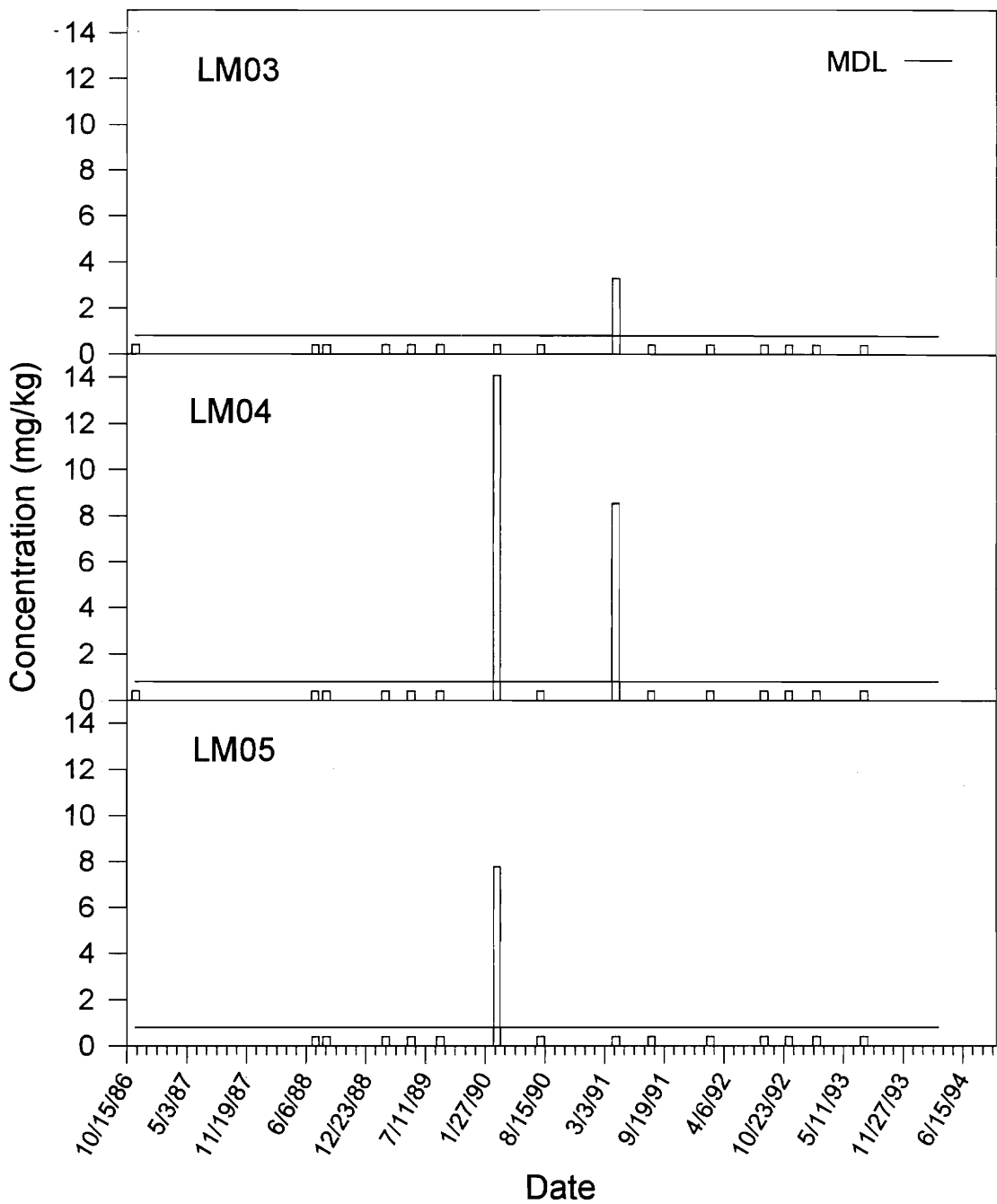


Figure 16. Atrazine Concentrations in Sediment obtained from LM03, LM04, and LM05, stations on Lake Manassas. MDL denotes the method detection limit (0.8 mg/kg). All values below the MDL are shown as one-half the MDL.

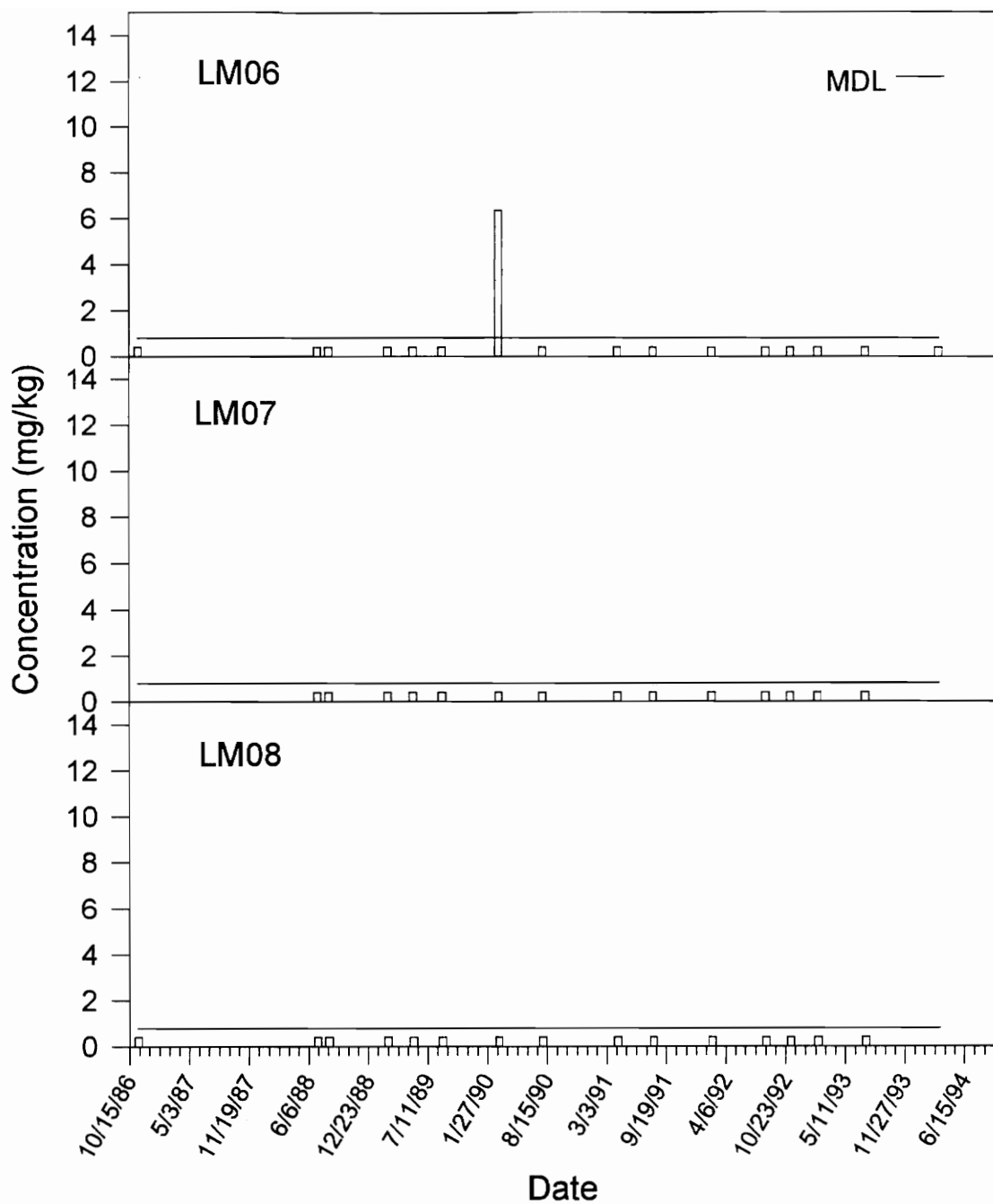


Figure 17. Atrazine Concentrations in Sediment obtained from LM06, LM07, and LM08, stations on Lake Manassas. MDL denotes the method detection limit (0.8 mg/kg). All values below the MDL are shown as one-half the MDL.

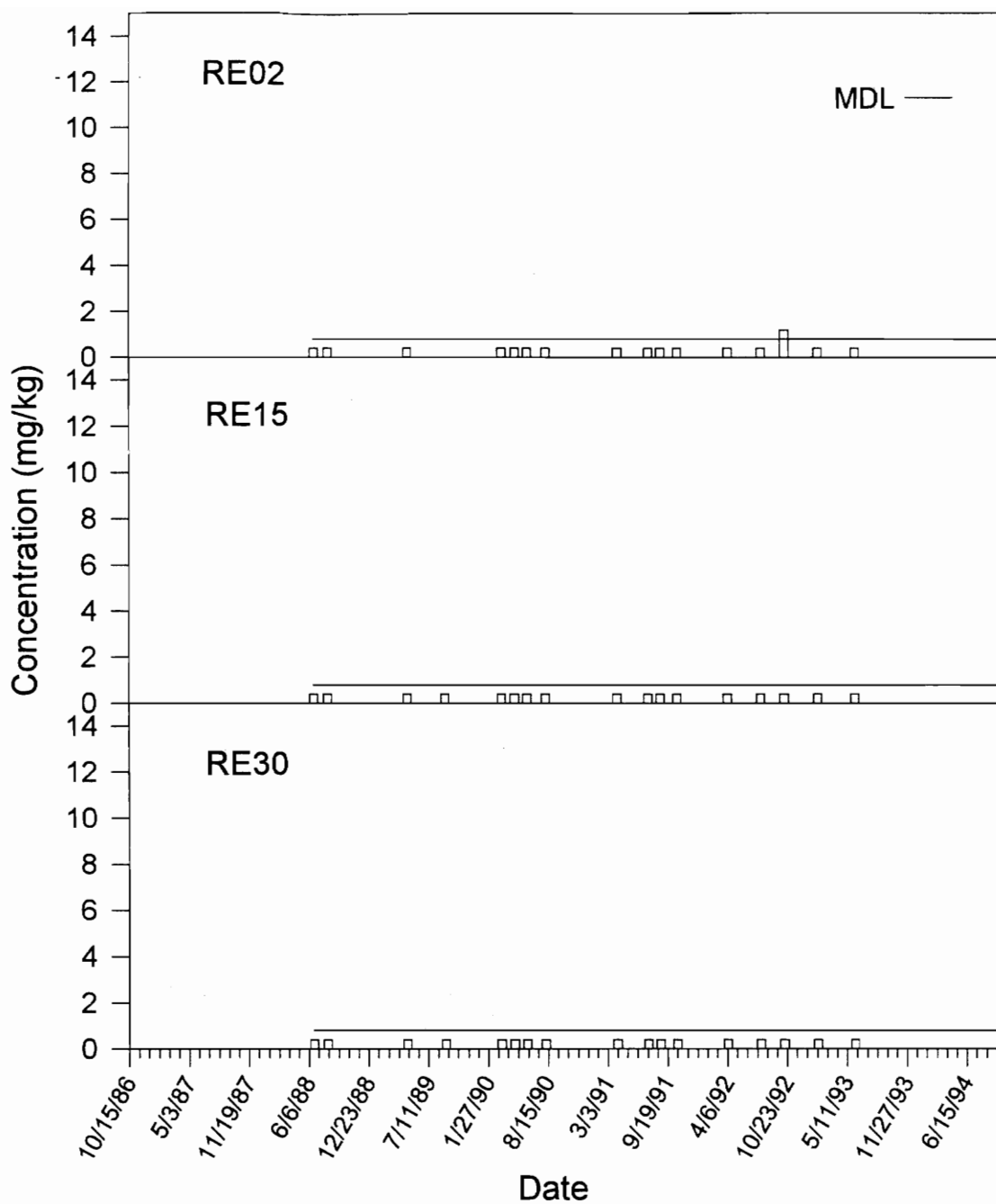


Figure 18. Atrazine Concentrations in Sediment obtained from RE02, RE15, and RE30, stations on the Occoquan Reservoir. MDL denotes the method detection limit (0.8 mg/kg). All values below the MDL are shown as one-half the MDL.

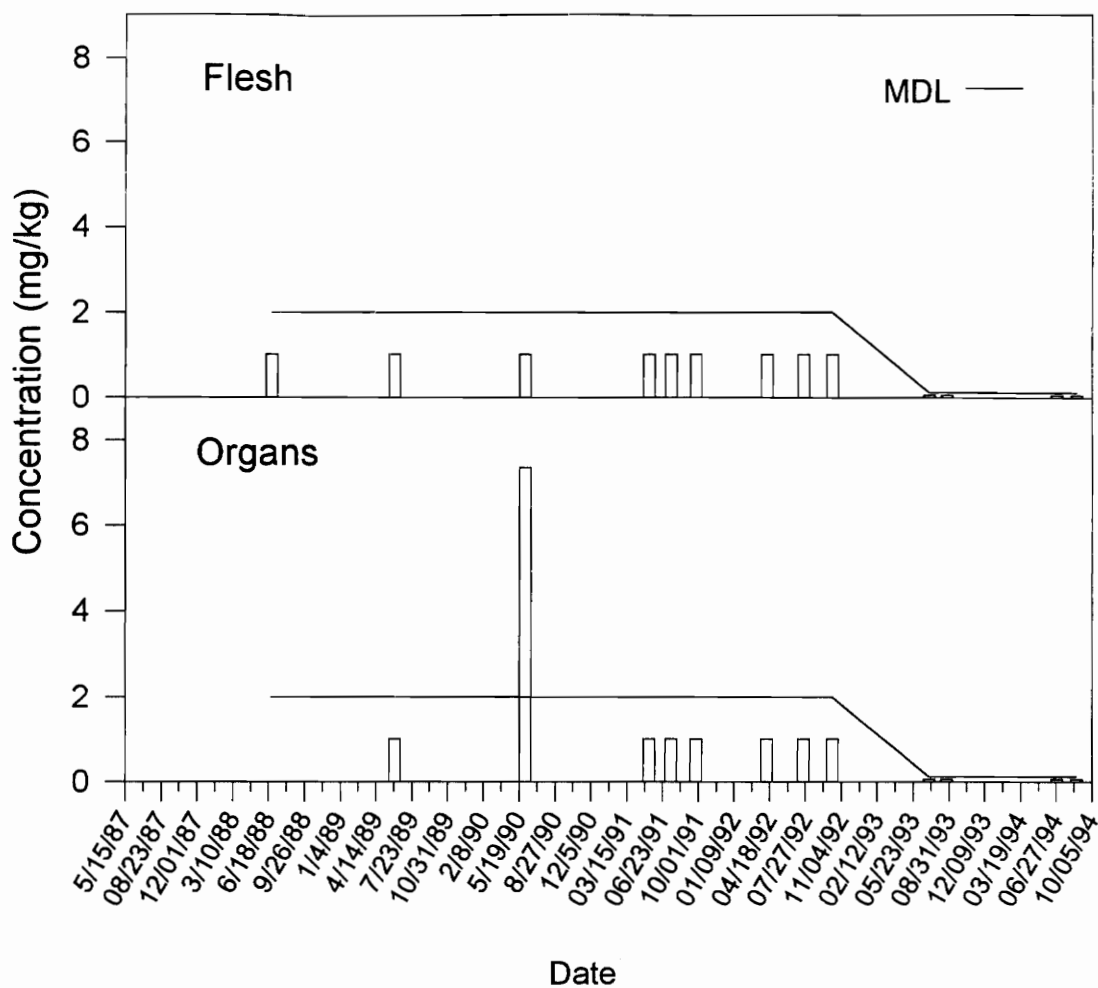


Figure 19. Atrazine concentrations in Largemouth Bass obtained from RE15, a station on the Occoquan Reservoir. Concentrations shown are on a wet weight basis. MDL denotes the method detection limit (2.00 and 0.12 mg/kg). All values below the MDL are shown as one-half the MDL.

Table 11. Rainfall and Atrazine Concentrations in Water

SOC Sampling Date	3 Day Composite Rainfall (in.)	Atrazine Concentration ($\mu\text{g/L}$)
9/29/82	1.10	1.49
9/29/82	1.10	3.31
6/7/83	0.49	1.17
6/7/83	0.29	2.38
6/7/83	0.29	1.25
6/7/83	0.29	1.14
7/11/85	0.63	1.15
2/22/89	0.27	2.60
8/23/89	0.18	1.36
8/30/89	0.71	1.26
8/29/90	0.14	2.46
8/29/90	0.14	1.28
5/20/91	0.16	5.51
12/2/91	2.01	5.61
7/27/92	1.65	1.28
7/28/92	0.59	1.88
7/28/92	0.59	1.38
7/29/92	0.57	1.29
8/18/92	0.12	1.36
8/19/92	0.12	1.77

C. Concurrent Atrazine Detections

Figures 20-24 show atrazine concentrations at all stations in all matrices on or about dates when multiple detections occurred. From left to right, the stations are in approximate upstream to downstream order. The MDLs for each matrix and the MCL for water are shown.

D. Aqueous Atrazine Concentrations Measured at Water Treatment Plants

The pre- and post-treatment atrazine concentrations and resulting percent removals for the two water treatment plants (Lorton and Lake Manassas) are shown in Table 12. These are only the data points where a value above the detection limit was found in the raw water and the raw and finished waters were sampled on the same day.

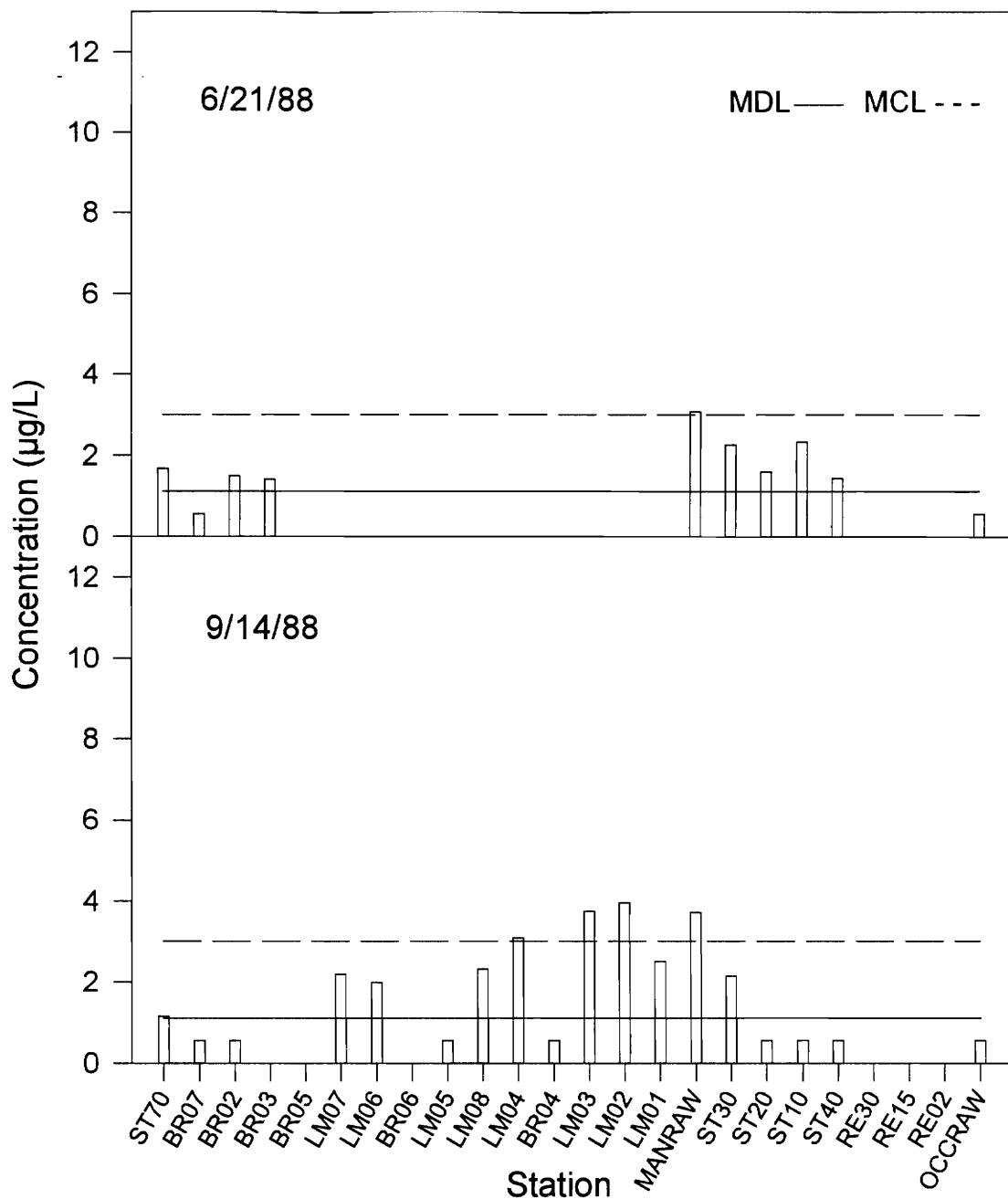


Figure 20. Atrazine Concentrations at all Stations on or about 6/21/88 and 9/14/88. Only water data were available for these dates. MDL denotes the method detection limit (1.11 µg/L). MCL denotes the Maximum Contaminant Level for drinking water (3 µg/L). All values below the MDL are shown as one-half the MDL.

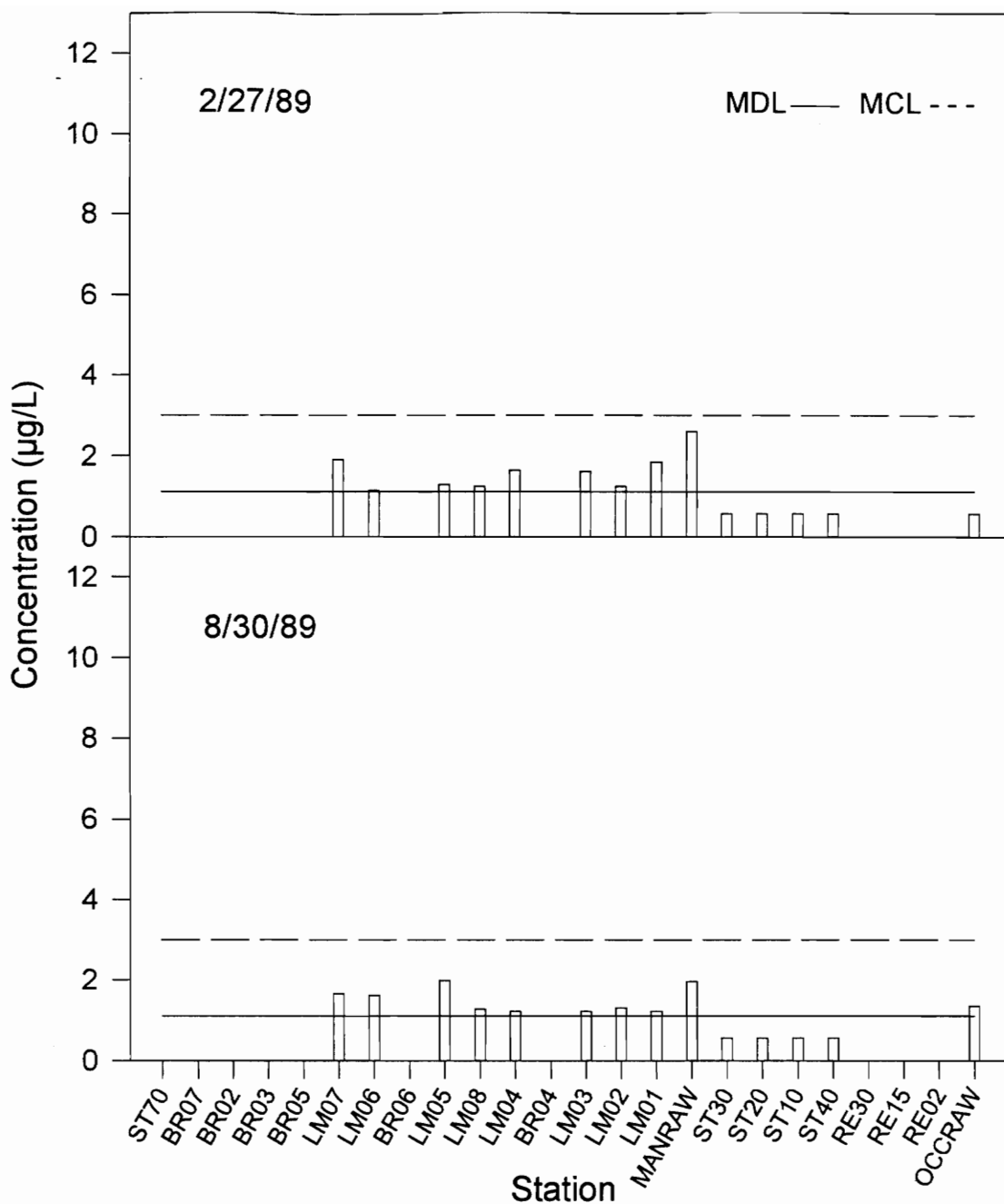


Figure 21. Atrazine Concentrations at all Stations on or about 2/27/89 and 8/30/89. Only water data were available for these dates. MDL denotes the method detection limit (1.11 µg/L). MCL denotes the Maximum Contaminant Level for drinking water (3 µg/L). All values below the MDL are shown as one-half the MDL.

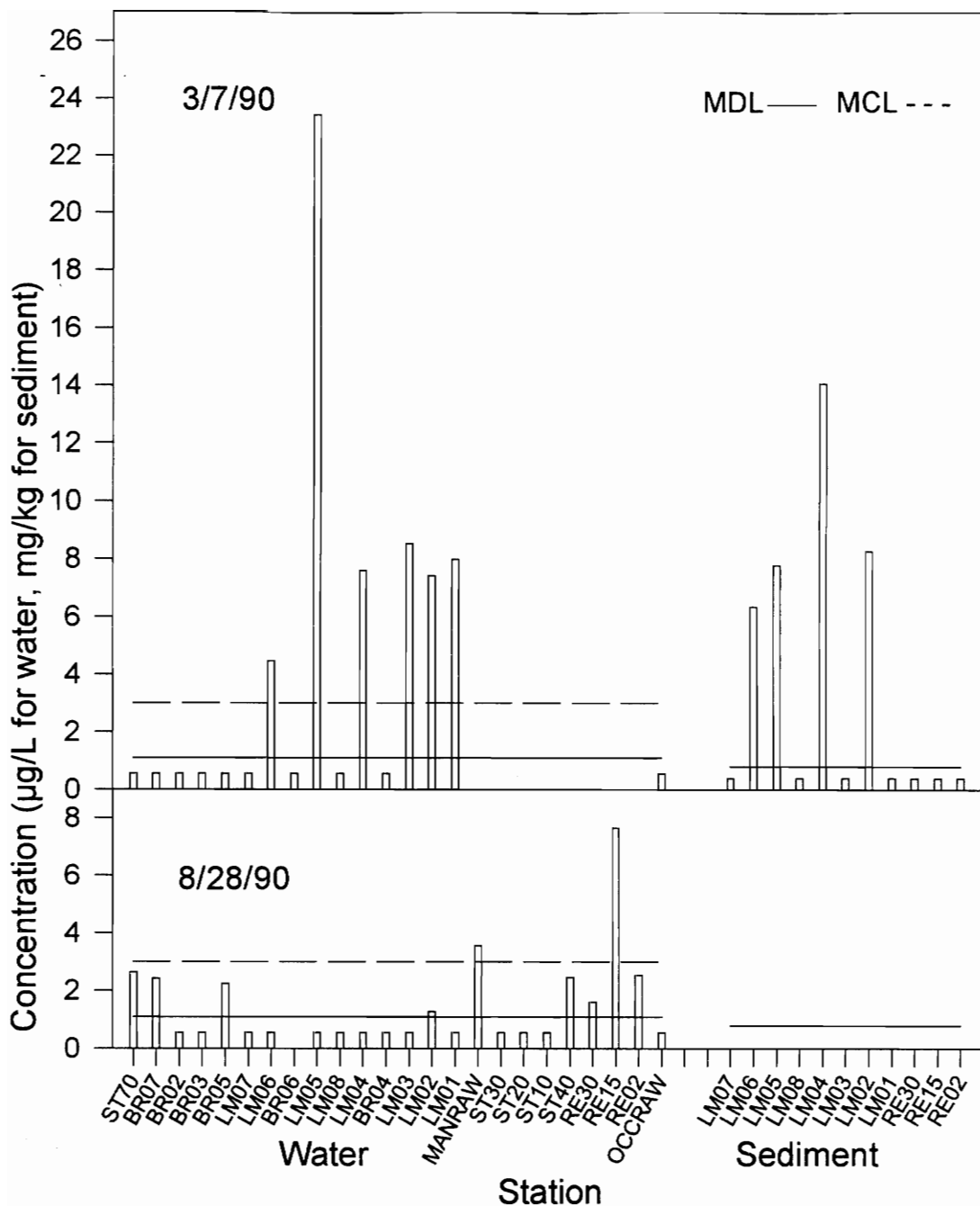


Figure 22. Atrazine Concentrations at all Stations on or about 3/7/90 and 8/28/90. Both water and sediment data were available for 3/7/90. MDL denotes the method detection limit (1.11 µg/L for water, 0.8 mg/kg for sediment). MCL denotes the Maximum Contaminant Level for drinking water (3 µg/L). All values below the MDL are shown as one-half the MDL.

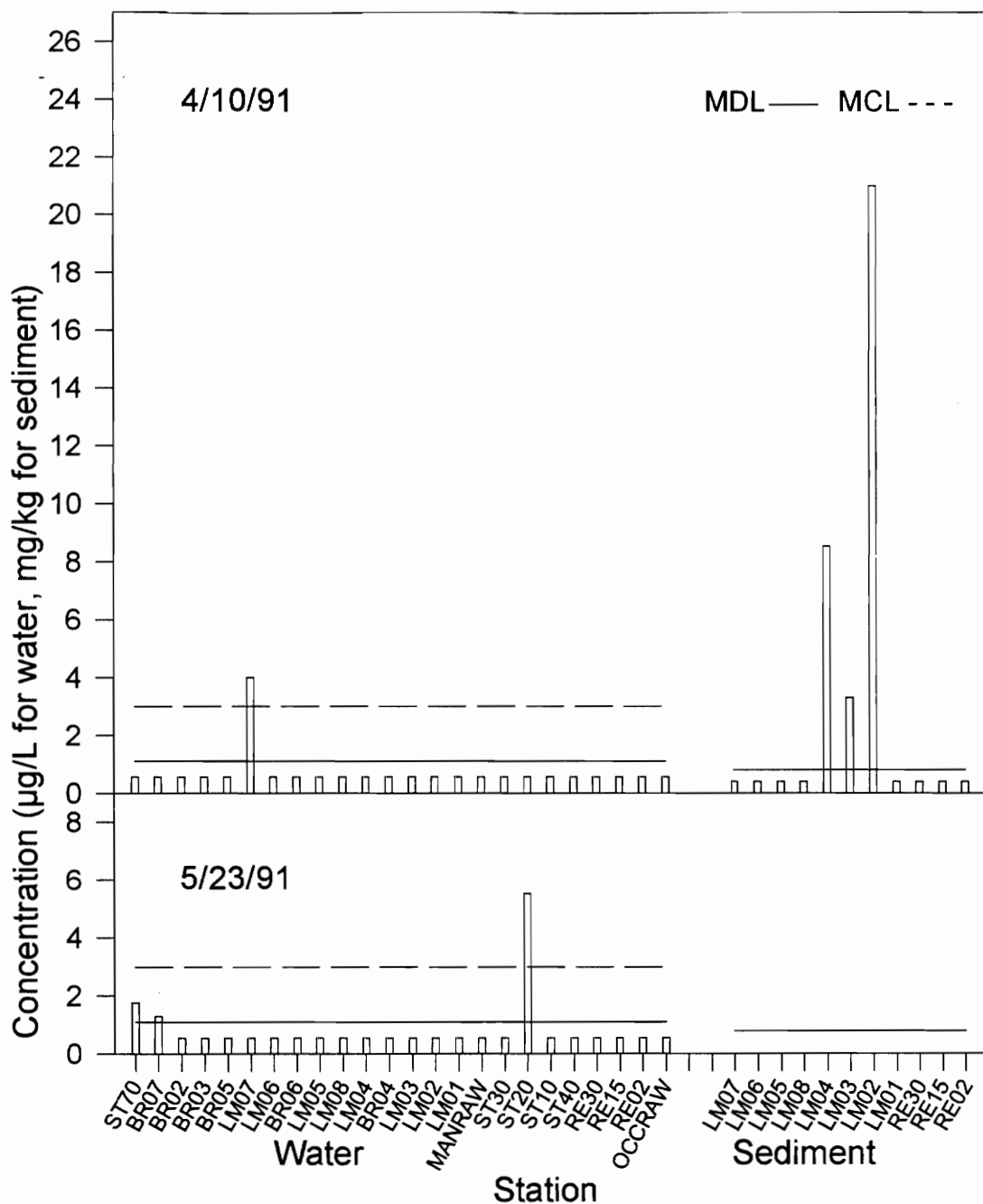


Figure 23. Atrazine Concentrations at all Stations on or about 4/10/91 and 5/23/91. Both water and sediment data were available for 4/10/91. MDL denotes the method detection limit (1.11 µg/L for water, 0.8 mg/kg for sediment). MCL denotes the Maximum Contaminant Level for drinking water (3 µg/L). All values below the MDL are shown as one-half the MDL.

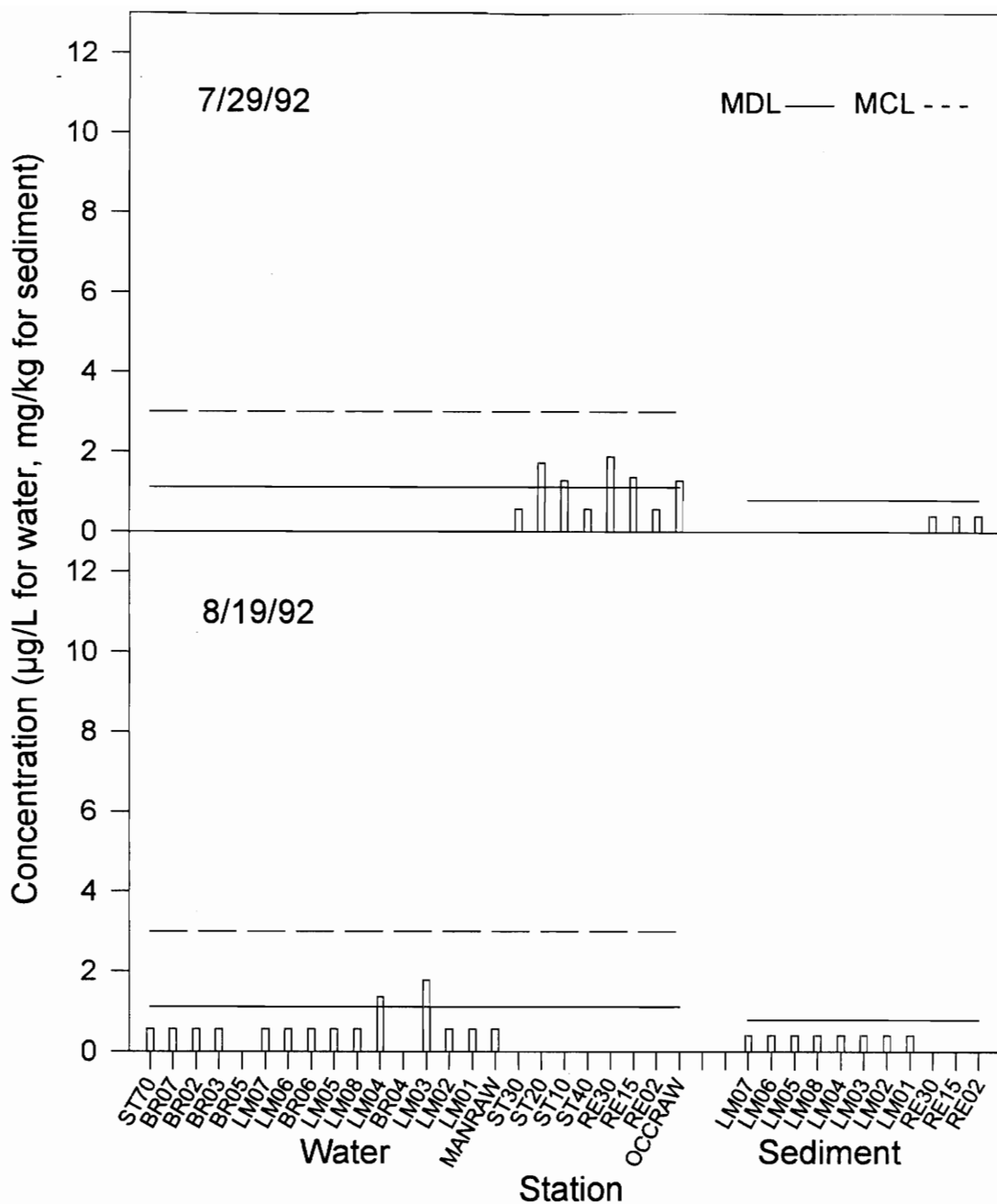


Figure 24. Atrazine Concentrations at all Stations on or about 7/29/92 and 8/19/92. Some water and sediment data were available for both dates. MDL denotes the method detection limit ($1.11 \mu\text{g/L}$ for water, 0.8 mg/kg for sediment). MCL denotes the Maximum Contaminant Level for drinking water ($3 \mu\text{g/L}$). All values below the MDL are shown as one-half the MDL.

Table 12. Atrazine Removal in Lorton and Lake Manassas Water Treatment Plants

Plant	Date	Raw Conc. ($\mu\text{g/L}$)	Finished Conc. ($\mu\text{g/L}$)	% Removal
Lorton	9/29/82	1.49	NS ¹	-
	6/7/83	2.38	1.92	19.3
	8/29/83	2.93	NS	-
	7/11/85	1.15	ND ²	(51.3) ³
	2/29/88	4.73	ND	(88.2) ³
	8/23/89	1.36	NS	-
	7/29/92	1.29	1.26	2.30
Plant Average				40.3
Lake	6/27/88	3.08	1.53	50.3
Manassas	9/14/88	3.73	1.83	50.9
	2/22/89	2.60	2.04	21.5
	9/7/89	1.97	1.2	39.1
	8/28/90	3.57	3.13	12.3
Plant Average				34.8
Average for both plants				37.2

¹NS = No sample collected on this date

²ND = Not detected or < MDL

³A finished water concentration of one-half the MDL (0.56) was assumed

The Lake Manassas Water Treatment Plant did not use any specific organic removal process, such as GAC, PAC, or oxidants other than the amount of chlorine needed for disinfection. The Lorton Water Treatment Plant sporadically used powdered activated carbon (PAC) at the intake in summer to combat taste and odor problems from algal blooms until February 1995. Since then, no PAC has been used and potassium permanganate has been used for taste and odor control.

E. Development of Fish Extraction Procedure

The extraction and cleanup procedure developed for OWML's fish samples consisted of methanol extraction followed by C-18 and alumina SPE cleanup. The procedure used equipment and materials already available at OWML. Recoveries varied from 15-92%, with an average of

60% (see Table 13). One compound, Benzo(g,h,i)perylene, was not recovered. Percent recoveries tended to be lowest for the very early and very late eluting compounds.

1. Qualitative results

Other extraction methods that were tested and rejected included soxhlet extraction with methylene chloride, sonication with acetone/hexane, and shaking with acetonitrile. Methylene chloride extract mixed with water clogged a C-18 column. The shaking method didn't seem to solvate enough fat and did not recover Fensulfothion, Ronnel, Di-n-butyl phthalate, and Bis(2-ethylhexyl) phthalate.

Cleanup methods designed to remove fats that were tried in addition to the C-18 and alumina combination included C-18 or alumina alone and C-18 followed by Florisil. Alumina SPE alone did not remove sufficient amounts of fat from the methylene chloride and acetone/hexane extracts. C-18 alone did not provide sufficient fat removal following acetonitrile or methanol extraction. Some analytes, including atrazine, 2,4,5-T, and Silvex, were not recovered from Florisil.

For the final method, sonication times, solvent volumes, methanol/water ratios, and elution solvents were adjusted to obtain the best recoveries. Addition of NaCl to the methanol was found to have no significant effect on recoveries.

2. QA/QC Results

The results of the various quality control samples and measures for the method developed to analyze fish caught in 1993-94 are shown in this section. Table 13 shows the average recoveries for matrix spikes and surrogates; Table 14 shows the detections in the laboratory blanks; and Table 15 shows the MDL for each compound. Control charts for the two surrogates were developed and presented in Figures 25 and 26.

Table 13. Matrix Spike and Surrogate Recoveries for Fish Extraction Method¹

Compound	Mean % Recovery	Compound	Mean % Recovery
<u>Analytes</u>			
Acenaphthene	69 ± 8	γBHC (Lindane)	73 ± 26
Acenaphthylene	81 ± 8	δBHC	44 ± 12
Anthracene	76 ± 16	Dacthal	60 ± 10
Benzo(a)anthracene	37 ± 22	Dieldrin	40 ± 16
Benzo(a)pyrene	76 ± 30	Hexachlorobenzene	53 ± 11
Benzo(b)fluoranthene	68 ± 16	Heptachlor epoxide	58 ± 9
Benzo(k)fluoranthene	71 ± 21	Mevinphos	26 ± 6
Benzo(g,h,i)perylene	NR ²	Diazinon	29 ± 5
Carbazole	90 ± 18	Mocap	62 ± 11
Chrysene	55 ± 37	Pendimethalin	83 ± 17
Fluoranthene	82 ± 10	Phorate	62 ± 18
Fluorene	80 ± 9	Ronnel	59 ± 16
Naphthalene	42 ± 11	Terbufos	57 ± 13
Phenanthrene	78 ± 12	Vapona	19 ± 3
Pyrene	77 ± 9	Silvex	81 ± 8
Parathion	89 ± 45	2,4,5-T	74 ± 20
Benzyl butyl phthalate	62 ± 17	Atrazine	64 ± 14
Bis(2-ethylhexyl) phthalate	81 ± 28	Carbaryl	28 ± 18
Di-n-butyl phthalate	93 ± 18	Dual (Metolachlor)	57 ± 10
Di-n-octyl phthalate	15 ± 94	Fensulfothion	18 ± 15
Diethyl phthalate	90 ± 13	Heptachlor	37 ± 17
Dimethyl phthalate	29 ± 16	Propazine	58 ± 9
αBHC	92 ± 13	<u>Surrogates</u>	
βBHC	73 ± 11	Terphenyl d ₁₂	89 ± 26
		Fluoranthene d ₁₀	89 ± 29

¹n = 8 for matrix spikes (includes the 7 MDL flesh samples and 1 spiked flesh sample) and n = 57 for surrogates (includes all flesh and organ samples, MDL samples, spikes, and blanks).

²Not recovered, possibly due to its long retention time and the age of the GC column.

Three method blanks using the fish extraction method with solvent alone were analyzed to evaluate contamination. A total of four compounds, all phthalates, were detected in the laboratory blanks. The amounts present were quantified and are shown in Table 14. Concentrations of these compounds in samples were adjusted by subtracting the concentration detected in the blank sample analyzed immediately prior to matrix sample. The blank analyzed with the MDL samples (10/21/95) was applied only to the MDL results.

Table 14. Blank Results for Fish Extraction Method

Compound Found	Concentration ($\mu\text{g/mL}$) in Sample Extract			Mean
	Date Blank Analyzed			
	9/15/95	10/21/95	10/31/95	
Diethyl phthalate	0.06	0.18	0.63	0.26
Di-n-butyl phthalate	-	-	0.01	0.003
Bis(2-ethylhexyl) phthalate	2.41	1.81	0.85	1.69
Di-n-octyl phthalate	0.57	0.37	0.27	0.40

Precision-based MDLs were found by determining the mean and standard deviation of pesticide concentrations in seven replicates of one full matrix spike concentration level. The MDL was calculated by multiplying the standard deviation by the 99.0% t distribution quantile for $7-1 = 6$ degrees of freedom (3.14). The remaining tissue of an actual fish flesh sample in which no contaminants were detected was used to prepare samples for the MDL study. The spike concentration was 0.4 mg/kg wet weight. The calculated MDLs are shown in Table 15.

Table 15. MDL Values for Fish Extraction Method

Compound	MDL (mg/kg wet weight)	Compound	MDL (mg/kg wet weight)
Acenaphthene	0.10	βBHC	0.12
Acenaphthylene	0.10	γBHC (Lindane)	0.6
Anthracene	0.22	δBHC	0.13
Benzo(a)anthracene	0.09	Dacthal	0.11
Benzo(a)pyrene	0.22	Dieldrin	0.11
Benzo(b)fluoranthene	0.10	Hexachlorobenzene	0.10
Benzo(k)fluoranthene	0.10	Heptachlor epoxide	0.18
Benzo(g,h,i)perylene	NR	Mevinphos	0.03
Carbazole	0.10	Diazinon	0.04
Chrysene	0.5	Mocap	0.12
Fluoranthene	0.12	Pendimethalin	0.09
Fluorene	0.11	Phorate	0.17
Naphthalene	0.06	Ronnel	0.08
Phenanthrene	0.14	Terbufos	0.09
Pyrene	0.10	Vapona	0.02
Parathion	0.15	Silvex	0.10
Benzyl butyl phthalate	0.22	2,4,5-T	0.07
Bis(2-ethylhexyl) phthalate	0.8	Atrazine	0.12
Di-n-butyl phthalate	0.25	Carbaryl	0.06
Di-n-octyl phthalate	0.37	Dual (Metolachlor)	0.13
Diethyl phthalate	0.17	Fensulfothion	0.07
Dimethyl phthalate	0.22	Heptachlor	0.18
αBHC	0.17	Propazine	0.11

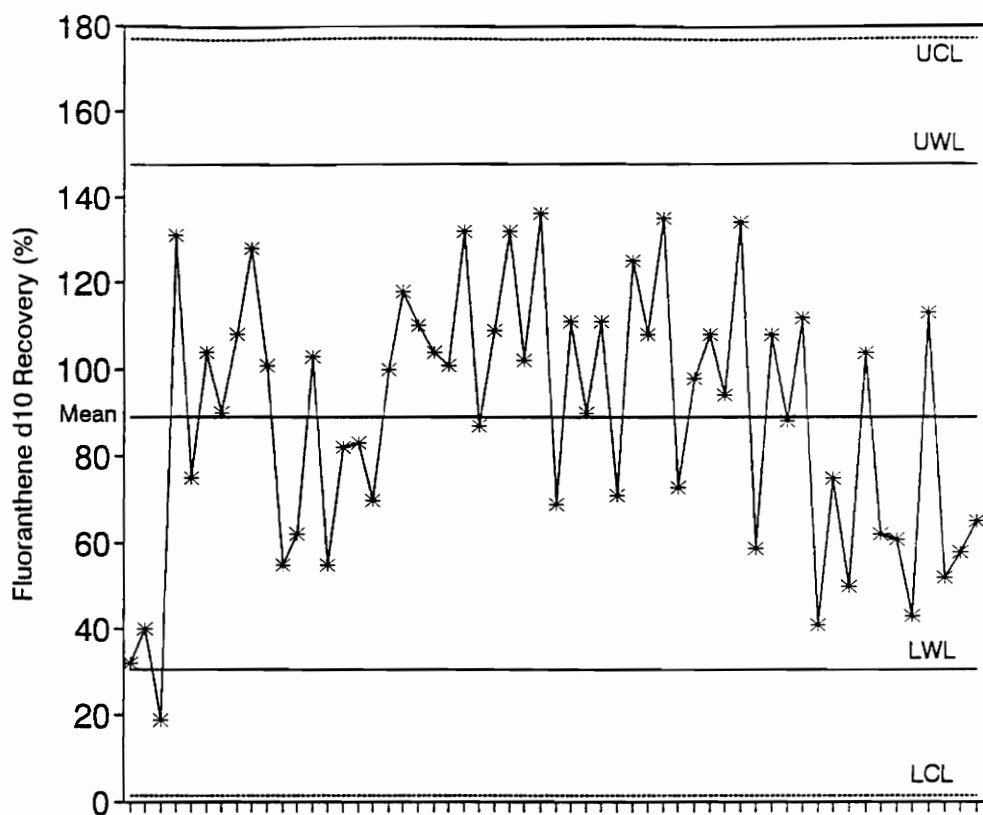


Figure 25. Control Chart for Fluoranthene d₁₀ (surrogate) measured in 1993-94 fish flesh and organ samples. The central line denotes the mean of the recoveries (89%). UCL and LCL denote the upper and lower control limits, located at $\pm 3\sigma$ ($\sigma=29\%$). UWL and LWL denote the upper and lower warning limits, located at $\pm 2\sigma$.

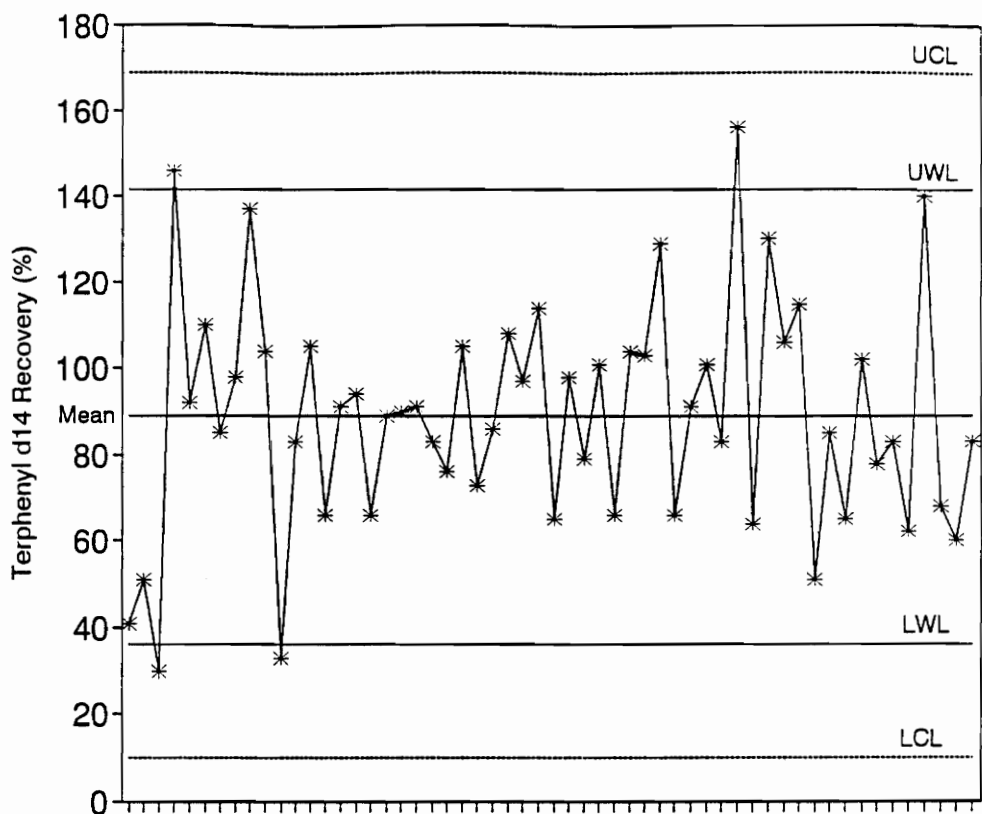


Figure 26. Control Chart for Terphenyl d₁₄ (surrogate) measured in 1993-94 fish flesh and organ samples. The central line denotes the mean of the recoveries (89%). UCL and LCL denote the upper and lower control limits, located at $\pm 3\sigma$ ($\sigma = 26\%$). UWL and LWL denote the upper and lower warning limits, located at $\pm 2\sigma$.

V. DISCUSSION

It often happens in environmental monitoring that contaminants are found in concentrations close to or below levels where they can be confidently detected. While this is certainly preferable to finding large quantities of substances present, it does make it more challenging to analyze the data and draw conclusions from it.

A. Atrazine Occurrence

Very few compounds were detected in the water, sediment, and fish of the Occoquan Watershed, and many of the concentration values were below calculated MDLs. Whenever a particular value, such as the one-half of the MDL used here, is chosen to represent the ND values, the mean will be close to the value chosen and the median will be that number. This was the case with the mean and median values found using all the data in this study. Thus, these numbers are estimates that may be inaccurate. However, when looking at those atrazine concentration values which are above the MDL, a few points did become clear.

1. Seasonal trends

The seasonal averages indicated that summer was the season in which detections most commonly occurred, while spring was the period when the highest concentration values occurred. The high spring values may indicate runoff from large applications, while the frequent summer detections may represent inputs from smaller mid-season applications and residual leaching. These results concur with Stamer (1996), who found that spring and summer atrazine concentrations were higher than those in fall and winter, and the highest values were found during the growing season following intense rains. Atrazine concentrations in the month of May ranged from 0.17 $\mu\text{g/L}$ to as high as 30 $\mu\text{g/L}$, while February values

stayed in the 0.08-0.1 $\mu\text{g/L}$ range. Pereira and Hostettler in a study of the Mississippi River (1993) also found that atrazine concentrations were highest following spring application. They sampled at three periods of the year, April-May, July-August, and October-November. The spring and summer concentrations were similar to each other (around 1 $\mu\text{g/L}$) and significantly higher than the fall values (about 0.2 $\mu\text{g/L}$).

In another river study, Schottler *et al.* (1994) found that application of atrazine tended to occur in May and atrazine flux into the river peaked in June. Atrazine, alachlor, and cyanazine concentrations ranged from 500-6500 ng/L during the first significant storm event following application, as opposed to atrazine concentrations in base flow of 20-65 ng/L. In a study of the tributaries to Lake Erie, atrazine was again present in water at concentrations similar to those observed in the Occoquan Watershed (averaging about 1.9 $\mu\text{g/L}$) (USEPA 1988). Peak atrazine concentrations (20-30 $\mu\text{g/L}$) occurred in late May, June, or July (USEPA 1988). Multiple storms of sufficient intensity produced multiple peak concentrations in the same year, even when pesticides had been on the field for several months (USEPA 1988). The same phenomenon appears to have occurred in this study.

2. Rainfall

The amount of rainfall associated with the 20 aqueous atrazine detections did not correlate with the concentration found. While the presence of atrazine is most likely due to agricultural runoff during storms, a definitive correlation cannot be made using this data. This is not surprising considering that the sampling dates only accidentally coincided with an occasional storm. Correlation with streamflow was equally impossible for the same reason. Streamflow correlations and calculation of loadings are more meaningful when done with data sampled frequently

enough to include most storms, as in the case of Schottler *et al.* (1994). In that study, concurrent samples and flow measurements were taken three times a week. Intensive sampling throughout the course of a storm would be the best way to establish a relationship between rainfall and atrazine concentration.

3. Other transport mechanisms

Transport of atrazine to the surface waters may have occurred through atmospheric deposition or groundwater discharge. Atrazine may be applied by spraying, as described by Tan *et al.* (1993), so there is the potential for wind to transport the spray. Soil with adsorbed atrazine may also have been transported by dry atmospheric deposition. Groundwater discharge was found to result in atrazine inputs to the base flow of the Mississippi River (Pereira and Hostettler 1993). It is likely that one or both of these mechanisms were responsible for a portion of the atrazine loading to the surface waters of the Occoquan Watershed.

4. Concurrent detections

The bar graphs showed that detections did appear concurrently at multiple stations, indicating that there were periodic instances when atrazine pollution was widespread. Figures 20-24 show some of these episodes. In those figures, the stations were shown roughly upstream to downstream. The BR stations and ST70 were on tributaries to Lake Manassas and the LM stations were in Lake Manassas. ST30 and ST10 are downstream of Lake Manassas and ST20 is on a branch (Cedar Run) that enters between ST30 and ST10. ST40 is on Bull Run (tributary to the Occoquan Reservoir and unrelated to Lake Manassas). The RE stations are in the Occoquan Reservoir. See Figures 1 and 2 in the Literature Review to review these locations. The following section describes each episode, what may have caused each one, and what might be concluded from each.

6/7/83 Only ST stations were sampled here, near the beginning of the monitoring program. The value at ST70 indicated that atrazine was entering Lake Manassas from Broad Run, perhaps from farmland to the west. Three day composite rainfall amounts were 0.29 in. at OWML and 0.49 in. at Lorton, so this episode could be attributed to runoff or wet deposition.

6/21/88 Again, the atrazine value at ST70, this time along with those at BR02 and BR03, suggested use to the west of Lake Manassas. Atrazine was also present in Bull Run (ST40), so this stream probably carried some agricultural runoff or groundwater inputs and should not be characterized as strictly urban. Cedar Run (ST20) and Broad Run (ST30) both showed detections, and after they combined, the atrazine concentration below Lake Jackson (ST10) was higher than the two upstream values. No rain fell at this time. LM and RE stations were not sampled.

9/14/88 All LM stations except LM05 showed atrazine detections. The only tributary to Lake Manassas with a detection was ST70, again pointing to a source west of Lake Manassas; however, BR05 and BR06 cannot be ruled out as contributors because they were not sampled. The value at MANRAW was above the later promulgated MCL of 3 $\mu\text{g/L}$ (this regulation was not in place yet), so this is one case where some level of removal in the treatment plant would have been desirable. Downstream of Lake Manassas, there was a pattern of dilution, as atrazine was detected at ST30, but not at ST20 or ST40, and not further downstream at OCCRAW. RE stations were not sampled. A small amount of rain (0.02 in.) fell at OWML during this sampling period and none fell at Lorton.

2/27/89 All LM stations showed atrazine detections, but the direction of the source(s) cannot be clarified because ST70 and the BR stations were not sampled. Downstream, there were no detections at the ST stations or OCCRAW, indicating dilution; the RE stations were not sampled. Again, a very small amount of rain (0.01 in.) was recorded at OWML.

8/30/89 Again, BR stations and ST70 were not sampled. All LM stations except LM03 (North Fork) had atrazine concentrations above the MDL. Values at ST10, 20 and 30 were all below the MDL. OCCRAW showed a detection on 8/23/89, which could mean that there was another source closer to the reservoir which was affected by the rain at Lorton (0.18 in.). No rain was recorded at OWML during the period 8/28-8/30.

3/7/90 LM stations in the middle of the lake showed atrazine values above the MDL in both water and sediment (this is the first of these episodes where sediment samples were taken as well as water). Note that the sediment concentrations are about 10 times as large as the water concentrations. BR stations were sampled on 3/12, ST stations on 2/21, and RE stations on 3/13, but no concentrations above the MDL were found. No rain was recorded.

8/28/90 The furthest upstream tributaries, ST70, BR07, and BR05 all showed atrazine concentrations above the MDL, so there were apparently sources in all three directions. All other BR and LM stations had results below the MDL except LM02 and MANRAW. Bull Run (ST40) had a value above the MDL, while Cedar Run (ST20), lower Broad Run (ST30), and Occoquan Creek (ST10) did not. All RE stations had concentrations above the MDL, with the value at RE15 being particularly high, but nothing was

detected at OCCRAW. Of the 14 values below the MDL during this period, 11 of them were recorded as estimated values rather than as NDs.

Although these values were below the MDL, they might be considered to indicate the presence of atrazine. Sediments were not collected at this time. The one fish with a detected value for atrazine was caught earlier in the Summer of 1990 (6/4/90). No rain was recorded during this sampling period.

4/10/91 All water stations were sampled at this time, but the only atrazine value above the MDL was that at LM07. However, fairly large sediment concentrations were found at LM02 and LM04 (20.98 and 8.52 mg/kg, respectively), with a lower value at LM03 (3.30 mg/kg). Sediment atrazine concentrations were below the MDL at the other LM stations and the RE stations. No rain was recorded during the period.

5/23/91 Two of the far upstream sites, ST70 and BR07 showed atrazine values above the MDL, again indicating use west of Lake Manassas. Cedar Run (ST20) had a concentration above the MDL on 5/20 which may have been brought on by the 0.16 in. of cumulative rainfall before and during that time. No rain was recorded closer to 5/23. All other stations showed values below the MDL.

8/8/91 An isolated detection occurred at BR06. No other stations in the watershed were sampled at this time and no rainfall was recorded.

8/26/91 Another isolated detection occurred, this time at ST20 (Cedar Run). Again, no rain was recorded.

7/29/92 ST70 and the BR and LM stations were not sampled. From upstream to downstream, one series of stations that had aqueous atrazine detections was ST10, ST20, and OCCRAW. Water and sediment at RE stations showed values below the MDL.

8/19/92 LM03 and LM04 were the only stations with aqueous atrazine concentrations above the MDL; ST70 and the BR and other LM stations had ND values. RE stations were not sampled. No atrazine was detected in LM sediment samples.

A few generalizations can be drawn from these episodes. First, Lake Manassas was more susceptible to atrazine contamination than the Occoquan Reservoir. The LM and BR stations had the highest average values and the LM stations had the greatest frequency of detection (see Table 10). A general trend of dilution downstream of Lake Manassas was demonstrated as downstream values tended to fall below the MDL. The elevated concentrations in Lake Manassas were probably due to the lake's proximity to the more agricultural part of the watershed. Another possible explanation for the values at Lake Manassas would be use of atrazine for weed control at the nearby golf courses. This sounds like a somewhat unusual use for atrazine, but one study (Morioka 1993) found another triazine herbicide, simazine, in a pond receiving golf course runoff, so it may be a possibility.

While Lake Manassas possessed the highest concentrations found, other branches of the system, such as Bull Run (ST40) and Cedar Run (ST20), also contained atrazine. This is not surprising since the headwaters of both streams lie in rural parts of the basin. The Occoquan Reservoir seemed to be far enough downstream of the potential sources of atrazine in

the basin that there were few concentrations found above the MDL. The Lorton Water Treatment Plant has been able to and should in the future be able to meet the drinking water MCL of 3 $\mu\text{g/L}$. There was only one detection in the sediment of the reservoir; it occurred in the Fall of 1992 at RE02, the station just above the Occoquan Dam. This finding may indicate the occurrence of scouring in the reservoir. Shifts in PAH concentrations between summer and fall possibly caused by scouring were noted by Mastran (1992).

There was a fairly even mixture of results as compared to rainfall; some detections did coincide with rain events and some did not. The occurrence of detections not brought on by an obvious storm event point to the idea that there may be a background concentration of atrazine present, and low flow conditions or a slight addition to the amount present will result in a value rising above the MDL. These detections without rain also may mean that dry deposition and groundwater contamination were important atrazine sources.

5. Fate in the water treatment plants

The water treatment plants at Lake Manassas and Lorton did remove a small percentage of atrazine from the influent water. In most cases, removals were large enough to produce a finished water concentration less than the MCL of 3 $\mu\text{g/L}$. Based on this data set, no violations of the MCL have occurred since the MCL was promulgated in 1991 (Pontius 1996). Randtke (1988) concluded in his review that conventional coagulation can remove some SOC's in cases where they can adsorb to floc particles, and the degree of removal may be influenced by coagulant dose, pH, and presence of other particles and natural organic matter in the raw water. Coagulation may account for the removals, and variations in raw water quality or coagulant dose may explain the variability in removals found. At

the Lorton Water Treatment Plant, use of PAC may have enhanced removals.

6. Fish

Atrazine contamination in fish is probably not of great concern. Only one sample, the organs of a largemouth bass caught in summer 1990, was found to contain atrazine. If organic compounds are to be found in fish, it is most likely that they would be found in the liver, so finding pesticides in the organs but not the muscle tissue is an expected result. The liver removes xenobiotic compounds from the bloodstream and metabolizes them (Heath 1987). A detection could only occur if the fish was caught at just the right time--after absorbing the compound but before the liver had time to break it down--or if the fish was continuously exposed to atrazine. If atrazine metabolites had also been considered in this study, perhaps they would have been found more frequently in fish than the parent compound. In any case, fish organs are not typically consumed by humans, so exposure to atrazine from fish must be considered unlikely.

B. Fish Extraction Method

The fish extraction method succeeded in recovering most analytes at acceptable levels. The one compound not recovered, Benzo(g,h,i)perylene, was a late eluting PAH. This compound had been recovered in water earlier in the life of the column used. It is likely that the problem was not in the extraction but in the chromatography, and with a new column, Benzo(g,h,i)perylene would probably be recovered. Most of the methods found in the literature report high recoveries (about 80-105%) for a smaller set of compounds (organochlorine pesticides alone, triazine herbicides alone, etc.). One broad spectrum method, that in the USFDA's PAM (1994), reported recoveries for a wide range of compounds as either not recovered, small (<50%), partial (50-80%), or complete (>80%). The

MDLs found in this study appear reasonable as compared to available values from the literature. Turin and Bowman (1993) reported a detection limit of about 10 $\mu\text{g/kg}$ for herbicides in soil extracted by shaking. NIST (1994) reported certified concentrations of 3-445 $\mu\text{g/kg}$ wet weight for organochlorine compounds in whale blubber extracted by the soxhlet method.

From the control charts for the surrogates (Figures 25 and 26), the method appeared to be in statistical control (i.e. 95% of points lie within the $\pm 2\sigma$ boundaries, and 99% are within the $\pm 3\sigma$ limits). The first few samples were outliers, probably because adjustments to the vacuum assembly were still being made when these samples were extracted. Beyond the first few samples, no significant bias was observed. The average surrogate recovery was good (89%) but the standard deviations were rather large (26 and 28%). The standard deviations should decrease with continued experience and the use of a commercial vacuum manifold that is easier to control than the manual one.

VI. CONCLUSIONS

The Occoquan Watershed generally had low (1-2 $\mu\text{g/L}$) or non-detectable aqueous concentrations of the 47 SOC's monitored. Very few compounds in OWML's SOC database were found at concentrations above method detection limits.

In water, atrazine was the most commonly detected compound (87 concentrations measured above the MDL for 610 samples analyzed). It was also found in 8 sediment samples and 1 fish organ sample. Atrazine concentrations were highest in the spring, while summer provided the most frequent detections. Detections occurred at multiple locations during the same sampling period; stations furthest west (nearest to agricultural areas) tended to show the highest values. Rainfall events were associated with 23% of atrazine detections.

Atrazine is the SOC with the greatest likelihood of being detected in the drinking water supplies of the basin, more so in Lake Manassas than to the Occoquan Reservoir. In OWML's records (1982-1994), the aqueous atrazine concentration in finished drinking water exceeded the MCL once at the Lake Manassas Water Treatment Plant (on a date prior to the promulgation of the MCL) and never exceeded it at the Lorton Water Treatment Plant. The raw and finished water samples from the two water treatment plants showed that they achieved an average of 37% removal of atrazine by conventional treatment.

The method for fish tissue extraction and cleanup developed in this study was able to recover all but one of the 47 analytes (recoveries were 15-92% with standard deviations of 5-94%). A few recoveries were low but most were reasonable. Reproducibility should improve with experience and use of a better vacuum manifold system. MDLs for the method

developed in this research improved as compared to those found by the previously used Soxhlet extraction method. For the 47 compounds investigated, MDLs ranging from 0.03-0.37 mg/kg wet weight were found.

Monitoring of SOC_s in the Occoquan Watershed should be continued. The results will help to determine the effects of future changes in land use in the basin and protect the public water supplies. The target compound list should be reevaluated periodically to delete compounds that are never found and add others that might be present. Since atrazine has the potential to exceed the MCL in Lake Manassas, having PAC on hand or installing an optional GAC contactor at the Lake Manassas Water Treatment Plant might be recommended. Storm sampling of Lake Manassas and its tributaries during a May or June rain event could provide an estimate of loading to the lake and a clearer picture of the locations of atrazine sources. The fish extraction and cleanup method should continue to evolve and methods like accelerated solvent extraction could perhaps be considered in the future.

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VIII. APPENDIX A: Atrazine and Rainfall Data

Table A-1. Atrazine Data for Water, Sediment, and Fish (1982-1994)
WATER (Lake Manassas, Occoquan Reservoir, tributaries, treatment plants)

Station	Date	Conc.ppb	Station	Date	Conc.ppb	Station	Date	Conc.ppb
BR02	05/11/87	ND	LM05	05/13/87	ND	ST10	09/29/82	1.72
BR02	08/03/87	ND	LM05	08/05/87	ND	ST10	03/04/83	ND
BR02	11/16/87	ND	LM05	11/18/87		ST10	06/07/83	1.17
BR02	02/25/88	0.41	LM05	02/26/88	ND	ST10	08/29/83	0.96
BR02	06/21/88	1.51	LM05	09/14/88	ND	ST10	03/19/84	ND
BR02	09/14/88	ND	LM05	02/27/89	1.29	ST10	06/18/84	1.05
BR02	05/25/89	ND	LM05	05/24/89	ND	ST10	09/19/84	ND
BR02	03/12/90	ND	LM05	08/30/89	1.99	ST10	03/08/85	ND
BR02	08/28/90	ND	LM05	03/07/90	23.44	ST10	07/11/85	ND
BR02	04/08/91	ND	LM05	08/29/90	0.39	ST10	09/06/85	ND
BR02	05/23/91	ND	LM05	04/10/91	ND	ST10	02/03/86	ND
BR02	08/08/91	ND	LM05	05/22/91	ND	ST10	06/06/86	ND
BR02	12/02/91	ND	LM05	08/07/91	ND	ST10	08/18/86	ND
BR02	02/03/92	ND	LM05	12/02/91	ND	ST10	02/17/87	ND
BR02	06/08/92	ND	LM05	02/20/92	0.30	ST10	05/11/87	ND
BR02	08/24/92	ND	LM05	06/10/92	0.56	ST10	08/04/87	1.53
BR02	11/16/92	ND	LM05	08/19/92	ND	ST10	11/09/87	ND
BR02	02/01/93	-1.4	LM05	11/09/92	0.24	ST10	02/25/88	ND
BR02	05/03/93	-1.4	LM05	02/09/93	NF	ST10	06/21/88	2.33
BR02	07/12/93	-1.4	LM05	05/10/93	-1.4	ST10	09/12/88	ND
BR02	09/07/93	NF	LM05	07/19/93	-1.4	ST10	02/22/89	0.19
BR02	01/03/94	NF	LM05	09/13/93	-1.4	ST10	05/25/89	ND
BR02	05/02/94		LM05	03/23/94		ST10	08/23/89	0.71
BR02	07/11/94		LM05	05/10/94		ST10	02/21/90	ND
BR02	09/06/94		LM05	07/18/94		ST10	08/29/90	0.45
BR03	05/11/87	ND	LM05	09/14/94		ST10	04/03/91	ND
BR03	08/03/87	1.08	LM06	05/13/87	ND	ST10	05/20/91	ND
BR03	11/16/87	ND	LM06	08/05/87	ND	ST10	06/26/91	ND
BR03	02/25/88	0.07	LM06	11/18/87	ND	ST10	04/06/92	ND
BR03	06/21/88	1.41	LM06	02/26/88	ND	ST10	07/27/92	1.28
BR03	09/14/88	ND	LM06	09/14/88	1.99	ST10	10/05/92	ND
BR03	05/25/89	ND	LM06	02/27/89	1.14	ST10	02/08/93	-1.4
BR03	03/12/90	ND	LM06	05/24/89	ND	ST10	06/01/93	-1.4
BR03	08/28/90	ND	LM06	08/30/89	1.62	ST10	08/09/93	-1.4
BR03	04/08/91	ND	LM06	03/07/90	4.47	ST10	02/14/94	
BR03	05/23/91	ND	LM06	08/29/90	0.41	ST10	06/13/94	
BR03	12/02/91	ND	LM06	04/10/91	ND	ST10	08/29/94	
BR03	06/08/92	ND	LM06	05/22/91	ND	ST20	09/29/82	0.99
BR03	08/24/92	ND	LM06	08/07/91	ND	ST20	03/04/83	0.71
BR03	11/16/92	ND	LM06	12/02/91	ND	ST20	06/07/83	1.25
BR03	02/01/93	-1.4	LM06	02/20/92	0.18	ST20	08/29/83	1.62
BR03	05/03/93	-1.4	LM06	06/10/92	0.52	ST20	03/19/84	ND
BR03	07/12/93	-1.4	LM06	08/19/92	0.77	ST20	06/18/84	0.97
BR03	09/07/93	NF	LM06	11/09/92	0.23	ST20	09/19/84	ND

BR03	01/03/94	-1.4	LM06	02/09/93	NF	ST20	03/08/85	0.95
BR03	05/02/94		LM06	05/10/93	-1.4	ST20	07/11/85	ND
BR03	07/11/94		LM06	07/19/93	-1.4	ST20	09/06/85	ND
BR03	09/06/94		LM06	09/13/93	-1.4	ST20	02/03/86	ND
BR04	05/11/87	ND	LM06	03/23/94		ST20	06/06/86	ND
BR04	08/03/87	ND	LM06	05/10/94		ST20	08/18/86	ND
BR04	11/16/87	ND	LM06	07/18/94		ST20	02/17/87	ND
BR04	02/25/88	ND	LM06	09/14/94		ST20	05/11/87	ND
BR04	06/21/88	ND	LM07	05/13/87	ND	ST20	08/04/87	ND
BR04	09/14/88	ND	LM07	08/05/87	ND	ST20	11/09/87	ND
BR04	05/25/89	ND	LM07	11/18/87	ND	ST20	02/25/88	ND
BR04	03/12/90	ND	LM07	02/26/88	ND	ST20	06/21/88	1.60
BR04	08/28/90	ND	LM07	09/14/88	2.20	ST20	09/12/88	ND
BR04	04/08/91	ND	LM07	02/27/89	1.89	ST20	02/22/89	1.11
BR04	05/23/91	ND	LM07	05/24/89	ND	ST20	05/25/89	ND
BR04	12/02/91	ND	LM07	08/30/89	1.66	ST20	08/23/89	0.56
BR04	02/03/92	ND	LM07	03/07/90	ND	ST20	02/21/90	ND
BR04	06/08/92	0.25	LM07	08/29/90	0.44	ST20	08/29/90	0.53
BR04	11/16/92	ND	LM07	04/10/91	4.01	ST20	04/03/91	ND
BR04	02/01/93	-1.4	LM07	05/22/91	0.61	ST20	05/20/91	5.51
BR04	05/17/93	-1.4	LM07	08/07/91	nf	ST25	08/26/91	1.19
BR04	07/12/93		LM07	12/02/91	ND	ST25	04/06/92	ND
BR04	12/14/93		LM07	02/20/92	ND	ST25	07/27/92	1.72
BR04	01/25/94	NF	LM07	06/10/92	0.37	ST25	10/05/92	ND
BR04	05/02/94		LM07	08/19/92	1.03	ST25	02/08/93	-1.4
BR04	09/23/94		LM07	11/09/92	ND	ST25	06/01/93	-1.4
BR05	05/11/87	ND	LM07	02/09/93	NF	ST25	08/09/93	-1.4
BR05	11/16/87	ND	LM07	05/10/93	-1.4	ST25	02/14/94	.
BR05	02/25/88	ND	LM07	07/19/93	-1.4	ST25	06/13/94	
BR05	05/25/89	ND	LM07	09/13/93	-1.4	ST25	08/29/94	
BR05	03/12/90	ND	LM07	03/23/94		ST30	09/29/82	3.31
BR05	08/28/90	2.25	LM07	05/10/94		ST30	03/04/83	0.56
BR05	04/08/91	ND	LM07	07/18/94		ST30	08/29/83	1.31
BR05	05/23/91	ND	LM07	09/14/94		ST30	03/19/84	ND
BR05	12/02/91	ND	LM08	05/13/87	ND	ST30	06/18/84	0.55
BR05	02/03/92	ND	LM08	08/05/87	ND	ST30	09/19/84	ND
BR05	06/08/92	0.27	LM08	11/18/87	ND	ST30	03/08/85	ND
BR05	11/16/92	ND	LM08	02/26/88	ND	ST30	07/11/85	ND
BR05	02/01/93	-1.4	LM08	09/14/88	2.32	ST30	09/06/85	ND
BR05	05/17/93	-1.4	LM08	02/27/89	1.25	ST30	02/03/86	ND
BR05	07/12/93		LM08	05/24/89	ND	ST30	06/06/86	ND
BR05	12/14/93	NF	LM08	08/30/89	1.28	ST30	08/18/86	ND
BR05	01/25/94	NF	LM08	03/07/90	ND	ST30	02/17/87	ND
BR05	05/02/94		LM08	08/29/90	0.46	ST30	05/11/87	ND
BR05	09/23/94		LM08	04/10/91	ND	ST30	08/04/87	ND
BR06	05/11/87	ND	LM08	05/22/91	ND	ST30	11/09/87	ND
BR06	11/16/87	ND	LM08	08/07/91	ND	ST30	02/25/88	1.00
BR06	02/25/88	ND	LM08	12/02/91	ND	ST30	06/21/88	2.26
BR06	05/25/89	ND	LM08	02/20/92	ND	ST30	09/12/88	2.15

BR06	03/12/90	ND	LM08	06/10/92	0.58	ST30	02/22/89	ND
BR06	08/28/90		LM08	08/19/92	0.69	ST30	05/25/89	ND
BR06	04/08/91	ND	LM08	11/09/92	0.21	ST30	08/23/89	0.41
BR06	05/23/91	ND	LM08	02/09/93	NF	ST30	02/21/90	ND
BR06	08/08/91	6.87	LM08	05/10/93	-1.4	ST30	08/29/90	0.60
BR06	12/02/91	5.61	LM08	07/19/93	-1.4	ST30	04/03/91	ND
BR06	02/03/92	ND	LM08	09/13/93	-1.4	ST30	05/20/91	0.72
BR06	06/08/92	0.27	LM08	03/23/94		ST30	08/26/91	ND
BR06	08/24/92	ND	LM08	05/10/94		ST30	04/06/92	0.37
BR06	11/16/92	ND	LM08	07/18/94		ST30	07/27/92	0.37
BR06	02/01/93	-1.4	LM08	09/14/94		ST30	10/05/92	ND
BR06	05/17/93	NF	MAN_RA	08/17/84	ND	ST30	02/08/93	-1.4
BR06	12/14/93	NF	MAN_RA	09/19/84	ND	ST30	06/02/93	-1.4
BR06	05/02/94		MAN_RA	03/08/85	ND	ST30	08/09/93	-1.4
BR06	05/02/94		MAN_RA	07/11/85	ND	ST30	02/14/94	
BR06	09/23/94		MAN_RA	09/06/85	ND	ST30	06/13/94	
BR07	05/11/87	ND	MAN_RA	02/03/86	ND	ST30	08/29/94	
BR07	08/03/87	ND	MAN_RA	06/06/86	ND	ST40	09/29/82	ND
BR07	11/16/87	0.42	MAN_RA	08/18/86	ND	ST40	03/04/83	ND
BR07	02/25/88	ND	MAN_RA	02/17/87	ND	ST40	06/07/83	0.16
BR07	06/21/88	ND	MAN_RA	05/12/87	ND	ST40	09/12/83	ND
BR07	09/14/88	ND	MAN_RA	08/04/87	ND	ST40	03/19/84	ND
BR07	05/25/89	ND	MAN_RA	11/10/87	ND	ST40	06/18/84	0.24
BR07	03/12/90	ND	MAN_RA	02/29/88	0.15	ST40	09/19/84	ND
BR07	08/28/90	2.42	MAN_RA	06/27/88	3.08	ST40	03/08/85	ND
BR07	04/08/91	ND	MAN_RA	09/14/88	3.73	ST40	07/11/85	ND
BR07	05/23/91	1.30	MAN_RA	02/22/89	2.60	ST40	09/06/85	ND
BR07	12/02/91	ND	MAN_RA	05/25/89	ND	ST40	02/03/86	ND
BR07	02/03/92	ND	MAN_RA	09/07/89	1.97	ST40	06/06/86	ND
BR07	06/08/92	ND	MAN_RA	03/12/90	76.96*	ST40	08/18/86	ND
BR07	08/24/92	ND	MAN_RA	08/28/90	3.57	ST40	02/17/87	ND
BR07	11/16/92	ND	MAN_RA	04/03/91	ND	ST40	05/11/87	ND
BR07	02/01/93	-1.4	MAN_RA	05/23/91	ND	ST40	08/04/87	ND
BR07	05/03/93	-1.4	MAN_RA	08/28/91	ND	ST40	11/09/87	ND
BR07	07/12/93	NF	MAN_RA	12/02/91	ND	ST40	02/25/88	1.04
BR07	09/07/93	NF	MAN_RA	02/06/92	ND	ST40	06/21/88	1.45
BR07	01/03/94		MAN_RA	05/20/92	0.46	ST40	09/12/88	ND
BR07	05/02/94		MAN_RA	08/24/92	ND	ST40	02/22/89	0.05
BR07	07/11/94		MAN_RA	12/02/92	0.44	ST40	05/25/89	ND
BR07	09/06/94		MAN_RA	02/01/93	-1.4	ST40	08/23/89	ND
LM01	05/13/87	ND	MAN_RA	07/19/93	-1.4	ST40	02/21/90	ND
LM01	08/05/87	ND	MAN_RA	09/13/93	-1.4	ST40	08/29/90	2.46
LM01	11/18/87	ND	MAN_RA	01/10/94	NF	ST40	04/03/91	ND
LM01	02/26/88	ND	MAN_RA	05/26/94	-1.4	ST40	05/20/91	ND
LM01	09/14/88	2.51	MAN_RA	07/18/94		ST40	08/26/91	ND
LM01	02/27/89	1.84	MAN_RA	09/04/94		ST40	04/06/92	0.32
LM01	05/24/89	ND	MAN_RA	09/14/94		ST40	07/27/92	0.55
LM01	08/30/89	1.26	MAN_RA	05/10/94		ST40	10/05/92	ND
LM01	03/07/90	7.99	OCC_RA	09/29/82	1.49	ST40	02/08/93	NF

LM01	08/29/90	0.40	OCC_RA	03/04/83	0.33	ST40	06/02/93	NF
LM01	04/10/91	ND	OCC_RA	06/07/83	2.38	ST40	08/09/93	-1.4
LM01	05/22/91	ND	OCC_RA	08/29/83	2.93	ST40	02/14/94	
LM01	08/07/91	ND	OCC_RA	03/19/84	ND	ST40	06/13/94	
LM01	12/02/91	ND	OCC_RA	06/18/84	0.12	ST40	08/29/94	
LM01	02/20/92	ND	OCC_RA	09/19/84	ND	ST70	06/07/83	1.14
LM01	06/10/92	0.47	OCC_RA	03/08/85	ND	ST70	05/11/87	ND
LM01	08/19/92	0.69	OCC_RA	07/11/85	1.15	ST70	08/03/87	ND
LM01	11/09/92	ND	OCC_RA	09/06/85	ND	ST70	11/16/87	ND
LM01	02/09/93	-1.4	OCC_RA	02/03/86	ND	ST70	02/25/88	ND
LM01	05/10/93	-1.4	OCC_RA	06/06/86	ND	ST70	06/21/88	1.68
LM01	07/19/93	-1.4	OCC_RA	08/18/86	ND	ST70	09/14/88	1.16
LM01	09/13/93	-1.4	OCC_RA	02/17/87	ND	ST70	05/25/89	ND
LM01	03/23/94		OCC_RA	05/12/87	ND	ST70	03/12/90	ND
LM01	05/10/94		OCC_RA	08/04/87	ND	ST70	08/28/90	2.64
LM01	07/18/94		OCC_RA	11/12/87	ND	ST70	04/10/91	ND
LM01	09/14/94		OCC_RA	02/29/88	4.73	ST70	05/23/91	1.76
LM02	05/13/87	ND	OCC_RA	06/27/88	ND	ST70	08/08/91	ND
LM02	08/05/87	ND	OCC_RA	09/12/88	1.08	ST70	12/02/91	ND
LM02	11/18/87	ND	OCC_RA	02/22/89	ND	ST70	02/03/92	ND
LM02	02/26/88	ND	OCC_RA	05/25/89	ND	ST70	06/08/92	0.64
LM02	09/14/88	3.96	OCC_RA	08/23/89	1.36	ST70	08/24/92	ND
LM02	02/27/89	1.24	OCC_RA	02/21/90	ND	ST70	11/16/92	ND
LM02	05/24/89	ND	OCC_RA	08/29/90	0.66	ST70	02/01/93	-1.4
LM02	08/30/89	1.32	OCC_RA	04/03/91	ND	ST70	05/03/93	-1.4
LM02	03/07/90	7.43	OCC_RA	05/23/91	ND	ST70	07/12/93	-1.4
LM02	08/29/90	1.28	OCC_RA	08/26/91	ND	ST70	09/07/93	
LM02	04/10/91	ND	OCC_RA	05/14/92	0.91	ST70	01/03/94	-1.4
LM02	05/22/91	ND	OCC_RA	07/29/92	1.29	ST70	04/13/94	
LM02	08/07/91	ND	OCC_RA	10/05/92	ND	ST70	04/27/94	
LM02	12/02/91	ND	OCC_RA	02/02/93	-1.4	ST70	05/02/94	
LM02	02/20/92	ND	OCC_RA	06/14/93	-1.4	ST70	05/26/94	
LM02	06/10/92	0.38	OCC_RA	08/23/93	-1.4	ST70	06/23/94	
LM02	08/19/92	0.78	OCC_RA	10/18/93	-1.4	ST70	06/29/94	
LM02	11/09/92	0.21	OCC_RA	03/15/94		ST70	06/29/94	
LM02	02/09/93		OCC_RA	06/06/94		ST70	07/11/94	
LM02	05/10/93	-1.4	OCC_RA	08/24/94		ST70	07/27/94	
LM02	07/08/93	-1.4	OCC_RA	10/18/94		ST70	08/15/94	
LM02	07/19/93	-1.4	RE02	04/26/90		ST70	09/06/94	
LM02	09/13/93	-1.4	RE02	06/06/90		MAN_FIN	08/17/84	ND
LM02	03/23/94		RE02	08/28/90	2.54	MAN_FIN	09/19/84	ND
LM02	05/10/94		RE02	04/04/91	ND	MAN_FIN	03/08/85	ND
LM02	07/18/94		RE02	05/21/91	ND	MAN_FIN	07/11/85	ND
LM02	09/14/94		RE02	07/16/91		MAN_FIN	09/06/85	ND
LM03	05/13/87	ND	RE02	08/27/91	ND	MAN_FIN	02/03/86	ND
LM03	08/05/87	ND	RE02	10/24/91	ND	MAN_FIN	06/06/86	ND
LM03	11/18/87	ND	RE02	04/08/92	ND	MAN_FIN	08/18/86	ND
LM03	02/26/88	ND	RE02	07/28/92	1.00	MAN_FIN	02/17/87	ND
LM03	09/14/88	3.75	RE02	10/19/92	ND	MAN_FIN	05/12/87	ND

LM03	02/27/89	1.60	RE02	02/03/93	NF	MAN_FIN	08/04/87	ND
LM03	05/24/89	ND	RE02	06/07/93	-1.4	MAN_FIN	11/10/87	ND
LM03	08/30/89	1.23	RE02	08/23/93	-1.4	MAN_FIN	02/29/88	ND
LM03	03/07/90	8.52	RE02	10/18/93	-1.4	MAN_FIN	06/27/88	1.53
LM03	08/29/90	0.86	RE02	03/15/94		MAN_FIN	09/14/88	1.83
LM03	04/10/91	ND	RE02	06/06/94		MAN_FIN	02/22/89	2.04
LM03	05/22/91	ND	RE02	08/24/94		MAN_FIN	05/25/89	ND
LM03	08/07/91	ND	RE02	10/18/94		MAN_FIN	09/07/89	1.20
LM03	12/02/91	ND	RE15	04/25/90		MAN_FIN	03/12/90	124.02*
LM03	02/20/92	ND	RE15	06/06/90		MAN_FIN	08/28/90	3.13
LM03	06/10/92	0.40	RE15	08/28/90	7.66	MAN_FIN	04/03/91	ND
LM03	08/19/92	1.77	RE15	04/04/91	ND	MAN_FIN	05/23/91	ND
LM03	11/09/92	0.50	RE15	05/21/91	ND	MAN_FIN	08/28/91	ND
LM03	02/09/93	-1.4	RE15	07/16/91		MAN_FIN	12/02/91	ND
LM03	05/10/93	-1.4	RE15	08/27/91	ND	MAN_FIN	02/06/92	ND
LM03	07/19/93	-1.4	RE15	10/24/91	ND	MAN_FIN	05/20/92	ND
LM03	09/13/93	-1.4	RE15	04/08/92	ND	MAN_FIN	08/24/92	0.33
LM03	03/23/94		RE15	07/28/92	1.38	MAN_FIN	12/02/92	ND
LM03	05/10/94		RE15	10/06/92	-1.4	MAN_FIN	02/01/93	-1.4
LM03	07/18/94		RE15	10/19/92	ND	MAN_FIN	07/19/93	-1.4
LM03	09/14/94		RE15	02/03/93	-1.4	MAN_FIN	09/13/93	-1.4
LM04	05/13/87	ND	RE15	06/07/93	-1.4	MAN_FIN	01/10/94	NF
LM04	08/05/87	ND	RE15	08/23/93	-1.4	MAN_FIN	05/10/94	
LM04	11/18/87	ND	RE15	10/18/93	-1.4	MAN_FIN	05/26/94	-1.4
LM04	02/26/88	ND	RE15	03/15/94		MAN_FIN	07/18/94	
LM04	09/14/88	3.09	RE15	06/06/94		MAN_FIN	09/04/94	
LM04	02/27/89	1.63	RE15	08/24/94		OCC_FIN	06/07/83	1.92
LM04	05/24/89	ND	RE15	10/18/94		OCC_FIN	03/19/84	ND
LM04	08/30/89	1.23	RE30	04/25/90		OCC_FIN	06/18/84	0.11
LM04	03/07/90	7.60	RE30	06/06/90		OCC_FIN	09/19/84	ND
LM04	08/29/90	0.54	RE30	08/28/90	1.60	OCC_FIN	03/08/85	ND
LM04	04/10/91	ND	RE30	04/04/91	ND	OCC_FIN	07/11/85	ND
LM04	05/22/91	ND	RE30	05/21/91	ND	OCC_FIN	09/06/85	ND
LM04	08/07/91	ND	RE30	07/16/91		OCC_FIN	02/03/86	ND
LM04	12/02/91	ND	RE30	08/27/91	ND	OCC_FIN	06/06/86	ND
LM04	02/20/92	ND	RE30	10/24/91	ND	OCC_FIN	08/18/86	ND
LM04	06/10/92	0.42	RE30	04/08/92	ND	OCC_FIN	02/17/87	ND
LM04	08/18/92	1.36	RE30	07/28/92	1.88	OCC_FIN	05/12/87	ND
LM04	11/09/92	ND	RE30	10/19/92	ND	OCC_FIN	08/04/87	ND
LM04	02/09/93	-1.4	RE30	02/03/93	-1.4	OCC_FIN	11/12/87	ND
LM04	05/10/93	-1.4	RE30	06/07/93	NF	OCC_FIN	02/29/88	0.24
LM04	07/19/93		RE30	08/23/93	-1.4	OCC_FIN	06/27/88	ND
LM04	09/13/93	-1.4	RE30	10/18/93		OCC_FIN	09/12/88	0.56
LM04	03/23/94		RE30	03/15/94		OCC_FIN	02/22/89	ND
LM04	05/10/94		RE30	06/06/94		OCC_FIN	05/25/89	ND
LM04	07/18/94		RE30	08/24/94		OCC_FIN	08/23/89	0.81
LM04	09/14/94		RE30	10/18/94		OCC_FIN	02/21/90	1.35
						OCC_FIN	08/29/90	0.62
						OCC_FIN	04/03/91	ND

OCC_FIN	05/23/91	ND
OCC_FIN	08/26/91	ND
OCC_FIN	05/14/92	ND
OCC_FIN	07/29/92	1.26
OCC_FIN	10/05/92	ND
OCC_FIN	02/02/93	NF
OCC_FIN	06/14/93	-1.4
OCC_FIN	08/23/93	-1.4
OCC_FIN	10/18/93	-1.4
OCC_FIN	03/15/94	
OCC_FIN	06/06/94	
OCC_FIN	08/24/94	
OCC_FIN	10/18/94	

SEDIMENT (Lake Manassas and Occoquan Reservoir)

LM01	11/13/86	ND	LM05	07/07/88	ND	RE02	06/23/88	ND
LM01	07/07/88	ND	LM05	08/14/88	ND	RE02	08/09/88	ND
LM01	08/14/88	ND	LM05	02/27/89	ND	RE02	05/02/89	ND
LM01	02/27/89	ND	LM05	05/24/89	ND	RE02	03/13/90	ND
LM01	05/24/89	ND	LM05	08/30/89	ND	RE02	04/26/90	
LM01	08/30/89	ND	LM05	03/07/90	7.78	RE02	06/06/90	
LM01	03/07/90	ND	LM05	08/01/90	ND	RE02	08/07/90	ND
LM01	08/01/90	ND	LM05	04/10/91	ND	RE02	04/04/91	ND
LM01	04/10/91	ND	LM05	08/07/91	ND	RE02	04/04/91	
LM01	08/07/91	ND	LM05	02/20/92	ND	RE02	07/16/91	
LM01	02/20/92	ND	LM05	08/19/92	ND	RE02	08/27/91	ND
LM01	08/19/92	ND	LM05	11/09/92	ND	RE02	10/22/91	ND
LM01	11/09/92	ND	LM05	02/09/93	ND	RE02	04/08/92	ND
LM01	02/09/93	ND	LM05	07/19/93	ND	RE02	07/28/92	0.11
LM01	07/19/93	ND	LM05	03/23/94		RE02	10/14/92	1.20
LM01	03/23/94		LM06	11/13/86	ND	RE02	02/03/93	ND
LM02	11/13/86	ND	LM06	07/07/88	ND	RE02	06/07/93	ND
LM02	07/07/88	ND	LM06	08/14/88	ND	RE02	11/09/93	
LM02	08/14/88	ND	LM06	02/27/89	ND	RE02	03/15/94	
LM02	02/27/89	ND	LM06	05/24/89	ND	RE02	06/06/94	
LM02	05/24/89	ND	LM06	08/30/89	ND	RE02	08/23/94	
LM02	08/30/89	ND	LM06	03/07/90	6.34	RE02	08/24/94	
LM02	03/07/90	8.25	LM06	08/01/90	ND	RE02	10/18/94	
LM02	08/01/90	ND	LM06	04/10/91	ND	RE15	06/23/88	ND
LM02	04/10/91	20.98	LM06	08/07/91	ND	RE15	08/09/88	ND
LM02	08/07/91	ND	LM06	02/20/92	ND	RE15	05/02/89	ND
LM02	02/20/92	ND	LM06	08/19/92	ND	RE15	09/06/89	ND
LM02	08/19/92	ND	LM06	11/09/92	ND	RE15	03/13/90	ND
LM02	11/09/92	ND	LM06	02/09/93	ND	RE15	04/25/90	
LM02	02/09/93	ND	LM06	07/19/93	ND	RE15	06/06/90	
LM02	07/19/93	ND	LM06	03/23/94		RE15	08/07/90	ND
LM02	03/23/94		LM06.1	11/13/86	ND	RE15	04/04/91	ND

LM03	11/13/86	ND	LM07	07/07/88	ND	RE15	04/04/91	
LM03	11/13/86	ND	LM07	08/14/88	ND	RE15	07/16/91	
LM03	07/07/88	ND	LM07	02/27/89	ND	RE15	08/27/91	ND
LM03	08/14/88	ND	LM07	05/24/89	ND	RE15	10/22/91	ND
LM03	02/27/89	ND	LM07	08/30/89	ND	RE15	04/08/92	0.13
LM03	05/24/89	ND	LM07	03/07/90	ND	RE15	07/28/92	0.42
LM03	08/30/89	ND	LM07	08/01/90	ND	RE15	10/14/92	ND
LM03	03/07/90	ND	LM07	04/10/91	ND	RE15	02/03/93	ND
LM03	08/01/90	ND	LM07	08/07/91	ND	RE15	06/07/93	ND
LM03	04/10/91	3.30	LM07	02/20/92	ND	RE15	11/09/93	
LM03	08/07/91	ND	LM07	08/19/92	ND	RE15	03/15/94	
LM03	02/20/92	ND	LM07	11/09/92	ND	RE15	06/06/94	
LM03	08/19/92	ND	LM07	02/09/93	ND	RE15	08/23/94	
LM03	11/09/92	ND	LM07	07/19/93	ND	RE15	08/24/94	
LM03	02/09/93	ND	LM07	03/23/94		RE15	10/18/94	
LM03	07/19/93	ND	LM07	12/28/94		RE30	06/23/88	ND
LM03	03/23/94		LM07	12/28/94		RE30	08/09/88	ND
LM04	11/13/86	ND	LM08	11/13/86	ND	RE30	05/02/89	ND
LM04	07/07/88	ND	LM08	07/07/88	ND	RE30	09/07/89	ND
LM04	08/14/88	ND	LM08	08/14/88	ND	RE30	03/13/90	ND
LM04	02/27/89	ND	LM08	02/27/89	ND	RE30	04/25/90	
LM04	05/24/89	ND	LM08	05/24/89	ND	RE30	06/06/90	
LM04	08/30/89	ND	LM08	08/30/89	ND	RE30	08/07/90	ND
LM04	03/07/90	14.07	LM08	03/07/90	ND	RE30	04/04/91	ND
LM04	08/01/90	ND	LM08	08/01/90	ND	RE30	04/04/91	
LM04	04/10/91	8.52	LM08	04/10/91	ND	RE30	07/16/91	
LM04	08/07/91	ND	LM08	08/07/91	ND	RE30	08/27/91	ND
LM04	02/20/92	0.22	LM08	02/20/92	ND	RE30	10/22/91	ND
LM04	08/19/92	ND	LM08	08/19/92	ND	RE30	04/08/92	0.04
LM04	11/09/92	ND	LM08	11/09/92	ND	RE30	07/28/92	0.46
LM04	02/09/93	ND	LM08	02/09/93	ND	RE30	10/14/92	ND
LM04	07/19/93	ND	LM08	07/19/93	ND	RE30	02/03/93	ND
LM04	03/23/94		LM08	03/23/94		RE30	06/07/93	ND
LM04.1	11/13/86	ND	LM08.1	11/13/86	ND	RE30	11/09/93	
LM04.1	11/13/86	ND				RE30	03/15/94	
						RE30	06/06/94	
						RE30	08/23/94	
						RE30	08/24/94	
						RE30	10/18/94	

FISH (Occoquan Reservoir)

Station	Date	Sample Type		Conc.ppm	Station	Date	Sample Type		Conc.ppm
RE02	06/27/88	LM BASS	FLESH	ND	RE15	04/09/92	CATFISH	ORGA	ND
RE02	06/27/88	LM BASS	ORGANS	IS	RE15	04/09/92	LM BASS	ORGA	ND
RE02	06/08/89	CATFISH	FLESH	ND	RE15	07/14/92	CATFISH	ORGA	0.44

RE02	06/08/89	CATFISH	ORGANS	ND	RE15	07/14/92	CATFISH	FLESH	ND
RE02	04/05/90	CATFISH	ORGANS	ND	RE15	07/21/92	LM BASS	ORGA	ND
RE02	04/05/90	CATFISH	FLESH	-0.01	RE15	07/21/92	LM BASS	FLESH	ND
RE02	06/04/90	CATFISH	FLESH	ND	RE15	10/10/92	LM BASS	FLESH	ND
RE02	06/17/90	LM BASS	FLESH	ND	RE15	10/10/92	LM BASS	ORGA	ND
RE02	06/17/90	LM BASS	ORGANS	ND	RE15	07/07/93	LM BASS	FLESH	NF
RE02	06/12/91	CATFISH	ORGANS	-	RE15	07/07/93	LM BASS	ORGA	NF
RE02	06/12/91	CATFISH	FLESH	-	RE15	07/13/93	CATFISH	ORGA	NF
RE02	06/12/91	CATFISH	ORGANS	-	RE15	07/13/93	CATFISH	FLESH	NF
RE02	06/12/91	CATFISH	FLESH	-	RE15	08/25/93	LM BASS	FLESH	NF
RE02	06/27/91	LM BASS	FLESH	-	RE15	08/25/93	LM BASS	ORGA	NF
RE02	06/27/91	LM BASS	ORGANS	-	RE15	10/12/93	CATFISH	FLESH	NF
RE02	06/27/91	LM BASS	FLESH	-	RE15	10/12/93	CATFISH	ORGA	NF
RE02	06/27/91	LM BASS	FLESH	ND	RE15	06/21/94	CATFISH	FLESH	NF
RE02	06/27/91	LM BASS	ORGANS	0.17	RE15	06/21/94	CATFISH	ORGA	NF
RE02	06/27/91	LM BASS	ORGANS		RE15	06/28/94	LM BASS	ORGA	NF
RE02	04/15/92	LM BASS	FLESH	ND	RE15	06/28/94	LM BASS	FLESH	NF
RE02	04/15/92	LM BASS	ORGANS	ND	RE15	08/23/94	LM BASS	FLESH	NF
RE02	08/19/92	LM BASS	FLESH	ND	RE15	08/23/94	LM BASS	ORGA	NF
RE02	08/19/92	LM BASS	ORGANS	ND	RE15	11/08/94	CATFISH	FLESH	NF
RE02	06/02/93	LM BASS	FLESH	ND	RE15	11/08/94	CATFISH	ORGA	NF
RE02	06/02/93	LM BASS	ORGANS	ND	RE20	05/21/86	CATFISH	ORGA	ND
RE02	08/17/93	LM BASS	FLESH	NF	RE20	05/21/86	CATFISH	FLESH	ND
RE02	08/17/93	LM BASS	ORGANS	NF	RE30	06/28/88	BLUEGILL	WHOL	ND
RE02	06/21/94	LM BASS	FLESH	NF	RE30	08/11/88	LM BASS	WHOL	ND
RE02	06/21/94	LM BASS	ORGANS	NF	RE30	09/06/88	CATFISH	WHOL	ND
RE02	08/16/94	LM BASS	FLESH	NF	RE30	08/27/89	LM BASS	WHOL	ND
RE02	08/16/94	LM BASS	ORGANS	NF	RE30	06/04/90	BLUEGILL	WHOL	0.38
RE02	08/22/94	LM BASS	ORGANS	NF	RE30	05/16/91	LM BASS	WHOL	ND
RE02	08/22/94	LM BASS	FLESH	NF	RE30	05/24/91	LM BASS	WHOL	ND
RE02	09/20/94	CATFISH	ORGANS	NF	RE30	05/24/91	LM BASS	FLESH	-
RE02	09/20/94	CATFISH	FLESH	NF	RE30	05/24/91	LM BASS	ORGA	NF
RE15	06/27/88	LM BASS	ORGANS	IS	RE30	10/22/91	LM BASS	FLESH	ND
RE15	06/27/88	LM BASS	FLESH	ND	RE30	10/22/91	LM BASS	ORGA	IS
RE15	06/28/88	CATFISH	ORGANS	ND	RE30	04/09/92	LM BASS	ORGA	ND
RE15	06/28/88	CATFISH	FLESH	ND	RE30	04/09/92	LM BASS	FLESH	ND
RE15	08/08/88	LM BASS	WHOLE	ND	RE30	07/14/92	LM BASS	ORGA	ND
RE15	09/02/88	CATFISH	WHOLE	ND	RE30	07/14/92	LM BASS	FLESH	ND
RE15	06/06/89	LM BASS	FLESH	ND	RE30	06/15/93	LM BASS	FLESH	ND
RE15	06/06/89	LM BASS	ORGANS	ND	RE30	06/15/93	LM BASS	ORGA	ND
RE15	06/08/89	CATFISH	FLESH	ND	RE30	07/13/93	CATFISH	FLESH	NF
RE15	06/08/89	CATFISH	ORGANS	ND	RE30	07/13/93	CATFISH	ORGA	NF
RE15	04/14/90	CRAPPIE	FLESH	ND	RE30	09/21/93	LM BASS	FLESH	NF
RE15	04/14/90	CRAPPIE	ORGANS	IS	RE30	09/21/93	LM BASS	ORGA	NF
RE15	04/24/90	CATFISH	FLESH	ND	RE30	10/26/93	CATFISH	ORGA	NF
RE15	04/24/90	CATFISH	ORGANS	ND	RE30	10/26/93	CATFISH	FLESH	NF
RE15	06/04/90	LM BASS	ORGANS	7.35	RE30	06/14/94	CATFISH	FLESH	NF
RE15	06/04/90	LM BASS	FLESH	ND	RE30	06/14/94	CATFISH	ORGA	NF
RE15	05/16/91	CATFISH	ORGANS	IS	RE30	07/06/94	LM BASS	ORGA	NF

RE15	05/16/91	LM BASS	FLESH	0.14	RE30	07/06/94	LM BASS	FLESH	NF
RE15	05/16/91	CATFISH	FLESH	0.19	RE30	08/09/94	CATFISH	ORGA	NF
RE15	05/16/91	LM BASS	ORGANS	0.45	RE30	08/09/94	LM BASS	FLESH	NF
RE15	07/16/91	LM BASS	FLESH	1.58	RE30	08/09/94	CATFISH	FLESH	NF
RE15	07/16/91	LM BASS	ORGANS	1.82	RE30	08/09/94	LM BASS	ORGA	NF
RE15	09/24/91	LM BASS	ORGANS	ND	RE30	10/04/94	CATFISH	FLESH	NF
RE15	09/24/91	LM BASS	FLESH	ND	RE30	10/04/94	LM BASS	FLESH	NF
RE15	04/09/92	CATFISH	FLESH	ND	RE30	10/04/94	LM BASS	ORGA	NF
RE15	04/09/92	LM BASS	FLESH	ND	RE30	10/04/94	CATFISH	ORGA	NF

NOTES

1982-92 samples analyzed by the Virginia Tech Pesticide Laboratory

*Indicates data points not used in analysis-suspect lab contamination

1993-94 samples analyzed by OWML

MDL's are as follows:

	Water	Sediment	Fish
1982-92	1.11 ppb	0.8 ppm	2.0 ppm
1993	1.4 ppb	-	.12 ppm
1994	0.3 ppb	-	.12 ppm

Table A-2. Rainfall Data from OWML and Lorton*

Date	Rainfall at OWML (in.)	Rainfall at Lorton (in.)	Date	Rainfall at OWML (in.)	Rainfall at Lorton (in.)
09/27/82	0.00	1.10	09/05/89	0.00	0.00
09/28/82	0.00	0.00	09/06/89	0.00	0.00
09/29/82			09/07/89	0.00	0.00
06/05/83			02/19/90	0.00	0.06
06/06/83	0.49	0.01	02/20/90	0.00	0.00
06/07/83	0.00	0.28	02/21/90	0.00	0.01
08/27/83			03/05/90	0.00	0.00
08/28/83	0.00	0.08	03/06/90	0.00	0.00
08/29/83			03/07/90	0.00	0.00
07/09/85	0.06	0.60	08/26/90	0.00	0.00
07/10/85	0.01	0.03	08/27/90	0.00	0.00
07/11/85			08/28/90	0.00	0.00
08/02/87	0.00	0.03	08/29/90	0.14	0.00
08/03/87	0.00	0.00	04/08/91	0.00	0.00
08/04/87	0.00	0.58	04/09/91	0.00	0.00
02/27/88	0.00	0.01	04/10/91	0.00	0.00
02/28/88	0.00	0.03	05/18/91	0.00	0.02
02/29/88			05/19/91	0.06	0.16
06/19/88	0.00	0.00	05/20/91	0.00	0.00
06/20/88			05/21/91	0.00	0.00
06/21/88			05/22/91	0.00	0.00
06/25/88			05/23/91	0.00	0.00
06/26/88			08/06/91	0.00	0.00
06/27/88			08/07/91	0.00	0.04
09/10/88	0.00	0.00	08/08/91	0.00	0.03
09/11/88	0.00	0.00	08/24/91	0.00	0.00
09/12/88	0.00	0.00	08/25/91	0.00	0.00
09/12/88	0.00	0.00	08/26/91	0.00	0.00
09/13/88	0.02	0.00	11/30/91	0.44	0.06
09/14/88	0.00	0.00	12/01/91	0.78	0.88
02/20/89	0.00	0.05	12/02/91	0.79	0.90
02/21/89	0.23	0.92	07/25/92	0.90	0.60
02/22/89	0.04	0.42	07/26/92	0.00	0.02
02/25/89	0.00	0.00	07/27/92	0.75	0.57
02/26/89	0.01	0.00	07/28/92	0.00	0.00
02/27/89	0.00	0.21	07/29/92	0.00	0.00
08/21/89	0.28	0.18	08/16/92	0.06	0.18
08/22/89	0.00	0.00	08/17/92	0.06	0.13
08/23/89	0.00	0.00	08/18/92	0.00	0.01
08/28/89	0.00	0.00	08/18/92	0.00	0.01
08/29/89	0.00	0.00	08/19/92	0.00	0.00
08/30/89	0.00	0.00			

*Dates two days before and the day of an aqueous atrazine detection

**VIV. APPENDIX B: QA/QC Data and Sample Chromatograms
for Fish Extraction Method**

Table B-1. Surrogate Recoveries for Fish Extraction Method

Lab ID	Tissue/ organ	Fluoranthene d10	Terphenyl d14	Lab ID	Tissue/ organ	Fluoranthene d10	Terphenyl d14
24709	T	128	137	27896	T	71	66
24709	O	108	98	27896	O	41	51
24754	T	104	110	27897	T	94	83
24754	O	32	41	27897	O	102	97
24755	T	75	92	27949	T	111	98
24755	O	40	51	27949	O	59	64
25018	T	62	83	28015	T	69	65
25018	O	19	30	28015	O	113	140
25139	T	82	91	28016	T	136	114
25139	O	61	83	28016	O	65	83
25289	T	101	104	28179	T	104	102
25289	O	90	85	28179	O	75	85
25426	T	83	94	28272	T	112	115
25426	O	55	33	28272	O	134	156
25572	T	103	105	28273	T	73	66
25572	O	55	66	28273	O	52	68
27479	T	111	101	28503	T	108	103
27479	O	43	62	28503	O	58	60
27515	T	70	66	blank2a2		135	129
27515	O	62	78	blankf		118	90
27516	T	90	79	24755TSP	T	131	146
27516	O	125	104	mdl1	T	104	83
27590	T	108	101	mdl2	T	110	91
27590	O	88	106	mdl3	T	101	76
27591	T	100	89	mdl4	T	87	73
27591	O	50	65	mdl5	T	109	86
27659	T	98	91	mdl6	T	132	108
27659	O	108	130	mdl7	T	132	105

Table B-2. MDL and Matrix Spike Data (after blank correction)*

Compound	MDL1	MDL2	MDL3	MDL4	MDL5	MDL6	MDL7	24755TS
ATRAZINE	0.314	0.268	0.242	0.202	0.24	0.222	0.194	0.228
CARBARYL	0.118	0.092	0.096	0.086	0.094	0.06	0.066	0.184
CARBAZOLE	0.344	0.35	0.34	0.276	0.3	0.342	0.382	0.334
DACTHAL	0.214	0.216	0.198	0.202	0.228	0.306	0.26	0.19
DIAZINON	0.094	0.106	0.102	0.096	0.114	0.13	0.126	0.094
DIELDRIN	0.13	0.158	0.134	0.126	0.148	0.234	0.19	0
DUAL	0.254	0.228	0.216	0.144	0.242	0.28	0.2	0.154
FENTHION	0.066	0.058	0	0.048	0.06	0.054	0.058	0.136
HCB	0.194	0.216	0.19	0.196	0.196	0.264	0.146	0.18
HEPTACHLO	0.106	0.118	0.118	0.112	0.064	0.16	0.254	0.162
HEPTEPOX	0.21	0.214	0.198	0.206	0.204	0.302	0.254	0.172
LINDANE	0.546	0.586	0.572	0.6	0.172	0.888	0.716	0.192
MEVINPHOS	0.096	0.096	0.096	0.096	0.096	0.096	0.098	0.102
MOCAP	0.276	0.236	0.248	0.158	0.244	0.28	0.218	0.202
PARATHION	0.308	0.312	0.304	0.202	0.234	0.338	0.338	0.51
PENDAMETH	0.296	0.304	0.28	0.272	0.294	0.352	0.344	0.312
PHORATE	0.202	0.24	0.226	0.184	0.138	0.302	0.292	0.242
PHTH_BB	0.246	0.248	0.228	0.096	0.242	0.344	0.274	0.2
PHTH_DB	0.358	0.38	0.306	0.25	0.396	0.518	0.412	0.218
PHTH_DE	0.374	0.348	0.354	0.27	0.348	0.462	0.414	0.22
PHTH_DO	0.784	0.34	0.338	-0.002	0.212	0.41	-0.482	0.458
PHTH_DM	0.104	0.102	0.108	0.282	0.096	0.058	0.072	0.058
PHTH_DNOC	0.122	0.046	-0.012	-0.05	-0.01	0.322	0.04	0.078
PROPAZINE	0.256	0.242	0.232	0.16	0.228	0.272	0.206	0.166
RONNEL	0.198	0.216	0.194	0.172	0.21	0.25	0.24	0.248
SILVEX	0.334	0.32	0.296	0.298	0.294	0.39	0.356	0.186
T245	0.266	0.282	0.254	0.246	0.234	0.306	0.278	0.31
TERBUFOS	0.196	0.198	0.194	0.17	0.202	0.262	0.246	0.218
VAPONA	0.082	0.068	0.068	0.068	0.068	0.066	0.068	0.068
ACENAPHTH	0.274	0.252	0.244	0.226	0.276	0.316	0.322	0.196
ACENAPHTH	0.336	0.36	0.324	0.29	0.37	0.276	0.342	0.184
ANTHRACEN	0.308	0.3	0.298	0.206	0.22	0.408	0.386	0.19
B_A_ANTHR	0.162	0.134	0.088	0.084	0.078	0.124	0.134	0.23
B_A_PYREN	0.258	0.23	0.23	0.238	0.232	0.434	0.23	0.356
B_B_FLUOR	0.23	0.246	0.242	0.23	0.238	0.332	0.256	0.26
B_K_FLUORA	0.23	0.246	0.242	0.23	0.238	0.332	0.256	0.304
B_GHI_PERY	0	0	0	0	0	0	0	0
CHRYSENE	0.12	0.136	0.134	0.12	0.56	0.31	0.26	0.072
FLUORENE	0.312	0.29	0.286	0.268	0.308	0.354	0.374	0.228
FLORANTH	0.306	0.302	0.29	0.28	0.312	0.378	0.376	0.244
NAPHTHALE	0.172	0.164	0.15	0.144	0.178	0.114	0.144	0.168
PHENANTHE	0.312	0.29	0.228	0.26	0.314	0.356	0.368	0.232
PYRENE	0.296	0.28	0.268	0.262	0.286	0.338	0.35	0.23
aBHC	0.366	0.348	0.36	0.318	0.336	0.486	0.42	0.202
bBHC	0.292	0.264	0.36	0.286	0.26	0.356	0.308	0.138
dBHC	0.158	0.16	0.134	0.108	0.164	0.252	0.182	0.156

*MDL spike level was 0.4 mg/kg, 24755TSP spike level was 0.25 mg/kg

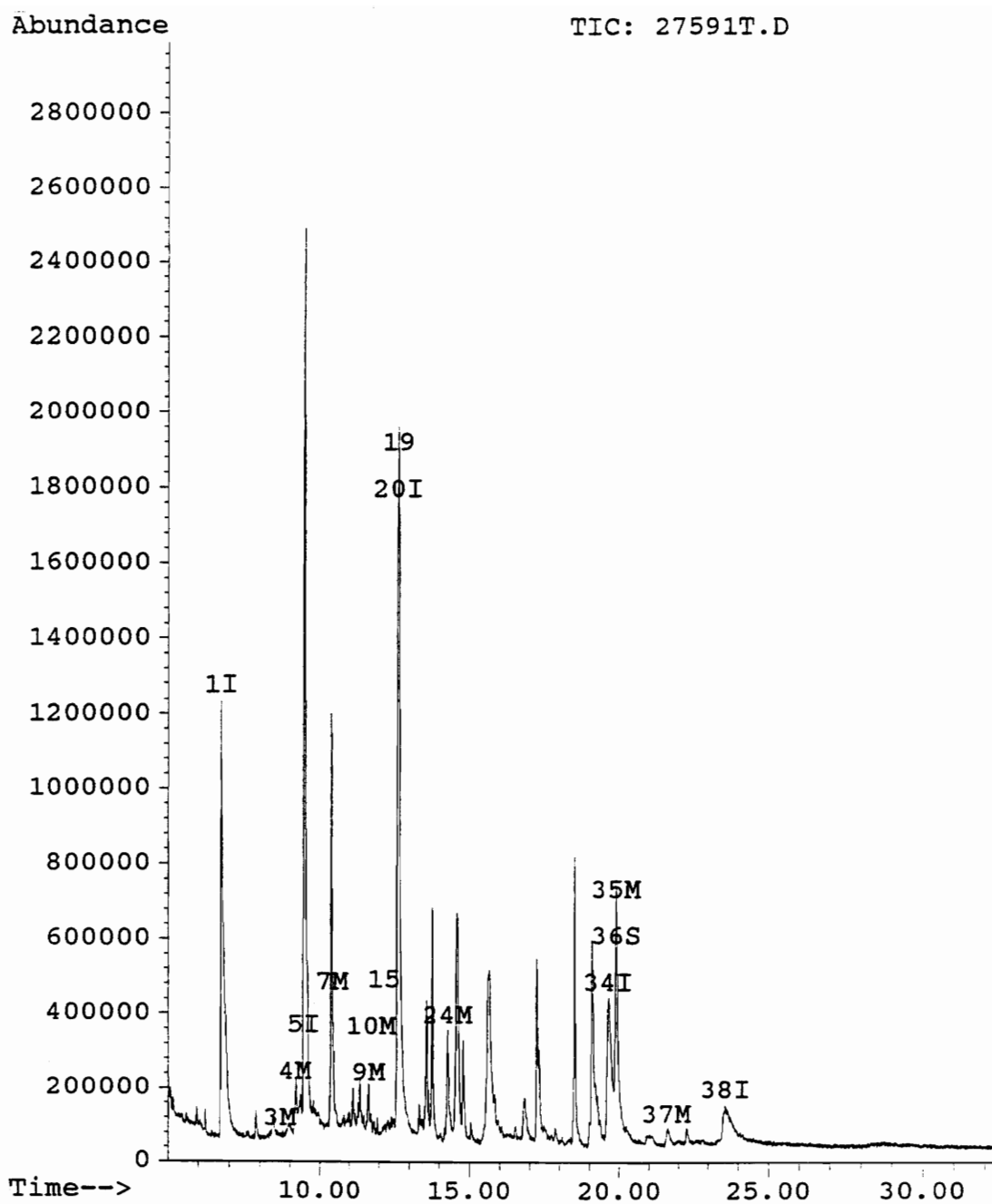


Figure B-1. Sample Chromatogram of Fish Flesh. Internal standards are labeled as 1I (Naphthalene d_8), 5I (Acenaphthene d_{10}), 20I (Phenanthrene d_{10}), 34I (Chrysene d_{12}), and 38I (Perylene d_{12}).

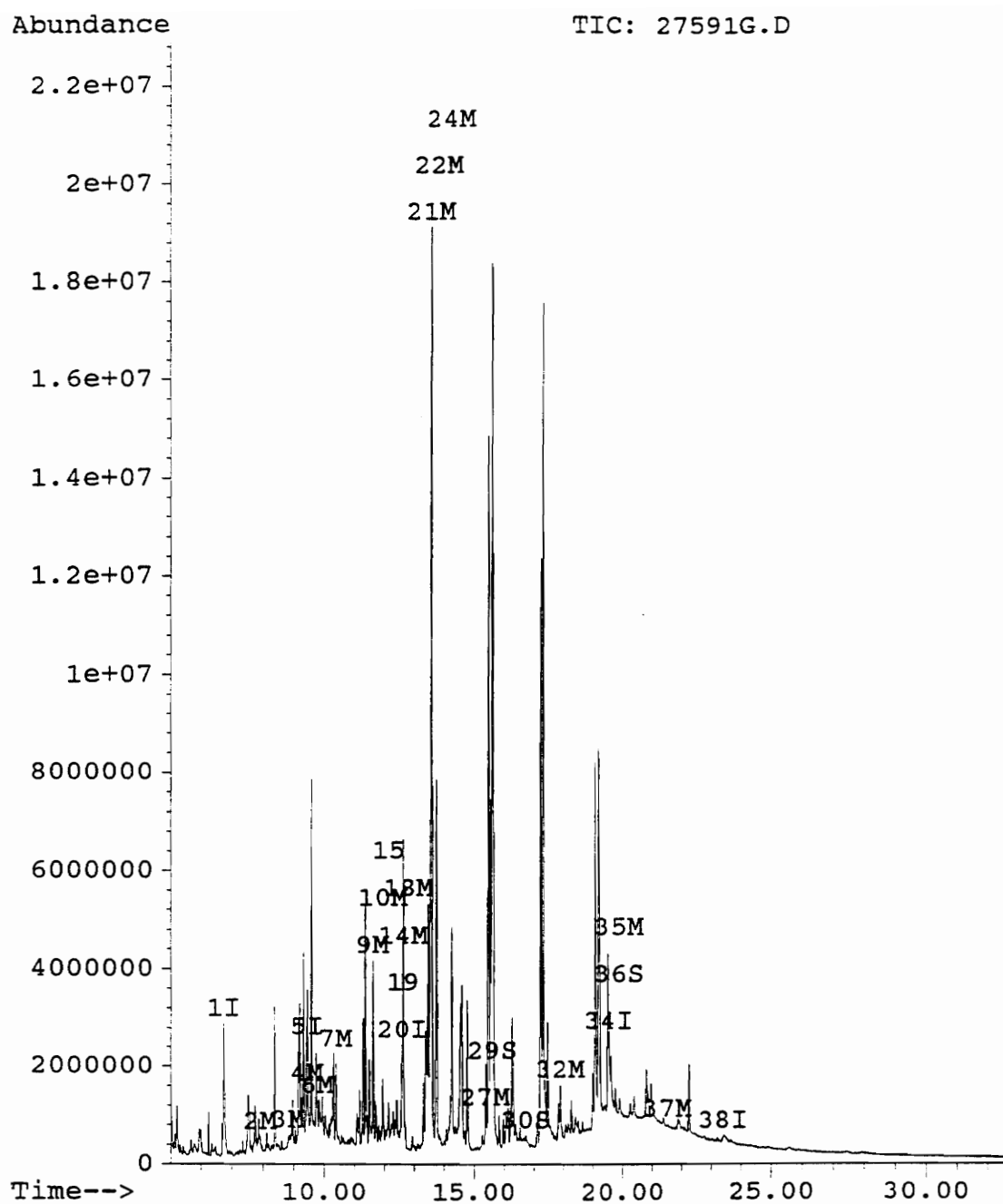


Figure B-2. Sample Chromatogram of Fish Organs. Internal standards are labeled as 1I (Naphthalene d_8), 5I (Acenaphthene d_{10}), 20I (Phenanthrene d_{10}), 34I (Chrysene d_{12}), and 38I (Perylene d_{12}).

X. VITA

Ellen Laurel Hall was born to Anita and Leon Hall in Johnson City, New York, on December 6, 1971. She attended Virginia Polytechnic Institute and State University in Blacksburg, Virginia as a University Distinguished Scholar and graduated with a Bachelor of Science in Civil Engineering, *Summa Cum Laude*, in May of 1994. She completed the degree of Master of Science in Environmental Engineering at VPI&SU in May of 1996.

A handwritten signature in cursive script that reads "Ellen L. Hall". The signature is written in black ink and features a large, stylized initial "E" and a decorative flourish at the end.