Evaluation of the behavior of caffeine in fresh watersheds and as a tracer of sewage contamination

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ABSTRACT
It has been suggested that reductions in nitrogen loading to estuaries should be accomplished by implementing watershed specific programs that target the dominant nitrogen sources. The area surrounding Long Island Sound has been intensively developed and the watersheds contributing water and nutrients to the Sound are subject to a variety of density in urbanization. The loading of nutrients due to urban development to the Sound is influenced by urban infrastructure and the density of human populations and their associated activities. Efficient management of water quality in urban systems requires the identification of elements that contribute most to the loading of various pollutants. Caffeine is unique to sewage sources in the Northern Hemisphere, and could be used as a tracer for sewage contamination and evaluation of landscape elements which contribute to nitrogen loading via sewage effluent. I measured caffeine concentration in a fresh watershed along an urban-rural gradient which exhibited a variety in development intensity and infrastructure connection. Caffeine was detected and resolved a pattern that increased with urban density and correlated to other water quality parameters. The evaluation of caffeine as a tracer for sewage contamination as well as a tool for understanding how urban landscapes contribute nutrients to the environment is promising but requires further study.

KEYWORDS
Urban ecology, caffeine, watershed management, infrastructure, waste water, nutrient contamination

Background

Eutrophication is a widespread problem in rivers, lakes, estuaries, and coastal oceans, caused by enrichment of the ecosystem with P and N, and subsequent increased growth of aquatic plants and algae. Non-point pollution, a major source of P and N to surface waters of the United States, results primarily from agriculture and urban activity. (Carpinter et. al. 1998) Long Island Sound, which receives drainage from several populous cities, including New York City, and agriculture from the Hudson and Connecticut River valleys has a well known history of eutrophication, and this issue has seen much effort over the years to manage and remediate the effects. With the decline in agricultural production in much of the region, as compared to other parts of the country, urban areas are likely to be the chief contributors of nutrients, particularly nitrogen compounds, to Long Island Sound.

Urban centers have been shown to increase the nitrogen concentration in rivers, chiefly in the form of ammonium and nitrate. Sources for nitrogen in urban areas include the maintenance of lawns and other vegetation, pet wastes, and waste water treatment infrastructure. The extent of the increase depends on wastewater treatment technology, degree of illicit discharge and leaky sewer lines, and fertilizer use. Nitrogen concentrations in streams draining agricultural catchments are usually much higher, but some studies show similar or even greater levels of nitrogen loading from urbanization (Paul and Meyer, 2001)

The loading of nutrients due to urban development to the Sound is influenced in part by urban infrastructure and the density of human populations and their associated activities. Drainage connection and infrastructure type may be two such variables (Hatt et al. 2004) that determine the mechanism by which urban areas contribute nutrients. The areas draining into Long Island Sound have been intensively developed and the contributing watersheds are subject to a variety of intensity in urbanization. Urban density is an important indicator in predicting water quality. Access to services such as sewer lines or other infrastructure types may explain variation in the contribution of nutrients from within urban areas (Carle et. al, 2005). It is uncertain how variations within the developed land-use classification, surburban, rural, and traditional urban development, and different infrastructure types, contribute to overall loading of nitrogen compounds attributed to urbanized portions of watersheds.

In the case of Long Island Sound, considerable investment has already been made to control nutrient contribution from municipal sewage and waste water. Waste water treatment plants (WWTPs) are utilized to remove nutrients and organic matter from sewage where it was once dumped raw into the Sound, and these plants are monitored to ensure removal of nutrients to targeted levels. Conventional water treatment technologies remove the most labile forms of nitrogen, ammonia and nitrate, from the water before it is discharged. Nitrogen that is bound in organic matter is prevalent in sewage effluent and appears to be slowly converted into the labile forms which contribute to eutrophication.(Pehlivanoglu and Sedlak 2004). Once in the environment, there is potential that these organic forms are mineralized by organisms or chemical processes. (Pehlivanoglu and Sedlak 2004), (Koopmans and Bronk 2002). Organic nitrogen compounds are also prevalent as part of the natural nutrient flux from undeveloped watersheds. (Hedin et al. 1995)

It has been suggested that reductions in nitrogen loading to estuaries should be accomplished by implementing watershed specific programs that target the dominant nitrogen sources (Castro et. al, 2003). Nitrogen loading is a major water quality issue in urban watersheds in general, and locally contributes to the problems of eutrophication and hypoxia in Long Island Sound. Effective and efficient management of water quality in urban systems requires the identification of those watershed elements that contribute to the loading of various pollutants.

Caffeine has the potential to be used as an indicator, conservative, or semi-conservative tracer of sewage effluent from either wastewater treatment plants (WWTPs) or septic systems. In the northeastern US, the only source for caffeine is from anthropogenic sources, specifically, waste water (Standley et al. 2000). Caffeine is a component of human waste and unfinished beverages or other products enter the waste stream directly via disposal into sinks or drains. Caffeine resists destruction in conventional water treatment (147,000 ng/L, Ternes et al. 2001), and persists after release into the environment (Lam et al. 2004). Caffeine can also be detected at extremely low levels of concentration in receiving waters after sewage effluent or septic leachate is diluted. The potential use of caffeine as a tracer of sewage effluent in Long Island Sound could be an important tool in identifying the source of nitrogen or other sewage-related contaminants, and allowing for focused management or remediation of specific sources.

Research Goals

The goal of this research project is twofold. First, is to characterize the behavior of caffeine in freshwater watersheds, and evaluate the use of caffeine as a tracer for sewage contamination; specifically nitrate and organic nitrogen pollution. Second, to explore the influence that different intensities of urban development have on the mechanism by which urban areas contribute nutrients to their watersheds. Specifically, what role does waste water infrastructure play in the magnitude of relative nutrient contribution, and what elements of the landscape affect this contribution.

A comparison of the ratio of caffeine to associated nitrogen levels has not been attempted, nor has the behavior of caffeine in fresh water watersheds been extensively documented. Caffeine levels measured in Long Island Sound could help to determine the separate the contribution of nitrogen from sewage sources than from other sources, such as agricultural runoff or natural ecosystem processes, and aid in the creation of targeted management strategies.

Site Description

The West River is an urbanized watershed draining land occupied by the New Haven metropolitan area, a significant urban area that borders Long Island Sound. The West River is useful to study nitrogen contribution from according to different infrastructure in that it contains a gradient of land uses, from Water Company land held in reserve to protect water quality, to sparse rural/suburban type development and dense urban development.

Methods:

Sub-watersheds within the West River system were identified by infrastructure type: a) combined sewers, b) separated sewers, c) septic systems and d) undeveloped, e.g. Water Company lands (Fig.1) The West River watershed was selected because it displays a gradient of these land uses and does not receive effluent from a waste water treatment plant, isolating caffeine sources to septic systems in the headwaters region and leaky sewer connections in the lower region. Population density and per capita nutrient contribution were considered, since the presence of sewers and high population density are likely to be correlated. Caffeine, nitrate, and dissolved organic nitrogen (DON) were measured and compared across the spatial gradient from undeveloped areas near the headwaters. Municipal sewer maps were acquired for the New Haven and West Haven sewer systems, which are adjacent to the West River. These maps were used to categorize the infrastructure type in detail for each basin and compared to the extent of sewer coverage in GIS layers.

Sampling sites (Table 1) were selected near the lower reach of each sub-basin, as determined by GIS data provided by the CT-DEP. Sites were also selected for accessibility and identification on GIS images, usually at road crossings or above reservoirs. 2002 Land Use/Land Cover data available from CT-DEP was used to characterize the intensity of urban development, and sewer service areas were used to differentiate between areas served by septic systems. Where possible, sites were duplicated from the West River Water Quality Assessment Report, which represents a large data set of water quality parameters for the watershed (Benoit, and Schiff, 2002).

GIS analysis was done with ESRI's ARCGIS 9.0 software suite.

Field Measurements

The entire watershed was sampled on the same day to avoid variation that may be caused by different weather conditions, especially precipitation and runoff. Two sampling events were conducted: on July 24, 2006 and November 7, 2006 under base flow conditions. Caffeine samples were taken using a grab method in acid washed, 1000ml polyethylene bottles. Nitrate samples were field filtered at .45um and collected in acid washed, 30ml polyethylene bottles. DON samples were collected using the grab method in 250ml bottles. All samples were stored on ice for transport to the lab. Caffeine samples were refrigerated at 40C and extracted within 1 week. Nutrient samples were frozen for a period of 1-3 weeks.

Temperature and conductivity was measured in-situ using a YSI-63 probe. Flow measurements were taken using an electromagnetic flow meter at 20% intervals of stream width. Depth was measured with a meter stick at 20% width intervals. The stream flow and profile data will be used to calculate discharge.

Lab measurements:

Nitrate is measured by standard colorimetric methods carried out on an Astoria 2 flow analyzer. DON is measured via NO3- produced after persulfate digestion. Caffeine was extracted from the water samples using a continuous liquid-liquid extraction into dichloromethane, followed by concentration. Caffeine was quantified using a Agilent G1800C GC/MS Gas Chromatograph with an isotopically marked C-13 Caffeine reference.

The liquid-liquid extraction process dissolves caffeine by evaporating a solvent dichloromethane, (DCM) and condensing it above the extractor (sample reservoir), where it forms droplets and falls through the 1000ml sample, collecting caffeine as it goes. The denser DCM collects at the bottom of the extractor and eventually through a gooseneck. The DCM is filtered through a drying bulb packed with Sodium Sulfate to prevent residual water from contaminating the sample flask. Caffeine is concentrated in the sample flask as DCM evaporates and continues the cycle (Figure 2). Each sample is extracted for 24 hours, yielding 500mL of solvent. This solvent is then concentrated to 1mL (a factor of 500) to aid in detection and quantification.

Quality Assurance/Quality Control

At least 30% of samples were taken for QA/QC purposes, including field blanks, recovery blanks and replicates. Field blanks were comprised of DI water poured into sample bottles in the field and extracted. Blanks were taken to ensure no contamination was introduced to the samples during field procedures, and as an instrument blank to ensure no contamination was introduced to samples via the extraction or concentration apparatus. Recovery blanks were spiked with known quantities of analytical grade caffeine in the lab, and used to ensure that the extraction was achieving a high rate of recovery, and that quantified caffeine concentrations reflected the level in the environment.

Results

Caffeine was detected in all samples with a range of 27-64 ng/L with error of +/- 1.7 ng/L. The detection level was ~10ng/L for the quantification. My current data (Figure 3) shows that caffeine is increasing in concentration as one moves from the headwaters, with more rural land use and less dense population, to the mouth of the West River, where land use is more urban and population much more dense. The caffeine concentration also mirrors the pattern in conductivity, which is often used to indicate more generally poor water quality. Nitrogen concentrations in the watershed do not follow such a clear pattern, and there is a high concentration detected near the headwaters that is not incident with a high caffeine measurement. There was apparent contamination of the field blank at concentrations similar to the background level, 35ng/L.

Discussion

The development of the liquid-liquid extraction method required a considerable time investment and methods development. The data presented above should be considered as preliminary, and more sampling is planned to reduce uncertainty introduced by blank contamination. However, the method appears to be working, and there is little reason to believe that the general trend revealed will not be more or less robust, and that the pattern of caffeine concentration seen in the watershed will persist through future sampling.

These data suggest that caffeine and nitrogen levels may be independent of each other; that is, high nitrogen levels can be observed even with low caffeine levels, possibly because nitrogen may be coming from different sources, such as agricultural runoff, of which there are some sources in the area, or lawn fertilizer runoff. Sampling sites in the septic area are likely to be receiving residential lawn runoff as well. How this will confound the establishment of a caffeine : nitrogen ratio for septic systems has not been determined. Caffeine**:** nitrogen ratios for WWTPs can be established directly by sampling effluent.

One issue with examining infrastructure as a landscape component is that they do not often follow natural boundaries, and in this case the “sewer-shed” of areas contributing wastewater to the water treatment plants is very different, and much larger, than the area drained by the basins of the natural watershed. In this sense, waste water from the sewer system is collected and the effluent distributed as a point source (at the plant), while septic systems act as a non-point source and are spatially related to the geographic watershed. Introduction of caffeine (and by extension, sewage contamination) is highly reliant upon the type of infrastructure in place. Ideally, any caffeine entering the environment above a WWTP in the watershed is from septic systems (though leaky sewer pipes contributing nitrogen to shallow sub-surface runoff may be an important, if unknown, factor).

Further Work

To better understand how caffeine is introduced and transported in the environment, I would like to do more in depth analysis of caffeine data compared against population density, septic tank density, distance of the rivers to sewage sources, and land use classification are other factors that I will be comparing with an expanded database of caffeine concentration. The septic-sewer boundary, where infrastructure changes to being connected to a sewer system, along the river north of Konold’s Pond, might be an interesting place to investigate the role of leaky sewer pipes in contributing caffeine; which might be indicated by a sudden increase in caffeine concentration.

A useful additional project would be to determine the ratio of nitrate and DON with caffeine directly from sewage effluent, hopefully to establish a kind of signature for associating caffeine with sewage. The unique source of caffeine in sewage clearly makes it a useful indicator of sewage contamination, but its conservative properties can not been established without more data collection on the watershed scale.

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FIGURES

FIGURE CAPTIONS

Figure 1: This overview map shows the West River watershed, subdivided into sub-catchments. Sampling sites are identified by mark and numbered for watershed position.

Figure 2: The continuous liquid-liquid extractor set up, a battery of 3 extractors. The water bath is visible at the bottom of the picture. Just visible are the condensers at top.

TABLES

Table 1: Sampling Sites in West River Watershed

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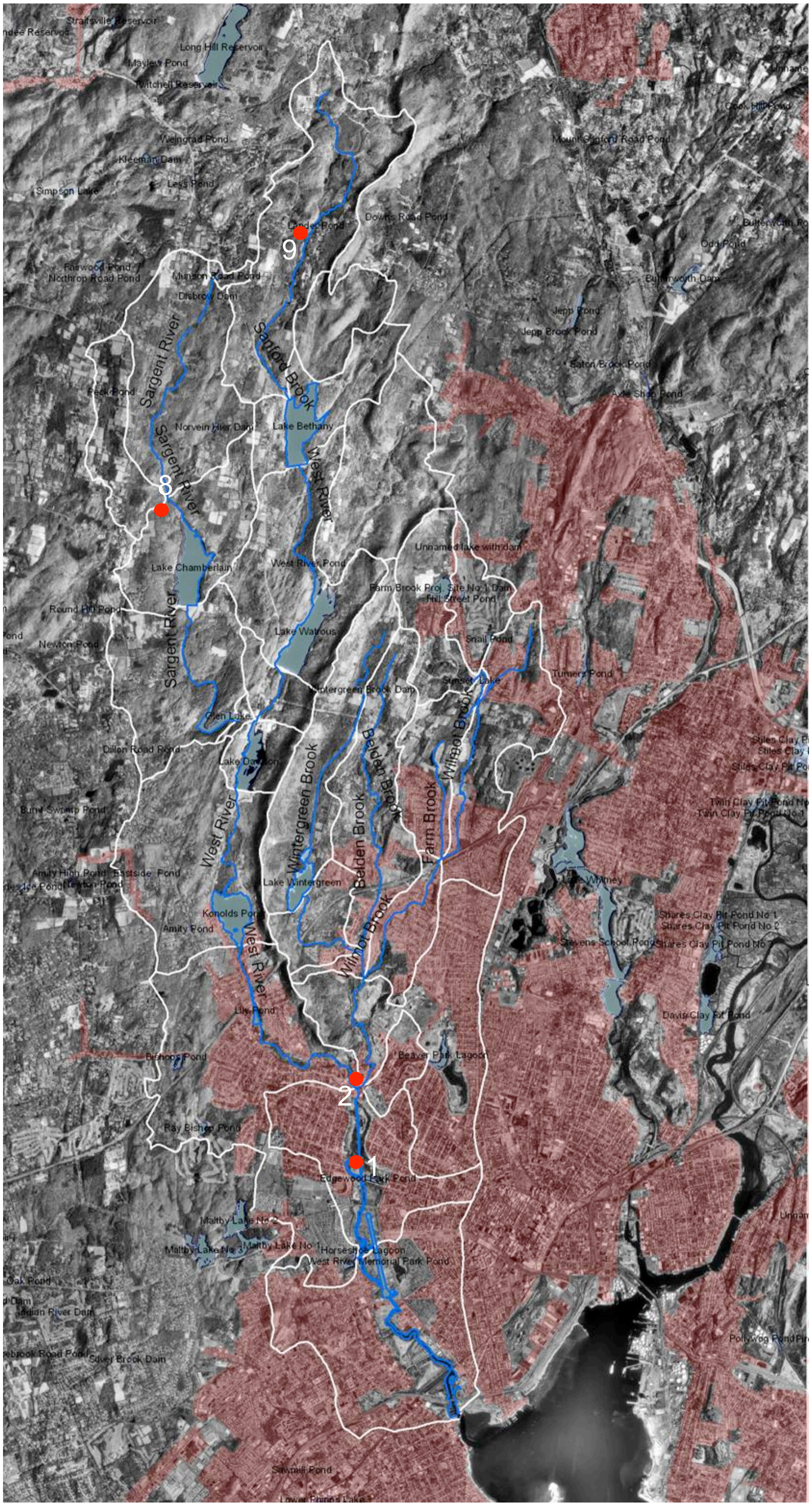
Figure 1



Long Hill Reservoir
Sargent River
Sanford Brook
Lake Bethany
West River
Lake Chamberlain
West River Pond
Lake Watrous
Wintergreen Brook
Belden Brook
Farm Brook
Wilmot Brook
Lake Dawson
Lake Wintergreen
Konolds Pond
Lily Pond
Beaver Park Lagoon
Edgewood Park Pond
Horseshoe Lagoon
West River Memorial Park Pond
Maltby Lake No 1
Maltby Lake No 3
Sawmill Pond
Glen Lake
Round Hill Pond
Newton Pond
Dillon Road Pond
Amity Pond
Bishops Pond
Ray Bishop Pond
Peck Pond
Snail Pond
Turners Pond
Lake Whitney
Davis Clay Pit Pond
Stevens School Pond
Simpson Lake
Downs Road Pond
Jepp Pond
Jepp Brook Pond
Wintergreen Brook Dam
Unnamed lake with dam
Hill Street Pond
Farm Brook Proj. Site No 1 Dam
Norvein Hier Dam
9
8
2
1

Figure 2

Figure 3

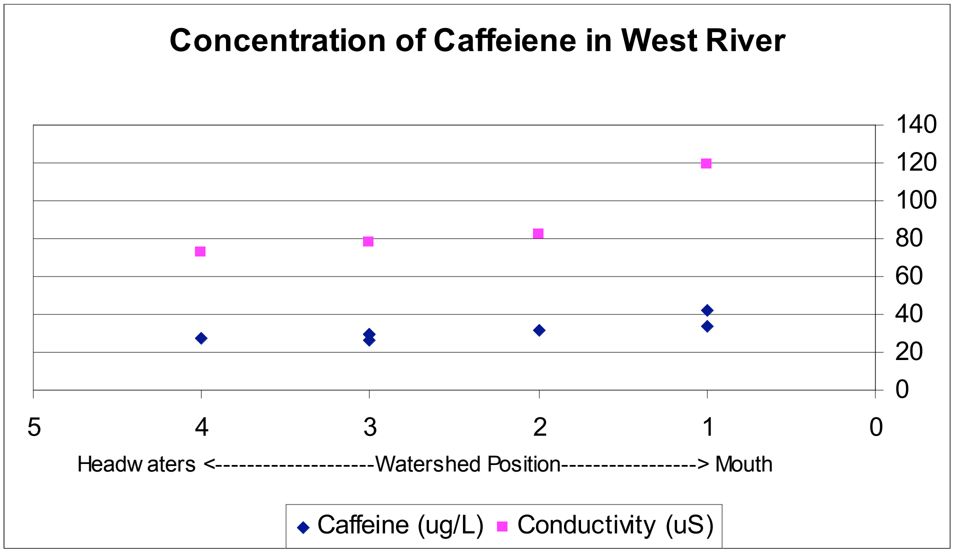


Table 1

Sample #	Type	Location	Qty	Measurement	Class
1	Sample	Lower WR	1L	caffeine	Sample
1B	Duplicate	Lower WR	1L	caffeine	QA/QC
1C	Duplicate	Lower WR	1L	caffeine	QA/QC
3	Blank	Lab Blank	1L	caffeine	QA/QC
4	Recovery	Lab Blank	1L	caffeine	QA/QC
2	Sample	Blake Ctr	1L	caffeine	Sample
8	sample	Sargent R	1L	caffeine	Sample
8B	duplicate	Sargent R	1L	caffeine	QA/QC
8C	duplicate	Sargent R	1L	caffeine	QA/QC
9	sample	Sanford Bk	1L	caffeine	Sample
Sample #	**Type**	**Location**	**Qty**	**Measurement**	**Class**
N1	sample	Lower WR		TN, Nitrate	Sample
N2	Sample	Blake Ctr		TN, Nitrate	Sample
N2-A	Recovery	Blake Ctr		TN, Nitrate	QA/QC
N7	Sample	Sargent R		TN, Nitrate	Sample
N7-A	Recovery	Sargent R		TN, Nitrate	Sample
N9	Blank	Lab Blank		TN, Nitrate	QA/QC