AN INVESTIGATION OF THE INFLUENCE OF WATER QUALITY ON THE MERCURY, METHYLMERCURY, ARSENIC, SELENIUM AND CADMIUM CONCENTRATIONS IN FISH OF REPRESENTATIVE MARYLAND STREAMS

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An Investigation of the Influence of Water Quality on the Mercury, Methylmercury, Arsenic, Selenium and Cadmium Concentrations in Fish of Representative Maryland Streams

Final Report

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Introduction

Atmospheric deposition provides a large component of heavy metal and metalloid inputs [e.g. lead (Pb), cadmium (Cd), arsenic (As), selenium (Se), and mercury (Hg)] to many water bodies that are removed from local point source inputs. Metals in deposition are derived from both natural and anthropogenic (point and non-point) sources (Baker *et al.*, 1997; Mason *et al.*, 1997). Power plants and other industrial sources are important contributors of the more toxic elements, such as Hg, Cd, Pb, As and Se (DOE, 1996; USEPA, 1997a). For streams and rivers, direct deposition to the water's surface is less important than runoff from the watershed. Many metals deposited from the atmosphere are strongly retained within the terrestrial environment (Lawson and Mason, 2001). For example, a recent mass balance estimation for Hg and the Chesapeake Bay suggests that about 50% of the Hg entering the mainstem Bay is from direct deposition (Mason *et al.*, 1999). This is mainly a result of Hg being strongly retained within Bay watersheds with less than 20% of the atmospheric input being transported to the Bay. The other metals are more mobile in watersheds, as suggested by recent studies in western Maryland (MD) (Church *et al.*, 1998; Lawson and Mason, 2001) and in Chesapeake Bay tributaries (Lawson *et al.*, 2001). Atmospheric deposition is an important source for Pb, As, and Se, and to a lesser extent for Cd (Scudlark and Church, 1997; Mason *et al.*, 2000a). Overall, in MD, for regions away from point source inputs, deposition rates of metals are relatively uniform (Castro *et al.*, 2000; Mason *et al*., in press). Thus differences in atmospheric deposition cannot be invoked to account for any variation in the concentration of metals in fish in MD waters.

While there are few data available, an understanding of sources of metals and the impact of water chemistry on metal speciation and bioavailability leads to the conclusion that water chemistry is likely the most important factor influencing fish metal burdens, regardless of Hg source, such as food type (Mason *et al*., 2000b). Certainly, this has been demonstrated for Hg in a number of studies within the USA and elsewhere (e.g. Wren and MacCrimmon, 1983; Wiener and Stokes, 1990). Information within MD has been severely limited and it was for this reason that the current study was initiated. Indeed, most data to date has come from studies in western Maryland relating water chemistry to fish concentration (Castro *et al*., 2000; Mason *et al*., 2000b). The primary

objectives of this work were to measure stream water chemistry and metal concentrations and to investigate relationships between these parameters and fish tissue metal concentration. Our studies in Chesapeake Bay tributaries (Lawson *et al.*, 2001) and other results (Hurley *et al.*, 1995, 1996) suggest that pH and DOC are important factors controlling metal fate, transport and bioavailability. Our initial studies in western MD showed that fish in two streams of different water chemistry had different levels of Hg, MMHg, As, Se and Cd and that these differences appeared to be explained by noted differences in water concentrations and seasonal metal inputs (Mason *et al.*, 2000b; Lawson and Mason, 2001).

The current study was an attempt to look at these relationships on a larger spatial scale. The objectives of this study was to relate fish concentration to that of water chemistry and thus it were felt that sampling small fish in small streams would provide the best mechanism for testing these relationships. The advantage of using small fish was that the complications of food web structure would be minimized as differences in diet can have a substantial effect on fish mercury burden and of that of other metals (Mason *et al*., 2000b). Thus, smaller fish are better indicators of water chemistry as food preference is less variable between species for juvenile fish compare to adult fish. Additionally, growth rate will effects are minimized by focusing on small fish. Secondly, by focusing on small streams, multiple collections could be made within a small geographical area of streams of different chemistry. Streams were for the most part low order. Again, using such an approach would minimize other sources of difference, such as differences in atmospheric inputs, and differences in watershed characteristics. For the most part, streams chosen for study were in rural areas with the watersheds dominated by either forest or agricultural land (DNR, 2001). Maps showing the locations of the sampling sites are gathered in Appendix 1. Most of the sites were on the eastern shore of the Chesapeake Bay with only six sites on the western shore, in Charles County, MD.

Sampling Location, Fish Distribution and Sampling Methods

Fish samples were collected during the summer and early fall of 1999 from a total of 13 streams (Appendix 1). Three different excursions were made to the various sites. The first four sites

were part of the Mason Branch watershed in Queen Anne's County, bordering Caroline County (Fig. A1). The second set of four sites were in the Andover watershed, also in Queen Anne's County near the Maryland-Delaware border (Figs. A2 and A3). The six western shore sites were in the Mattawoman Creek watershed and surroundings (Figs. A4 and A5). The streams sampled, and the chemistry of each stream from the Maryland Department of Natural Resources (DNR) spring survey, are given in the following tables. Measurements by DNR of water chemistry in these streams are in conjunction with a yearly biological stream survey and no seasonal chemistry data is available for these streams. While information on nutrient concentrations and oxygen are available (DNR, 2000) these were not used in this study as they have not been found to be important criteria in such small streams. All streams were relatively shallow (<2 m) as fish were collected by wading personnel using electroshocking equipment. The streams in Queen Anne's County were predominantly surrounded by agriculatural land (>50% typically) with most of the remainder of the catchment being forested. In Charles County, watersheds were mostly forested with a small urban component (<10%).

In Table 1, streams are listed in terms of the main watersheds, and according to date of collection. In Table 2, information on fish collected is gathered and analytical QA/QC data are given in Table 3. Streams were chosen to span a range of pH and DOC, especially, if possible, within the same watershed. The choice of stream was based on baseline information available for each stream (Table 4). No extremely high pH streams were sampled and most streams had relatively high DOC (4-12 mg/L). Water samples were also collected on the sampling day and analyzed for DOC and alkalinity for comparison with the data from the routine DNR spring monitoring program (Table 4). These samples were analyzed by CBL Analytical Services for their alkalinity, as this is the standard procedure for this laboratory, while the samples analyzed by DNR were analyzed for ANC. Additionally, the alkalinity samples from the Andover/Red Lion batch of samples were lost between collection and analysis.

Fish were collected by electroshocking by DNR personnel. Given the stream size and depth, fish were likely juveniles (Table 2). As it was not known how many fish and what species would be found at each site, a larger number of fish were collected than were analyzed. In a number of

watersheds fish of similar species and size were caught and thus not all these fish were analyzed. The subsample of the fish analyzed was a representative distribution of species and size across all the watersheds. All of the larger fish sampled were analyzed. A listing of the fish sampled and the number of fish collected and analyzed is given in Table 2. Sunfish (Centrarchidae) were found at most sites. At least one species, and typically two or three species of sunfish (*Lepomis* sp. or *Enneacanthus* sp.), were found in each stream. The most widely distributed was the bluespotted sunfish - in all streams except Piney Branch and Marbury Run - and bluegill, which were not in Mason 101 and Mason 104. Pickerel (both species) were less widely distributed, being absent from Mason 106, Piney Branch, Marbury Run and Mattawoman Creek. Minnows were present at some locations, but were not targeted, and thus are absent from the dataset for Mason Reference, Andover Reference, Timothy Branch and Mattawoman Creek. Catfish were only found in the Mason Branch watershed and at Andover Reference. Largemouth bass were collected from all sites except Mason 101, Mason 106, Red Lion Reference, Piney Branch and Mattawoman Creek.

Table 1: Location of each stream sampled.

MBSS Code	Stream Name	Sample Date	Location
QA-N-094-101Q-99	Mason 101	7/27/99	39^{O}06"34' N; 75^{O}50"10'W
QA-N-052-104Q-99	Mason 104	7/27/99	39^{O}05"19' N; 75^{O}50"50'W
QA-N-074-106Q-99	Mason 106	7/27/99	39^{O}06"52' N; 75^{O}49"20'W
QA-N-098-REFQ-99	Mason Reference	7/27/99	39^{O}02"02' N; 75^{O}52"55'W
QA-N-024-102Q-99	Andover 102	9/2/99	39^{O}12"52' N; 75^{O}45"14'W
QA-N-124-103Q-99	Andover 103	9/2/99	39^{O}12"26' N; 75^{O}45"58'W
QA-N-111-REFQ-99	Andover Reference	9/2/99	39^{O}13"40' N; 75^{O}46"43'W
QA-N-033-REFQ-99	Red Lion Reference	9/2/99	39^{O}11"23' N; 75^{O}54"04'W
CH-S-030-Q103-99	Timothy Branch	10/7/99	38^{O}40"04' N; 76^{O}52"38'W
CH-S-252-Q108-99	Piney Branch	10/7/99	38^{O}39"06' N; 76^{O}58"17'W
CH-S-296-Q112-99	Marbury Run	10/7/99	38^{O}34"08' N; 77^{O}09"00'W
CH-S-046-Q202-99	Mattawoman Creek	10/7/99	38^{O}31"37' N; 76^{O}51"24'W
CH-S-181-Q205-99	Mattawoman Creek	10/7/99	38^{O}39"18' N; 77^{O}00"10'W

Table 2: Summary statistics for stream sampling in 1999. Abbreviations for fish species are given below.

Fish Type	# of Fish Sampled	# of Fish Analyzed	Species Breakdown for Analysis	Average Weight (g)
Sunfish	209	106	RBS 21, BSS 34, BG 26, PS 25	19.8 ± 25.4
Pickerel	26	24	CP 8, RP 16	45.2 ± 79.9
Minnows	40	25	FF 13, GS 12	36.8 ± 62.5
Bass	18	11	LMB 11	61.4 ± 89.0
Catfish	10	9	MT 8, BB 1	11.1 ± 11.4

The fish species found in the streams were:

Sunfish: bluespotted sunfish (BSS), redbreast sunfish (RBS), pumpkinseed (PS), and bluegill (BG)

Pickerel: chain pickerel (CP) and redfin pickerel (RP)

Minnows: fallfish (FF) and golden shiner (GS)

Bass: largemouth bass (LMB)

Catfish: madtom (MT) and brown bullhead (BB)

Table 3: Quality control parameters for the various metals analyses. The detection limit, percentage relative standard deviation for laboratory and field duplicates, typical spike recoveries and field blanks are given for each metal (mercury (Hg), methylmercury (MMHg), cadmium (Cd), lead (Pb), arsenic (As) and selenium (Se)).

Metal	DL Water*	DL Fish	% RSD	% Typical Recovery of Matrix Spike	Field Blank*
Hg	0.1	0.05	<20	80-120	<1
MMHg	0.01	0.015	<20	80-120	<DL
Cd	0.01	0.005	2	95-105	<DL
Pb	0.02	-	2	90-110	<DL-0.15
As	0.03	0.05	<5	90-110	<DL
Se	0.03	0.05	<5	90-110	<DL

*Detection limit (DL) and blank values are given in μg/L and μg/g for all metals except Hg and MMHg which are given in ng/L and ng/g.

After collection, fish were briefly transferred to a plastic container of distilled water to rinse them of adhering material and were handled and rinsed by gloved personnel, and transferred to plastic ziplock bags. Samples were kept on ice until arrival at CBL. Fish were weighed individually, and were then frozen until analysis. Individual fish were ground whole in a small plastic blender in a non-contaminating environment and were subsampled for analysis of each parameter. The blender was washed with dilute hydrochloric acid (HCl) and distilled water between fish. Samples were separately digested, as discussed below, for total Hg, MMHg and for Cd, As, and Se.

All sampling devices, where appropriate, were acid cleaned with dilute HCl or concentrated nitric acid prior to use and in between deployments. Stream water was sampled for Hg and MMHg by dipping 2 L Teflon bottles into the stream. Given funding constraints it was not possible to sample the streams more than once for water quality even though it was recognized at the outset that this was not ideal in terms of characterizing the watersheds. However, it was felt that comparison of the measurements at time of sampling with those of the spring survey by DNR would provide some indication of potential variability in water quality parameters. Water was filtered for Hg and MMHg under a Class 100 clean bench, using a peristaltic pump, acid-washed Teflon tubing and pre-cleaned 0.45 µm pore size filters, at the end of each collection. An aliquot was transferred to an acid-cleaned polyethylene bottle and stored for metal analysis after acidification. Filters were stored in acid-cleaned petri dishes and frozen. Water was also collected for dissolved organic carbon (DOC) and alkalinity (Alk) while filters were analyzed for total suspended load (SPM) and for particulate carbon (POC) and nitrogen (PON). CBL Analytical Services performed all ancillary measurements. In addition, the following parameters are measured yearly during the DNR spring survey - pH, ANC, DOC. Comparison could therefore be made between the two datasets (Table 4).

Samples were analyzed for total Hg and Hg speciation using standard techniques (Bloom and Fitzgerald 1988; Bloom 1989; EPA 1995). Total Hg was measured in water samples after oxidation of samples with 0.5 mL of 2N bromine monochloride)(Bloom and Crecelius 1983;

USEPA, 1995) and pre-reduction with hydroxylamine hydrochloride. Samples were then reduced with a tin chloride solution and purged to remove elemental Hg to a gold trap. Hg was determined by two-stage gold amalgamation cold vapor atomic fluorescence spectroscopy (CVAFS; Bloom and Fitzgerald 1988). Particulate (filter) samples were digested overnight in a 70:30 nitric/sulfuric acid mixture at 60^{o} C in Teflon digestion vessels prior to bromination. Methylmercury measurements were made on samples by distillation separation followed by derivitization with sodium tetraethylborate, chromatographic separation, and CVAFS (Horvat *et al.* 1983; Bloom 1989; Mason *et al.* 1997).

As noted above, water samples were taken for metal analysis but these were inadvertently discarded before they could be analyzed. Given the results of the study in western MD (Mason *et al*., 2000), that showed little relationship between water concentration of As, Se and Cd and fish tissue concentration, the lack of information on water chemistry is not considered significant.

For fish tissues, analysis followed the same procedures outlined above with digestion of about 1 g of tissue using the same techniques as described above for particulate samples. Metal analysis relied on a Hewlett-Packard 4500 Inductively Coupled Plasma Mass Spectrometer (ICP-MS). These methods are consistent with those proposed by EPA (USEPA, 1997b). The metalloids were analyzed by hydride generation-atomic fluorescence techniques, using an automated Merlin PSA analyzer or by ICP-MS (Lawson *et al*., 2001).

Standard calibration curves were run daily, and a standard addition spike (added to one in every 15 samples) was used to check for matrix interferences. Externally certified reference samples (digestates of NIST SRM 1646a Sediment for Cd, Pb, As, and Se and IAEA SRM 142 for Hg and MMHg) were also regularly included in the analytical protocols to verify the accuracy of the results. Furthermore, the Mason laboratory participated in the Canadian National Water Research Institute intercalibration in late summer, 1997 to confirm the analytical methods for trace metals. All results were within the accepted variability. In another study, we compared our sample collection and analysis of river water with those of the Maryland USGS and a commercial analytical company, Frontier Geosciences. All laboratories obtained comparable results (unpublished data). Additionally, the Mason laboratory is a regular participant in intercomparisons

for Hg and MMHg; the most recent being a comparison of the analysis of Hg and MMHg in Florida Everglades waters organized by Florida Department of Environmental Protection for USEPA. Overall, our results compare with those of others (within 20% of the mean for Hg and MMHg, within 10% for the other metals, which is considered normal for trace Hg and MMHg analysis). Samples were run in duplicate when possible and replicate samples were run on separate days to represent true analytical reproducibility.

For water samples, the typical detection limits for the various metals and metalloids analyzed are: total Hg 0.1 ng/L; MMHg 0.01 ng/L; Cd 0.01 μg/L; Pb 0.02 μg/L; As 0.03 μg/L; and Se 0.03 μg/L (Table 3). Detection limits for particulate samples depended on the sample volume filtered but were generally of the same order as the total metal detection limits. Field and travel blanks were typically less than the detection limit. For tissue samples, detection limits were 0.05 ng g^{-1} for total Hg, 0.015 ng g^{-1} for MMHg, 0.005 μg g^{-1} for Cd and 0.05 μg g^{-1} for As and Se (Table 3), similar values to those of our other studies (Mason *et al.*, 2000).

For correlation between parameters, linear regression techniques were used. In addition, stepwise regression techniques were used to examine the importance of more than one variable and to determine statistical relationships for fish MMHg concentration with the water chemistry parameters. These statistical approaches utilized the tools available in the software packages Microsoft Excel and Quattro Pro. Graphical representation of data relied mostly on the software package, Sigmaplot.

Results and Discussion

Water Chemistry

The DNR measurements of ANC, pH and DOC were made in spring while the measurements made by CBL were made at the time of collection (late summer/early fall). It is possible that spring concentrations would have lower pH and ANC (due to the influence of spring runoff) than samples collected in summer, when ANC or alkalinity may be increased due to higher temperatures (i.e. increased CO_2 solubility), and pH increased as a result of enhanced productivity. The streams sampled were still turbid on some sampling days and it is difficult to ascertain how this

may have hindered productivity. From spring data, it can be seen that the range in ANC was large (Table 4). ANC changes did not correlate directly with changes in pH, although there is some correspondence between the two parameters. This is somewhat unexpected and suggests that other constituents besides carbonate species is contributing to ANC, most likely DOC. In a general sense, the expected trends are observed. The highest pH stream (pH 7.06) was Andover 102 (Table 4) which also had the highest ANC (595.4μeq/L). The lowest pH stream (Mattawoman Crk.) had nearly the lowest ANC (2.2 μeq/L in spring; Table 4). Mason Reference branch, which was a high DOC stream, had a lower ANC, and a somewhat higher pH (6.31). This stream falls within the batch of low pH streams, but it is clear that the high spring DOC concentration (11.3 mg/L) decreased the ANC; i.e. increased the acidity.

For most waters, there should be little difference between ANC and alkalinity if the acid–base chemistry is controlled by the concentration of dissolved CO_2 and its dissociation products (bicarbonate and carbonate). In systems with elevated dissolved organic acids or other acid-base pairs, ANC and alkalinity may not be equivalent. In the Mason watershed, differences between the spring ANC and summer alkalinity values are most marked while they are very similar for the Mattawoman watershed. This is likely a function of sampling time with all Mason Branch samples being collected in July while those of the Mattawoman region were collected in October, when productivity is likely decreased. In the Mason watershed, all values of alkalinity were substantially elevated in July compared to the DNR ANC values as expected if primary productivity is affecting alkalinity (Table 4).

DOC concentrations also varied to a larger degree in the Mason watershed compared to the Mattawoman watershed where DOC concentrations were fairly similar between the two collections. Again this reflects the role of summer productivity in controlling water chemistry and differences in values highlights the difficulty in characterizing a stream based on samples collected only once per year. For the Andover/Red Lion sampling, the alkalinity samples were not run and thus comparison is not possible. However, DOC concentrations were typically lower in summer (Table 4) suggesting that there were differences for this watershed as well on a seasonal basis. These differences must be kept in mind when comparing the fish metal concentrations to these water quality parameters.

Table 4: Concentration of alkalinity (Alk) or ANC, dissolved organic carbon (DOC), particulate matter (SPM) and particulate organic carbon (POC) in the streams. DNR = from DNR spring survey; CBL = from samples collected at the time of fish collection.

Stream	**pH DNR**	**DOC* (DNR) (mg/L)**	**ANC (DNR) (μeq/L)**	**Alk (CBL) (μeq/L)**	**DOC* (CBL) (mg C/L)**	**SPM (CBL) (mg/L)**	**POC (CBL) (mg C/L)**
Mason 101	6.47	4.92	20.0	309	4.5	8.6	1.5
Mason 104	6.45	8.38	110.2	413	3.9	2.4	0.47
Mason 106	6.61	7.60	282.9	626	9.6	40.9	3.01
Mason Ref.	6.31	11.31	-7.9	262	2.6	2.4	0.22
Andover 102	7.06	8.09	595.4	-	5.9	2.9	0.48
Andover 103	6.27	8.57	45.6	-	7.7	6.1	1.1
Andover Ref.	6.98	9.42	10.60	-	5.4	3.8	1.2
Red Lion Ref.	6.62	7.50	95.8	-	3.1	5.2	0.74
Timothy Branch	6.18	7.56	95.8	153	7.6	12.6	1.3
Piney Branch	6.53	5.59	118.4	109	5.5	2.9	0.61
Marbury Run	6.24	4.77	70.3	76	4.6	3.3	4.6
Mattawoman Crk.	5.24	8.38	2.2	13.4	8.0	13	3.2
Mattawoman Crk.	6.20	7.25	48.2	84	8.6	7.6	0.94

Note: * DOC and ANC are measured by DNR personnel during their spring sampling while the data from CBL are those for the summer sampling at the time of fish collection.

Mercury and Methylmercury in Water

Hg and MMHg concentrations are given in Table 5. Total Hg concentrations were around 1 ng/L (5 pM) and relatively consistent between sites, except for Andover Reference (2.03 ng/L), Timothy Branch (3.84 ng/L), Mattawoman Creek Q202 (5.20 ng/L) and Q205 (3.92 ng/L). These values are at the lower end of the range in Hg concentrations found in rivers in MD (Lawson *et al*., 2001; Lawson and Mason, 2001).

Table 5: Total mercury, and total and dissolved methylmercury in each stream.

Stream	Total Hg (ng/L)	MMHg (ng/L)	Diss. MMHg (ng/L)
Mason 101	0.83	0.10	0.043
Mason 104	0.94	0.02	0.016
Mason 106	1.80	0.10	<0.005
Mason Ref.	1.20	0.02	0.021
Andover 102	1.27	0.09	0.065
Andover 103	1.00	0.07	0.041
Andover Ref.	2.03	0.14	0.097
Red Lion Ref.	1.38	0.09	0.046
Timothy Branch	3.84	0.19	0.094
Piney Branch	1.44	0.13	0.099
Marbury Run	1.45	0.10	0.066
Mattawoman Crk. (Q202)	5.20	0.94	0.621
Mattawoman Crk. (Q205)	3.92	0.24	0.195

The Mattawoman Creek and surrounding streams had the highest total MMHg concentrations with the highest concentration (0.94 ng/L) at Mattawoman Creek (Q202), coincident with the high total Hg concentration. Mattawoman Creek (Q202) also had the highest percent MMHg (18%; Table 5) while in the other streams the %MMHg ranged from 1-12%, and the overall average was 7 ± 5%. The average %MMHg is typical of large and small streams (Lawson *et al.*, 2001; Lawson and Mason, 2001). The high value represents a somewhat anomalous situation although such high %MMHg has also been found by others, with a similar average value (e.g. Hurley *et al.*, 1995). The total Hg concentrations vary by about a factor of 5 while the difference in MMHg concentration is larger (0.01 to 0.9 ng/L, or a factor of 90). It is likely that the high MMHg values for the Mattawoman sites reflect the fact that there is significant wetlands within these watersheds (Fig. A4 and A5). While these MMHg concentrations are high relative to the other sites, they are comparable to those found in the MD reservoirs (0.1-0.4 ng/L, and as high as 0.7 ng/L; Sveinsdottir, 2002). Further study of the Mattawoman watershed should investigate the relationship

between extent of wetlands and the MMHg in water as this relationship has been shown to be important in boreal lakes (Heyes, pers. comm..).

Thus, MMHg concentration in the water may be an important factor in controlling fish tissue concentration. However, it is useful to compare the dissolved concentration rather than the total concentration as the total suspended load in each stream is different. Bioavailability will presumably depend more on dissolved concentration, which controls accumulation into algae at the base of the food chain (Mason et al., 1996). Based on the measurements of particulate Hg and MMHg and the SPM (Table 4), the average log K_D was determined as 5.9 for total Hg and 5.0 for MMHg. These values are similar to those found in other rivers within MD (Lawson *et al.*, 2001; Lawson and Mason, 2001; Mason and Sullivan, 1998). Based on these values, the estimated dissolved MMHg concentrations are reported in Table 5.

Fish Concentration- Mercury and Methylmercury

Average concentrations of MMHg for each fish group are given in Table 6, and the percent MMHg for each fish group is also listed. Individual fish data is collected in appendix 2. For Hg, the concentration of MMHg in the fish is the parameter that will be discussed during most of the report as it the species of Hg that bioaccumulates through all levels of the food chain while the inorganic Hg does not (Mason *et al*., 2000; 1996). Thus, the relationship between MMHg in fish and MMHg in water, and with the water quality parameters, is the most relevant comparison that can be made.

To some degree the differences in the concentration of MMHg in the fish and the %MMHg can be related to the feeding preferences of the fish. Clearly, these change with fish size and age and can confound the associations between water chemistry and fish concentration. Indeed, this was one reason for focusing the study on smaller fish as their MMHg concentration would be less impacted by changes in feeding strategy during growth. Furthermore, the higher the trophic level of the fish, the less strongly the fish concentration is coupled to water chemistry because of these differences in feeding patterns.

Given the size and fish species analyzed, the only species that have significantly different feeding strategy are catfish (Table 7), which are benthic feeders and consume primarily benthic invertebrates. The differences in MMHg concentration for the catfish compared to the other species, even considering their relatively small size compared to the other fish, was noticeable (Fig. 1). Also, the catfish had the lowest %MMHg of all species. The small sunfish sampled in this study likely are dominantly invertivores, while the pickerel and bass are piscivorous. However, most of the fish at the small size found in the streams feed on a mixture of insects and small fish and thus it is difficult to directly contrast the MMHg concentration in these fish as they occupy a similar trophic niche (Table 7).

Table 6: Average concentrations of methylmercury, arsenic, selenium and cadmium in whole fish. All concentrations are given on a wet weight basis.

Fish Type	n	Weight (g)	MMHg* (ng/g)	%Methyl Hg	As (μg/g)	Se (μg/g)	Cd (μg/g)**
Sunfish	106	19.8 ± 25.4	73 ± 80	77	0.26 ± 0.25	0.57 ± 0.25	0.10 ± 0.27
Pickerel	24	45.2 ± 79.9	76 ± 74	89	0.28 ± 0.27	0.53 ± 0.19	0.02 ± 0.04
Minnow	25	36.8 ± 62.3	96 ± 113	91	0.13 ± 0.15	0.41 ± 0.22	0.06 ± 0.06
Bass	11	61.4 ± 89.0	76 ± 51	94	0.20 ± 0.22	0.75 ± 1.08	0.10 ± 0.14
Catfish	9	11.0 ± 11.4	36 ± 34	41	0.25 ± 0.27	0.44 ± 0.26	0.02 ± 0.02

Note: ***** Average Total Hg can be determined by dividing the MMHg value by the MMHg fraction e.g. Sunfish Total Hg = 73 ± 80/0.77 = 95 ± 104 ng/g.

** 0.01 ppm is the detection limit for Cd**.**

When comparing the average fish weight and the average concentration, there is a reasonably similar correlation between these two parameters for all the fish except catfish (Fig. 1). When individual fish are plotted (Fig. 2), there is the most scatter for sunfish, but this may be partly because of the larger sample size. The correlation between fish concentration and size (weight) is poor since this relationship combines different species across all streams. To compare among species, the concentration in fish of less than 50 g was compared. For sunfish and pickerel,

concentrations were generally less than 250 ng/g; for carp and bass, less than 150 ng/g, and for catfish, less than 100 ng/g. Again, this shows clearly the discrepancy between catfish concentrations and those of the other species. Interestingly, for the small bass, concentrations on a weight-comparative basis are lower than for sunfish.

Table 7: List of fish species sampled and details of their feeding preferences. Taken from Eddy and Underhill (1976), Smith (1979) and Murdy et al. (1997).

Name	**Common Name**	**Food Preferences**
Micropterus salmoides	Largemouth bass	Small fish eat plankton and insects, and amphipods. Larger fish eat crustaceans (crayfish preferred), frogs, small fish (minnows, sunfish, perch)
Lepomis gibbosus	Pumpkinseed	Invertebrates including snails, amphipods and insects, and for older fish, other small fish.
Lepomis macrochirus	Bluegill	Aquatic insects, worms, amphipods with older fish eating snails, crayfish and some small fish
Lepomis auritus	Redbreast sunfish	Invertebrates including insects, plankton; crayfish, small fish
Enneacanthus gloriosus	Bluespotted sunfish	Crustaceans, insects, worms
Notemigonus crysoleucas	Golden shiner	Mud, plankton, plant material, mollusks, amphipods, terrestrial insects
Semotilus corporalis	Fallfish	Plant and animal materials from algae and invertebrates to small fish
Ictalurus nebulosus	Brown bullhead	Insects, bottom-dwelling crustaceans and mollusks
Noturus gyrinus	Tadpole madtom	Amphipods, insect larvae, small crustaceans, algae,
Esox niger	Chain pickerel	If >15 cm, fish and crayfish
Esox americanus	Redfin pickerel	Invertebrates when young; fish when older

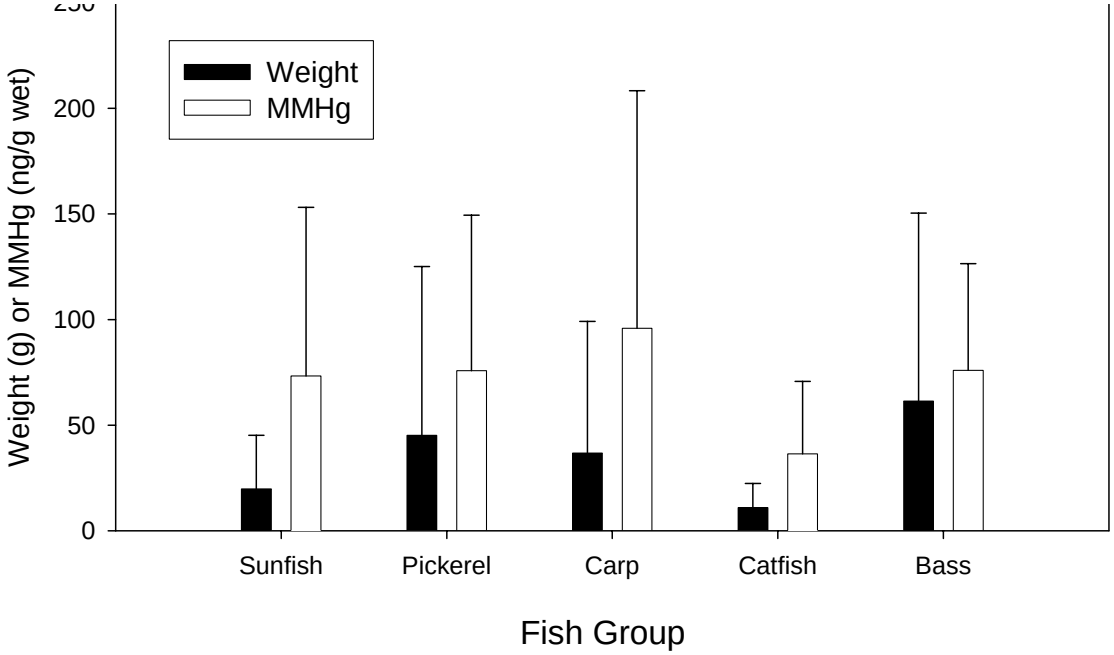


Figure 1: Average weight of fish (grams) and average methylmercury tissue concentration (ng/g wet weight) for each fish group.

Pickerel and bass, because they were the larger of the fish caught, show a stronger relationship between concentration and weight as MMHg concentration is cumulative with age given its slow depuration from tissue. For minnows, one large fallfish had a high MMHg concentration with others showing little trend with size. For all species, the higher concentration fish were not concentrated in a single watershed and not just in one location so these fish do not have a skewed influence over any correlations between parameters. Because of the limited weight range in most cases, other factors besides age-related accumulation govern fish MMHg concentration. This is discussed below. The largest dataset was for sunfish and thus these results will be examined in terms of the individual species (Fig. 3) - bluespotted sunfish (BSS), bluegill (BG), pumpkinseed (PS) and redbreast sunfish (RBS). The streams are referred to in this and further figures by codes that represent their location - M=Mason Branch; A=Andover; REDL=Red Lion Reference; and Q=the Mattawoman Creek series (see Table 1 for details in terms of which stream each code represents).

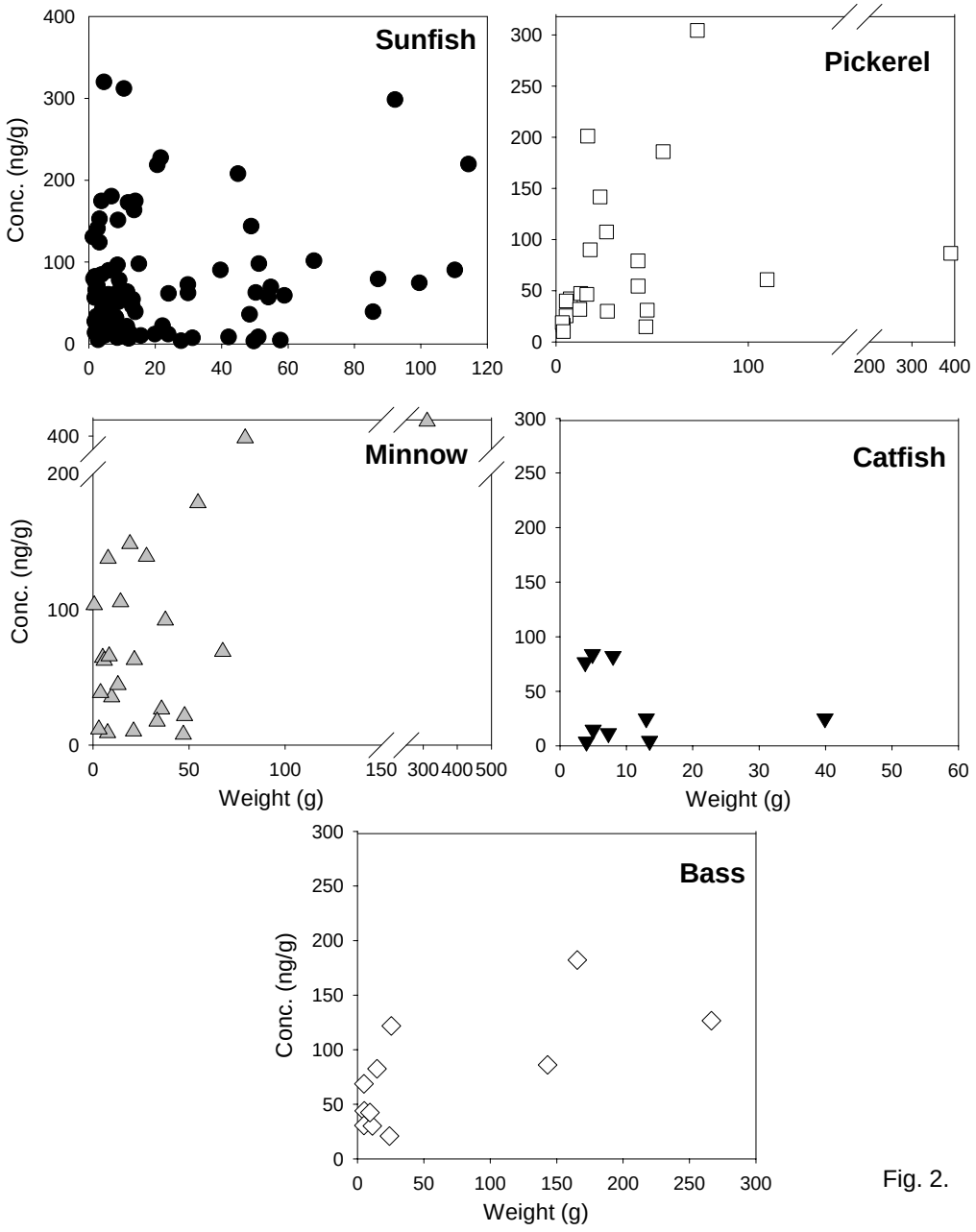


Fig. 2.

Figure 2: Graph of individual fish tissue methylmercury (in ng/g wet weight) against fish weight, in terms of each fish grouping (sunfish, pickerel, minnows, catfish and bass).

In streams where all sunfish species were found it appeared that there was no consistent trend between MMHg concentration and species. For example, in Andover 102, the highest concentration was in redbreast sunfish with the lowest in bluespotted sunfish (Fig. 3) while their

MMHg concentrations were comparable and higher than other species in Mattawoman Creek (Q205). From an examination of these results, it appears that inter-species differences were not consistent and it is therefore reasonable to combine these fish into one group, as has been done mostly throughout the rest of the report. It is worth noting that redbreast sunfish occasionally had very high concentrations relative to the others - e.g. for Q112 and A102 . The reason for this is not known.

It is clear that there were large differences in concentration between streams and between locations, as predicted (Fig. 3). The concentrations of MMHg in the sunfish from the Mason Branch watershed were substantially lower than other locations (Fig. 4). In the Mason Branch streams, except for one fish, the highest concentration was <100 ng/g compared with much higher values in the other systems (Fig. 4). The difference cannot be explained in terms of fish size. Indeed, most sunfish in the Mattawoman Creek region were small but had the highest concentrations (Fig. 4b). These tissue concentration differences will be discussed below in terms of water chemistry but the reason for the large differences is not simple and does not just depend on differences in a single water quality parameter, nor was it strongly dependent on the measured MMHg concentration. The correlation between fish concentration and either total MMHg, or dissolved MMHg concentration, was weak (Table 8; r = 0.13 for sunfish; 0.075 for pickerel). Note that for this multiple regression, data from only the 9 streams that had both sunfish and pickerel are used. The only significant correlation for a single water chemistry parameter was for pickerel and ANC ($r = 0.646$; $p \leq 0.05$) Overall, the concentrations of sunfish and pickerel were correlated but not significant (r = 0.33; Table 8). Thus, in the broadest sense, factors controlling MMHg in fish are reasonably similar for both fish types.

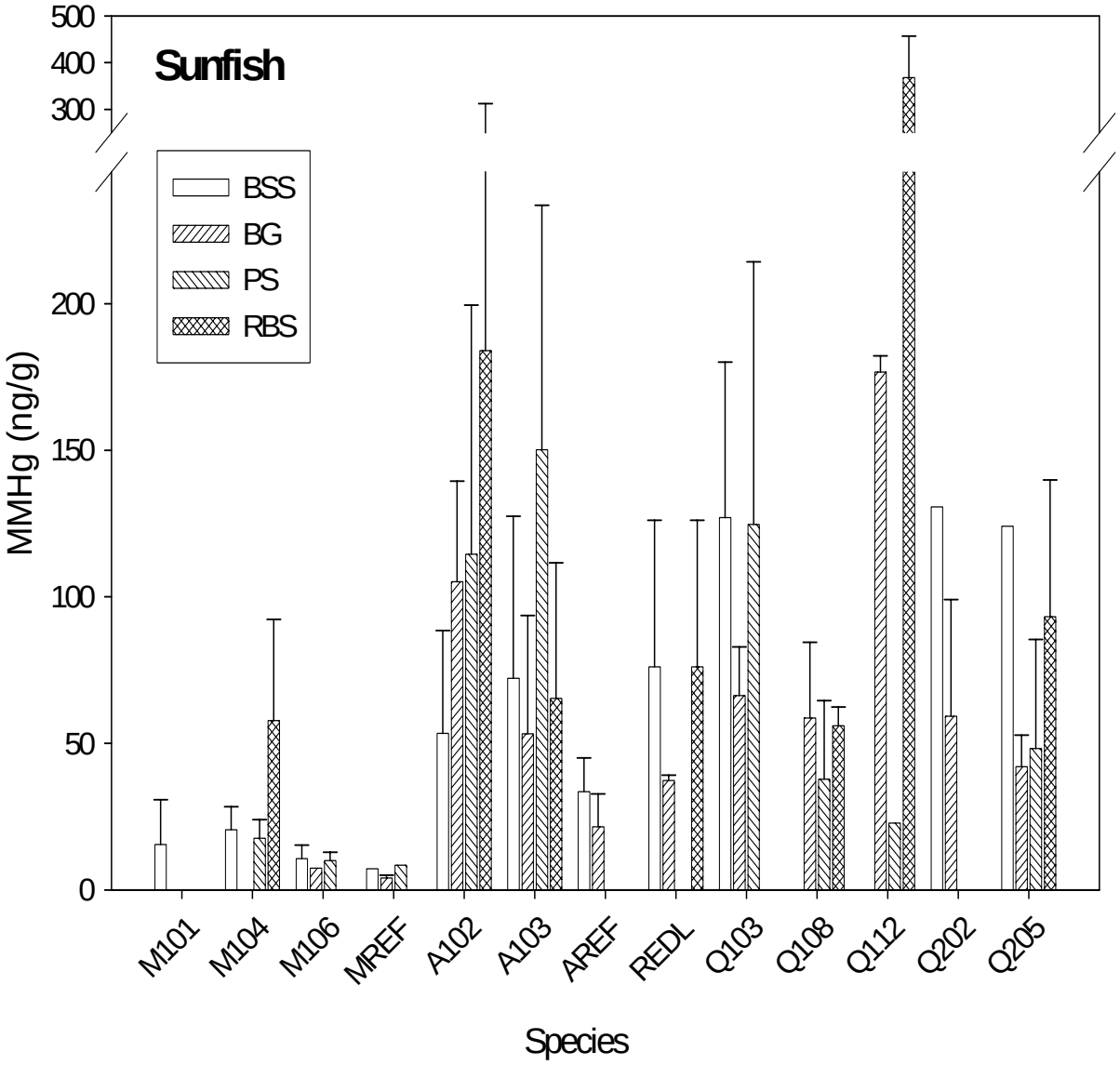


Figure 3: The concentration of methylmercury (ng/g wet weight) in sunfish, separated according to species (BSS=bluespotted sunfish, BG=bluegill, PS=pumpkinseed, RBS=redbreast sunfish). Streams are listed according to each watershed (M=Mason Branch, A=Andover, REDL=Red Lion, Q=Mattawoman Watershed; see text for details).

To put these measured fish concentrations into perspective, data are plotted against other recently collected data (Gilmour *et al.*, 1999) for freshwater fish, or that from the reservoir fish project currently underway (Fig 5; Sveinsdottir, 2002). The stream data fall on linear correlation lines with those collected by Gilmour *et al.* (1999) (ANSERCPax), and the reservoir fish. Acknowledging that there is little data for fish of intermediate size, the correlation lines for both bass (r^2=0.29) and pickerel (r^2=0.79) are significant and suggest that the overall fish concentration of these species is related broadly to their size (Fig. 5) even though such relationships were not apparent for the smaller size range of the current study. Thus, if these fish from the streams sampled continue to grow, then it would be expected that their concentration might be similar to reservoir fish. This suggests that processes controlling bioaccumulation are somewhat similar in the streams and in the reservoirs, and this most likely reflects the fact that the prey items are similar for each fish species in the two systems.

USEPA has recently issued a health advisory update in which they are suggesting that 0.3 ppm MMHg in fish be used as a criterion to determine if a waterbody is impaired in terms of MMHg. As can be seen from Fig. 5, the largemouth bass in the reservoirs exceed this guideline for the older fish, typically >1000 g, but none of the bass from the streams exceed this limit, but nor are they of legal size. Again, the implication of the data in Fig. 5 is that these fish may have concentrations approaching this new limit if, and when, they grow to a legal size. For pickerel, the results are similar to that of the bass. Large chain pickerel from Deep Creek Lake (DCL/ANSERC) analyzed by Gilmour *et al.* (1999) had very high concentrations compared to the stream fish but they were large fish.

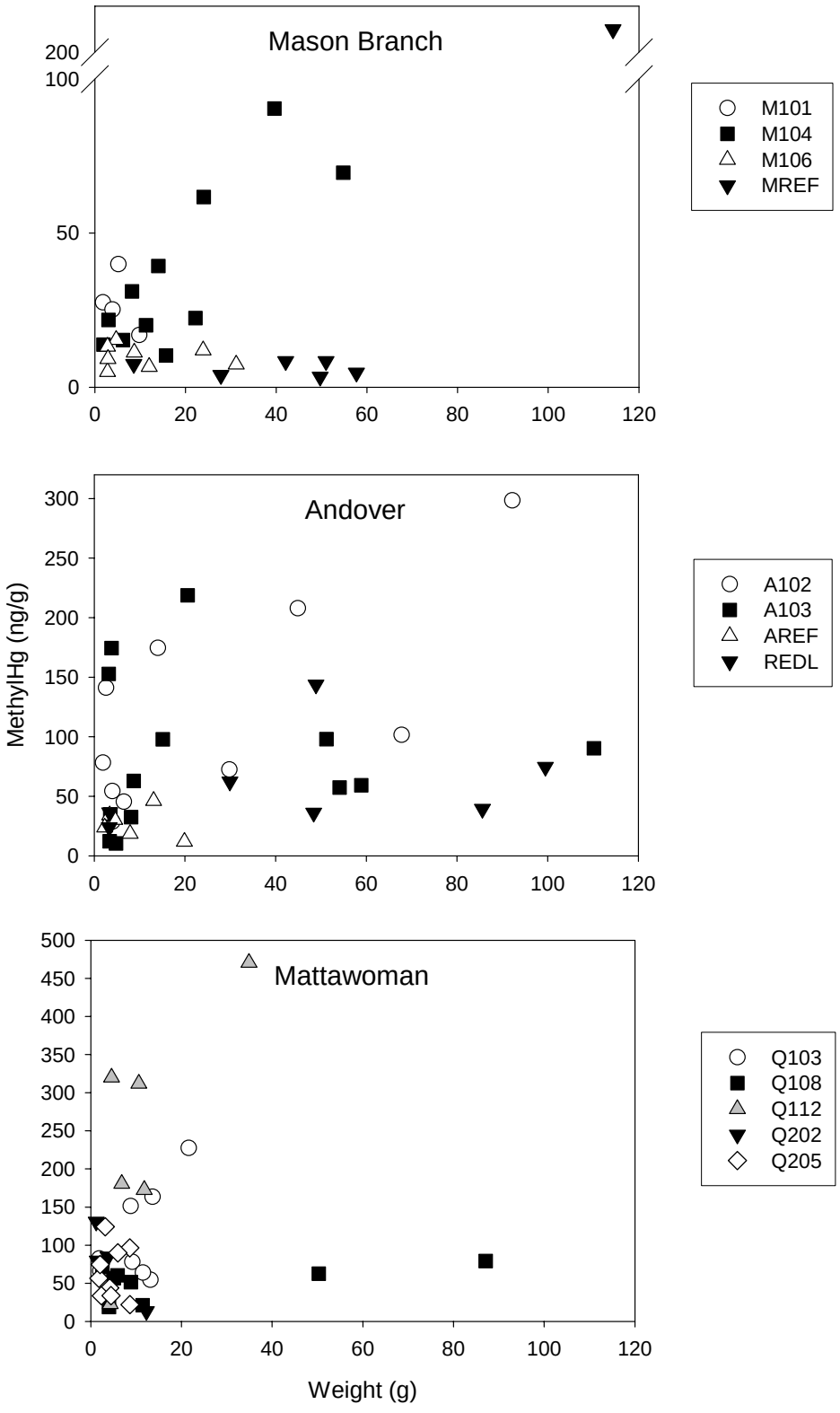


Figure 4a: Concentrations of methylmercury (ng/g wet weight) in sunfish according to each stream sampled and by watershed.

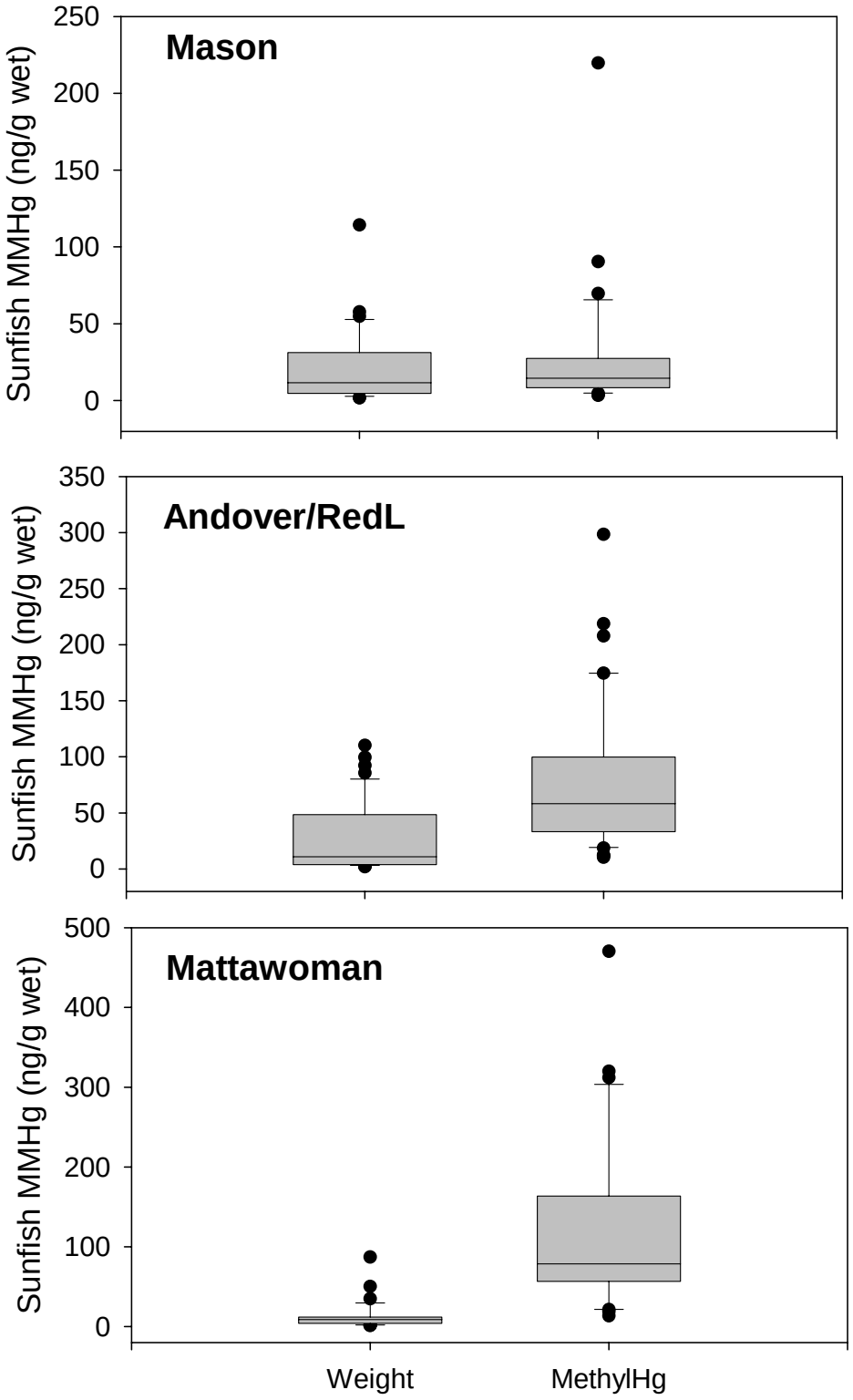


Figure 4b: Box plots of sunfish weight and methylmercury concentration (ng/g wet weight) according to each region sampled.

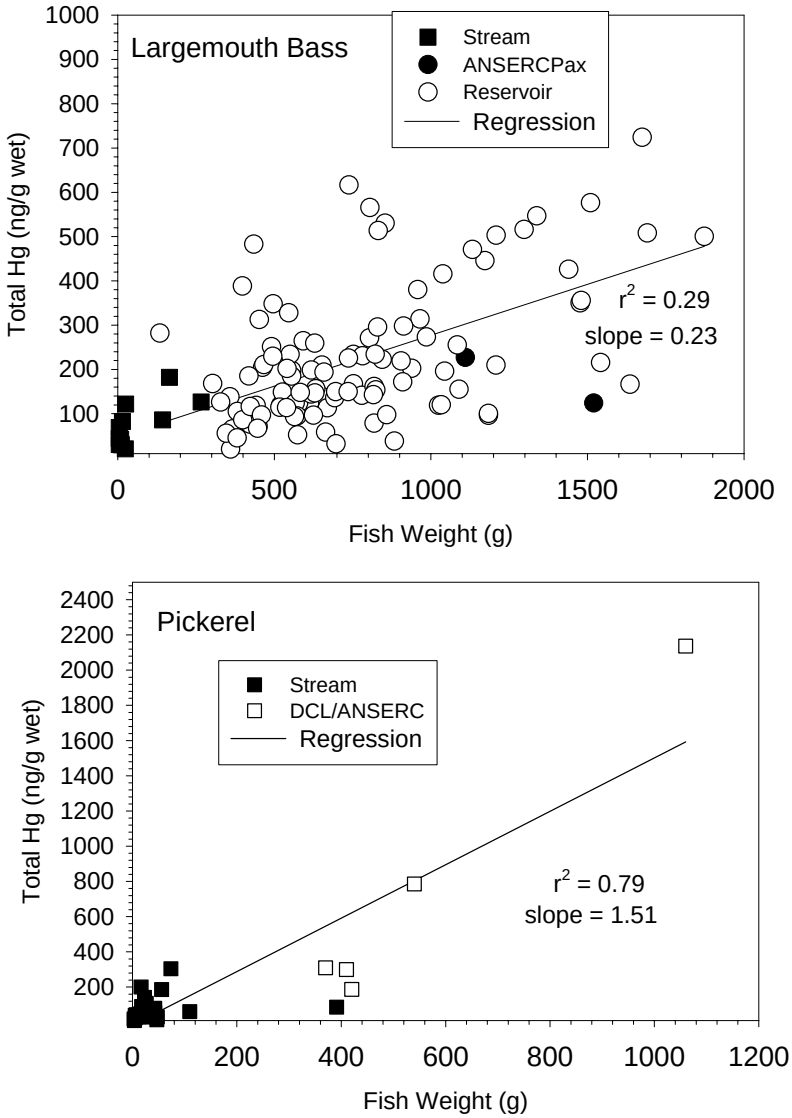


Figure 5: Comparison of stream fish concentrations with similar species from other studies. a) largemouth bass and b) pickerel. See text for details.

It is interesting to note that the slope of the line for pickerel is much steeper than that for bass, but this slope is driven to a large degree by the two large fish. To fully understand the differences implied in these relationships, age-weight relationships are needed for both classes of fish. The reservoir studies have shown that for the different reservoirs, the relationships between largemouth bass length and weight are similar and growth curves for largemouth bass in different reservoirs are similar (DNR, 2000). Thus, it is not these differences that account for differences in fish concentration across sites. For the fish collected in the reservoirs, which were all above

minimum size and generally >300 g, the relationship between size and weight is:

Bass weight (g) = 53.3exp(0.007*bass length (cm)); $r^2 = 0.72$.

It is well known that older fish change their weight-length ratio more slowly than younger fish and thus age-weight relationships between species cannot be directly compared. According to Stafford and Haines (1997), chain pickerel in Maine of similar weight, in the size range of 300-500 mm (comparable to most of the fish being discussed here), are about 20% older than largemouth bass of similar weight. It is possible that the same is true in MD. The age of the fish of similar weight are likely relatively similar and differences in the fish weight-mercury concentration plots discussed above cannot be accounted for purely by age differences. The fact that chain pickerel eat mostly fish even at a young age probably accounts for the differences in mercury concentration with weight as it is known from observation that bass in the reservoirs prefer crayfish to small fish (Sveinsdottir, 2002). From our studies in Maryland (Mason *et al*., 2000; Sveinsdottir, 2002), it is apparent, and expected, that crayfish, which are omnivores, have lower mercury burdens than small fish, which are more invertivores. These small fish may feed on insects that are themselves predatory (feeding on other insects). Thus, pickerel are potentially at a somewhat higher trophic status, when large, than the largemouth bass.

Correlations Between Fish Methylmercury Concentration and Water Quality Parameters

The average sunfish concentration for each stream is plotted against the various water quality parameters, total Hg and dissolved MMHg concentration in Fig. 6. The general expectation, based on other studies such as those in Wisconsin, is that the fish MMHg concentration would be inversely correlated with pH. This is a generally accepted, although not conclusively proven tenet, and would be influenced by DOC. The influence of DOC on fish MMHg is complex (Mason and Benoit, in press). It could enhance accumulation by increasing the standing stock concentration in the water as it strongly binds to MMHg, but this strong binding and the large MMHg-DOC complex size likely hinders its bioaccumulation into microorganisms and thus the high DOC could

hinder uptake. These two effects are opposite and so the net impact has been found to be different for different systems (Mason and Benoit, in press).

There is only a weak correlation between the measured DOC and MMHg concentrations at the time of sampling ($r = 0.37$) and thus the notion that DOC strongly enhances the dissolved MMHg concentration is not strongly supported for these basins. There is a stronger correlation between pH and MMHg concentration ($r = -0.78$) which may be controlled by the fact that the highest MMHg concentration was in the lowest pH stream. This suggest that pH may be an important variable influencing fish concentration while DOC would have a lesser effect. However, this was not found.

A multiple regression of all parameters against each other show that for sunfish, DOC concentration is most closely linked to fish concentration (Table 8). However, a stepwise analysis of the data using the SAS Program did not show that this correlation was significant nor that addition of the other variables into the model improved the correlation (Table 9). However, the regression equations are still given in Table 9, in which the values listed represent the coefficients for the variables in each equation. The result of the stepwise analysis clearly shows that DOC is the only variable that has any relationship with sunfish MMHg concentration, and that this is weak. The lack of a DOC impact in this study may be the result of the different SPM concentrations across the streams, which lead to differences in partitioning of MMHg to solids, and the relationship between SPM and DOC is not simple for these streams. Additionally, because DOC is relatively high in all streams, there may be no effect of DOC concentration on Hg methylation i.e. DOC concentration is not limiting methylation.

The relationship between sunfish tissue MMHg and water MMHg is shown in Fig. 6. The high MMHg concentration in water, but low fish MMHg concentration, in the two Mattawoman locations appear as potential outliers, or they reflect the impact of some other factors on MMHg bioaccumulation and fish concentration. Again, the caveat that must be remembered is that the water samples collected with the fish may not be representative of the seasonal average concentration, and thus this may be the cause of the lack of correlation. The rationale for collecting only one sample, and its likely impact, has been discussed above.

There is obviously no relationship with total Hg concentration, as has been found in many studies. Given the influence of DOC over many aspects of water chemistry and system productivity, the actual cause of the relationship found, whether positive or negative, is not easy to ascertain. Here a negative correlation is found for sunfish MMHg and DOC (Table 8 & 9). There is no discernible trend with pH for sunfish concentration (Fig. 6), except perhaps that MMHg is higher in fish for streams of intermediate DOC. This may be expected given that contrasting effects of DOC on MMHg production and bioaccumulation. As all the parameters are interlinked, direct correlations between parameters can be discerned in some instances, as discussed above (Table 8). Overall, however, the impacts and relationships are best examined using a stepwise multiple regression approach (Table 9).

Table 8: Correlation matrix for the water column parameters (pH, ANC, DOC and MMHg) and sunfish and pickerel concentration for those streams having both fish groups. Values given are the correlation coefficient, r; n=9.

Parameter	pH	ANC	DOC	Diss. MMHg	Sunfish	Pickerel
pH	**1**					
ANC (μeq/L)	**0.665**	**1**				
DOC (mg/L)	**0.0365**	**0.072**	**1**			
Diss. MMHg (pg/L)	**-0.199**	**-0.194**	**-0.379**	**1**		
Sunfish (ng/g)	**-0.053**	**0.211**	**-0.552**	**0.126**	**1**	
Pickerel (ng/g)	**0.062**	**0.646**	**0.051**	**0.0748**	**0.330**	**1**

It is apparent that both pH and MMHg concentration alone explain none of the variability in sunfish MMHg concentration (Table 9). If fact, DOC changes appear to be the controlling parameter of those measured, explaining about 30% of the variability (r^2 = 0.30 for the 9 streams; Table 9). The consistency in the magnitude of the coefficient for DOC in all the regression equations is an indication of how important it is relative to the other parameters. The relationship is however not significant. Including all the parameters in the regression increases the r value but statistically this does not improve the relationship which is still not significant (Table 9). Overall, DOC and ANC are the two most important variables and together they account for 37% of the fish tissue concentration variability (r^2 = 0.37; Table 9).

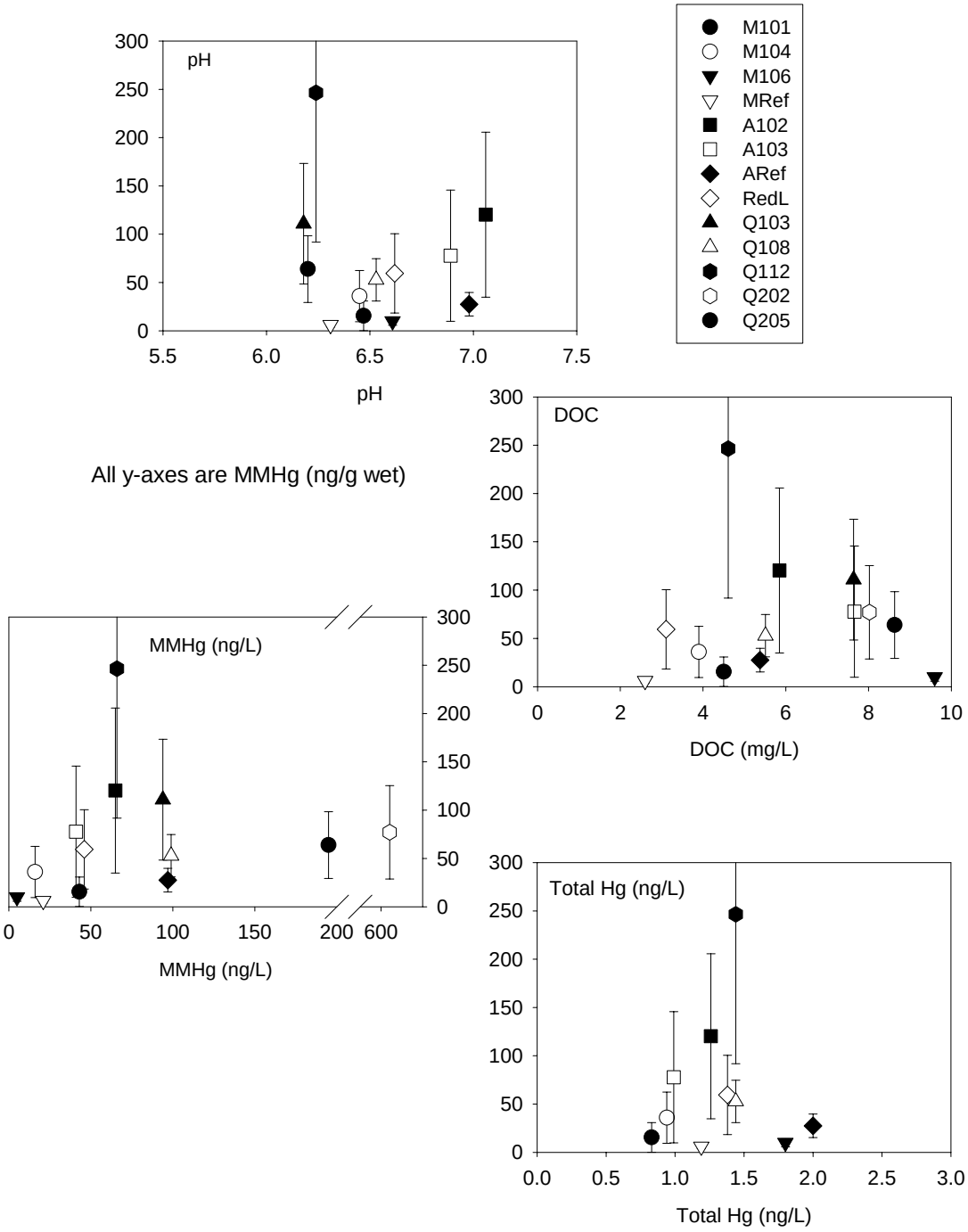


Figure 6: Comparison of methylmercury in sunfish (ng/g wet weight) with water quality parameters (pH, DOC, water dissolved methylmercury and total Hg).

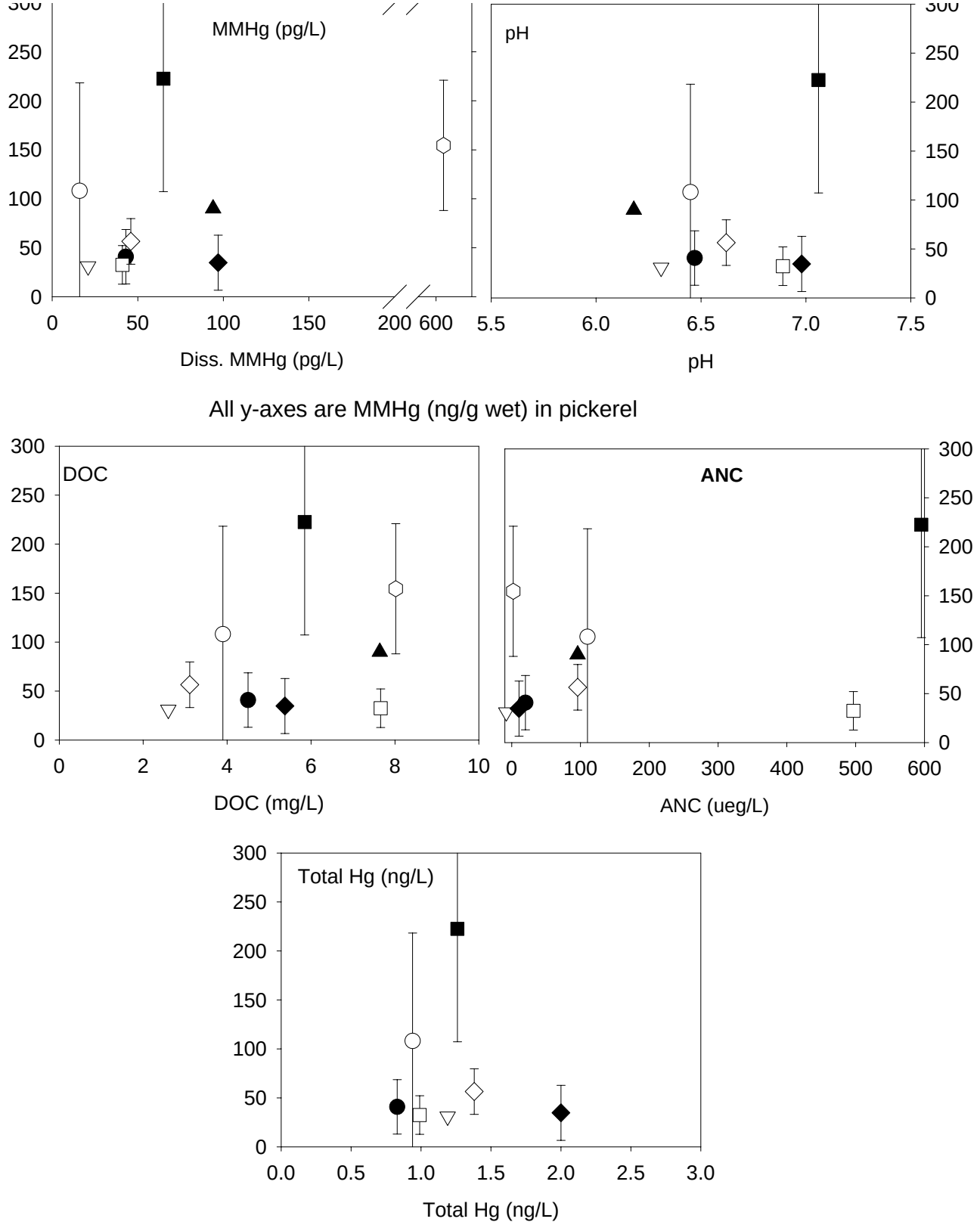


Figure 7: Comparison of methylmercury in pickerel (ng/g wet weight) with water quality parameters (pH, DOC, water Dissolved methylmercury and total Hg). Symbols as in Fig. 6.

Thus, the results of the multiple regression analysis suggest that DOC may be an important parameter for understanding sunfish tissue concentration and the relationship is negative; i.e. fish concentrations are decreasing with increasing DOC. Secondly, alkalinity or ANC is a better measure of the influence of stream chemistry than pH. That the influence of MMHg concentration is marginal may indicate that the effects of changes in water quality, and their influence over MMHg bioavailability and bioaccumulation, are more important than differences in dissolved MMHg concentration in the water, or that the single measurements of MMHg in the water are not representative. Note that these results are true for sunfish and may not apply to the other species.

In contrast, a similar analysis with pickerel showed that DOC did not have the dominating influence over the fish concentration and that a combination of parameters explained the fish MMHg concentrations best (Fig. 7). For pickerel, ANC and pH were the best predictors, but only ANC was significantly correlated for the individual variables (Table 10). However, the relationship for ANC and pH was also significant. The correlation coefficient is very small with DOC. Overall, the correlations were better for the pickerel than for the sunfish (Table 9). For the other fish species, it was considered that the data was too limited for a significant analysis to be performed.

Table 9: Multiple linear regression equations for sunfish concentration versus the various water quality parameters and the concentration of methylmercury. The data is given in terms of : $y = a_0 + a_1.[MMHg] + a_2.[DOC] + a_3.[ANC] + a_4.[pH]$ with the associated correlation coefficient (r value). Bold values for r indicate the overall relationship was significant.

Intercept (a_0)	MMHg coeff. (a_1)	DOC Coeff. (a_2)	ANC coeff. (a_3)	pH coeff (a_4)	Corr. Coeff., r
161.1		-14.32			0.551
41.43			0.48		0.213
153.2		-14.79	0.057		0.607
540.6		-14.90	0.112	-61.85	0.667
563.1	-0.069	-15.69	0.110	-63.72	0.668

Table10: Multiple linear regression equations for pickerel concentration versus the various water quality parameters and the concentration of methylmercury. The data is given in terms of : $y = a_0 + a_1.[MMHg] + a_2.[DOC] + a_3.[Alk] + a_4.[pH]$ with the associated correlation coefficient (r value). Bold values for r indicate the overall relationship was significant.

Intercept (a_0)	MMHg coeff. (a_1)	DOC Coeff. (a_2)	ANC coeff. (a_3)	pH coeff (a_4)	r
25.61			0.168		**0.646**
			0.282	-129.7	**0.813**
11.55	0.197		0.178		0.677
837.1		-0.104	0.282	-129.7	0.813
778.74	0.177	1.93	0.285	-124.8	0.830

While second order or higher relationships between variables may have improved the correlations, these were not attempted as it was not clear the scientific significance of such relationships. Thus it appears that the factors controlling bioaccumulation into the different fish groups - sunfish (DOC) versus pickerel (ANC and pH) - were different. This is intriguing and may relate to the different feeding patterns of the two fish groups. More data would however be required to make a definitive conclusion. While food preferences are similar for these two species, in that older fish eat smaller fish and crustaceans, it is likely that there is a difference in feeding for smaller fish. Relationships to water quality parameters described above likely reflect that pickerel are eating small fish predominantly (as discussed above) while the sunfish are feeding more on the invertebrates – zooplankton and invertebrates which may be migrating between the water column and the sediment. This conclusion is supported by the likely relationships among DOC, and sediment POC, and MMHg concentration, which exist through the complex interaction of the factors controlling methylation in sediments, as well as the role of organic matter in controlling sediment bioavailability to amphipods and other sediment dwellers (Lawrence and Mason, 2001).

These results suggest that sunfish are feeding at a lower trophic level and that the water quality parameters do not therefore directly influence their bioaccumulation. The relationship to DOC reflects the interaction of the sediment and water column through the benthic food chain as DOC is to some degree controlled by sediment organic carbon and watershed type in these small

streams. For chain pickerel, their feeding on organisms that directly consume plankton in the water column results in the relationship to water quality parameters being stronger and reflects the effects of pH on bioavailability. To clearly test if these proposed ideas are true, gut content analysis would be needed. Unfortunately this was not done.

Arsenic, Selenium and Cadmium in Fish

Arsenic, Se and Cd concentrations in fish species sampled are shown in Fig. 8 and Table 6. The concentration of As in the fish shows a wide variability for any particular fish weight and differences in the concentration distribution amongst species is difficult to discern (Figs. 8 and 9). There is no definite trend with fish weight and it appears that the larger fish have lower As concentrations. This result is expected as As does not tend to accumulate through all trophic levels (Mason *et al*., 2000b) and thus organisms at a higher trophic level often have lower As concentrations. Typically, As concentrations are highest in phytoplankton, algae and invertebrates and decline in concentration in consumers as demonstrated in the study by Mason *et al*. (2000b) in western Maryland, where the concentration of As in insects was above 1 ppm (1 μg/g wet weight) on average for some species but the concentration in fish (e.g. brook trout) was less than 0.5 μg/g. Indeed, the concentration in the brook trout was lower overall than that of sculpin in one stream.

Similarly, both Cooper and Gillespie (2001) and Chen and Font (2000) found a decrease in the concentration of As between zooplankton and fish, and Cooper *et al.* (2001) showed that the concentration in fish was highest for omnivores, followed by benthivores, with filter feeders having the lowest As concentration, less than 0.05 μg/g on average. The As concentration in the omnivores averaged 0.11 ± 0.20 μg/g, suggestive of some high concentration fish in the sample.

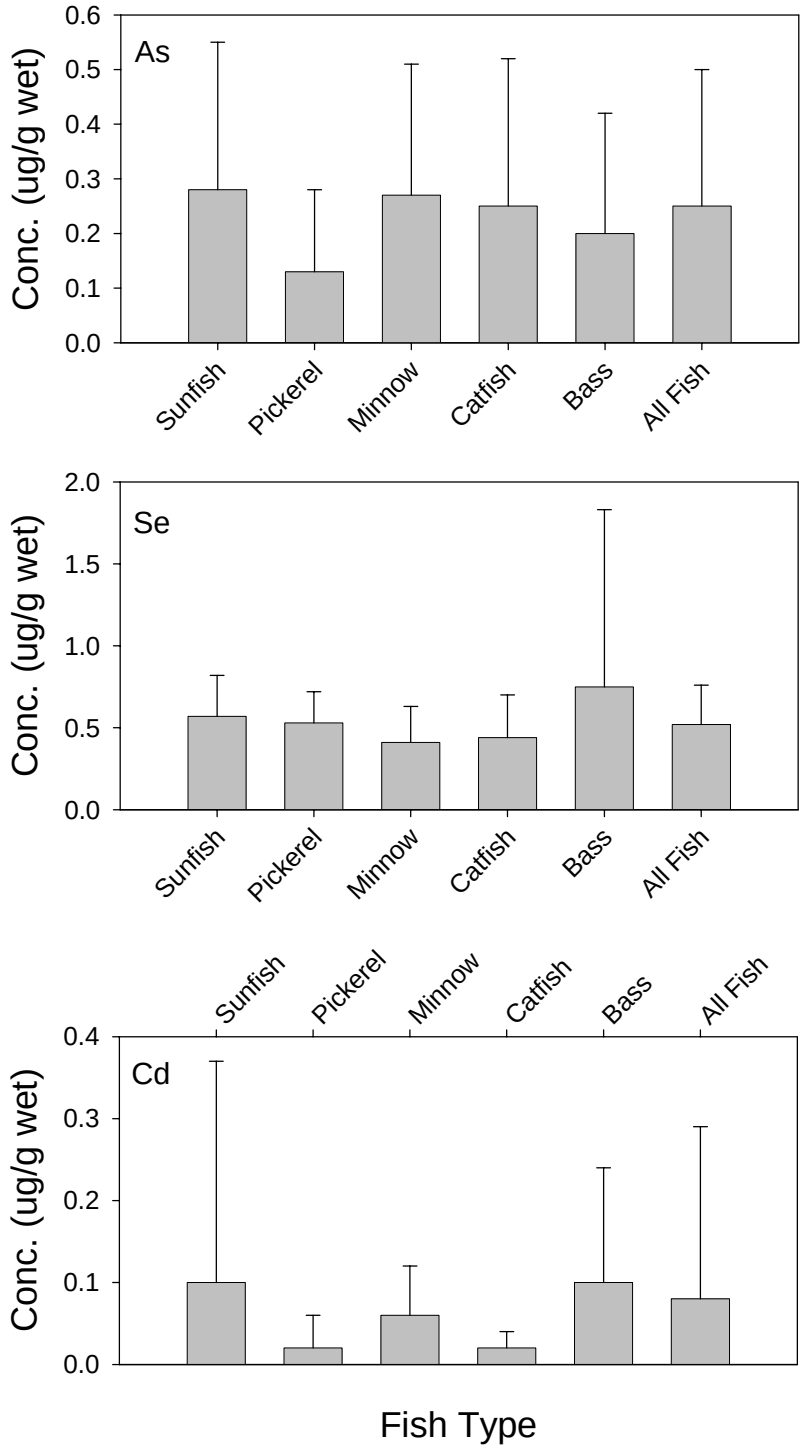
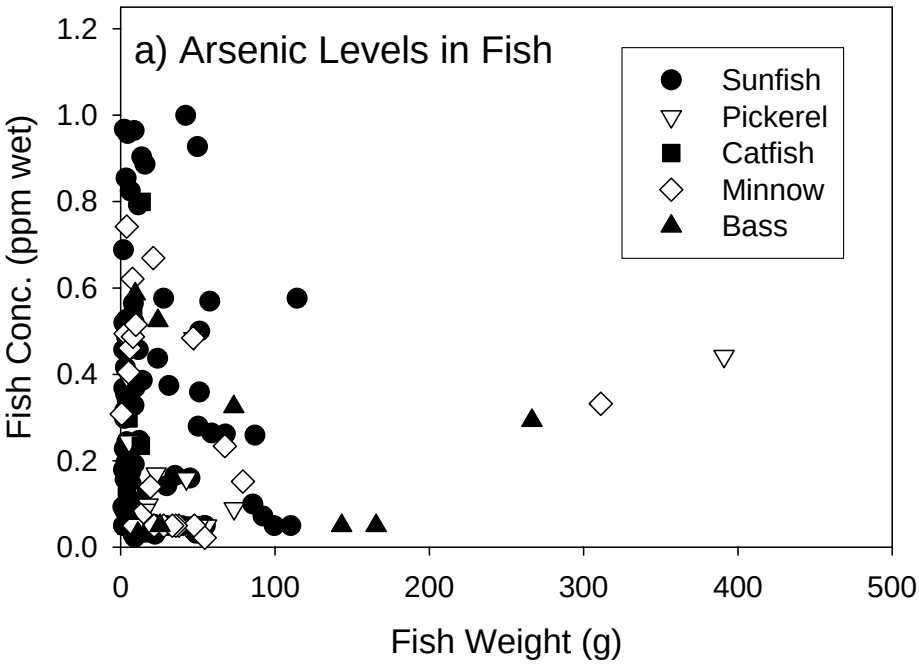
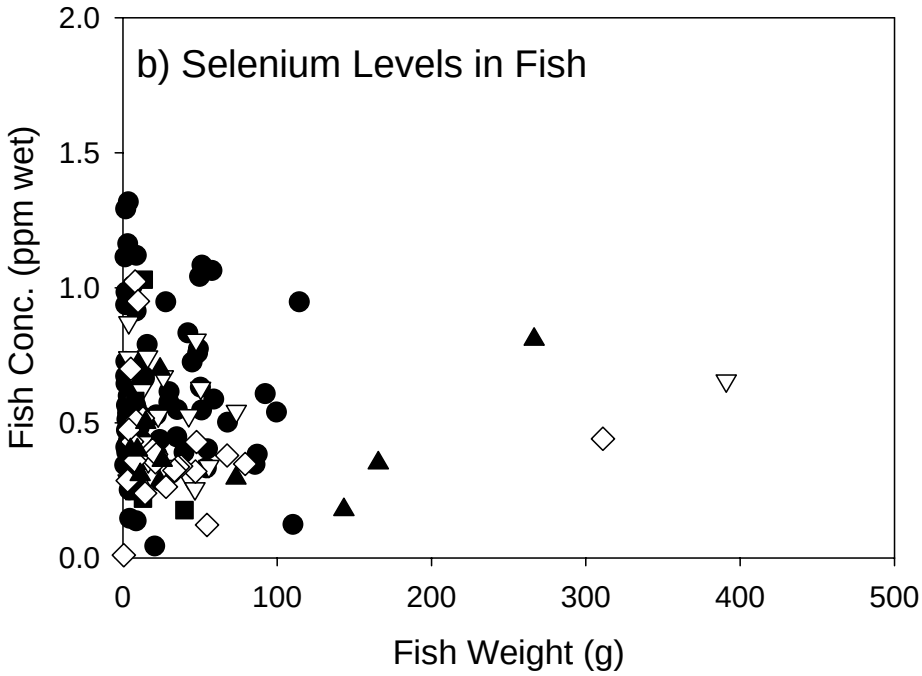


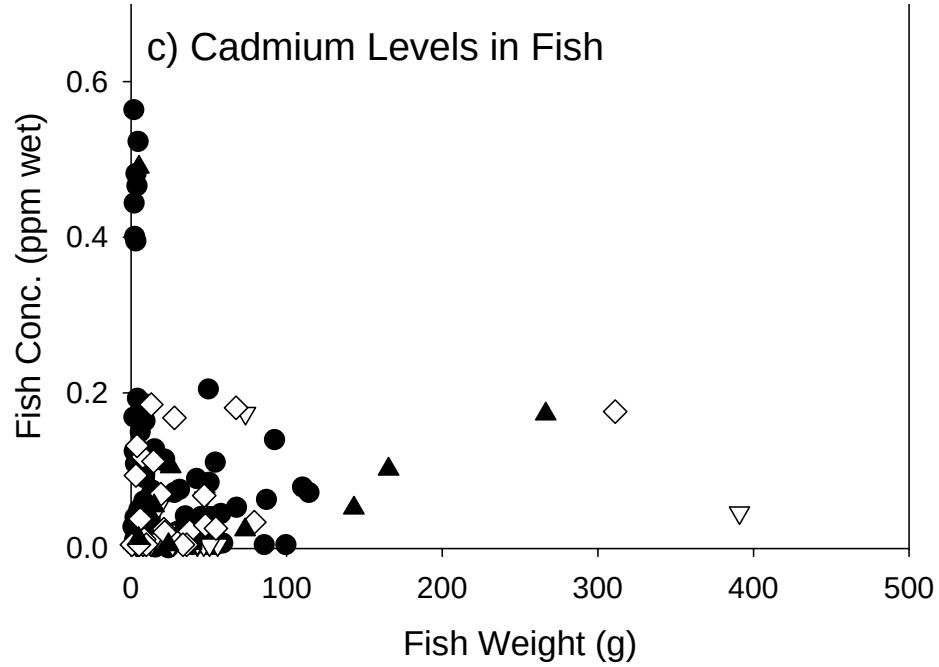
Figure 8: The average wet weight concentrations of arsenic (As), selenium (Se) and cadmium (Cd) in each fish group and the overall average for all fish analyzed. Error bars indicate standard deviations of the mean.

Other recent studies of the As concentration in fish in the USA have found similar values to our study. The current dataset has values that range from the detection limit (0.05) to 1 μg/g wet weight. The overall average value for the fish of this study was 0.26 μg/g (Fig. 8). It should be noted that there were a few fish of much higher concentration and these have been excluded from the dataset. Interestingly, these fish were high in As and Se, and to some degree, Cd. The fish were a redbreast sunfish from site Q112 (As 5.43, Se 6.43, and Cd 0.52 μg/g); a bluegill from Q202 (As 7.67, Se 1.11, and Cd 2.57 μg/g); and a largemouth bass from Andover 103 (As 0.41, Se 3.96, and Cd 0.49 μg/g). The reason for these high values is unknown and they could be analytical outliers, but it is not clear how they came to have such high concentration; whether through contamination or because these fish were indeed elevated in concentration. Given the size of the fish there was not enough tissue available for re-analysis.

The concentrations for As are somewhat difficult to compare to the literature because most of the published data are for larger fish and for fish that are piscivorous and are thus not comparable with the small fish in this study that are feeding dominantly on invertebrates. The national monitoring program of the Fish and Wildlife Service reports a geometric mean concentration for the fish they collect of 0.14 μg/g with a maximum of 1.5 μg/g and a 85^{th} percentile value of 0.27 μg/g (Schmitt and Brumbaugh, 1990), but again these are for larger fish. Values reported here (Fig. 8) are somewhat higher than the average for the USA but not substantially different. Furthermore, interpretation of fish As data in terms of environmental concern is complicated by the fact that most of the As in the fish is bound up in large organic As compounds (arsenobetaine; e.g. Shiomi *et al*., 1995) and this organic As is not of concern from a health point of view compared to inorganic As Shiomi *et al*., 1995). Thus, to fully interpret the concentrations of As would require tissue speciation measurements that were beyond the scope of this study.


a) Arsenic Levels in Fish
Sunfish
Pickerel
Catfish
Minnow
Bass
Fish Conc. (ppm wet)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
Fish Weight (g)


b) Selenium Levels in Fish
Fish Conc. (ppm wet)
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
Fish Weight (g)



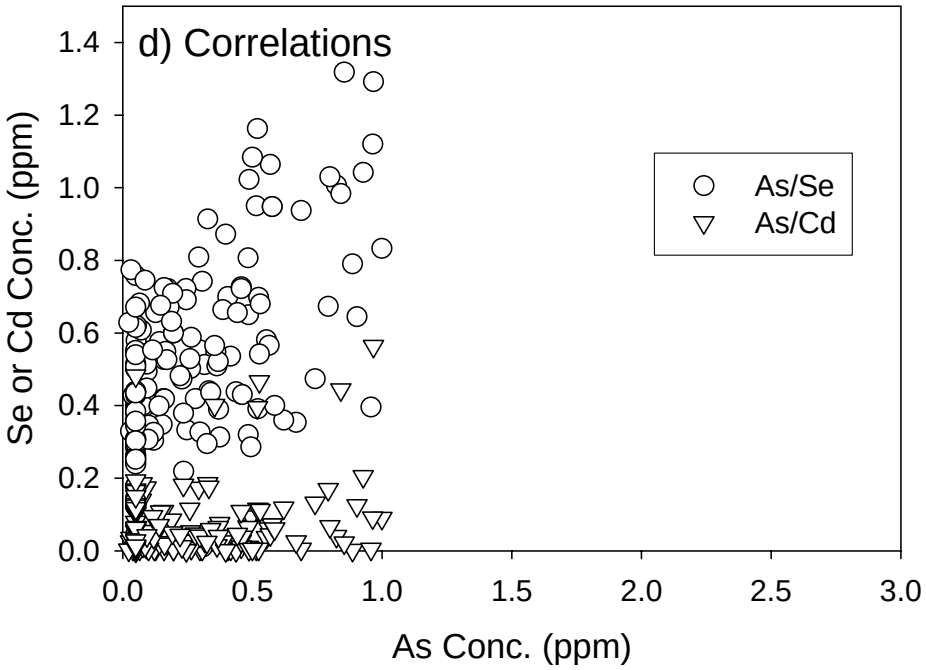


Figure 9: Concentration of a) arsenic b) selenium and c) cadmium in individual fish plotted against fish weight. Fish are divided into respective groups. d) The correlations between the different metals.

Selenium concentrations were comparable but somewhat higher than the As levels in the fish. The overall average concentration was 0.52 ± 0.24 μg/g wet weight. Again there was little difference in concentration between the different fish groups with the lowest concentrations being in catfish and minnows (Fig. 8). The scatter in fish concentration for a particular weight was less for Se (Fig. 9) but there was again no evident trend of increasing fish concentration with increasing size. In many respects, As and Se behave similarly during trophic transfer as these metalloids can both be incorporated into organic molecules. Both are regulated to some degree in higher organisms, and are fairly readily depurated if their concentration becomes too elevated. It is only in highly contaminated environments that the uptake is sufficient that regulation of concentration is no longer possible. The study in western Maryland by Mason *et al.* (2000b) showed that Se concentrations in those streams in insects were generally above 1 μg/g but that the concentration showed high variability seasonally. As was similarly variable. The Se concentrations in the fish analyzed during that study were also similar to the values found in the current study. The USA geometric mean value reported by Schmitt and Brumbaugh (1990) for Se was 0.42 μg/g, with a maximum value of 2.3 μg/g, and a 85^{th} percentile value of 0.73 μg/g. Again, the current values fall within this range of concentrations.

Cadmium levels were the lowest of all the analytes measured in fish and many concentrations were at the detection limit of 0.01 μg/g. The overall average value was 0.08 ± 0.21 μg/g. These values are equivalent to the USA geometric mean and range – 0.03 μg/g average, 0.22 μg/g as a maximum and 0.05 μg/g as the 85^{th} percentile (Schmitt and Brumbaugh, 1990). Cadmium levels also decrease with trophic level (Mason *et al.*, 2000b) and as seen in Fig. 9c. There were six sunfish and one bass that had Cd concentrations over 0.4 μg/g and these were all very small fish (Fig. 9c). The largest bass had one of the lowest concentrations. Overall, the pickerel and catfish had the lowest average concentrations while for the sunfish and bass, the higher average is to some degree driven by the elevated concentrations in a few fish. A correlation exists between fish concentrations for As and Se, but not between the metalloids and Cd (Fig. 9d). The relationship for As and Se had an r^2 value of 0.41 and a slope of 0.52 with a positive intercept. This reinforces the notion that As and Se behave similarly upon accumulation and during trophic transfer.

The concentrations of As, Se and Cd in sunfish on a watershed basis are shown in Fig. 10. Overall, the highest concentrations of As were found in the Mason watershed, with the highest stream average for the Mason Reference stream (Table 11). This contrasts the Hg concentration found in sunfish, which was lowest in fish in the Mason watershed. Except for two high values, the Andover/Red Lion watershed had the lowest As concentrations, with the Red Lion Reference stream having the lowest average value. For Se, Mason Reference was the highest average value, with the lowest values in Mattawoman (Q112 and Q202). However, it must be remembered that two high concentration fish were removed from consideration for these two streams. For Cd, the highest average value was for Q205 but Cd was also high relatively in Mason Reference, and Andover 103 and Andover Reference. Mason 101 had the lowest Cd with most fish at the detection limit. While these observations based on average values appear to designate trends between streams, it should be noted that the standard deviations of the sunfish concentration in each stream are similar or greater than the mean indicating a wide variability in concentration. Additionally, the differences for most streams are likely not significant given the high variability. Because of the high variability between fish, it was not considered realistic to compare the fish concentration data to water quality parameters in any detail as it is likely that the correlations, if found, would not be statisdtically valid. No correlations between water quality parameters and fish concentration are apparent. Similarly, Chen *et al.* (2000) found in their study of a multiple of lakes that fish As and Cd concentration did not correlate with any water column parameter. Clearly, other factors including the ability of individual fish species to regulate their As, Se and Cd body burden are as important as water quality parameters in controlling fish concentration.

Summary

The analysis of fish from a number of streams with contrasting pH, alkalinity and DOC did not show a strong influence of water quality parameters on fish MMHg concentration. Also, there appeared to be no strong correlation between fish As, Se and Cd concentration and water quality. Fish species collected could be assigned into four broadly-defined groups: sunfish, minnow, bass and catfish. The streams chosen for study differed in the water quality parameters both within each

watershed and between watersheds. Fish tissue burden of MMHg increased with fish weight for most species examined except for sunfish where the relationship was not apparent. For the other analytes, concentrations appeared to decrease with fish size. While fish MMHg concentrations were low, comparison with other data suggested that it is possible that the concentrations would approach those of larger fish in other water bodies if the fish were able to attain that size. For sunfish, the concentration of DOC appeared to have the most influence over the measured MMHg concentration This was not true for pickerel where pH appeared to be the most important parameter controlling fish MMHg concentration. For the other fish groups, number of fish were too small to fully investigate these relationships.

Table 11: Average arsenic, selenium and cadmium concentrations for sunfish in each stream.

Stream	**As (µg/g)**	**Se (µg/g)**	**Cd (µg/g)**
Mason 101	0.34 ± 0.30	0.73 ± 0.14	0.006 ± 0.003
Mason 104	0.27 ± 0.34	0.51 ± 0.21	0.013 ± 0.019
Mason 106	0.30 ± 0.17	0.39 ± 0.05	0.045 ± 0.047
Mason Ref.	0.62 ± 0.26	0.90 ± 0.17	0.10 ± 0.07
Andover 102	0.25 ± 0.12	0.62 ± 0.10	0.039 ± 0.035
Andover 103	0.29 ± 0.32	0.59 ± 0.38	0.12 ± 0.17
Andover Ref.	0.27 ± 0.30	0.55 ± 0.34	0.11 ± 0.15
Red Lion Ref.	0.05 ± 0.02	0.56 ± 0.24	0.061 ± 0.10
Q103	0.39 ± 0.31	0.57 ± 0.14	0.095 ± 0.042
Q108	0.21 ± 0.16	0.58 ± 0.13	0.080 ± 0.027
Q112	0.33 ± 0.30	0.40 ± 0.41	0.037 ± 0.037
Q202	0.05 (n=2)	0.39 ± 0.07	0.019 ± 0.013
Q205	0.30 ± 0.36	0.57 ± 0.42	0.27 ± 0.3
Overall Mean	0.30 ± 0.36	0.57 ± 0.42	0.27 ± 0.3

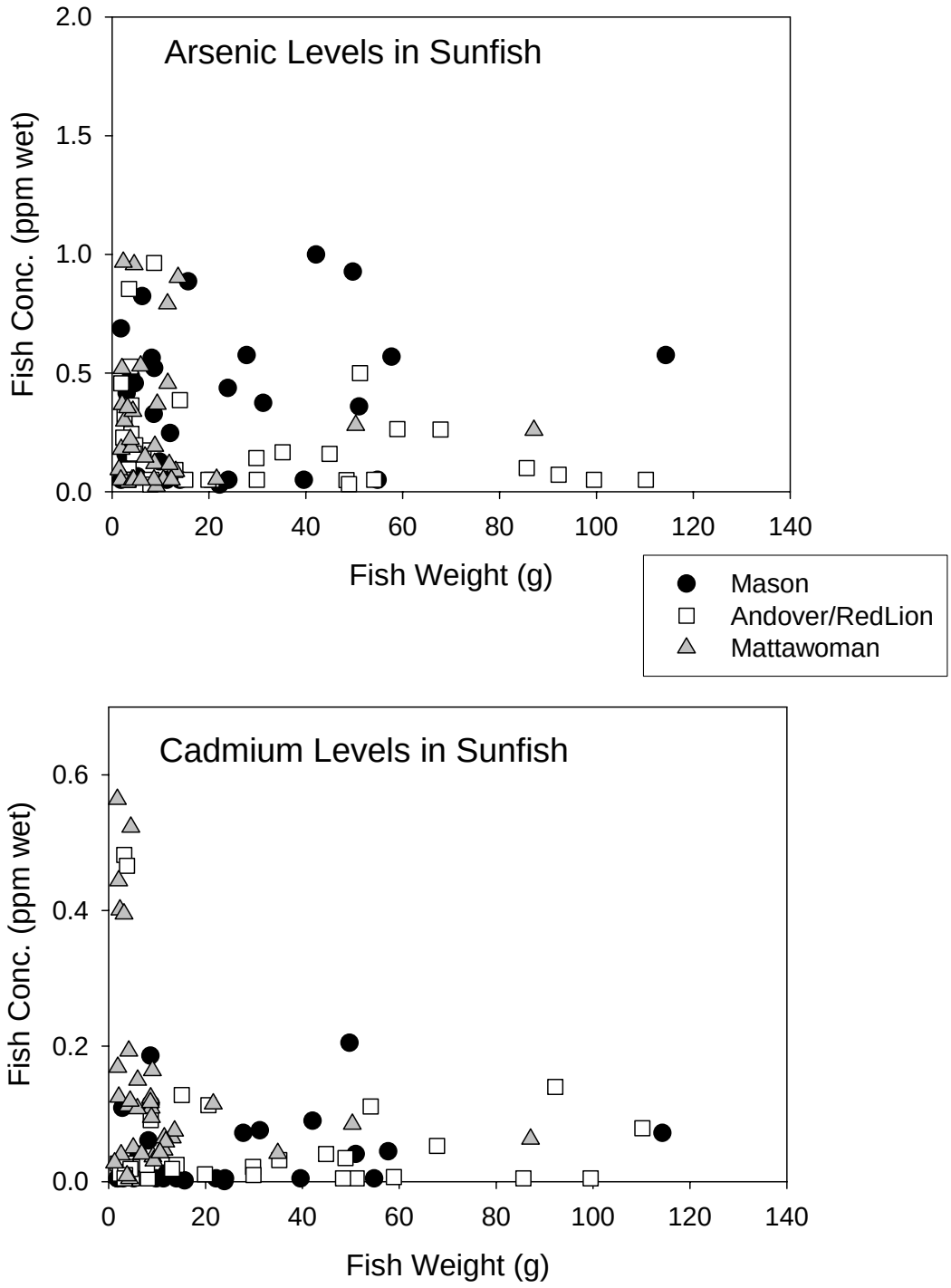


Figure 10: Concentrations of Arsenic and Cadmium in Individual Sunfish Separated by Watershed.

Acknowledgments

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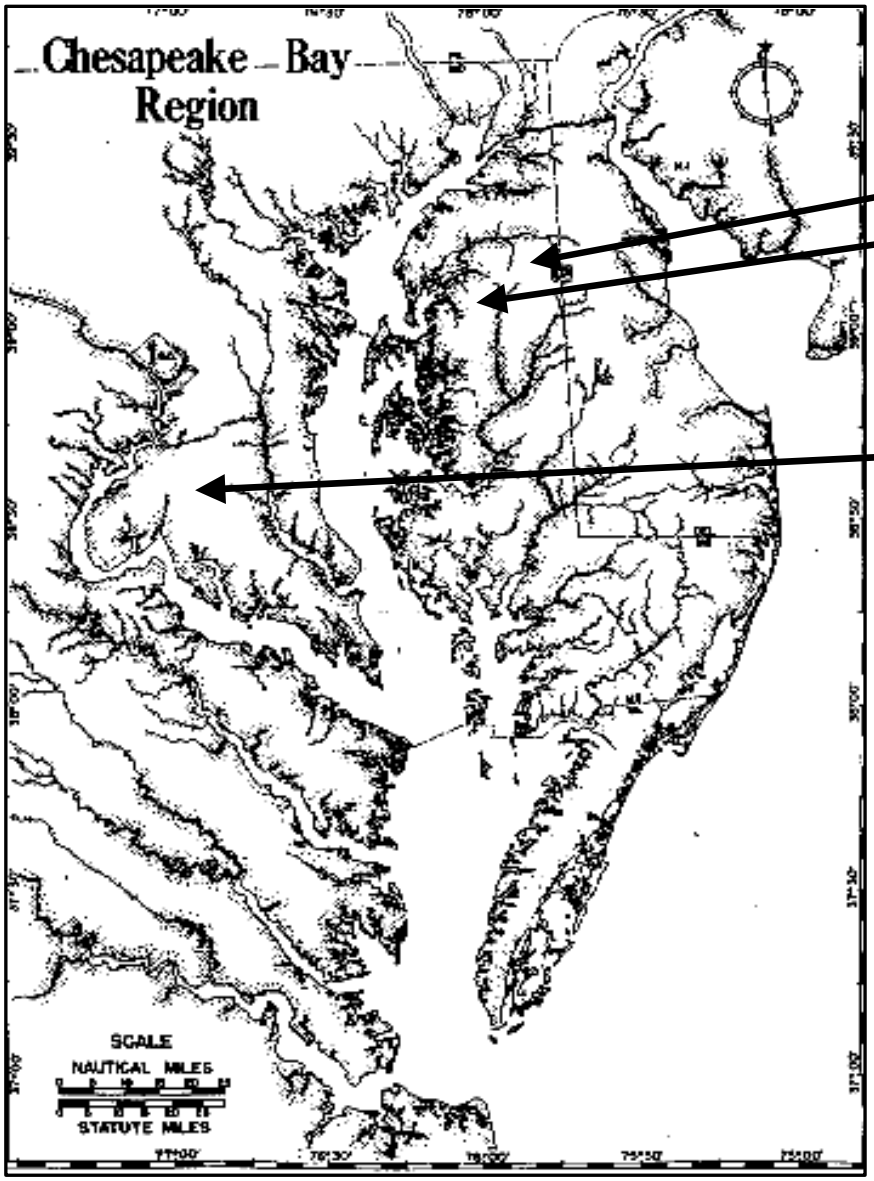
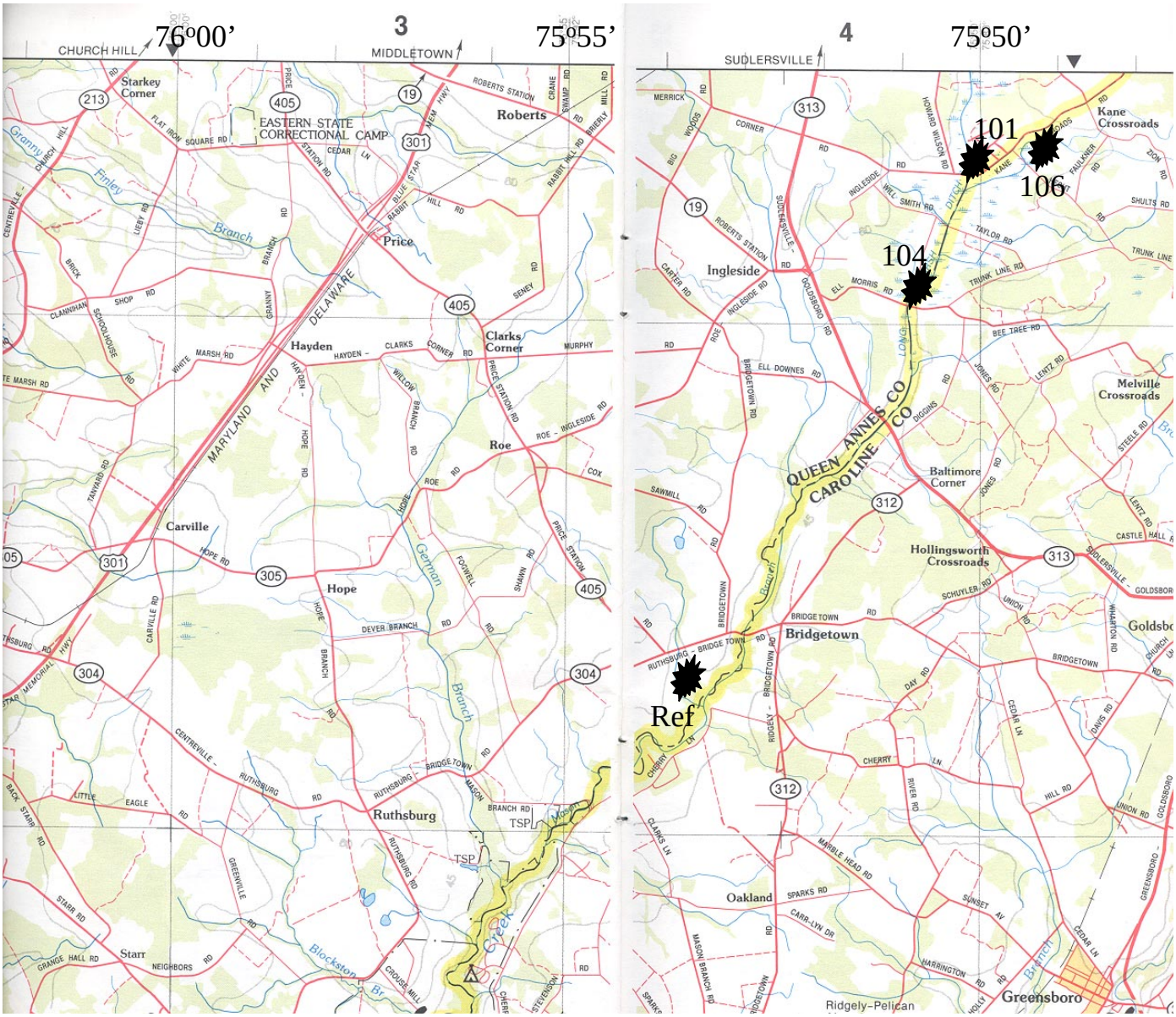
Appendix 1: Maps of the Locations of the Stream Sampling Sites



Map of the Chesapeake Bay Region showing the approximate location of the following maps of the streams sampled in the study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106
104
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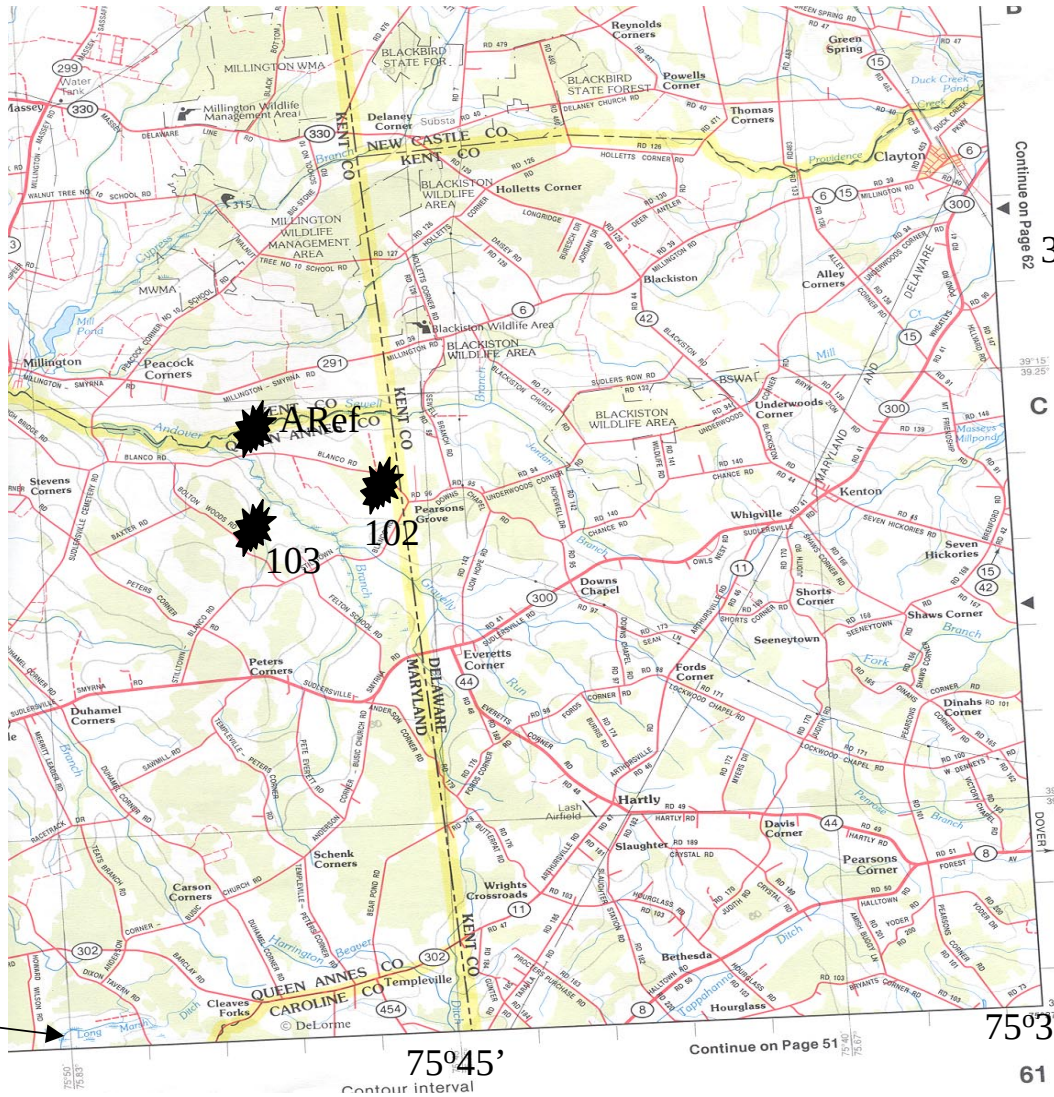
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103
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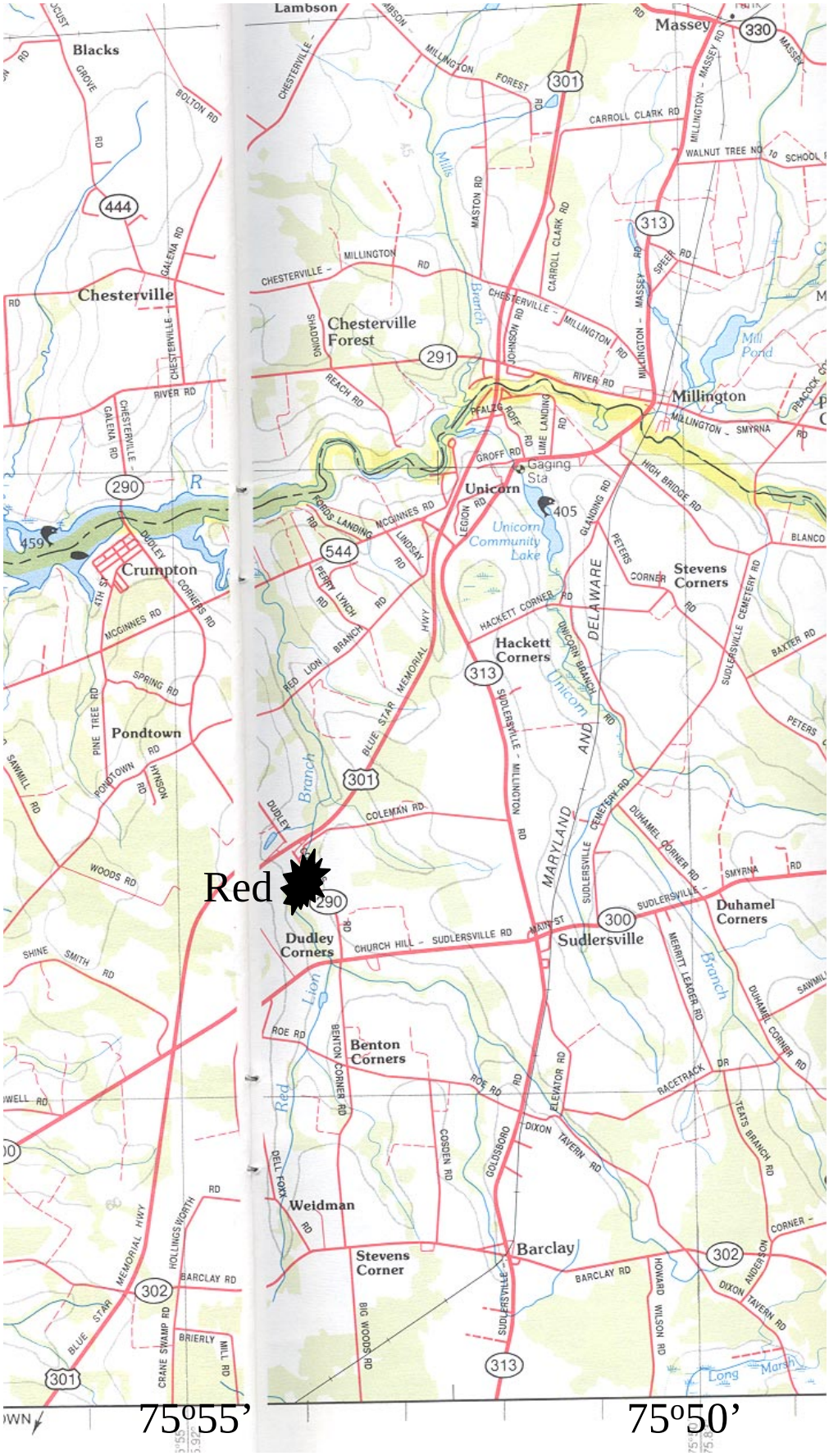
61
Contour interval
© DeLorme

Fig. A2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Blacks
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MILLINGTON - MASSEY RD
WALNUT TREE NO 10 SCHOOL
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313
Chesterville
MILLINGTON RD
CHESTERVILLE - MILLINGTON RD
Chesterville Forest
291
RIVER RD
Millington
MILLINGTON - SMYRNA
39º15’
Gaging Sta
Unicorn
405
Unicorn Community Lake
290
Crumpton
544
Stevens Corners
HACKETT CORNER RD
Hackett Corners
313
Pondtown
SPRING RD
301
COLEMAN RD
Red
290
Dudley Corners
CHURCH HILL - SUDLERSVILLE RD
MAIN ST
300
Sudlersville
Duhamel Corners
SMYRNA RD
Benton Corners
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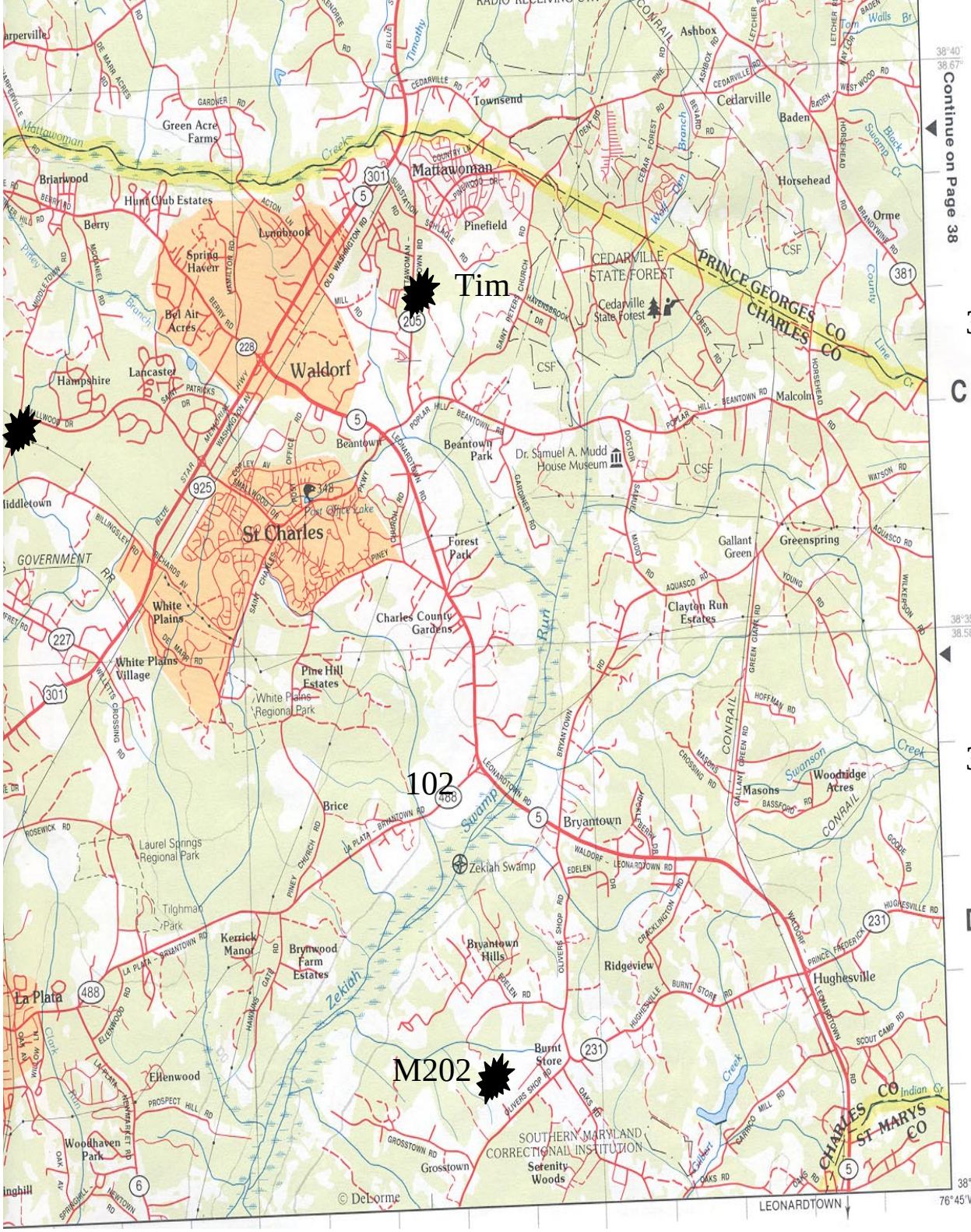
Fig. A3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Bryantown
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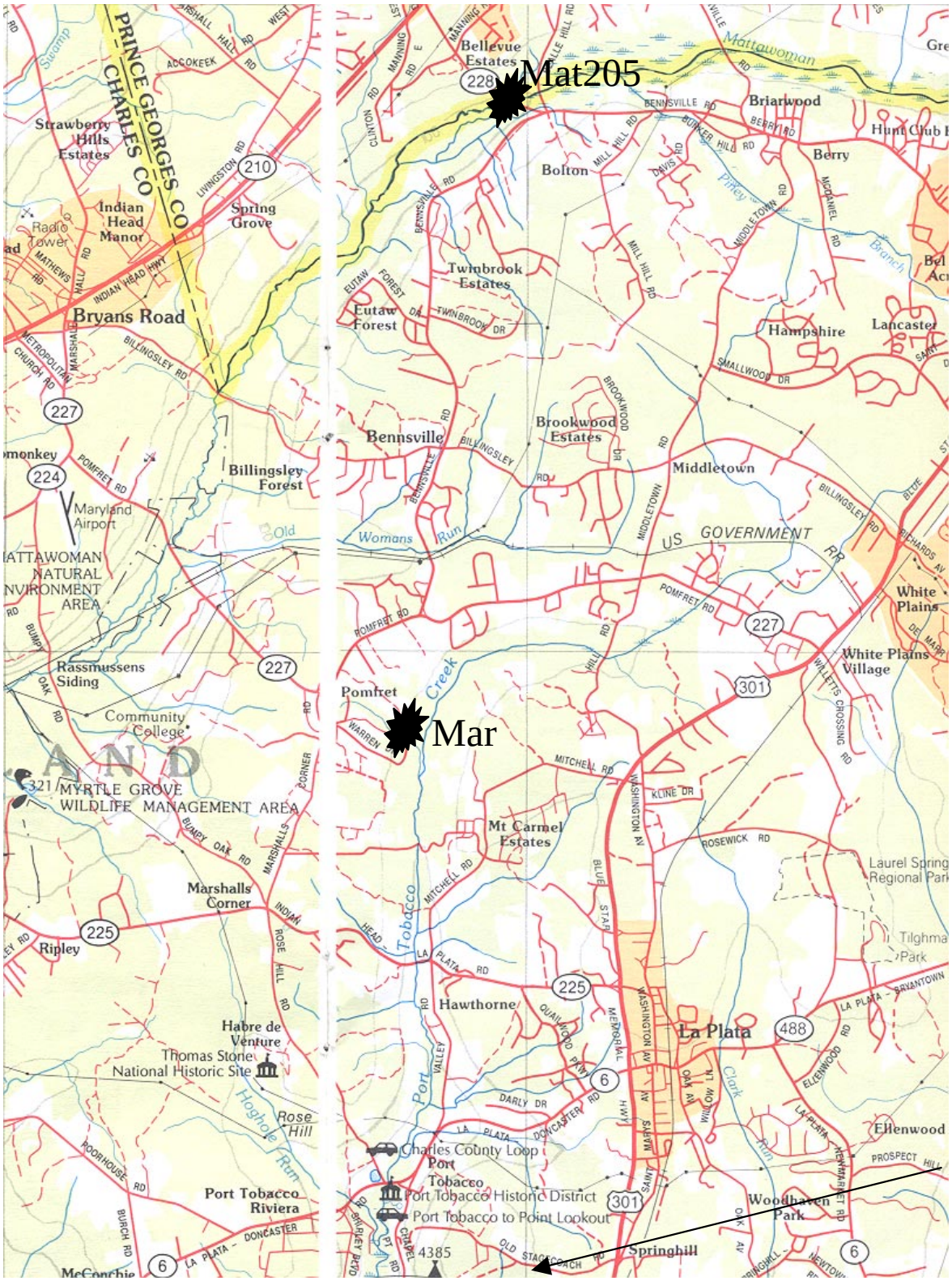
Fig. A4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Spring Grove
Bryans Road
Billingsley Forest
Maryland Airport
MATTAWOMAN NATURAL ENVIRONMENT AREA
Rassmussens Siding
Community College
MYRTLE GROVE WILDLIFE MANAGEMENT AREA
Marshalls Corner
Ripley
Habre de Venture
Thomas Stone National Historic Site
Rose Hill
Port Tobacco Riviera
Bellevue Estates
Bolton
Briarwood
Berry
Twinbrook Estates
Eutaw Forest
Hampshire
Lancaster
Bennsville
Brookwood Estates
Middletown
Womans Run
US GOVERNMENT RR
White Plains
White Plains Village
Pomfret
Creek
Mt Carmel Estates
Laurel Spring Regional Park
Hawthorne
La Plata
Charles County Loop
Port Tobacco
Port Tobacco Historic District
Port Tobacco to Point Lookout
Woodhaven Park
Springhill
Ellenwood

Fig. A5

Appendix 2: Raw Data for Fish

All fish concentration data. Concentrations are in ppb for Hg and MMHg and in ppm for other metals.
M = Mason Branch streams; A= Andover streams; RL = Rel Lion Reference; Q series streams in Charles County. See Table 1 for locations.

Fish are identified as follows:
Sunfish: bluespotted sunfish (BSS), redbreast sunfish (RBS), pumpkinseed (PS), and bluegill (BG)
Pickerel: chain pickerel (CP) and redfin pickerel (RP)
Minnows: fallfish (FF) and golden shiner (GS)
Bass: largemouth bass (LMB)
Catfish: madtom (MT) and brown bullhead (BB)

Numbers refer to individual fish e.g. M 101 BSS1 = the first bluespotted sunfish taken from Mason Branch 101.

Sunfish	Fish	Total Hg			
Sample ID	Wt. (g)	Aver	STD	MMHg	%MMHg
M 101 BSS1	9.8	21.8	4.3	16.9	77.5
M 101 BSS3	1.8		5.5	27.5	
M 101 BSS4	3.9	49.4	4.7	25.2	51.1
M 101 BSS5	5.2	54.0	4.4	39.9	73.8
M104BSS1	6.2	56.4		15.3	27.1
M104BSS4	8.2	118.7		31.1	26.2
M104BSS6	1.9	13.4	4.1	13.8	102.8
M104BSS8	3.0	24.1	7.5	21.8	90.1
M104P1	22.2	28.1	2.9	22.4	79.8
M104P3	11.3	29.3	4.0	20.1	68.5
M104P4	15.7	18.0		10.3	57.4
M104RBS1	24.0	39.9	4.2	61.7	154.5
M104RBS2	14.0	29.1	4.1	39.3	135.0
M104RBS3	54.8	71.6	4.4	69.6	97.1
M104RBS4	39.6	101.3	4.6	90.4	89.3
M 106 BG1	31.2	45.3	4.2	7.4	16.3
M 106 BSS2	4.7	80.0	4.1	15.4	19.2
M 106 BSS3	2.8	53.4	4.6	13.2	24.8
M 106 BSS4	2.8	16.0	4.8	5.0	31.0
M 106 BSS5	2.9	50.9	5.8	9.2	18.0
M 106 P1	23.9	65.6	4.6	12.0	18.2
M 106 P2	12.0	23.2	4.2	6.6	28.3
M 106 P5	8.7	54.5	4.0	11.3	20.8
MR BG1	57.7	32.3	3.9	4.7	14.4
MR BG2	49.7	26.6	1.7	3.4	12.7
MR BSS2	8.6	53.2	3.0	7.5	14.2
MR P1	42.1	59.3	6.7	8.4	14.2
MR RBS1	27.8	45.6	1.4	3.9	8.6
MR RBS2	114.3	194.0		219.7	113.2
MR RBS4	51.0	68.6	21.0	8.4	12.3
A102BG3	2.6	74.1	12.0	141.1	190.4
A102BG4	67.8	134.6	4.3	101.6	75.5
A102BG5	29.8	74.8	3.6	72.5	97.0
A102BSS3	1.9	72.2	4.7	78.2	108.3
A102BSS4	4.0	96.7	0.2	28.6	29.6
A102P1	14.0	134.0	2.1	174.6	130.3
A102P2	4.0	38.4	2.6	54.4	141.6
A102P3	35.2	156.3	0.9		
A102 RBS1	92.2	133.7		298.5	223.3
A102RBS2	6.5	97.6	3.5	45.5	46.7
A102RBS3	44.9	149.8	2.9	207.9	138.7
A102BG2	4.8	80.7	1.3	10.4	12.8
A103BSS1	5.3	68.2	1.7		0.0
A103BSS2	3.4	63.7	2.8	12.3	19.4
A103 BSS3	15.1	168.1		97.9	58.3

Sunfish	Fish	Total Hg			
Sample ID	Wt. (g)	Aver	STD	MMHg	%MMHg
A103BSS4	8.7	125.8	6.6	62.9	50.0
A103BSS5	3.5	92.8	2.8	34.9	37.6
A103 BSS6	3.2	92.5		152.8	165.2
A103 P1	3.8	112.6		174.5	154.9
A103 P3	20.6	193.6		218.7	113.0
A103 P4	54.1	65.8		57.29	87.1
A103RBS1	8.1	67.3	0.9	32.5	48.3
A103RBS3	51.2	173.2	0.3	98.0	56.6
AR BG3	3.4	113.9	0.2	34.0	29.8
AR BG4	19.9	89.9	0.2	11.9	13.3
AR BG6	7.9	113.5	2.2	18.6	16.3
AR BSS1	2.3	78.5	11.7	23.9	30.4
AR BSS2	13.1	230.3	7.3	46.3	20.1
AR BSS5	4.5	87.7	0.4	30.3	34.6
RL BG3	85.6	31.0		39.4	126.9
RL BG4	3.4	30.7		36.3	118.1
RL BG 6	48.4	44.3		36.13	81.5
RL BSS1	3.3	37.0		23.9	64.6
RL RBS1	29.9	70.5		62.27	88.4
RL RBS2	99.5	83.5		74.56	89.3
RL RBS3	48.9	147.6		143.73	97.4
Q103 BG1	13.15	75.2		54.55	72.5
Q103 BG2	9.14	108.92		78.03	71.6
Q103 BSS7	2.08	95.34		66.12	69.4
Q103 BSS13	8.79	186.24		151.36	81.3
Q103 BSS14	13.62	178.22		163.53	91.8
Q103 P1	11.49	75.96		63.98	84.2
Q103 P5	1.88	91.6		82.44	90.0
Q103 P12	21.61	903.36		227.61	25.2
Q108 BG5	11.43	37.56		21.35	56.8
Q108 BG9	87.09	68.05		79.24	116.4
Q108 BG10 OR 11	50.29	62.83		62.65	99.7
Q108 BG13	2.57	45.87		71.26	155.4
Q108 P2	4.02	38.7		18.72	48.4
Q108 P3	5.08	56.31		56.74	100.8
Q108 RBS1	5.92	70.4		60.51	86.0
Q108 RBS5	8.84	53.77		51.47	95.7
Q112 BG1	6.83	106.42		180.57	169.7
Q112 BG3	11.8			172.75	
Q112 P8	4.3			22.79	
Q112 RBS1	4.58	354.03		320.06	90.4
Q112 RBS2	10.59	156.96		312.05	198.8
Q112 RBS11	34.9	627.98		470.53	74.9
Q202 BG2	3.8	48.08		84.76	176.3
Q202 BG4	1.41			79.59	
Q202 BG5	12.25			13.41	
Q202 BSS1	1.21			130.71	

Sunfish Sample ID	Fish Wt. (g)	Total Hg Aver	STD	MMHg	%MMHg
Q205 BG5	9.04	25.94		-	
Q205 BG7	1.8	54.38		56.57	104.0
Q205 BG9	4.17	27.22		43.83	161.0
Q205 BG12	2.34	28.66		33.62	117.3
Q205 BG13	4.45	30.32		33.87	111.7
Q205 BSS1	3.19	78.23		124.09	158.6
Q205 LM1	73.31	31.8		90.04	283.3
Q205 P1	8.66	18.6		21.91	117.9
Q205 P6	2.06	102.3		74.55	72.9
Q205 RBS1	8.61	79.8		96.49	120.9
Q205 RBS2	5.98	95.96		89.9	93.7

Pickerel	Fish	Total Hg			
Sample ID	Wt. (g)	Aver	STD	MMHg	%MMHg
M 101 CP1	5.2	34.1	6.0	25.5	74.6
M 101 RP1	42.6	10.5	4.0	79.3	755.1
M 101 RP2	3.7	176.1	7.0	16.4	9.3
M 101 RP3	7.4	39.1	5.1	42.1	107.8
M104CP1	3.3	19.2	4.9	18.9	98.4
M104RP1	26.7	102.4	21.4	30.1	29.4
M104RP2	55.7	246.4		186.0	75.5
M104RP2		163.4			0.0
MR RF1	47.4	208.6	11.2	31.0	14.9
A102 RP1	73.5	452.2		304.4	67.3
A102RP2	22.9	97.3	0.7	141.7	145.7
A103CP2	3.8	139.2	1.1	10.2	7.3
A103CP3	5.3	98.5	7.2	40.1	40.7
A103RP2	12.8	180.7	4.5	47.3	26.2
AR RP2	42.7	242.3	15.7	54.5	22.5
AR RP1	46.7	204.9	11.1	14.8	7.2
RL CP1	391.0	102.7		86.6	84.3
RL CP2	109.8	709.8		60.9	8.6
RL CP3	12.3	39.0		31.88	81.7
RL RP1	16.0	55.7		46.48	83.4
RL RP2	50.4	72.7		<10	<10
Q103 CP1	17.73	114.22		90	78.8
Q202 RP1	16.43	183.02		201.15	109.9
Q202 RP2	26.23	90.68		107.52	118.6

Carp		Total Hg			
Sample ID	**Wt. (g)**	**Aver**	**STD**	**MMHg**	**%MMHg**
M 101 GS1	9.8	35.9	4.2	35.4	98.6
M 101 GS2	5.1	64.3	4.4	64.5	100.3
M104FF1	21.6	62.8	5.6	62.9	100.1
M104GS1	35.7	18.3	4.1	26.4	144.1
M104GS2	33.4	59.4	3.9	17.4	29.3
M 106 GS1	47.0	36.2	4.4	7.9	21.8
M 106 GS2	21.1	26.1	4.1	10.2	39.0
M 106 GS3	7.6	36.7	4.3	9.0	24.6
M 106 GS5	3.1	39.5	5.6	11.6	29.5
A102FF1	79.2	305.8	0.6	391.5	128.0
A102FF2	37.7	67.2	0.8	92.1	137.0
A102FF5	5.9	60.8	4.4	62.4	102.6
A103 GS1	14.4	70.2		105.5	150.2
A103GS3	7.9	197.3	8.4	137.6	69.7
A103 FF1	13.0	66.9		44.4	66.4
A103 FF2	27.9	122.7		139.0	113.3
RL FF2	47.7	25.7		21.52	83.6
RL FF4	8.5	31.3		65.61	
RL FF5	311.2	8.6		455.58	
Q103 LB1	11.22	84.37		30.07	35.6
Q108 FF3	3.98	38.27		38.51	100.6
Q108 FF4	67.53	74.26		68.89	92.8
Q112 FF1	19.22	501.64		148.51	29.6
Q112 FF2	54.59			178.64	
Q112 LM1	9.42	130.06		42.46	32.6
Q112 LM3	4.93	37.02		68.79	185.8
Q202 GS1	0.68			103.3	

B ass		**Total Hg**			
Sample ID	**Wt. (g)**	**Aver**	**STD**	**MMHg**	**%MMHg**
M104LM1	24.1	44.0		20.9	47.6
MR LB1	143.2	716.1		86.1	12.0
MR LB3	266.5	546.6		126.6	23.2
A102 LM1	165.5	558.9		182.2	32.6
A102LM3	14.8	72.7	3.3	82.6	113.7
A103 LM2	5.1	41.0		43.9	107.2
A103 LM3	25.5	157.1		121.8	77.6
AR LM1	4.9	135.0	2.8	30.6	22.7
Catfish					
M 101 MT1	8.0	123.9	4.7	82.2	66.3
M 101 MT2	5.0	49.8	4.6	14.7	29.4
M104MT1	7.3	62.4	4.6	11.5	18.4
M104MT2	3.8	99.8	4.2	76.5	76.7
M104MT3	4.9	98.5	4.4	83.9	85.1
M 106 MT1	13.0	101.0	4.8	25.1	24.9
MR MT1	13.5	36.2	2.9	4.5	12.5
MR MT2	4.0	20.6	0.8	3.7	17.9
AR BBH1	39.9	68.2	0.8	25.1	36.8

	Fish concentrations in μg/g wet weight				
Sample ID	**Class**	**wt. (g)**	**As**	**Se**	**Cd**
M 101 BSS1	sun	9.8000	0.1270	0.6560	5.0000e-3
M 101 BSS3	sun	1.8000	0.6880	0.9370	5.0000e-3
M 101 BSS4	sun	3.9000	0.4850	0.6500	0.0100
M 101 BSS5	sun	5.2000	0.0650	0.6820	5.0000e-3
M104BSS1	sun	6.2000	0.8240	1.0070	0.0400
M104BSS4	sun	8.2000	0.5640	0.5660	0.0610
M104BSS6	sun	1.9000	0.0500	0.4100	5.0000e-3
M104BSS8	sun	3.0000	0.4160	0.5360	5.0000e-3
M104P1	sun	22.2000	0.0300	0.3810	5.0000e-3
M104P3	sun	11.3000	0.0500	0.4310	5.0000e-3
M104P4	sun	15.7000	0.8860	0.7900	2.0000e-3
M104RBS1	sun	24.0000	0.0500	0.2850	5.0000e-3
M104RBS2	sun	14.0000	0.0500	0.3880	5.0000e-3
M104RBS3	sun	54.8000	0.0500	0.4040	5.0000e-3
M104RBS4	sun	39.6000	0.0500	0.3900	5.0000e-3
M 106 BG1	sun	31.2000	0.3740	0.3130	0.0760
M 106 BSS2	sun	4.7000	0.4570	0.4310	0.0110
M 106 BSS3	sun	2.8000	0.1570	0.4190	0.1090
M 106 BSS4	sun	2.8000	0.0830	0.3960	0.0270
M 106 BSS5	sun	2.9000	0.0910	0.4130	0.0100
M 106 P1	sun	23.9000	0.4370	0.4380	1.0000e-3
M 106 P2	sun	12.0000	0.2470	0.3330	0.0130
M 106 P5	sun	8.7000	0.5210	0.3910	0.1150
MR BG1	sun	57.7000	0.5690	1.0640	0.0450
MR BG2	sun	49.7000	0.9270	1.0420	0.2050
MR BSS2	sun	8.6000	0.3280	0.9140	0.1860
MR P1	sun	42.1000	0.9990	0.8330	0.0900

Sample ID	Class	wt. (g)	As	Se	Cd
MR RBS1	sun	27.8000	0.5760	0.9480	0.0720
MR RBS2	sun	114.3000	0.5760	0.9480	0.0720
MR RBS4	sun	51.0000	0.3590	0.5470	0.0410
A102BG3	sun	2.6000	0.3160	0.5130	0.0270
A102BG4	sun	67.8000	0.2620	0.5020	0.0530
A102BG5	sun	29.8000	0.1420	0.5760	0.0220
A102BSS3	sun	1.9000	0.4570	0.7270	0.0270
A102BSS4	sun	4.0000	0.2440	0.7220	0.0270
A102P1	sun	14.0000	0.3860	0.6640	0.0250
A102P2	sun	4.0000	0.3630	0.5090	0.0150
A102P3	sun	35.2000	0.1660	0.5490	0.0320
A102 RBS1	sun	92.2000	0.0720	0.6080	0.1400
A102RBS2	sun	6.5000	0.1740	0.7220	0.0220
A102RBS3	sun	44.9000	0.1600	0.7250	0.0410
A104BG2	sun	4.8000	0.1960	0.6000	5.0000e-3
A103 BG4	sun	110.2000	0.0500	0.1240	0.0790
A103BG6	sun	58.9000	0.2640	0.5880	7.0000e-3
A103BSS2	sun	3.4000	0.1960	0.6000	5.0000e-3
A103 BSS3	sun	15.1000	0.0500	0.3580	0.1280
A103BSS4	sun	8.7000	0.9640	1.1200	0.0910
A103BSS5	sun	3.5000	0.8540	1.3180	0.0220
A103 BSS6	sun	3.2000	0.0500	0.3460	0.4820
A103 P1	sun	3.8000	0.5270	0.5420	0.4660
A103 P3	sun	20.6000	0.0500	0.0440	0.1130
A103 P4	sun	54.1000	0.0500	0.3330	0.1110
A103RBS1	sun	8.1000	0.0500	0.5490	5.0000e-3
A103RBS3	sun	51.2000	0.5000	1.0840	5.0000e-3
AR BG3	sun	3.4000	0.0940	0.4940	0.0140
AR BG4	sun	19.9000	0.0500	0.3250	0.0110
AR BG6	sun	7.9000	0.0300	0.3290	0.0250
AR BSS1	sun	2.3000	0.2280	0.4730	0.0120

Sample ID	Class	wt. (g)	As	Se	Cd
AR BSS2	sun	13.1000	0.0920	0.5140	0.0190
AR BSS5	sun	4.5000	0.1610	0.4180	0.0190
RL BG3		85.6000	0.1000	0.3460	5.0000e-3
RL BG4		3.4000	0.0500	0.5150	0.0100
RL BG 6		48.4000	0.0490	0.7580	5.0000e-3
RL BSS1		3.3000	0.0500	0.5520	5.0000e-3
RL RBS1		29.9000	0.0500	0.6150	0.0100
RL RBS2		99.5000	0.0500	0.5400	5.0000e-3
RL RBS3		48.9000	0.0320	0.7740	0.0350
Q103 BG1		13.1500	0.0860	0.5210	0.0650
Q103 BG2		9.1400	0.0230	0.3260	0.0370
Q103 BSS7		2.0800	0.3680	0.6450	0.1250
Q103 BSS13		8.7900	0.1190	0.7220	0.1090
Q103 BSS14		13.6200	0.9030	0.6710	0.0750
Q103 P1		11.4900	0.4570	0.4340	0.0650
Q103 P5		1.8800	0.1790	0.6730	0.1690
Q103 P12		21.6100	0.0530	0.5290	0.1150
Q108 BG5		11.4300	0.7920	0.4190	0.0470
Q108 BG9		87.0900	0.2590	0.3840	0.0630
Q108 BG10		50.2900	0.2800	0.6320	0.0850
Q108 BG13		2.5700	0.0500		
Q108 P2		4.0200	0.1880	0.6800	0.1120
Q108 P3		5.0800		0.7090	0.0500
Q108 RBS1		5.9200	0.5300	0.6760	0.1080
Q108 RBS5		8.8400	0.1920	0.5530	0.0950
Q112 BG1		6.8300	0.1460	0.3270	0.0410
Q112 BG3		11.8000	0.1150	0.4360	0.0590
Q112 P1		2.5700	0.2980	0.3900	0.0400
Q112 P8		4.3000	0.3390	0.3960	5.0000e-3
Q112 P11		9.3300	0.3690	0.3080	0.0310
Q112 RBS1		4.5800	0.9570	0.5230	

Sample ID	Class	wt. (g)	As	Se	Cd
Q112 RBS2		10.5900	0.0500	0.4820	0.0430
Q112 RBS11		34.9000		0.4480	0.0420
Q202 BG2		3.8000	0.2210	0.4380	9.0000e-3
Q202 BG4		1.4100	0.0930	1.1140	2.5730
Q202 BG5		12.2500	0.0500		
Q202 BSS1		1.2100		0.3440	0.0280
Q205 BG5		9.0400		0.3030	0.1640
Q205 BG7		1.8000	0.0500	1.2920	0.5640
Q205 BG9		4.1700	0.0500	0.2520	0.1930
Q205 BG12		2.3400	0.9670	0.5650	0.4010
Q205 BG13		4.4500	0.0500	0.1460	0.1190
Q205 BSS1		3.1900	0.3540	1.1630	0.3950
Q205 P1		8.6600	0.0500	0.1370	0.1240
Q205 P6		2.0600	0.5190	0.9840	0.4440
Q205 RBS1		8.6100		0.4390	0.1170
Q205 RBS2		5.9800	0.0500	0.4350	0.1500

Pickerel Sample ID	Total Fish Wt. (g)	As	Se	Cd
M 101 CP1	5.2000	0.1220	0.5490	5.0000e-3
M 101 RP1	42.6000	0.1590	0.5270	5.0000e-3
M 101 RP2	3.7000	0.3070	0.7420	5.0000e-3
M 101 RP3	7.4000	0.0520	0.5790	5.0000e-3
M104CP1	3.3000	0.0500	0.2860	5.0000e-3
M104RP1	26.7000	-0.1490	0.3400	5.0000e-3
M104RP2	55.7000	0.0500	0.3400	5.0000e-3
MR RF1	47.4000	0.4830	0.8070	0.0650
A102 RP1	73.5000	0.0900	0.5430	0.1740
A102RP2	22.9000	0.1700	0.5260	0.0230
A103CP2	3.8000	0.3970	0.8720	5.0000e-3
A103CP3	5.3000	0.2450	0.6910	5.0000e-3
A103RP2	12.8000	0.0500	0.4280	5.0000e-3
AR RP2	42.7000	0.0500	0.2950	7.0000e-3
AR RP1	46.7000	0.0500	0.2570	5.0000e-3
RL CP1	391.0000	0.4420	0.6560	0.0460
RL CP3	12.3000	0.0530	0.6210	0.0110
Q103 CP1	17.7300	0.0980	0.3070	0.0540
Q202 RP1	16.4300	0.0500	0.3570	0.0120
Q202 RP2	26.2300	0.0500	0.6710	0.0140
RL RP1	16.0000	0.0860	0.7450	0.0150
RL RP2	50.4000	0.0500	0.6290	5.0000e-3

Carp Sample ID	Total Fish Wt. (g)	As	Se	Cd
M 106 GS1	47.0000	0.4840	0.3200	0.0680
M 106 GS2	21.1000	0.6690	0.3540	0.0250
M 106 GS3	7.6000	0.6210	0.3600	0.1180
M 106 GS5	3.1000	0.4940	0.2860	0.0940
A102FF1	79.2000	0.1520	0.3480	0.0340
A102FF2	37.7000	0.0500	0.3400	0.0220
A102FF5	5.9000	0.4610	0.4300	0.0380
A103 GS1	14.4000	0.0500	0.2390	0.1120
A103GS3	7.9000	0.4870	1.0230	5.0000e-3
A103 FF1	13.0000	0.0750	0.5170	0.1850
A103 FF2	27.9000	0.0500	0.2630	0.1680
RL FF2	47.7000	0.0500	0.4290	0.0300
RL FF4	8.5000	0.0500	0.5080	0.0120
RL FF5	311.2000	0.3320	0.4410	0.1760
Q108 FF3	3.9800	0.7420	0.4740	0.1320
Q108 FF4	67.5300	0.2340	0.3790	0.1810
Q112 FF1	19.2200	0.1400	0.3990	0.0700
Q112 FF2	54.5900	0.0220	0.1220	0.0260
Q202 GS1	0.6800	0.3080	0.0100	5.0000e-3
M 101 GS1	9.8000	0.5150	0.9500	5.0000e-3
M 101 GS2	5.1000	0.4050	0.7000	5.0000e-3
M104FF1	21.6000	0.0500	0.3830	0.0210
M104GS1	35.7000	0.0500	0.3370	5.0000e-3
M104GS2	33.4000	0.0500	0.3240	5.0000e-3

Bass Sample ID	**Total Fish Wt. (g)**	**As**	**Se**	**Cd**
MR LB1	143.2000	0.0500	0.1780	0.0520
MR LB3	266.5000	0.2930	0.8090	0.1730
A102 LM1	165.5000	0.0500	0.3510	0.1020
A102LM3	14.8000	0.0260	0.5010	0.0550
A103 LM2	5.1000		0.4900	
A103 LM3	25.5000	0.0500	0.3610	0.1050
AR LM1	4.9000	0.0780	0.4000	0.0130
Q103 LB1	11.2200	0.0320	0.3080	0.0590
Q112 LM1	9.4200	0.5860	0.4000	0.0610
Q112 LM3	4.9300			
Q205 LM1	73.3100	0.3250	0.2950	0.0240
M104LM1	24.1000	0.5240	0.6980	5.0000e-3
Catfish				
M 101 MT1	8.0000	0.5540	0.5810	0.0370
M 101 MT2	5.0000	0.2980	0.5530	5.0000e-3
M104MT1	7.3000	0.0500	0.2470	5.0000e-3
M104MT2	3.8000	0.0500	0.4350	5.0000e-3
M104MT3	4.9000	0.0500	0.4090	5.0000e-3
M 106 MT1	13.0000	0.2350	0.2190	0.0300
MR MT1	13.5000	0.7990	1.0300	0.0670
MR MT2	4.0000	0.1190	0.3040	0.0280
AR BBH1	39.9000	0.0500	0.1770	0.0100