

**Quinnipiac River Fund Final Report- 2015**

February 25, 2016

Quinnipiac University

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Project Name: A study of phthalate and organotin plasticizers in an effort to characterize contamination from industrial and municipal sources in the Quinnipiac River and New Haven tidal basin.

Grant Number: 20150081

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Summary

The focus of this study was to identify and quantify known pollutants diethyl hexyl phthalate and benzyl butyl phthalate, along with other phthalate plasticizers and organotins in water from the Quinnipiac River, with particular attention to the parts of the river from Community Lake in Wallingford to the mouth of the tidal basin in New Haven. Efforts were also directed to known industrial discharge points on Toelles Road, specifically effluent pipes, which discharge water into the Quinnipiac River.

Environmental chemical pollutants have continuously been found in our studies from 2010 to 2015. The project period for this investigation was: March 19, 2015 to March 18, 2016.

Project Objectives

* Collect and analyze water from the Quinnipiac River at predetermined locations in Wallingford, North Haven, Hamden, and New Haven harbor, in order to identify the presence of phthalate plasticizers and organotins.
* Measure water quality and climatic parameters at sample sites during collection. This project will map the sampling sites along the Quinnipiac River and compare weather, river depth and flow, along with any chemical analysis results
* Communication to the community-at-large.

Background

Phthalate esters are plasticizers commonly used to soften polyvinyl chloride products such as electrical conduit and sewage piping. Several of these plasticizers, specifically diethyl hexyl phthalate, are manufactured in Wallingford by Cytec Industries who has a discharge permit allowing outflow into the Quinnipiac River. Our studies over the past years have sought to identify and quantify phthalate chemical pollutants which are known to be present in the Quinnipiac River and which have a high likelihood of being found in the tidal basin of the Quinnipiac River and New Haven harbor. In addition to plasticizers, we have expanded our study to characterize the presence of organotin pollutants. Organotins are known to leach into the aquatic environment through antifouling paints containing tributyltin, and through leaching and normal weathering of PVC products. Organotins are known endocrine disrupting chemicals, which have been responsible for imposex in mollusks (male genital imposed on females), suppressed immune systems and suppressed expression of cytochrome P4501A in fish.

Samples were collected at these locations going from north to south along the River: 1) Hall Avenue, below the bridge in Wallingford, just below Community Lake; 2) Quinnipiac River State Park just below the Wallingford town line; 3) Toelles Road, water and discharge pipe effluent in the Quinnipiac River State Park, Wallingford; 4) Valley Service Road in North Haven where the Quinnipiac River meets town owned land; 5) The entrance to Quinnipiac River State Park behind the service station on the Wilbur Cross Parkway in North Haven; 6) State Street in North Haven, behind the River Street Tavern directly across from Agway; 7) Sackett Point Road, before the bridge over the River; 8) The Department of Energy and Environmental Protection's boat ramp behind the Tilcon paving plant in North Haven; 9) In the tidal marshes, at multiple points, in North Haven and Hamden via boat, from State Street to the Amtrak yard near the fuel storage tanks.

Laboratory Analysis and Sampling

We collected and analyzed water from the Quinnipiac River at locations noted above. These field tests included temperature, flow, and depth. All of the sampling and determination was performed by Harry Pylypiw, Courtney McGinnis, and John Chiari a Quinnipiac University undergraduate student. Analysis of water samples were performed at Quinnipiac University and the Connecticut Agricultural Station.

The technique and detection method we chose for analysis was first an extraction of water by solid phase micro-extraction (SPME) followed by detection and determination via gas chromatography with a mass selective detector (GC-MSD). SPME is a solvent-free (no hazardous waste disposal) sample prep technology that is quick and versatile. SPME uses a fiber coated with a solid (sorbent). The fiber coating extracts the compounds, from the sample, by adsorption of the target analytes in each water sample. The SPME fiber is then inserted directly into the chromatograph for desorption and analysis. We use SPME as our extraction technique for the analysis of phthalates and volatile compounds (MW 60-275) in water. Example target phthalate analytes of the method: benzyl butyl phthalate; bis-2-ethylhexyl phthalate (diethyl hexyl phthalate); dibutyl phthalate; diethyl phthalate. Other analytes such as pesticides, herbicides, and plastic additives are also detected.

Extraction of all water samples were performed using a polydimethylsiloxane (PDMS) fiber with a fused silica/ss core (Supelco Inc., 57342-U) solid phase microextraction (SPME) assembly (Supelco Inc., 57330-U) that was capable of specific adsorption of the target group of volatile analytes (MW 60-275) in the water. Prior to sample extraction and analysis, the SPME was conditioned by placing the SPME in the GC injection port of the GC-MSD and the 40-minute sample program was run. All water samples were SPME extracted by inserting the PDMS fiber into a 100 mL beaker containing 40 mL of sample for 15 minutes. The fiber was then placed into the GC-MSD inlet and desorbed at 250°C for the entire 40 minute run; the SPME fiber was also considered conditioned for the next sample run.

Analyses of all samples were performed using an Agilent Technologies Model 6850 Gas Chromatograph attached to an Agilent 5973N Mass Spectrometric Detector (GC-MSD). An Agilent Technologies HP-5MS, 20 m x 0.25 µm capillary column equipped with a Merlin High Pressure Septum (Supelco Co., 24816-U) was used for analyte separation. Experimental conditions were as follows: initial temperature of 110°C with a ramp of 5°C/minutes, to 250°C, and a total run time of 40 minutes. Spectra were collected using Enhanced Chemstation Software (Agilent Technologies MSD Chemstation Ver D.03.00.552).

The technique for analyzing organotins is liquid chromatography with tandem mass spectrometry (LC-MS/MS), which is utilized because it can achieve low detection limits of organotins. The advantage of using these types of techniques are that the analytical methods separates, detects, and identifies chemical compounds in a simple simultaneous procedure.

Results of Testing River Water

This study started in May 2015 and proceeded well into the November 2015. In samples taken from the locations listed earlier we found low levels of phthalate esters, specifically dibutyl phthalate, benzyl butyl phthalate, and diethyl hexyl phthalate. All were found at very low levels roughly at less than 50 parts-per-billion (ppb). There were no trends with the phthalate findings noted. Samples obtained in May 2015 were tested for heavy metals, specifically tin and lead, to see if the likelihood was high or low of us finding organotin plasticizers in the water samples. All samples tested had no detectable metals with a method that had a detection limit of 50 ppb.

Results of Testing Pipe Effluent Water Located at Toelles Road

In May 2015, we started sampling the effluent from the pipe located on the south side and eastern side of the Toelles Road Bridge over the Quinnipiac River. The temperature of the water being discharged through the pipe was roughly 4 to 5 °C higher than the River water temperature. This led us to believe that the pipe was not from a storm drain source but an industrial discharge source. It was in November that we learned from DEEP that the discharge pipe was from Nucor Steel in Wallingford, CT.

The samples collected in May 2015 contained detectable levels of phenothiazine; they also had a pink color. We measured the pH of the samples and found them to be neutral. Phenothiazine is used in polymer processes as an additive. According to the chemical's MSDS, phenothiazine is soluble in water to roughly 120-130 mg/L (ppm) and has no color in dilute water solutions. In our lab we confirmed its solubility in water, but also found that fish tanks dosed to roughly 1-2 ppm phenothiazine turned pink after roughly 2-weeks, which, when looking into the literature, is consistent with oxidized phenothiazine. We also purchased a standard of phenothiazine to confirm that we correctly identified the compound using our extraction method with mass spectrometry detection. We concluded that the pink color in the water was likely due to the presence of oxidized phenothiazine in the water. In November 2015 we reported that all of our results were qualitative, and no absolute concentrations could be assigned to the samples. However, by calculation of total ion peaks on our mass spec, it appears that the samples from May 2015 had phenothiazine to levels in the 0.5-3 ppm range.

All June 2015 and July 2015 samples showed the presence of what appeared to be monomers, or fragments of monomers from a methyl vinyl ether based polymer. Also noted was that the pink color was absent, and detectable levels of phenothiazine were not found in all samples. However, the temperature of the discharge water still was roughly 4 to 5 °C higher than the River water temperature. Our conclusions, using both low and high resolution mass spectrometry on the methyl vinyl ether based polymer, was that in each sample we regularly found five or six congeners, all likely present as monomers or monomer/small polymer fragments ranging in masses, based upon chromatograph retention time, ranging from approximately 58 daltons to approximately 300 daltons. The identity of the parent molecule, or polymer, could not be determined as no standard could be obtained, but pipe discharges appeared to be consistent with an industrial process where the polymer was in use or manufactured.

Sampling in July 2015 was not as consistent as June samplings. Some pipe discharge samples in July had no detectable chemicals in the water by our method and some samples had the same polymer compounds as in June. We did find one sample set to be interesting. A set of samples taken June 16th, when the pipe appeared to be flowing much slower than its usual flow, showed the presence of a Cytec compound that was identified as Cymel Resin. This resin is in the chemical family of methylated melamine formaldehyde, CAS # 068002-20-0; no standard was obtained for this resin. Additionally, the sample contained the herbicides sulfometuron methyl and metolachlor; all findings in this sample are qualitative. Drawing conclusions on the source, or sources, of this sampling, which likely has some back-flow from the River are uncertain, however, the presence of the resin and herbicides were determined by mass spectrometry and were not present in any system blanks. This non-typical sample was taken 1-day after a heavy rain when the River level was higher than the pipe; the sample was likely contaminated with upstream River water.

After September 3rd samplings were not performed until November 2015, since the pipe was not actively running. We did find the pipe running in November 17th but analysis showed nothing remarkable.

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| Table of Collection Dates at Toelles Road | |
| Date | Notes |
| 05-14 | Phenothiazine and pink color |
| 05-18 | Phenothiazine and pink color |
| 05-19 | Phenothiazine and pink color |
| 05-20 | Phenothiazine and pink color |
| 06-05 | Trace monomers/polymer, no color |
| 06-08 | Monomer/polymer |
| 06-09 | Monomer/polymer |
| 06-12 | Monomer/polymer |
| 06-16 | Cymel Resin, sulfometuron methyl, metolachlor, monomers/polymer, pipe under water |
| 06-17 | Monomer/polymer |
| 06-19 | Monomer/polymer |
| 07-07 | Monomer/polymer |
| 07-13 | Monomer/polymer |
| 08-03 | No findings |
| 09-03 | Possible oil contamination, unable to perform confirming analysis |
| 11-17 | No findings |

Dissemination of Research - Community Outreach

Our findings were presented by us to the community-at-large via a press release disseminated by the Public Relations Department at Quinnipiac University, and an article in the New Haven Independent. We also presented our findings at the Graduate Student Sigma Xi Poster Conference in held at Quinnipiac University. The results from this research were disseminated to the following interested organizations: The Connecticut Fund for the Environment and The State of Connecticut Department of Energy & Environmental Protection Water Permitting and Enforcement Division.