Hixon Center for Urban Ecology
Student Research Fellowship
Research Report

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Introduction

Mercury is a potent neurotoxin with significant human health effects (Franzblau, 1994) that readily bioaccumulates to harmful levels in food chains (Mikac & Picer, 1985). It has many anthropogenic sources, stemming mainly from industrial activity, including the manufacture of electrical apparatus and computers, the amalgamation of metals, the production of hydrochloric acid and sodium hydroxide, and the production of pesticides (Laws, 1981). Its primary anthropogenic sources to the environment, however, are waste incineration and coal burning (Nriagu & Pacyna, 1988). Many components of municipal solid waste contain mercury, and mercury is present in coal primarily in the form of mercuric sulfide (HgS), or cinnabar. Due to its heavy industrial use, mercury is present in relatively high concentrations in urban areas and industrial centers. Rice (1999) has shown that mercury concentrations in streambed sediments across the United States are positively correlated with population density in a stream's watershed. Because of its high abundance in populated areas and its threat to human health, it is important to understand the biogeochemistry of mercury in urban watersheds.

Because of its high binding affinity for mineral particles, most anthropogenic mercury released to the atmosphere adheres to dust particles and either settles to the earth's surface or is washed out in rain. Although direct atmospheric deposition of mercury is the most important source to the world oceans (Mason *et al.*, 1994), it comprises a relatively low proportion of riverine mercury budgets, due to rivers' low surface area (Mason & Sullivan, 1998). The mercury that is deposited on a river's watershed, however, can be much more significant than what is deposited in the river itself, as most watersheds are many times larger than the streams that drain them. This watershed-deposited mercury washes into streams, during storm events, as surface runoff. In watersheds with a low degree of urbanization (and therefore a low degree of impervious surface cover), there is little surface runoff, and what runoff does occur is usually low in total suspended solids (TSS), and therefore provides little transport medium for mercury. More urbanized watersheds, however, produce more surface runoff during storm events, as water cannot easily soak into the ground. This runoff is higher in TSS, and therefore often higher in mercury concentrations as (Balogh *et al.*, 1997).

Mason and Sullivan (1998) have shown that mercury concentrations in an urbanized river, the Anacostia River in Washington, D.C., account for a much higher percentage of atmospheric deposition to the watershed than do rivers in less urbanized watersheds. They also demonstrated that storm flow is the most important transport mechanism for aquatic mercury, with storm mercury concentrations three to five times higher than base flow. Although New Haven County, in south central Connecticut, has watersheds with a similar degree of urbanization as those in Washington, D.C., the relationship between land use and the mercury cycle has not been studied in these rivers.

Balcom *et al.* (2004) estimated that Connecticut rivers contribute 59% of Long Island Sound's total mercury budget, but that figure is based on base flow mercury concentrations. The storm flow mercury levels in New Haven County rivers have not been studied. The relationship between land use change and mercury cycling in the New

Haven area has also received little study. In order to better understand these important components of the regional mercury cycle, in this study, I tested the following hypotheses:

1. Watershed mercury concentrations are positively correlated with the degree of urbanization in the watershed, defined as the percentage of the ground covered with impervious surfaces.
2. Mercury concentrations under conditions of storm flow are significantly higher than base flow concentrations, in addition to following the trend outlined in Hypothesis 1.
3. Mercury concentrations are positively correlated with TSS under base and storm flow.

Methods

I selected four sites (Fig. 1) in the three major watersheds of the City of New Haven. The sites contained streams of similar order, discharge, and watershed size. The sites were selected based on the land use in their watersheds, and represent a gradient from non-urbanized (3.20% impervious surface cover) to almost entirely urbanized (77.29% impervious surface cover) (Fig. 2). The sites are Sanford Brook (Site 1050), a tributary to the West River, in Bethany, CT, 1.21 mi^2 watershed, 3.20% impervious surface cover; Butterworth Brook (Site 2026), a tributary to the Mill River, in Hamden, CT, 1.64 mi^2 watershed, 6.43% impervious surface cover; an unnamed tributary to the Quinnipiac River (Site 3025), in between Route 15 and the Old Hartford Turnpike, in Wallingford, CT, 0.91 mi^2 watershed, 18.79% impervious surface cover; and an unnamed tributary to Lake Whitney (Site 2005), an impoundment of the Mill River, in the Spring Glen neighborhood of Hamden, CT, 0.43mi^2 watershed, 77.29% impervious surface cover. The site numbers were generated by an earlier study, the Mastodon Project, and the first digit of each number corresponds to a major watershed: 1 – West River, 2 – Mill River, 3 – Quinnipiac River (Benoit, G., Personal Communication). Three of the four watersheds were selected from within the 0-20% impervious surface cover range based on the belief that that range represents the majority of variability in watershed effects.

Watershed size and impervious surface cover estimates were created using the Environmental Systems Research Institute's (ESRI) ArcGIS 9.0 software package. Due to a lack of sufficient detail in the statewide digital elevation model (UCONN MAGIC, 2005), watershed boundaries were delineated manually, rather than using ESRI's automated "Watershed" tool. The base data used for this operation were the United States Geological Survey (USGS) topographic map quadrangles for the study area and the statewide minor drainage basins map layer (UCONN MAGIC, 2005). Where watershed boundaries differed from minor drainage basin boundaries, lines were drawn based on contours on the USGS quadrangles. The accuracy of the delineations was confirmed by converting the USGS quadrangles into a three dimensional projection, using the statewide digital elevation model, and visually ensuring that watershed boundaries corresponded logically with slopes, ridge lines, and valleys. Impervious surface cover estimates were made using the 1990 Connecticut Orthophotos (UCONN MAGIC 2005) as base data. All buildings, parking lots, and visible roads were hand digitized. This method achieved a much higher precision than would have been achieved by using the statewide land cover map layer (UCONN MAGIC, 2005), which has a 30 m x 30 m pixel resolution.

Each stream was sampled every month under base flow conditions in order to monitor seasonal variations in stream chemistry. Storm flow has not been sampled, at the time of writing, due to delays in method development. Storm flow will be sampled once in the future, and the results published in a subsequent paper. Base flow samples were collected by hand in acid-cleaned Teflon® bottles. Samples were preserved with 0.5% bromine monochloride (BrCl) prior to storage.

Water samples were analyzed for total and dissolved mercury, total suspended solids (TSS), pH, conductivity, and turbidity. Dissolved mercury samples were filtered through 0.45µm sealed capsule filters in a Class 100 clean room, prior to preservation and storage. Mercury was analyzed using oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry (CVAFS) on a Tekran Model 2600 Aqueous Mercury Analyzer, following EPA Method 1631 (EPA, 2001). Calibration blanks and standards were run daily, to guarantee low contamination and high recovery. An ongoing precision and recovery standard was measured at several points throughout each analytical run to ensure the stability of the signal. A certified reference material (ORMS-3, National Research Council, Canada) was analyzed several times throughout the course of the study to ensure consistency of results.

TSS samples were filtered through Whatman GF/F filters (0.7µm pore size). Filters were dried in an oven at 115°C for 48 hours and weighed, following Standard Methods (APHA, 1998). pH and conductivity were measured using field probes and turbidity was measured in the field using a handheld fluorometer.

All samples were collected and analyzed following trace metal clean techniques (Fitzgerald, 1999; Benoit, 1994; Benoit *et al.*, 1994). Samples only came in contact with tubing and containers that have been thoroughly acid-cleaned in a Class 100, mercury-free clean room. All sample collection was done wearing arm-length polyethylene gloves. Field blanks of nanopure deionized water were collected at field sites during every sampling trip, and were transported, stored, and analyzed under the same conditions as the samples. Sample containers were transported to and from the field double-bagged in polyethylene, and atmospheric exposure time was kept to a minimum. All analysis took place in the clean room, to prevent atmospheric contamination of samples.

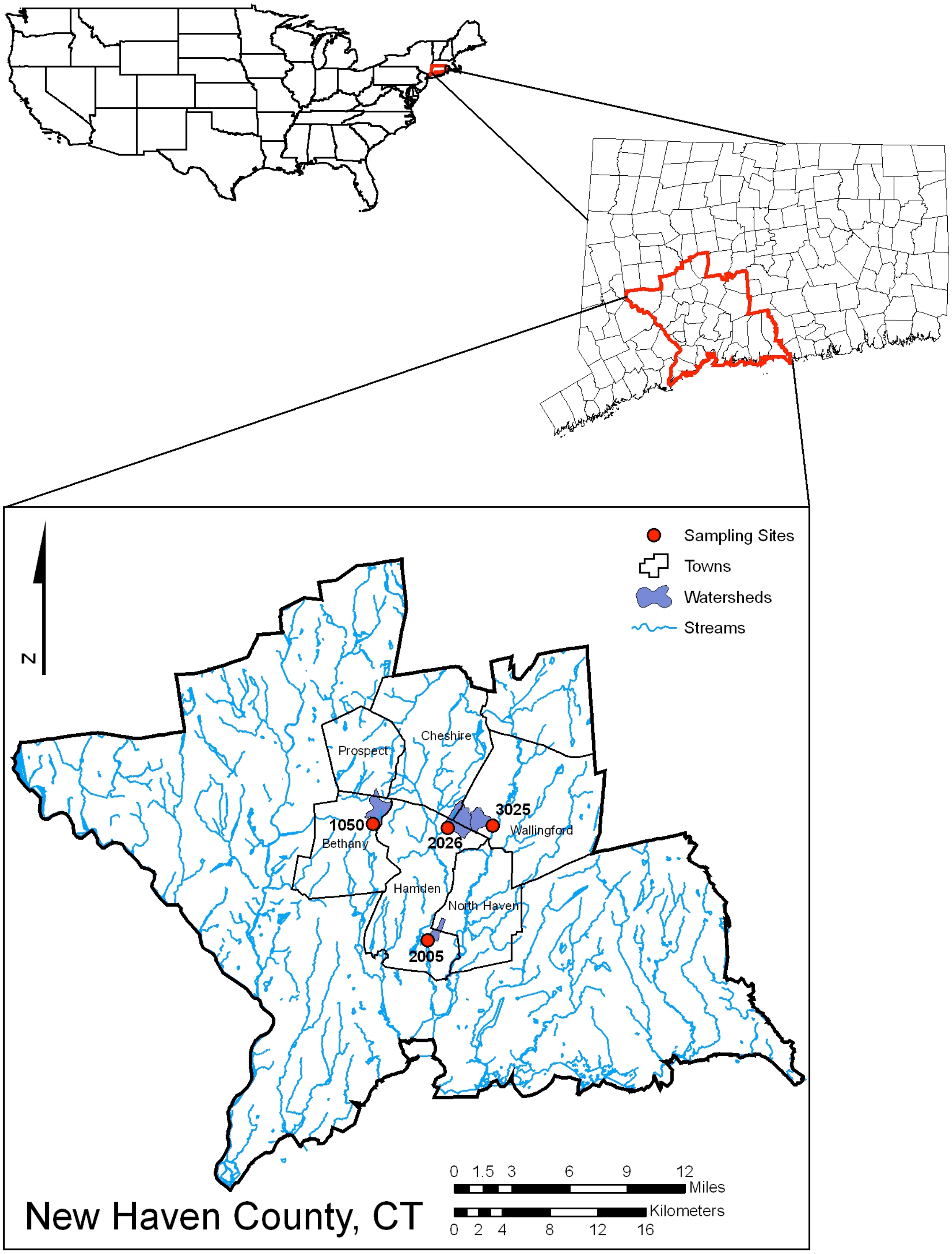

Figure 1: Study sites, watershed areas, and encompassing towns.

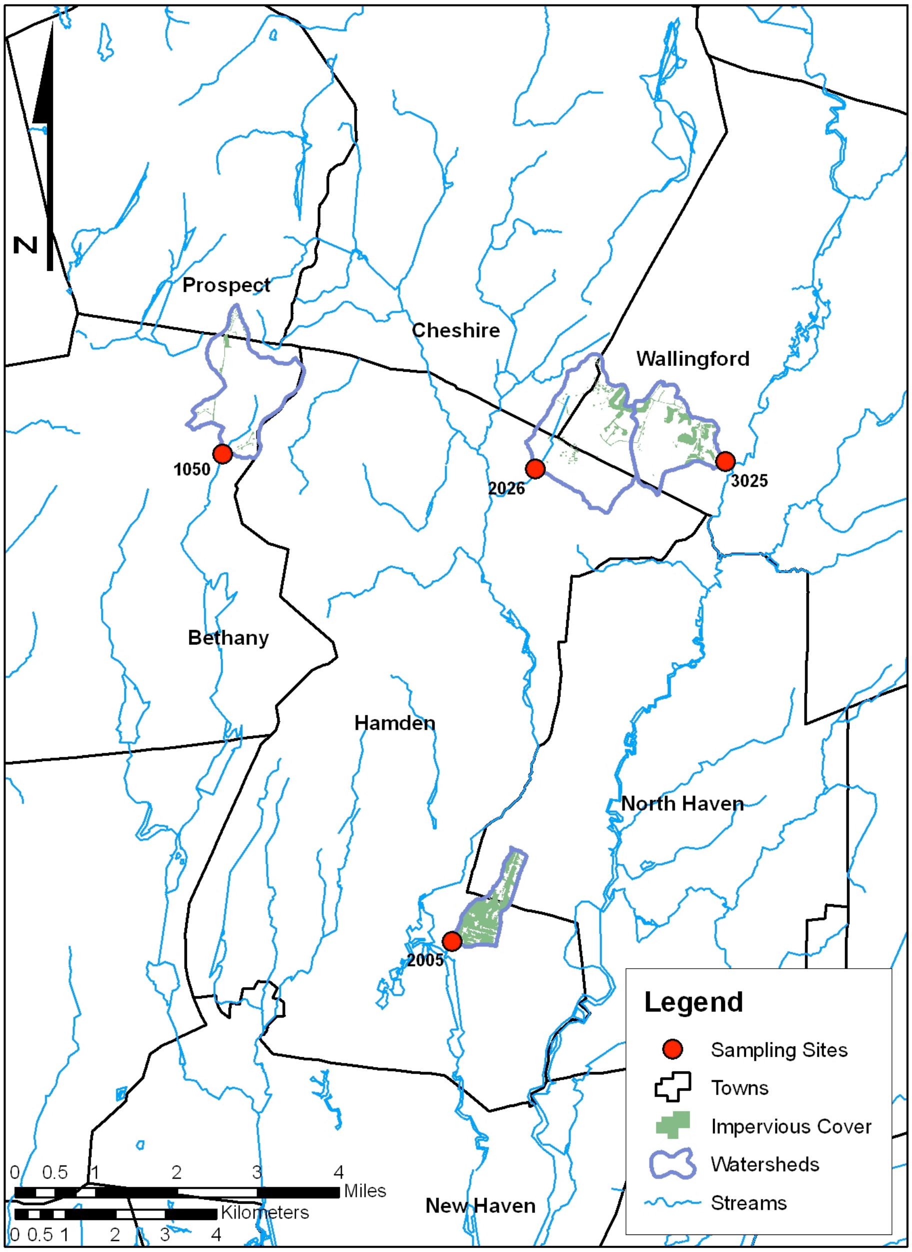

Figure 2: Study sites and impervious surface cover in their watersheds.

Results and Discussion

Total and dissolved mercury data vary from 0 to roughly 2 parts per trillion (ppt, or ng/L), excepting one outlier (Fig. 3). The numbers show a trend throughout the sampling season of decreasing during the summer months and increasing in the fall. It is interesting to note that the mercury levels are low in late July and August, when stream flows were low, however, all concentrations increased between August and September, despite stream flow remaining fairly low throughout that period. This indicates that, while stream flow may explain some variation in mercury concentration at base flow levels, it is not the only contributing factor. Samples collected on July 29 are difficult to compare to the rest of the data as the mercury analyzer malfunctioned that day, giving results with poor reproducibility and thus questionable reliability.

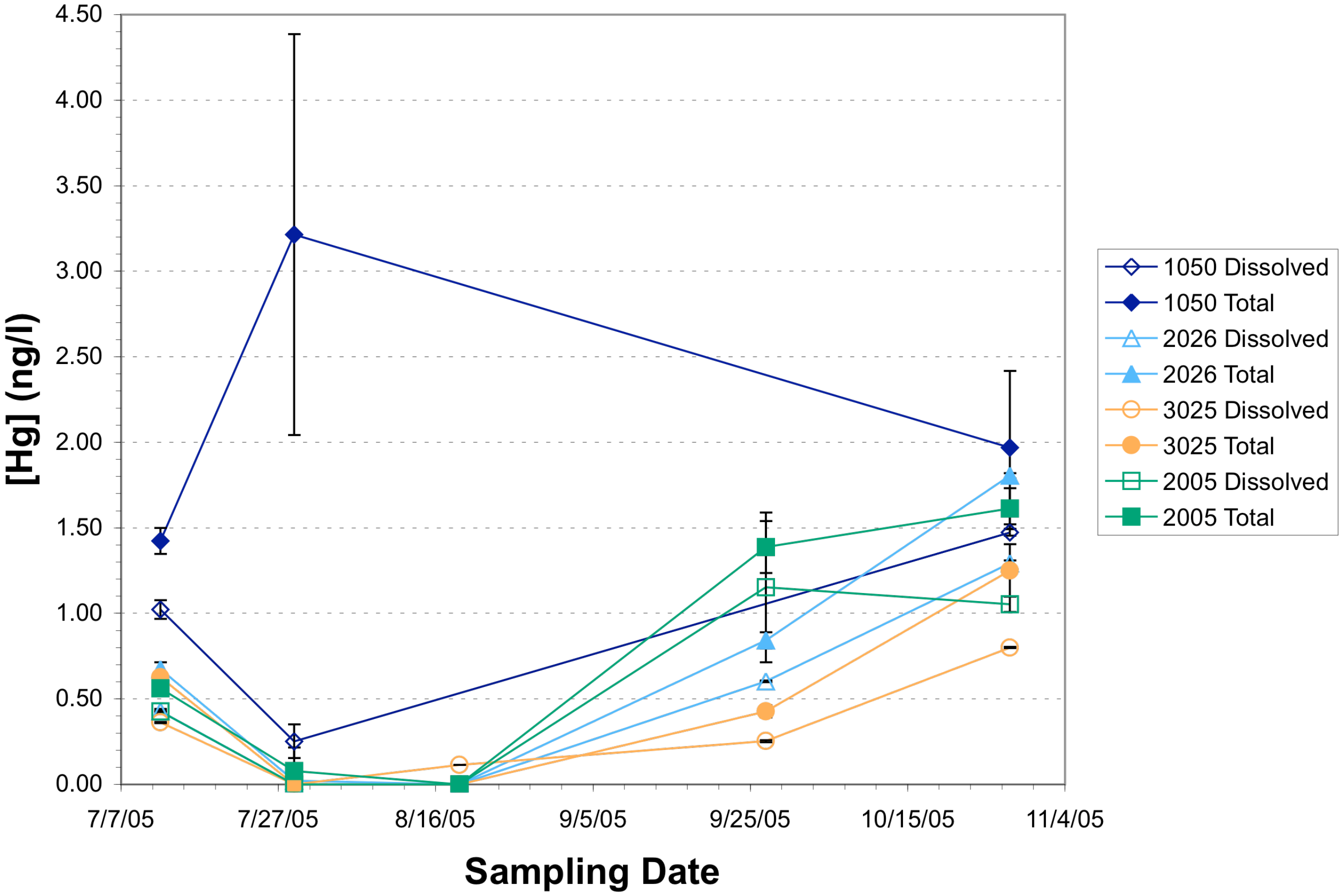

Figure 3: Raw mercury data plotted by sample site and date. Error bars indicate the standard deviations of replicate measurements. Every measurement was made in duplicate or triplicate except for Site 2026 Dissolved and Total Mercury on 8/19/05, which were only made once, due to a software error. Data also available in numeric form in Table 1.

	Date	7/12/05			7/29/05			8/29/05			9/27/05			10/28/05		
Site		Average	σ	n	Average	σ	n	Average	σ	n	Average	σ	n	Average	σ	n
1050	**Dissolved**	1.02	0.05	3	0.25	0.10	2	No water in stream			No water in stream			1.47	0.02	2
	Particulate	0.40			2.96									0.49		
	Total	1.42	0.08	3	3.21	1.17	3							1.97	0.45	3
2026	**Dissolved**	0.43	0.01	2	0.00	0	2	0.00	0	1	0.60	0.00	2	1.29	0.02	2
	Particulate	0.25			0.02			0.00			0.24			0.51		
	Total	0.67	0.04	3	0.02	0.03	2	0.00	0	1	0.84	0.05	3	1.80	0.02	2
3025	**Dissolved**	0.36	0.00	2	0.00	0	3	0.11	0	2	0.25	0.01	2	0.80	0.00	2
	Particulate	0.27			0.00			0.00			0.17			0.45		
	Total	0.63	0.02	2	0.00	0	3	0.00	0	2	0.43	0.04	2	1.25	0.15	3
2005	**Dissolved**	0.43	0.00	2	0.00	0	2	0.00	0.00	2	1.15	0.44	3	1.05	0.05	3
	Particulate	0.14			0.08			0.00			0.23			0.56		
	Total	0.56	0.00	2	0.08	0.14	3	0.00	0.00	2	1.39	0.15	3	1.61	0.12	3

Table 1: Raw mercury data. Particulate mercury concentrations were calculated as
$Hg_{particulate} = Hg_{total} - Hg_{dissolved}$

TSS data were highly variable throughout the period of the study, with no apparent trends in this short time frame (Fig. 4). Based on previous studies, such as Mason and Sullivan's (1998), I would expect TSS to correlate with stream discharge, dropping to low levels in the summer and higher levels in the fall. Although no quantitative discharge data are available for these streams, it is clear that TSS does not follow the expected seasonal pattern of varying with stream discharge: some of the highest points are in the summer, and some of the lowest in the fall.

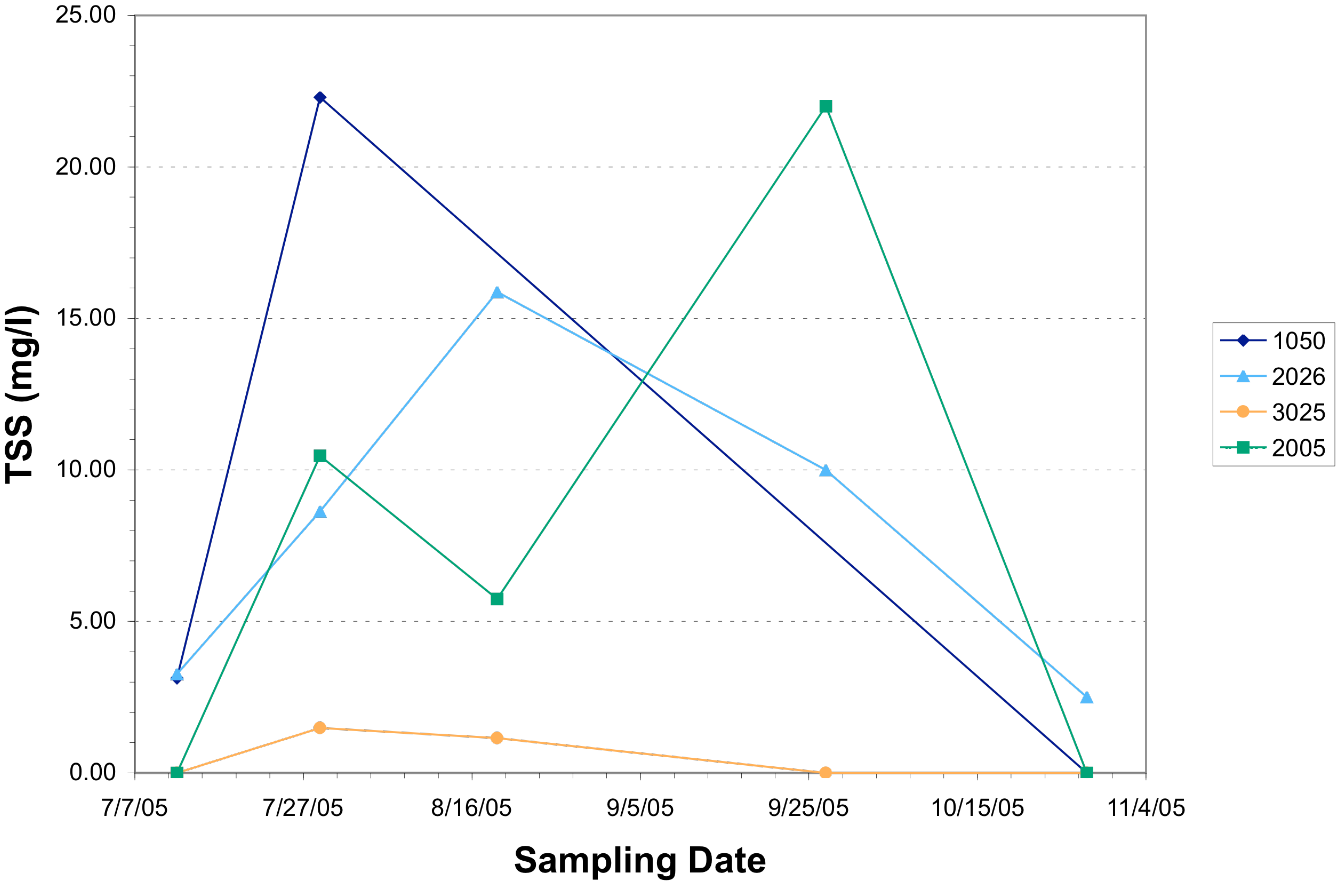

Figure 4: TSS data plotted by sample site and date. TSS data are also available in numeric form in Table 2.

Date Site	07/12/05	07/29/05	08/19/05	09/27/05	10/28/05
1050	3.14	22.29	No water	No water	0.00
2026	3.27	8.63	15.87	10.00	2.50
3025	0.00	1.49	1.16	0.00	0.00
2005	0.00	10.47	5.74	22.00	0.00

Table 2: Raw TSS data.

When the mercury data are plotted against TSS, some extremely weak trends emerge (Fig. 5). There is a slight negative correlation between total mercury and TSS (r^2=0.04), and a steeper negative correlation between particulate mercury and TSS (r^2=0.07). Thus mercury concentrations in these streams are not positively correlated with TSS under base flow conditions, and hypothesis 3 can be rejected.

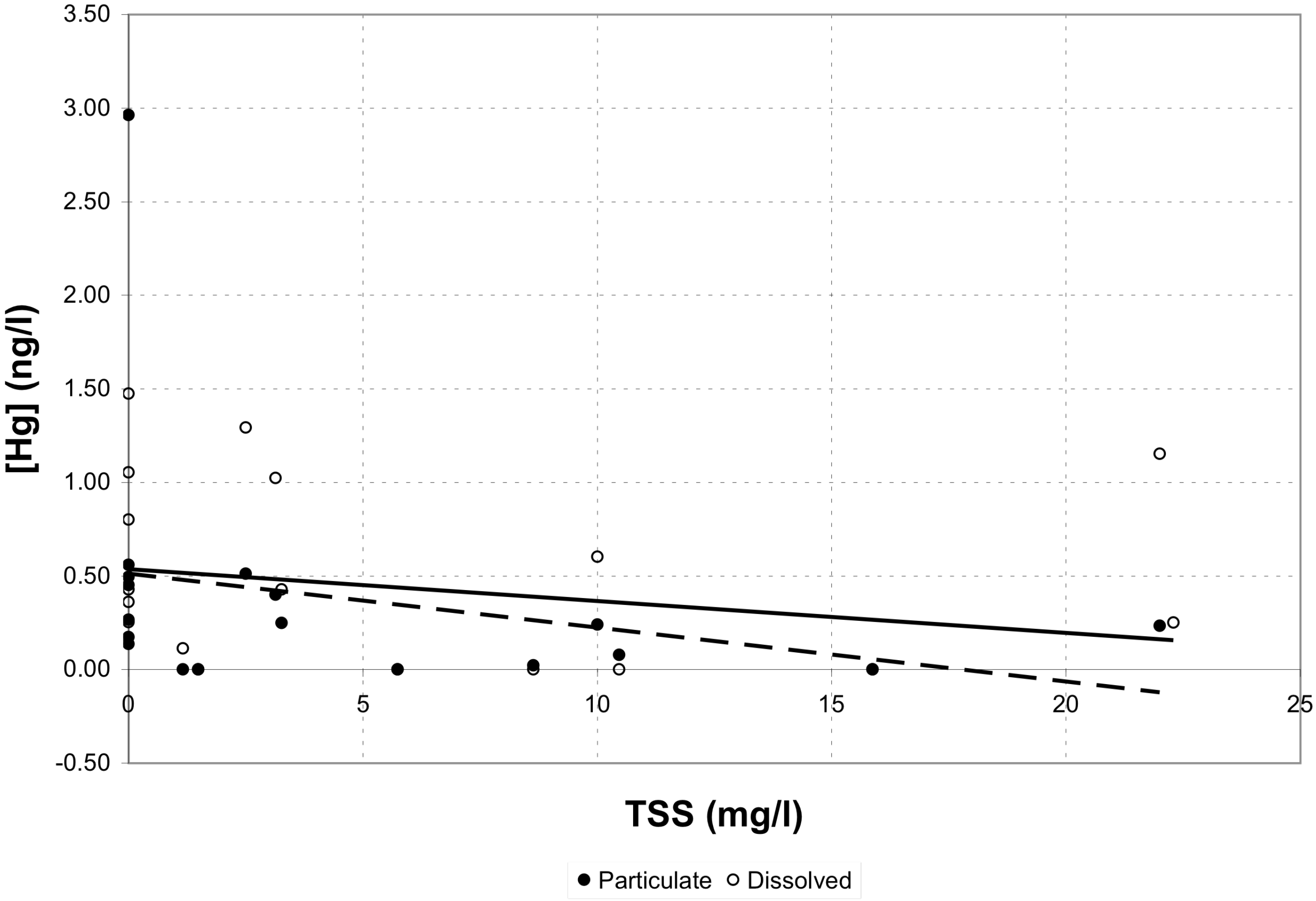

Figure 5: Particulate and dissolved mercury concentrations plotted against Total Suspended Solids (TSS). The solid line represents a linear regression between total mercury and TSS, the dashed line is a linear regression between particulate mercury and TSS.

When compared to the percentage of impervious surface cover in each site's watershed, mercury data also show a very weak (r^2=0.02) negative correlation (Fig. 6). This is the opposite of what was predicted in hypothesis 1. A possible cause for the negative trend is that, under base flow conditions, less-urbanized watersheds, in which streams have more direct contact with soil and natural substrates, are dominated by natural mercury sources. In urbanized watersheds, streams are more likely to be channelized, with concrete sides, or diverted through culverts, such that they have less contact with soils and other potential natural sources of mercury than their less-urbanized counterparts. This is the case in the stream sampled at site 2005, which flows through a culvert for much of its length. In cases such as these, it is likely that, during storm flow conditions, the trend is reversed. In less-urbanized watersheds, a substantial amount of rainwater percolates into the soil, where mercury is usually retained by soil particles. In addition, surface runoff from less-urbanized watersheds tends to have low concentrations of TSS. In urbanized watersheds, more rainwater is discharged directly to streams, potentially carrying both higher mercury concentrations and higher TSS than in less-urbanized areas. I plan to resolve this issue in the spring of 2006, when I conduct storm sampling.

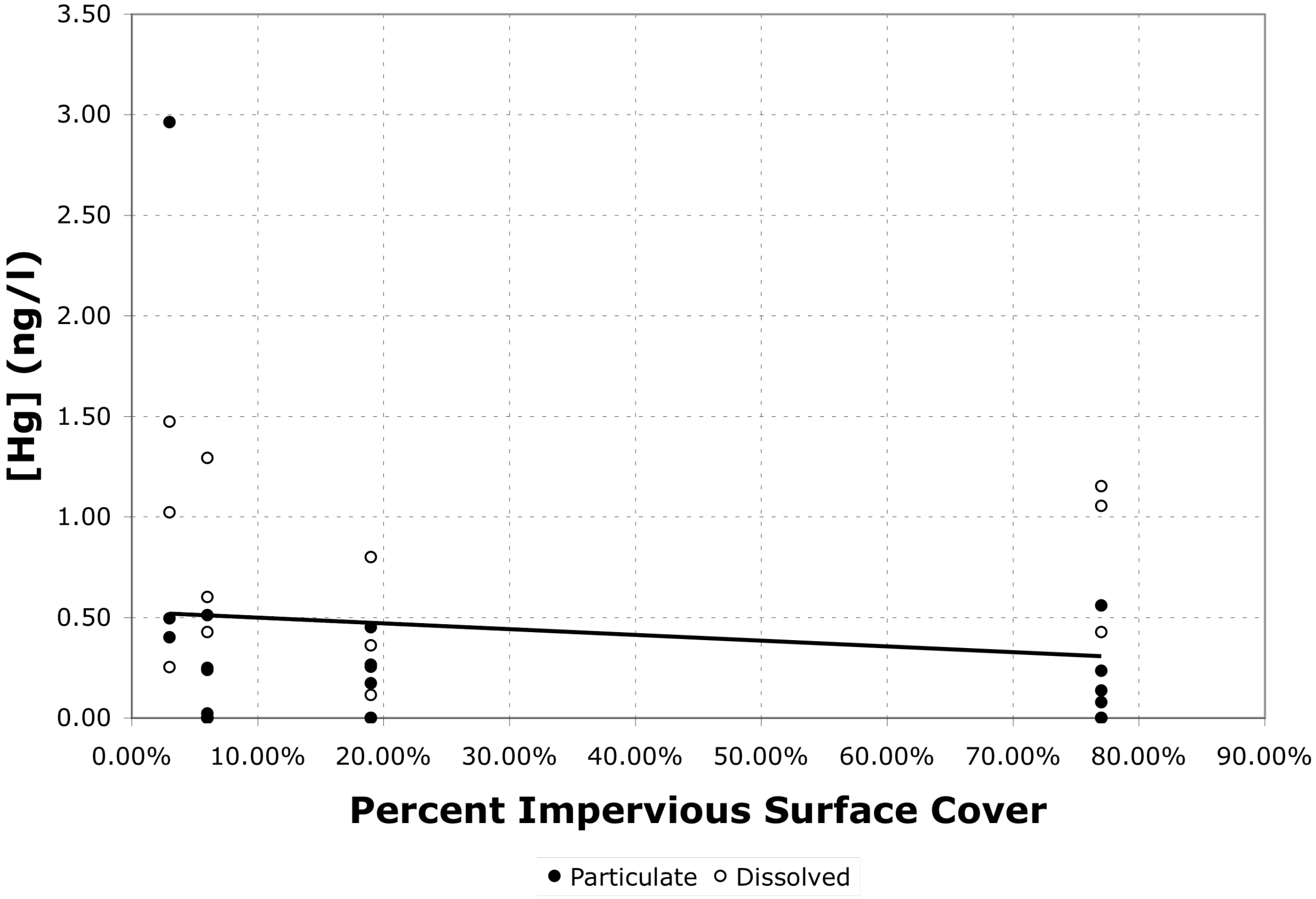

Figure 6: Particulate and dissolved mercury concentrations plotted against the percentage of impervious surface cover in each watershed. The solid line represents a linear regression between total mercury and impervious surface cover.

A relatively strong negative correlation (r^2=0.35) was found between dissolved mercury concentrations and pH (Fig. 7). This is expected, as the solubility of mercury is a direct function of pH, and it forms complexes more easily at high pH. There is a weaker and less-steep negative correlation (r^2=0.24) between particulate mercury and pH.

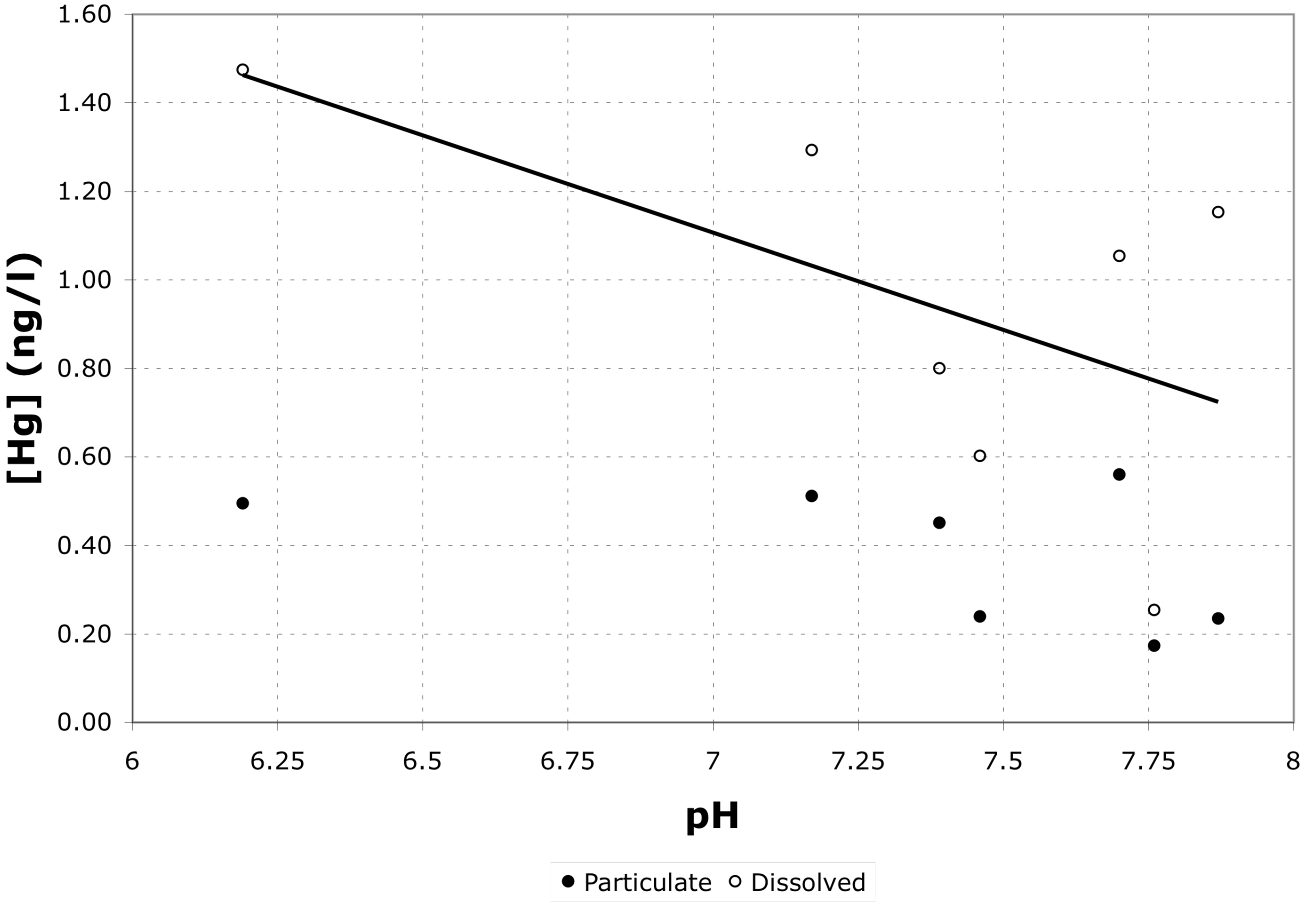

Figure 7: Particulate and dissolved mercury concentrations plotted against pH. The solid line represents a linear regression between total mercury and pH.

Conclusions

This study would benefit from a larger data set, of at least a year, and one or more sets of storm samples. Without storm flow data, it is impossible to accept or reject hypothesis 2. Given the time constraints commensurate with a master's program, it was not possible to conduct more sampling by the time of this writing. This research will continue through early summer of 2006, and will include storm sampling as well as methylmercury analysis of samples from most sampling dates.

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