Senator George J. Mitchell Center for Environmental & Watershed Research
Annual Technical Report
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Introduction

The Maine Water Resources Research Institute is the locus of research, graduate student support, and outreach for freshwater issues at the University and for the state. During the past year the Maine Institute has supported three research projects: The Role of Dissolved Organic Carbon in the Loss of Metals from Biosolids; The Effect of Background Chloride Concentration on the Formation of Disinfection-Byproducts; A Pilot Study to Evaluate the Effect of Dam Removal on River Toxicity; and An Evaluation of Economic Change Related to Dam Removal. In addition one specific Information Transfer project was supported: The Penobscot Synthesis. Three of the funded projects were selected to support research on the effects of dam removal on rivers in Maine. These projects alone provided support to four graduate students and several undergraduate students. Funding from a variety of sources provides support to a total of 12 graduate students that were directly associated with the Mitchell Center.

This year marked the 11th anniversary of our highly successful Maine Water Conference. We are grateful for continued support from a broad array of sponsors. We take great pride bringing people together to learn and debate important water issues in Maine. We are continuing to increase active participation in the conference by high school students.

The Water Resources Research Institute program is a key component of the Mitchell Center. The Institute program is vital to the support of small projects that address important local needs. It also helps us to develop and attract funding from other agencies. This program is strongly supported by our Vice-President for Research who has contributed $50,000 to the 104b research projects. In 2005, the Maine Institute had projects funded by state agencies (Atlantic Salmon Commission, Department of Inland Fish and Wildlife, Department of Environmental Protection, Drinking Water Program), federal agencies (Department of Agriculture, Environmental Protection Agency, NOAA-Fisheries, National Park Service), and foundations. Total external funding, including USGS support, exceeded $1 million in 2005.

During this past year, Institute Director Peckenham served as Interim Director of the Senator George J. Mitchell Center for Environmental and Watershed Research. During this time a national search was launched for a new Director of the Mitchell Center. We are pleased to announce that David Hart will be starting as Director in FY2007. David, formerly the Director of the Patrick Environmental Science Center at the Philadelphia Academy of Science, will be a welcome addition to the University of Maine.

Research Program

Metal mobilization from municipal biosolids stockpiles: The role of dissolved organic matter.

Basic Information

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Release of Nitrogen and Trace Metal Species from Field Stacked Biosolids

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Abstract

The goal of this study was to measure the amount and speciation of nitrogen (N) and metals leaving stockpiled biosolids and traveling through soil column. Biosolids were placed on plastic lined cells to collect all leachate. Ammonium (NH_4^+) was the dominant species (90% of total N) released from the Class B lime-stabilized biosolids in the lined cell experiment. NO_3^- and nitrite (NO_2^-) concentrations were essentially negligible, remaining below 0.25 mg L^{-1} and 0.1 mg L^{-1}, respectively. NH_4^+ levels ranged from 2,000 to 4,900 mg L^{-1} in the leachate. Dissolved organic carbon (DOC) concentrations as high as 8,900 mg L^{-1} and chemical oxygen demand (COD) as high as 37,000 mg L^{-1} were measured in the leachate leaving the lined cell. Fifteen pan lysimeters were installed in an 90 m^2 plot at depth intervals of 30, 60, and 100 cm. Leachate passing through the soil column underlying the biosolid stockpile was collected in the zero tension pan lysimeters. Average lysimeter NH_4^+ concentrations ranged from 1,400 mg L^{-1} at 60 cm depth to 145 mg L^{-1} at 90 cm depth. Average lysimeter DOC concentrations ranged from 2,000 mg L^{-1} at 60 cm to 525 mg L^{-1} at 90 cm. At day 30, the cumulative loading of N species from the lined-cell was 20 times typical agronomic levels.

Trace metal determinations of the leachates collected from the lined cell and lysimeters showed arsenic loading rates exceeded the MRSA Chapter 419 limits of 0.5 kg ha^{-1} yr^{-1} by an order of magnitude. Arsenic concentrations were in excess of several thousand mg L^{-1} in the lined-cell leachate and several hundred mg L^{-1} in the lysimeters as deep as 90 cm under the biosolid stockpile. Phosphorus, iron and manganese in excess of several thousand mg L^{-1} were observed in both the lined-cell leachate and lysimeters. Significant concentrations of other trace metals were found at depth in the zero-tension lysimeter plot. Trace metals were largely mobilized by the DOC from the biosolids, and/or due to the presence of anaerobic environment, especially in the underlying soil.

Introduction

Biosolids are derived from sewage sludge and have been treated to meet specific land-application criteria in accordance with the US EPA part 503 rules developed in 1993 to ensure safe agronomic use. Sewage sludge contains pathogens and biosolids are defined by the processing method used to reduce pathogen content. Class A biosolids have been treated to reduce pathogens to natural background concentrations. Class B biosolids have been treated to reduce pathogens, but not to background concentrations. The uses of Class B biosolids are restricted by well-defined site suitability and access control regulations; land application is a primary outlet for this class.

Field application of biosolids, especially in agricultural areas, is practiced widely (Stevens et al., 2002; Wang, 1997). Field stacking of biosolids prior to their application is an allowed practice in many countries and states, under local licensing standards, enforcement rules and regulations. Field stacking of biosolids is necessary to accommodate cropping schedules and in northern climates where land application is precluded during the winter season (USEPA, 2000). Field stacking allows for efficiency of operation at the farm as hundreds to thousands of m^3 of material can be stored and then applied in one application. Field stacking is typically done in agricultural areas that are remote from public access and may occur on bare ground (USEPA, 2000; Peckenham, 2004).

Biosolids generated in Maine (USA) contain nutrients such as: nitrogen (0.1 to 8%), phosphorus (0.1 to 3.2%), and potassium (0.0 to 0.8%) (Peckenham, 2005). Biosolids may also contain trace metals in concentrations > 100 ppm; e.g. Chromium, Copper, Iron, Lead, Manganese, Nickel, and Zinc, and a variety of other metals in lower concentrations (Cappon, 1984; Bell et al., 1991; Basta, 2005; McBride et al., 2004). Field application of biosolids, both as amendments and for storage purposes, can therefore, result in the release of nutrient and metal species into the surrounding environment (Gerritse et al., 1982; Clapp et al., 1994; McBride et al., 1997; Shober et al., 2002). Elevated NO_3^- levels in groundwater surrounding agricultural and grazing lands are well documented (Smith et al., 1998a, b; Maticic, 1999; Smith and Frost, 2000; Maeda et al., 2003). However, there is little information about the release of NO_3^- from biosolids stockpiles. Leaching of NO_3^- from biosolids stockpiles was suggested as the source of nitrogen plumes measured in a gravel pit reclamation site, and also from repeated stacking of chicken manure at the same site was reported (Hillier, 1993; McDowell and Chestnut, 2002). Even

though some studies have reported the significant impacts of manure stockpiling and cattle slurry lagoons on groundwater quality (Gooddy et al., 2002), research that exclusively measured the N losses from field stacked biosolids is lacking.

Trace metal release from biosolids has been linked to microbiological activity (Qureshi et al., 2003), water solubility (McBride, 1998) and breakdown of organic compounds that bind metals in the soil (Martinez et al., 2003). McBride et al. (1999) showed that shallow groundwater collected via tension lysimeters from an experimental plot that had a single high-dosage application of biosolids 15 years prior had elevated levels of several trace metals when compared to a nearby control plot that had received no biosolids application. Richards et al. (1998) found elevated trace metal levels such as cadmium (Cd), nickel (Ni), zinc (Zn) and boron (B) in soil pore water of a site treated with biosolids 20 years earlier. The evidence of increased trace metal concentrations in waters surrounding biosolids application sites, including a 20-year long watershed scale experiment in Minnesota (Clapp et al., 1994), is mixed due to natural heterogeneity of soils, uncertainties in biosolids compositions, and lack of control sites (Gerritse et al., 1982; Stukenberg et al., 1993; Berti and Jacobs, 1998; Babarick et al., 1998; Sloan et al., 2000; National Research Council, 2002).

Materials and Methods

Plot Designs: Two experimental plots were constructed and stacked with municipal biosolids at the University of Maine's research farm. The local soils are formed in a dense glacial till, Marlow silt loam (coarse loamy isotic frigid oxyaquic Haplorthod) and Woodbridge silt loam (coarse loamy mixed mesic aquic Dystrudept) that meets Maine's stockpiling suitability criteria for slope (<5%), drainage class (moderately well-drained), and texture (silt loam).

The plots consisted of: (1) a pair of lined cells designed to capture and measure all leachate and runoff generated, and (2) a zero-tension pan lysimeter plot designed to capture flow through the soil beneath field-stacked biosolids. The design of the lined cell and the lysimeters is described in detail elsewhere (Peckenham et al, 2005). Briefly, one 3.6×22.5 m cell and one 1.8×30.5 m cell were constructed by removing the vegetation and sloping the base inward. A 1.27 mm thick impermeable PVC sheet was cut to size and placed over the base area. A slotted flexible plastic pipe was placed along the centerline to collect the leachate from the pile. The PVC barrier and the drain pipe were covered with 12 – 18 cm of fine sand to facilitate flow of the leachate. Lime-stabilized class-B biosolids were stacked to a depth of 0.6 to 0.8 m as unloaded from truck or tractor bucket.

The water, or snow melt, shed from stockpile surfaces was collected using an open pipe system placed along the perimeter of the stockpile. The leachate and runoff flow rates were measured using 90° v-notch weirs and flow meters (ISCO[®] 4230). The leachate samples were collected with auto-samplers that were triggered by the flow meters and collected a 100 ml sample for every 100 L of flow (Peckenham et al, 2005).

The zero-tension pan lysimeter plot was 6×15 m, and consisted of fifteen $45 \times 45 \times 5$ cm stainless steel pan lysimeters. Placement of the lysimeter pans at depth was accomplished by digging a 0.6 m wide trench to the desired depth (0.3, 0.6, and 1 m), placing the pans, collection bottles and sampling tubes in place, then filling the trench with the material that was originally removed (Figure 1). The lysimeters were individually drained into buried polyethylene containers. Samples were collected using a manual vacuum pump. Lime-stabilized biosolids were stacked to a maximum thickness of ~1 m.

The stockpiling experiments for both the lined cell and the lysimeters were performed twice. The first stockpile was in place from December 2002 to May 2003, and consisted of 125 m^3 of biosolids to the lined cells and 90 m^3 to the lysimeter plot. In this run, freezing

temperatures made flow quantification difficult to impossible. The second stockpile was in place from July 2003 to May 2004 and consisted of 52.5 m^3 of biosolids to the lined cell and 90 m^3 to the lysimeter plot. The road sand on the bottom of the lined cell was allowed to be rinse by several rain storms between stackings, while the lysimeter plot was scraped and aerated for 30 days then restacked.

Sampling Methods. Composited biosolids samples were collected for analysis immediately after the stacking and just before the removal of biosolids at the completion of each stacking period. Composited samples consisted of 10 individual samples, collected utilizing a three-dimensional random grid approach. Composited biosolids were mixed in a bucket by hand and then re-sampled. The biosolids were analyzed as shown in Table 1.

Composited soil samples from beneath the lysimeter plot were collected before and after stockpiling and analyzed as shown in Table 1. All composited samples consisted of 10 individual samples, collected utilizing a random grid approach using a soil sampling tube (25.4 cm). All soil and biosolids samples were stored on ice during transportation and kept at 4° C until analyzed (within 7 days).

Data reported here are for the second stockpiling experiment. Aqueous samples from the lined cells were collected from the auto-samplers every 3 to 14 days. The individual 500 ml polyethylene bottles in the auto-samplers were transferred into Whirl-Pak® bags, placed on ice in coolers and transported to the lab. The aqueous samples were analyzed as shown in Table 1. Daily rain fall information, collected at the farm, was used in this study. Four field rain gauges were deployed in the experimental field to verify farm precipitation data.

The lysimeters were sampled approximately monthly from June 2003 to October 2003. Additional samples were collected in May and July 2004. Samples from each individual lysimeter were placed in an acid-washed 500 ml polyethylene bottle. The bottles were kept on ice until transferred to the lab for analysis. The remaining liquid in the submerged containers was completely drained after each sampling event. Dissolved organic nitrogen was determined by subtracting the concentrations of NH_4^+, NO_3^- and NO_2^- from total Kjeldahl nitrogen (TKN).

Analytical Methods. Laboratory pH was measured using a Corning Model 430 meter with an Orion Model 8104-BN probe. Field pH measurements were performed using a Hach pH pen calibrated at pH 4 and 7. Biosolids pH was determined by adding 70 ml of DI water to

approximately 35 ml of biosolids in a Nalgene® bottle. The bottle was capped, thoroughly shaken and pH of the slurry measured after 15 min.

Samples for NH_4^+ measurement were filtered through 0.45 μm polypropylene filters and acidified to a pH of 2.0 with 1:1 H_2SO_4. NH_4^+ was analyzed on an ALPKEM Flow Solution™ IV Automated Analyzer using the Berthelot reaction [EPA Method 353.2]. Nitrate was measured calorimetrically after its reduction by cadmium to NO_2^- at pH 7.5, while nitrite was determined directly without the reduction step. Total Kjeldahl Nitrogen (TKN) was determined on approximately 5 ml of leachate or 5 g of biosolids. Solids were dried at 105°C to remove adsorbed moisture. Samples were digested in a mixture of sulfuric acid, potassium sulfate and cupric sulfate at 400° C for 1 hr to convert amino-nitrogen from most organic materials into NH_4^+. Free NH_3 was also converted to NH_4^+. The digested sample was concentrated by heat distillation into a standardized acid in a receiving flask. Total Nitrogen was quantified as ammonium by neutralization with a standardized NaOH solution.

Organic carbon in the leachate, runoff and lysimeter samples were determined using an OI Analytical Model 1010 Total Carbon Analyzer. Chemical oxygen demand was determined using Hach Method 430/435, Hach COD reactor Model 45600 and a DR/2000 spectrophotometer. Percent solids were determined gravimetrically after heating the samples for 24 hours at 110° C. Loss on ignition (LOI) of the solid samples was determined by heating the samples at 550° C in a muffle furnace for 3 hours.

Metal concentrations were measured on an ICP-AES (Perkin-Elmer Optima 3300XL), after filtering through 0.45 μm membranes. Standard additions of a stock solution with known metal concentrations were made to a leachate sample to test the matrix effect on the ICP-AES measurements.

Results and Discussion

Liquid Release from Biosolids

The biosolids stockpile generated negligible volumes of leachate for several days (10 to 14 days), then leachate flux increased and peaked at ~60 days followed by a gradual decline. No measurable runoff was generated as all liquid on the surface either flowed into the biosolids or was evaporated. The predicted leachate volume was calculated from available precipitation data (not shown here) and a collection area of 81 m^2 with no surface runoff or evaporation. During the first three weeks, the leachate volume produced was less than the precipitation input. After three weeks, leachate volume increased in excess of precipitation input and remained in excess for nearly two months. The initial lag between the measured and the calculated leachate volume may be attributed to the absorption of water by the newly stockpiled biosolids. Eventually the stockpiled biosolids released the stored liquid with a net increase in total solids from 25.8% to 31.0 %. The total volume of leachate released was approximately 40,000 liters.

Leachate Chemistry-Nutrients and pH

Concentrations of N species, DOC and COD in the leachate are shown in Table 2. The dominant N species was NH_4^+ with maximum concentrations exceeding 4800 mg/L. NO_3^- and NO_2^- concentrations remained below 0.21 mg/L and 0.07 mg/L, respectively, constituting a very small fraction of total N. On average, dissolved organic nitrogen (DON) represented approximately 10% of the total N released. All nitrogen species' concentrations increased over time. COD and DOC concentrations were greatest at day 36 at 37,000 and 8,900 mg/L, respectively. This was followed by a slow and steady decrease for the remainder of the experimental period. The dissolved oxygen (DO) concentration was measured at the collection point for the auto-sampler (where the leachate drained into a collection bucket) with a portable field meter during several rain events, and was consistently <0.1 mg/L.

Application rates of land-applied biosolids are regulated to account for N demand of crops. When calculating these application rates, the percent inorganic (mineral) N and organic N in the biosolids are considered. Approximately 90% of the total N in the leachate is mineral (NH_4^+, NO_3^- and NO_2^-). Comparing an average crop value of 225 kg/ha nitrogen demand with the calculated loadings shows that the agronomic demands at the stockpile are exceeded by a factor of approximately 20 in the first 30 days of stockpiling. This factor increases to

approximately 60 and 70 times agronomic demands at 60 and 90 days, respectively. The loss of N from biosolids stockpiles exceeds agronomic demand and will likely lead to N saturation in the soil near the stockpile with subsequent losses of NH_4^+, NO_3^- and NO_2^- into groundwater (Jacobsen, 1998; Smith et al. 1998a, b; Roelle et al., 2002).

The biosolids composition changed during the second experiment with a net decrease in organic carbon as estimated by LOI from 27.6 weight % to 24.9 weight %, an insignificant decrease in NH_4^+ (2500 to 2300 mg kg^{-1}), a net decrease in $NO_3^- + NO_2^-$ (6.7 mg kg^{-1} to 2.5 mg kg^{-1}) and a net decrease in TKN (3.2 weight % to 0.9 weight%). Calculating the carbon loss by difference, based on the biosolids analyses, shows a 350 kg loss from the stockpile compared to a calculated loss of 290 kg based on the leachate composition. The same calculations show an N loss of 240 kg based on biosolids analysis compared to 145 kg N loss based on the leachate. This discrepancy may be largely attributed to the production of gaseous CO_2 and N_2 due to the mineralization of the organic matter and microbially-catalyzed denitrification. Release of CO_2 and N_2 from biosolids-amended soils have been estimated at between 10 and 25% of the total released from the biosolids (Smith et al., 1998a, b; Balint et al., 2002; Roelle et al., 2002).

Lime was added to the biosolids to increase pH to ~12. Calcium loss and pH decline are closely correlated as shown in Figure 2. Calcium concentrations in the leachate reached a maximum of 1,000 mg/L near day 20, then rapidly decreased to <100 mg/L. The pH declined simultaneously from >11 to approximately 7.5 during this same time period.

Leachate Chemistry – Trace Metals

Time-series trends in concentrations of selected metals (Al, As, Cd, Cu, Fe, Mn, Ni, Se, and Zn) and P in the leachate of lined cells are shown in Figure 3. Leachate Fe and Mn concentrations peak at 130 and 17 mg L^{-1}, respectively, by day 20, after which they decreased. For Fe, the concentration began to increase slowly after day 40. Leachate Mn concentration, however, remained very low after day 30. It is likely that Fe and Mn are released during microbially-catalyzed reductive dissolution of their respective oxyhydroxides that happens under anoxic conditions typical of the environment inside the stacked biosolids (Lovley and Phillips,

1988). The sharp drop in the concentrations observed after day 20 may be due to the depletion of the available Fe- and Mn-oxyhydroxides (von Gunten and Zobrist, 1993; Amirbahman et al., 2003), and the increase in the Fe concentration after day 40 may be due to the slow dissolution of the more crystalline Fe-containing minerals. The pH decrease to a circumneutral value (Fig. 2) coincides especially with the drop in Mn concentration. Mn minerals are quite insoluble at both alkaline and circumneutral pH values regardless of the redox potential (Krauskopf and Bird, 2003), and as such, it is unlikely that changes in biosolids pH as reported here would result in significant mobilization or removal of Mn. Also, precipitation of rhodochrosite ($MnCO_{3(s)}$) is favored at high pH, whereas in this study, Mn is mobile at a high pH.

Leachate Al, As, P, Zn and Cd concentrations were relatively constant for nearly the first 50 days, after which they increased (Fig. 4). By day 100, As, Al, P, Zn and Cd concentrations were nearly 2.5, 2, 8, 0.2 and 0.015 mg L^{-1}, respectively. The concentrations of these species do not directly correlate with that of Fe and Mn, and therefore, it is not likely that their mobilization is directly related to the mobilization of Fe and Mn. Considering the relatively strong affinity of these species especially with the Fe(III) (oxy)hydroxide surface (Dzombak and Morel, 1990), this lack of correlation with Fe may be attributed to the strong interaction of DOC with Fe colloids that results in the coverage of their reactive surface sites, and complexation of the species with DOC. The lack of correlation between the abrupt drop in pH observed between days 20 and 30 and release of these species also suggests that pH drop is not directly responsible for their release from the biosolids. One possible mechanism for the release of Al, As, P and Zn may, therefore, be due to the mineralization of organic matter with time.

Aluminum is mostly believed to be non-colloidal. However, considering the solubility of gibbsite ($Al(OH)_{3(S)}$), free Al concentration at a circumneutral pH should be < 1 µg L^{-1} (Stumm and Morgan, 1996), and therefore, Al is largely complexed by the fulvic acid or the low molecular weight organic acid fractions of DOC. Association of metal cations such as Zn and Cd with DOC is well-documented (Tipping, 2002). Redman et al. (2002) and Lin et al. (2004) observed complexation of As with DOC, especially in the presence of bridging cations, such as Fe. Therefore, As in the leachate may be truly dissolved or associated with DOC. P is also expected not to be associated with the Fe and Mn colloids. Soluble P, however, may possibly

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have a direct microbial association and be part of large biomolecules or associated with the DOC via bridging cations.

Concentrations of Cu and Ni were approximately 1 mg L^{-1} on day 6 and reduced to approximately 0.4 mg L^{-1} after that and remained relatively constant over the duration of the experiment. Selenium concentration remained relatively constant at approximately 0.17 mg L^{-1} until day 25 after which it consistently declined to approximately 0.03 mg L^{-1} by day 100.

Jensen and Christensen (1999) studied the physical size and colloidal nature of metals found in leachate from landfills. Their findings agree well with those of this study, were they observed that nearly 80-95% of Cd, Cu, K, Mg, Na, Ni, Pb and Zn were < 1 K Da, while nearly half of Ca and Mn were < 1 K Da, and Fe was 85% > 1K Da.

Lysimeter – Nitrogen Species

The average concentrations of N species DOC at various lysimeter depths are shown in Figure 4. Figure 4 depicts time-series trends for samples taken at 30, 60 and 90 cm depths at four different sampling dates. The June 2003 samples were collected after the removal of the first stockpile that was in place for six months, and before the emplacement of the second stockpile, which lasted from July 2003 to May 2004. The second date, September 2003, and third date, May 2004, were collected when the second stockpile was in place, and the fourth date, July 2004, was collected two months after the removal of the second stockpile.

Average DOC concentrations at 30 cm and 60 depths range between 1000 and 4000 mg kg^{-1}. DOC concentrations show a marked increase at all three depths from June to September 2003. This may be attributed to the fresh biosolids stockpile emplaced in July 2003. The average DOC increases consistently with time at a depth of 90 cm. The DOC concentrations are consistently higher at 60 cm depth compared to 30 cm depth. The higher DOC concentrations at 60 cm may be due to release and transport of the more soluble fraction of organic matter, as also observed with the DOC in the lined cell leachate. Alternatively, the DOC closer to the surface is subject to more rapid biological consumption. The decline in average DOC at 30 cm and 60 cm is perhaps attributable to passing of the DOC front and the readily degradable DOC fraction being consumed by soil organisms. Average NH$_4^+$ concentrations range between 589 and 1030

mg kg^{-1} at 30 cm with no clear trend over time. The lysimeter data at 60 cm and 90 cm, however, show a general increase in average NH_4^+ concentration with time. Nitrate concentrations were close to the detection limit of 0.01 mg/L at 30 cm and 60 cm depths prior to the emplacement of the biosolids stockpile

Results of the analyses of individual pan lysimeter filtrates sampled in June 2003 are shown in Table 3. The significant differences in concentrations seen at the same depth may be attributed to the existence of the preferential flow paths. The installation of pan lysimeters involves disturbing the existing soil structure, possibly creating preferential flow paths above the lysimeters. Subsurface flow may also be restricted locally by biological growth plugging the open pores and pathways in the soil, as has been reported in landfill leachate column studies (Jensen and Christensen, 1999). Evidence for the preferential flow paths was also the greatly varying yield of liquid from the lysimeters at the three different depths. Lysimeters especially at the 60 cm and 90 cm depth failed to yield as much liquid as lysimeters at the 30 cm depth. Preferential flow paths are commonly found in nature (e.g., worm holes, cracks and roots in soils) and have been documented to accelerate biosolids leaching into soil (Camobreco et al., 1996).

Lysimeter – Metals

Lysimeter results for metals are presented as: (1) average concentrations (composite samples) at a given depth over time (Fig. 5), and (2) one sampling round showing results of each of the 15 individual lysimeter pans sampled in June 2003 after the emplacement of the biosolid stockpile (Table 4). There is a wide range in concentrations for any given metal at the same depth; nevertheless systematic changes are observed with depth and over time.

Concentrations of Fe, Mn, P and Al were in the mg L^{-1} range in several of the samples (Table 4). These concentrations were generally lower in the deepest lysimeter at 90 cm. Arsenic concentrations showed a steady increase over time as well as depth, with the highest concentrations at 90 cm (Fig. 5). Cu and Zn concentrations increased in Sept. 2003, possibly due to the emplacement of a fresh biosolid stockpile in July 2003 (Fig. 5). Similar to As, highest Cu concentrations were observed at 90 cm. Soil extractions before the emplacement of the biosolid stockpile showed total As and Cu concentrations of 6.1 and 14.3 μg g^{-1}, respectively. Considering a soil bulk density of 2.6 g cm^{-1} and porosity ranging between 0.3 and 0.5, the soil

may potentially release two to three orders of magnitude more As and Cu than observed in the lysimeters. Therefore, the observed As and Cu in the lysimeters may indeed be released from the underlying soil. P concentrations showed a slight increase over time with highest concentrations at the 30 cm depth (Fig. 6), suggesting that biosolids are the source of P, and that the underlying soil and/or microorganisms act as a sink for P. Concentrations of Cd and Ni ranged between 5-20 and 20-250 μg L^{-1}, respectively, and remained relatively constant over time (data not shown here).

Conclusions

   Leachate from field stacked biosolids contains significant concentrations of DOC and N, well in excess of typical agronomic demands. NH_4^+ was the dominant species of N, and organic N, as a minor species, represented approximately 10% of the total dissolved N. Both species contribute to the formation of NO_3^- in soil and groundwater. In addition, P is mobilized from the biosolids in the low ppm concentration range.

   The results of this study also indicate that Al, Fe, Mn, and As are released from a lime-stabilized Class B biosolids stockpile during the first 90 days, which in this study exceed the annual soil loading limits. The other regulated metals studied (Cd, Cu, Ni, Se and Zn) were released during the first 90 days of stockpiling at rates below annual loading limits. Lysimeter data showed As, Cu, P and Se to be mobile through the soil column in the field. Soil-bound As and Cu were perhaps mobilized due to the presence of the anaerobic environment in the soil as their concentrations increased with depth. Other analytes, such as P and Se showed a general decreased with depth, suggesting that they directly originated from the biosolids.

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Table 1 – Sample Analytes by Matrix

Sample Location	Biosolids	Leachate/Runoff	Lysimeter	Soil
Sampling Frequency	Pre- and Post Test	3 to 14 days	monthly	Pre- and Post test
TKN	×	×	×	×
NO_3^-	×	×	×	×
NO_2^-	×	×	×	×
NH_4^+	×	×	×	×
Organic Carbon	TOC	DOC	DOC	TOC
COD		×	×	
Metals	×	×	×	×
pH	×	×	×	×
Percent Solids	×			

Table 2 – Nitrogen and COD concentrations in the leachate of lined cells

Time (Days)	Cumulative Flow (L)	COD (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)	NH_4^+ (mg/L)	TKN (mg/L)	DOC (mg-C/L)
6	49	20300	0	0.203	1860	2260	3900
19	4702	33125	0.036	0.134	2795	2944	8100
26	7034	36725	0.019	0.142	3168	3414	8900
29	12069	37525	0.025	0.087	3471	3693	8600
36	18297	36550	0.023	0.113	3939	3936	8100
50	26394	35400	0.022	0.089	3894	4275	8100
61	31353	30850	0.033	0.082	4120	4797	7900
83	34368	25250	0.039	0.137	4416	4826	6000
90	35888	27200	0.067	0.194	4832	4893	6800
100	38243	24000	0.042	0.110	4602	5085	7000

Table 3 – Zero tension pan lysimeter filtrate test results June 2003

| Lysimeter	DOC (mg/L)	COD (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)	NH_4^+ (mg/L)	TKN (mg/L)
1C1	67	1810	0.074	N.D.	167	223
1C2	725	6520	0.102	N.D.	600	715
1C3	1270	12660	0.218	N.D.	2400	2590
1E1	79	120	N.D.	N.D.	23.5	38.8
1E2	2030	20225	0.552	0.036	1960	2420
2C1	4860	26700	0.443	0.031	2384	2840
2C2	301	2690	0.062	N.D.	257	358
2C3	55	384	0.012	N.D.	87.8	112
2E1	6060	16075	0.036	N.D.	1340	3030
2E2	76	1680	0.031	N.D.	149	198
3C1	24	17	0.802	23.7	0.34	27.2
3C2	270	3480	N.D.	N.D.	342	468
3C3	54	246	12.5	8.8	0.88	24.6
3E1	39	54	1.0	43.1	1.19	52.5
3E2	37	422	N.D.	0.012	22.8	37.3

See Figure 1 for the location of the lysimeters.

Table 4 – Zero tension pan lysimeter metal concentrations June 2003

Lysimeter	Al (mg/L)	As (mg/L)	Cd (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Ni (mg/L)	P (mg/L)	Se (mg/L)	Zn (mg/L)
1C1	471	23.7	40.1	236.4	537	195	35.6	2761	79.9	28.2
1C2	930	43.8	0.5	70.1	41370	9415	145.8	2956	118.1	42.9
1C3	1613	128.0	8.1	291.8	10558	3564	307.6	10919	263.0	84.4
1E1	140	1.8	58.7	18.7	55	0	0	144	3.3	11.7
1E2	3248	302.2	3.4	167.5	47905	5049	474.1	28686	391.0	175.0
2C1	2518	267.7	8.5	246.6	53898	44032	500.4	21265	286.6	171.6
2C2	488	38.5	12.9	167.3	428	1184	82.3	1255	99.6	20.8
2C3	156	33.8	4.4	89.2	133	53	0.5	464	36.4	20.2
2E1	2802	134.5	0.4	507.8	82732	32654	514.4	3273	244.5	214.9
2E2	385	31.1	0	99.2	328	230	36.4	881	78.3	21.1
3C1	116	58.9	38.6	0.9	12	0	0	286	55.4	232.8
3C2	631	123.9	6.6	513.3	551	447	136.6	2165	194.2	115.0
3C3	135	33.7	36.7	17.5	31	0	0	112	59.4	78.1
3E1	179	60.0	9.6	14.8	76	5	0.5	670	64.0	43.6
3E2	156	26.9	5.8	23.9	84	14	10.0	121	57.1	45.0

See Fig. 1 for the location of the lysimeters.

Figure 1 – Lysimeter plot schematic –Lysimeters were labeled with a 3 digit code D-L-N where D was depth (1 = 30 centimeters, 2 = 60 centimeters and 3 = 90 centimeters), L was location (C=center E=edge) and N was a serial number 1 through 3
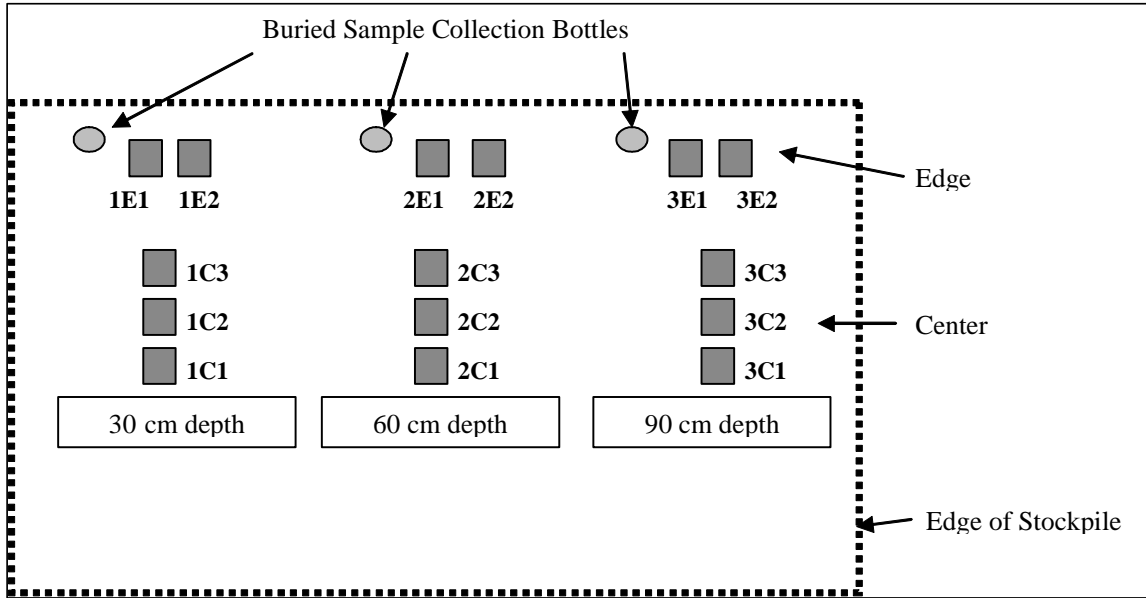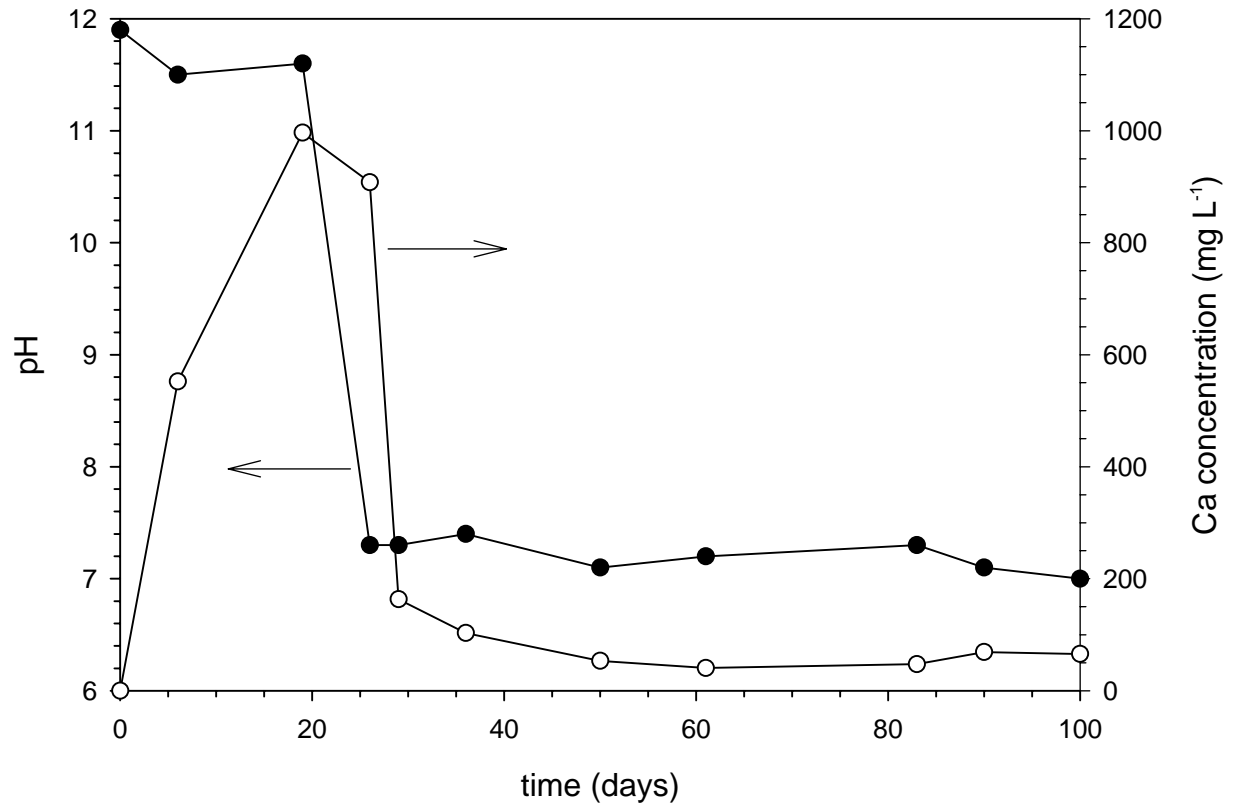
Figure 3 – Lined cell biosolids pH and lined cell leachate Ca concentration from July 9, 2003 to October 17, 2003.

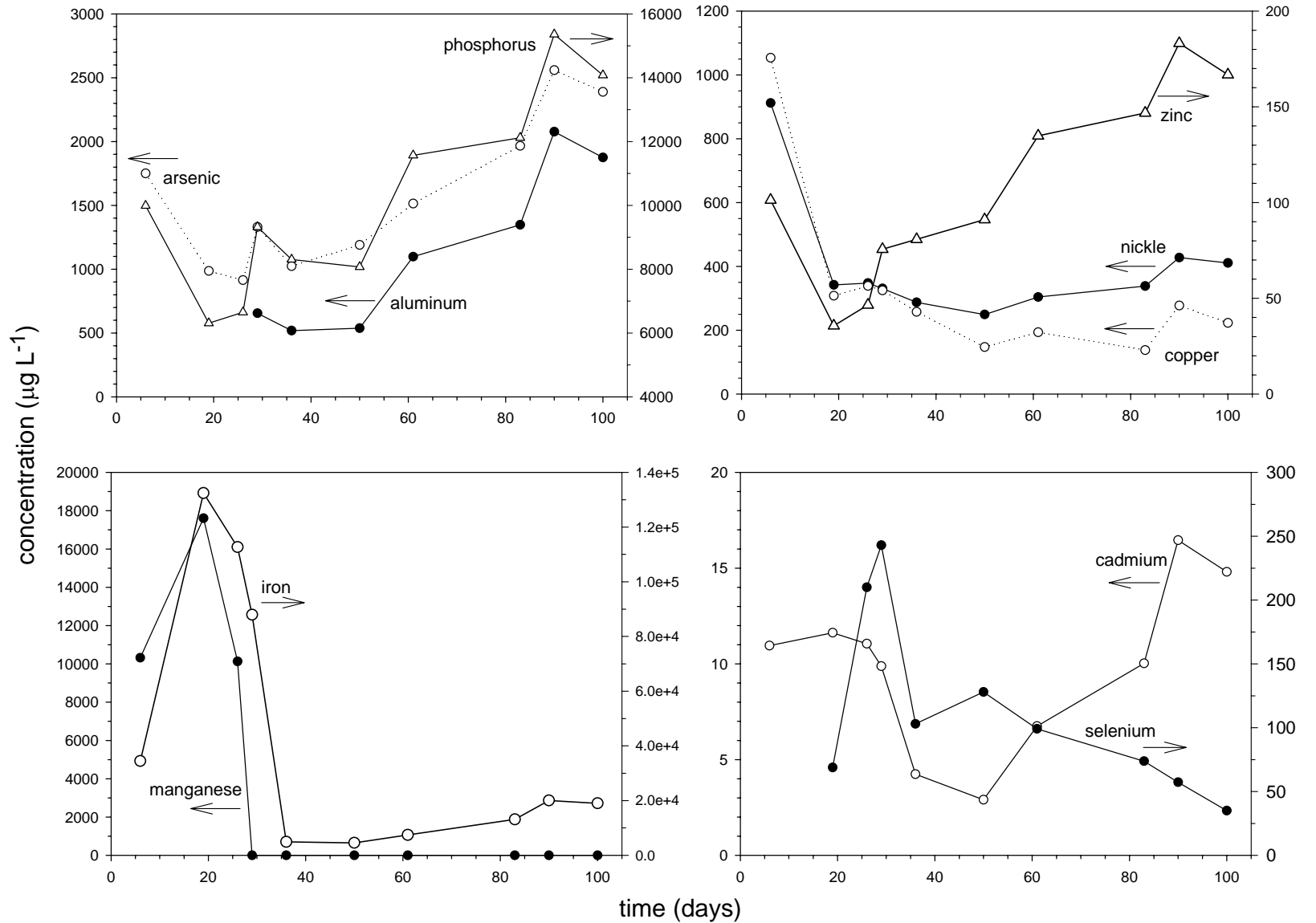**Figure 3 – Lined cell leachate trace metal concentration from July 9, 2003 to October 17, 2003.**

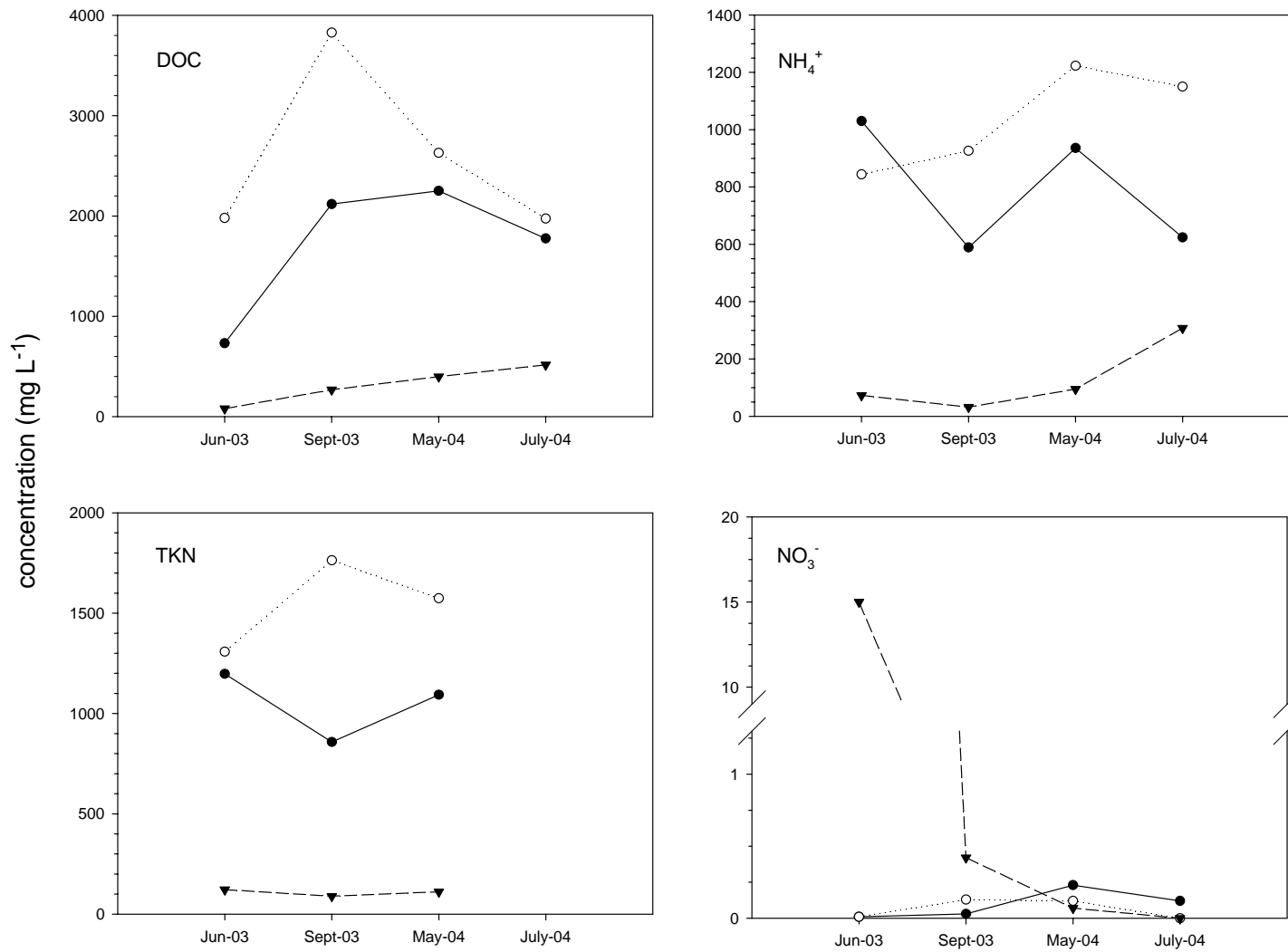**Figure 4** – **Zero-tension pan lysimeter DOC, NH_4^+, TKN and NO_3^- average concentrations 2003 – 2004.**
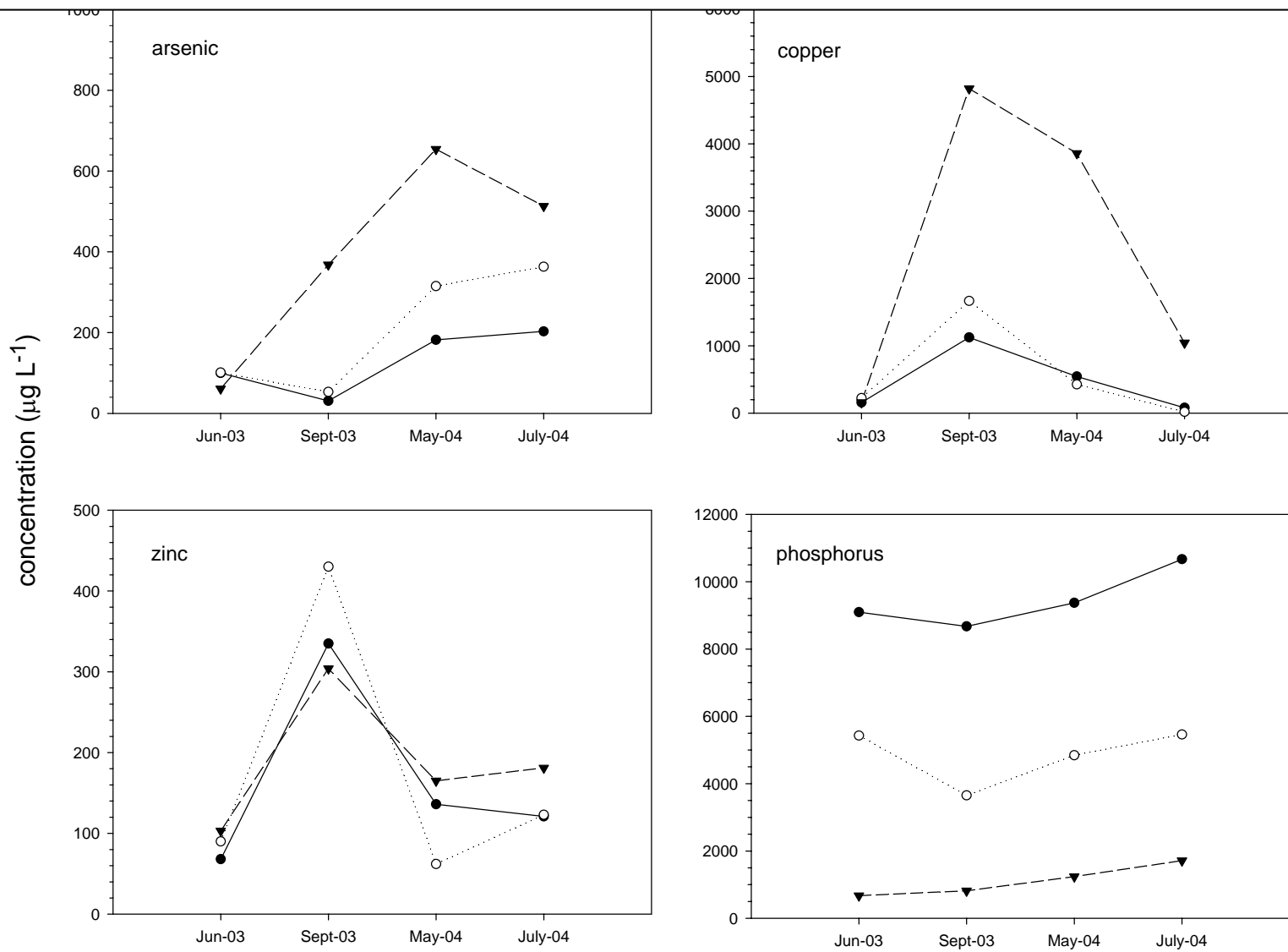
Figure 5 – Zero-tension pan lysimeter temporal average concentrations of As, Cu, Zn and Se at depth from 2003 to 2004.

Do Natural Chloride Gradients Affect the Formation of Disinfection

Basic Information

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DO NATURAL CHLORIDE GRADIENTS AFFECT THE FORMATION OF DISINFECTION BY-PRODUCTS IN PUBLIC WATER SUPPLIES?

ABSTRACT

This study assesses how chloride in source waters affects the formation of disinfection by-products (DBP). Preliminary analyses of DBPs in public water supplies in Maine showed a greater prevalence of trihalomethanes (THM) over haloacetic acids (HAA) with increasing distance from the ocean. Distance to the ocean could be related to a salt effect caused by deposition of marine aerosols. However, paired samples of raw and finished water show no correlation between the DBP ratio and chloride concentrations. While there is no linear correlation between total DBP concentrations and chloride concentrations; there is a decrease in both THM and HAA concentrations in water with high chloride concentrations. Since comparing multiple systems with diverse land uses and treatment procedures is complex, it is not yet possible to determine the process by which chloride affects DBP formation. Possibly, elevated concentrations of chloride in raw water are inhibiting the reactivity of hypochlorite with organic matter.

INTRODUCTION

January 2004 marked the start of the compliance cycle for small drinking water systems serving <10,000 customers (40 CFR Parts 9, 141, 142). The majority of 2,200 water systems in Maine, and in many other states, fall in this size range. During 2004, these small systems started monitoring for disinfection by-products and in 2005 they needed to have instituted control measures. However, there are numerous variables that contribute to the formation of DBPs, and not all are well understood. The presence of natural factors that affect the formation and type of DBPs will have a significant effect on the types of management techniques employed. The understanding and control of DBPs is the single biggest compliance challenge facing water utilities in the near future. Public water utility managers in Maine have requested help to understand how DBPs are forming in their systems so that they can best manage their risks.

Disinfection by-products (DBPs) are chlorinated or brominated compounds; tri-halomethanes (THM) and haloacetic acids (HAA) that are formed by disinfection chemicals reacting with natural organic matter (NOM) in the water. The EPA has set maximum contaminant levels (MCLs) of 0.08 mg/L for THM and 0.06 mg/L for HAA (USEPA, 2001; Safe Drinking Water Act, *e.g.* 40CFR 141 and revisions). Water systems may exceed the current MCLs during some reporting quarters and at some locations within the system. Although these systems are commonly in compliance based on average THM and HAA concentrations, Stage 2 of USEPA's DBP Rule, which requires that all monitoring sites within a system be compliant, will force many of those systems to undertake costly changes. Public water utility managers need help to understand how DBPs are forming in their systems so that they can best manage associated risks.

Efforts have been made recently to understand the controls on DBP formation and the steps necessary to prevent DBP formation. Regression techniques have been used to identify parameters responsible for DBP formation. Predictive models of DBP formation include variables such as: temperature, pH, bromine concentrations, chlorine dose, and measures of the content and nature of natural organic matter (NOM), such as total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV_{254}), and specific UV_{254} absorbance ($SUVA_{254}$), etc. (Sadiq and Rodriguez, 2004, Sohn et al., 2004). Although models developed using regression techniques can have high accuracy in laboratory studies or as defined through studies of single systems, accuracy decreases when models are applied across systems with differing water sources and treatment procedures.

TOC and the character of NOM are known factors in the formation of DBPs (Kitis et al., 2001; Leenheer et al., 2001; Charrois et al., 2004; Xie, 2004; Kim and Yu, 2005). In general, the higher the TOC content of the source water the greater the potential to form DBPs (Canale et al., 1997; Charrois et al., 2004). $SUVA_{254}$ is used as a surrogate parameter for aromaticity of NOM, which is related to a high proportion of humic content (Traina et al., 1990). $SUVA_{254}$ correlates positively with DBP formation potential (Kitis et al., 2001; Leenheer et al., 2001), and is used to predict DBP concentrations within a water system (Chow, 2006). The ratio of absorbance at 465 nm to 665 nm is also an indictor of the degree of humification and aromaticity of NOM (Stevenson and White, 1995; Chin at al., 1994). Korshin et al. (1997) have demonstrated that absorbance at 272 nm correlates with the formation of total organic halides (TOX) following chlorination. $SUVA_{280}$ was found to be an accurate predictor of the production of DBPs from chlorine reactivity with NOM (Kitis et al., 2001)

Much has been learned about the formation of by-products, and the occurrence of byproduct precursors in NOM (Reckhow et al., 1999; Karimi and Singer, 1991; Singer, 1994; Westerhoff et al., 1998), but it is clear that engineered systems do not entirely mitigate the occurrence of by-products. Recent data show the function of watersheds in controlling NOM and DBP precursors (LeChavelier and Volk, 2002; Garvey and Tobiason, 2003). The type of NOM in water supplies is dependent on the biological activity in the source watershed. The export of NOM to lakes is dependent upon such factors as watershed land uses, geology, topography, climate, (Schiff et al., 1997; Cronan et al., 1999; David et al., 1999) and hydrology is the driving force for mass loading of NOM. Several studies in the northeast have documented the relationships between watershed compositions and DOC (Thurman, 1985; Cronan et al., 1999), although few have addressed the issue from the perspective of drinking water supplies (Reckhow, 2002). These relationships have also been measured with respect to the potential to form tri-halomethane (Amy et al., 1987; Arruda et al., 1989; Garvey and Tobiason, 2003). The study on the Quabbin reservoir in Massachusetts clearly indicated that inputs and internal processes affect the formation of DBPs and that there is a need to differentiate between allochthonous and autochthonous DOC (Garvey et al., 1998; Stepczuk et al., 1998) in an understanding of DBPs.

The scope of this project encompasses public water supplies using surface waters in a spatial gradient from adjacent to the coast to 200 kilometers inland (Figure 1). Data collected by us and other researchers at the University of Maine have established a gradient of chloride in surface and ground waters that decreases inland from ~100 ueq/L to <10 ueq/L. Preliminary data from public water suppliers have demonstrated that DBPs occur in Maine's drinking water, including

several systems near or above the MCLs for THM or HAA. Since road salt can be a significant source of chloride seasonally at all locations, road salt is expected to overprint a natural chloride gradient. Water supplies that bracket the range from undeveloped to developed source areas can be mapped across the chloride gradient.

Preliminary analyses of DBPs in public water supplies in Maine showed that there are some unusual relationships between the distance from the ocean and the occurrence of trihalomethanes (THM) and haloacetic acids (HAA). In particular, the relative ratio of HAA to THM (HAA-THM ratio), defined as:

$$(HAA - THM) / (HAA + THM) \hspace{4cm} (equation 1).$$

The HAA-THM ratio is positive if HAA is the dominant DBP and negative if THM is dominant. In Maine, the HAA-THM ratio is positive near the coast and negative inland (Figure 2). This variation exhibits the same trend as chloride in surface waters generated from research on lakes in Maine. Chloride in lakes varies from relative highs near the ocean to trace concentrations in extreme northern Maine (Kahl et al., 2004; see also National Atmospheric Deposition Program, http://nadp.sws.uiuc.edu/). Other halides in seawater such as bromide and iodide may be equally important. As can be seen in Figure 2, there is a correlation between proximity to the ocean and the dominant type of DBP formed. Our initial hypothesis was that background chloride concentrations were affecting DBP formation. If natural chloride from oceanic aerosols (along with bromide and iodide), or from road salt, is affecting DBP formation in the source, in addition to disinfection processes, then very different control techniques will be needed. This research investigated the relationship between chloride concentrations and DBP formation.

The sites investigated in this report are public water supplies that utilize surface water throughout the state of Maine. The sites are located from 2 to 283 km (1.2 to 176 miles) from the ocean. The water sources for these utilities include lakes, ponds, rivers, streams, and reservoirs. Watershed hydrologic characteristics and land development for these sources vary considerably. Land use ranges from highly developed (urban to suburban) to undisturbed (forested), making a large gradient of influences for the delivery of NOM to surfaces waters.

METHODS

Two rounds of data were collected. In the first round, raw- and finished-water samples from 30 public water systems were analyzed for major cations, anions, acid neutralizing capacity (ANC), pH, conductivity, dissolved organic carbon (DOC), total organic carbon (TOC), and specific ultraviolet absorbance at 254 nm ($SUVA_{254}$). THM and HAA concentrations in finished water for round one were obtained from the water districts records for a date closest to the sample date for this project. In the second round, the same data were obtained, but THM and HAA concentrations were measured from samples collected at the same time.

Eight representative sites were selected from the first round sites for a second sampling round. The second round sites were sampled and analyzed as described above. Additionally, the major THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) and HAAs (monochloroacetic acid, monobromoacetic acid, dichloroloacetic acid, trichloroacetic acid, and dibromoacetic acid) were measured in raw and finished water that was collected at the same time.

Sample analysis was performed at the University of Maine for pH, specific conductance, acid neutralizing capacity, anions, major cations, DOC, and UV absorbance and at a commercial laboratory for DBPs. Analytical methods for tri-halomethanes followed EPA Method 524.2 and Standard Method 6251B for halo-acetic acids.

The pH and specific conductance were analyzed in accordance with standard methods. Acid neutralizing capacity was analyzed using an ARAS and TIM900 titrator system. Cations were analyzed using an Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Anions were analyzed by ion chromatography. UV absorbance was measured using a UV-VIS spectrophotometer at 254 nm. TOC and DOC were analyzed automated by persulfate digestion followed by infra-red detection of carbon dioxide.

RESULTS

First Round. Total trihalomethanes ranged from 3.3 to 224 μg/L and total halo-acetic acids ranged from 5.2 to 130 μg/L. Background chloride concentrations ranged from 14.8 to 1094 μeq/L (525 to 39,000 μg/L). TOC concentrations in raw water ranged from 1.8 to 18 mg/L. The HAA-THM ratio ranges from −1 to +0.6. Neither HAAs nor THMs consistently dominate the total DBP concentrations, although THM concentration is about 36 times HAA concentration at two sites. There is no pattern in THM or HAA dominance with source type. The HAA-THM ratio from the finished water decreased linearly ($R^2 = 0.30$) with distance from the ocean (Figure 3), indicating an increase in THM dominance away from the coast. Chloride concentrations decrease with distance from the ocean, but the correlation with the HAA-THM ratio is very weak ($R^2 = 0.10$). In spite of similar relationships of HAA-THM ratio and chloride concentrations with distance from the ocean, no correlation exists between the HAA-THM ratio in the finished water and chloride concentrations in the raw water (Figure 4). Total THM and HAA concentrations in finished water are lowest at highest raw-water chloride concentrations, but there are no linear correlations (Figure 5). Total THM concentrations decrease more sharply than total HAA with increasing chloride concentrations.

Chloride concentrations are higher in the finished water than in the raw water for all but one site. THM and HAA concentrations are highest at the greatest relative difference of chloride:
$$(Cl_{finished}-Cl_{raw})/Cl_{finished})*100 \qquad \text{(equation 2).}$$
There is a weak linear correlation ($R^2 = 0.26$) for the THM data (Figure 6) and insignificant correlation ($R^2 < 0.02$) for the HAA data .

Typically, DOC concentrations are within analytical error of the TOC concentrations (i.e. there is no significant difference between TOC and DOC for the same sample). All but one site had higher TOC concentrations in the raw water than the finished water. THM concentrations of finished-water samples correlate weakly with TOC of the raw water, but HAA concentrations show no correlation (Figure 7). No correlations were found between either ANC or pH and DBP concentrations.

Although correlations between $SUVA_{254}$ and both THM and HAA concentrations in finished water are not significant, the DBP concentrations are highest at highest $SUVA_{254}$ (Figure 8). Utilities with a river source have higher $SUVA_{254}$ than those with lake sources, but no correlation exists between DBP concentrations and $SUVA_{254}$ in those data (Figure 8).

Second Round. THM and HAA concentrations were measured for both raw and finished water, and only one sample had measurable DBP (1.6 µg/L trichloroacetic acid) in the raw water. Most of the finished water had HAAs with similar dichloroacetic acid and trichloroacetic acid concentrations, but two lake waters had considerably more trichloroacetic acid than dichloroacetic acid. Two river waters had minor monochloroacetic acid concentrations. Most of the total THMs in the finished water were composed of chloroform, with minor bromodichloromethane. Two river waters had minor dibromochloromethane.

Concentrations of both THM and HAA correlate positively with TOC (Figures 9 and 10) and with $SUVA_{254}$ (Figure 11). The lowest THM and HAA concentrations occur with the highest chloride concentrations.

DISCUSSION

There is a linear trend of decreasing HAA-THM ratio with distance from the ocean (Figure 3), indicating greater prevalence of THM concentrations inland. The initial hypothesis that this trend is due to a chloride gradient across the area is not supported by the data, which show no relationship between HAA-THM ratios and chloride concentrations (Figure 4). Distance from the ocean is associated with other changes, such as climatic gradients and land uses that affect NOM. The nature of NOM controls the formation of DBPs (Korshin et al., 1999; Kitis et al., 2001; Leenheer et al., 2001). THMs are more influenced by the hydrophobic fraction and HAAs are more influenced by the hydrophilic fraction (Kim and Yu, 2005). It is possible, therefore, that inland decreases in HAA-THM ratios may be controlled by differences in organic matter arising from other factors. $SUVA_{254}$ values are variable (73 to 238 L/mg-m) near the ocean, but all are above 180 L/mg-m at distances greater than 100 km from the ocean, suggestive of a spatial control on the humic factor of NOM.

Although there is no correlation between HAA-THM ratio and chloride concentrations, there is a relationship between total DBPs and chloride concentrations. In the first sampling round, the greatest DBP formation occurs in water with the lowest chloride concentrations, although the correlation is very weak (Figure 4). DBP and chloride concentrations in the second round of sampling show a similar decrease in both THM and HAA concentrations in water with high chloride concentrations, and have much better correlations (Figure 12).

TOC and $SUVA_{254}$ are known factors in the formation of DBPs (Kitis et al., 2001; Leenheer et al., 2001; Charrois et al., 2004; Xie, 2004; Kim and Yu, 2005). The data in the first sampling round show a poor correlation between DBP concentrations and TOC and $SUVA_{254}$. This is probably because of the time differential between data collection of the DBP concentrations and the other parameters in the first dataset. There is a better correlation of DBP concentrations and TOC and $SUVA_{254}$ in the second round of sampling than in the first, reflecting the simultaneous collection of all the data. Correlations between DBP concentrations and other parameters are compromised by the disconnect in sampling of DBP concentrations and other parameters in the first dataset, but the larger size of the dataset makes it useful, especially if similar relationships are detected in both datasets. General relationships, such as increases and decreases, show up in both datasets. Of particular importance is the occurrence of lowest DBP concentrations at the highest background chloride concentrations.

Assuming that a direct link exists between chloride and DBP concentrations, and chloride is not acting as a proxy, an explanation is needed for this relationship. Chloride is assumed to be a conservative element and is unlikely to participate in chemical reactions. Chloride does adsorb weakly, however, and can interfere with some surface reactions. For example, chloride, unlike other anions, acts as a linear inhibitor of NADH:nitrate reductase activity (Barber et al., 1989), and chloride adsorption onto iron filings inhibits perchlorate reduction (Moore and Young, 2005). Chloride adsorbs onto iron surfaces more at low pH (Moore and Young, 2005). THM concentrations differ considerably from low to high chloride concentrations, but HAA concentrations do not (Figure 5), suggesting that THM is more affected by chloride concentrations. It is known that THM formation increases with increasing pH, but HAA and total organic halide formation decreases with increasing pH (Reckhow and Singer, 1985; Xie, 2004; Malliarou et al., 2005). It may be that greater chloride interference at low pH prevents THM formation. There is, however, no trend in DBP concentrations with pH. Because of the complexity inherent in comparing multiple systems with diverse sources, source types, and treatment procedures, it is difficult to make conclusions as to the nature of the relationship between chloride concentrations and DBP formation. Possibly, elevated concentrations of chloride are inhibiting the activity of hypochlorite. Laboratory studies are being designed to investigate the nature of the effect of chloride on THM and HAA formation.

CONCLUSIONS
HAA dominance of total DBP concentrations decreases linearly with distance from the ocean. This relationship is not due to a chloride gradient, but may be related to the character of the NOM. Chloride concentrations in source water do appear to affect the total amount of DBP formed. DBP concentrations (particularly THM concentrations) are lowest at high chloride concentrations, implying potential chloride interference in DBP formation.

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FIGURES

Figure 1. Locations of Surface Water Intakes and Supply Wells for Public Water Supplies in Maine.
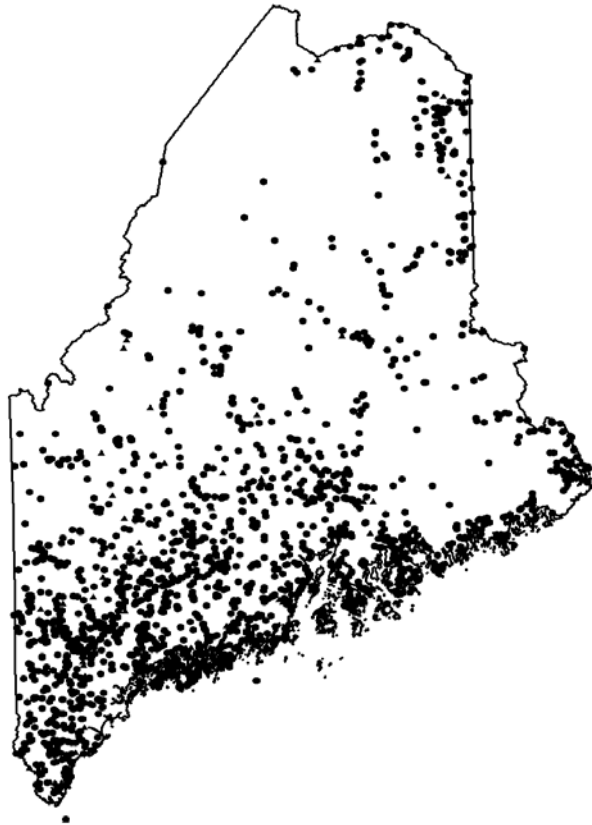
Figure 2. HAA-THM ratio in finished water (left axix) and Cl concentrations in raw water (right axis) versus distance from the ocean, preliminary data.

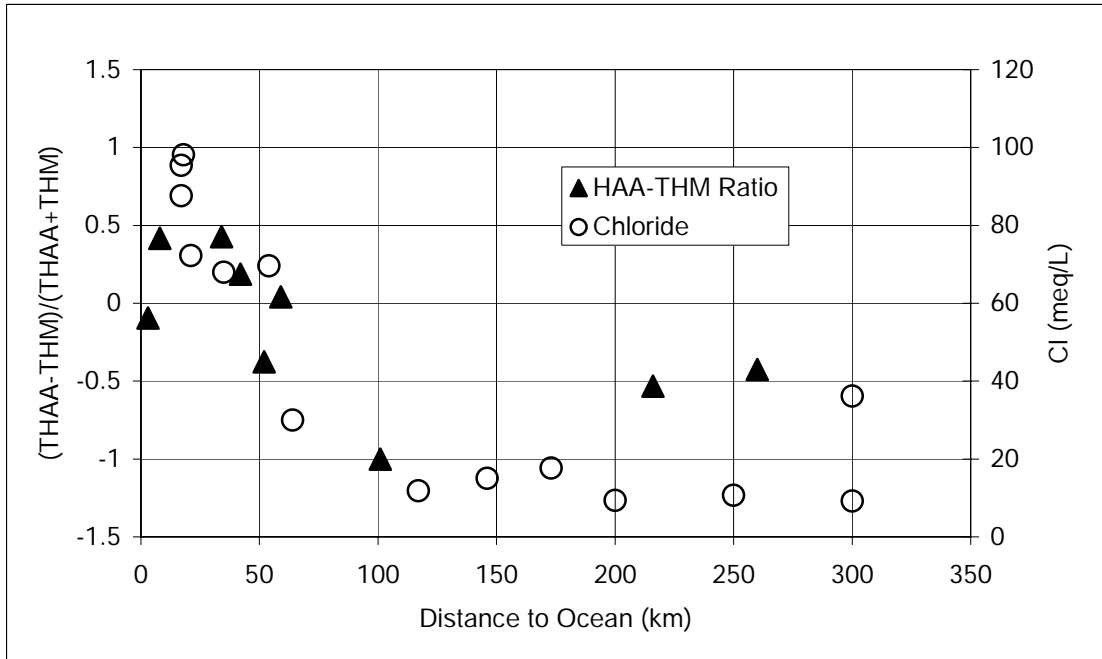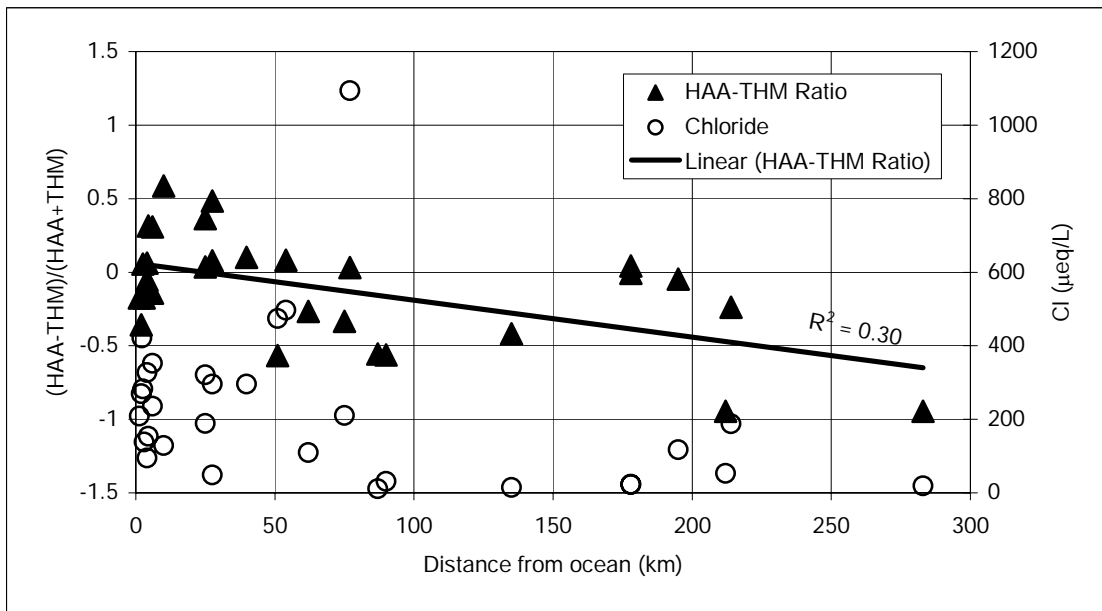**Figure 3. HAA-THM ratio in finished water (left axis) and Cl concentrations in raw water (right axis) versus distance from the ocean, first-round samples.**
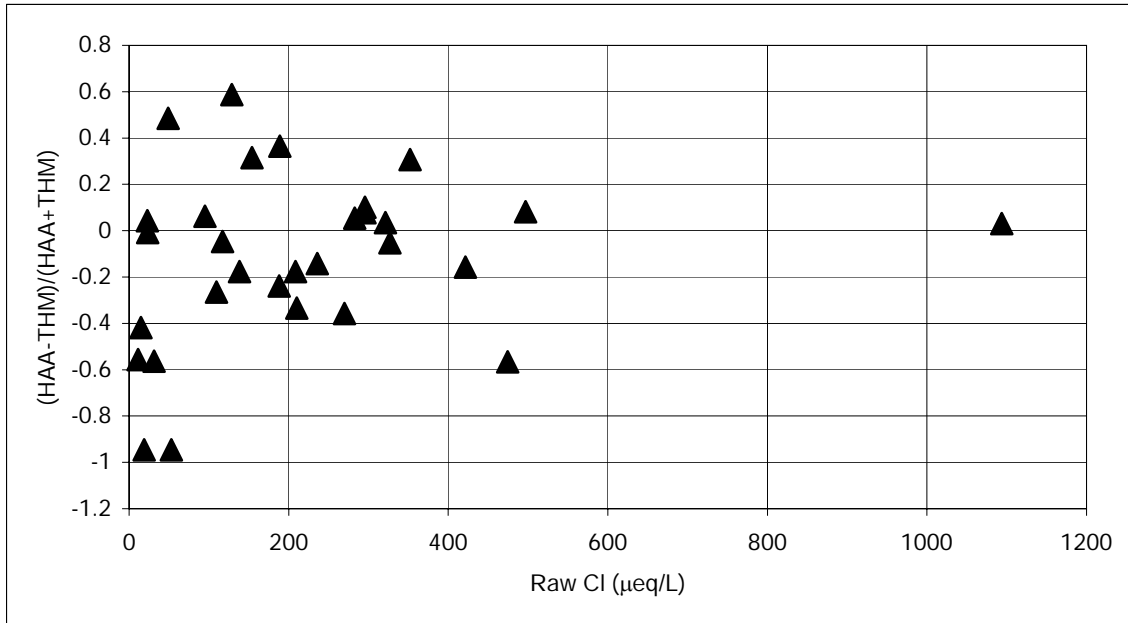
Figure 4. HAA-THM ratio in finished water versus Cl concentrations in raw water, first-round samples.
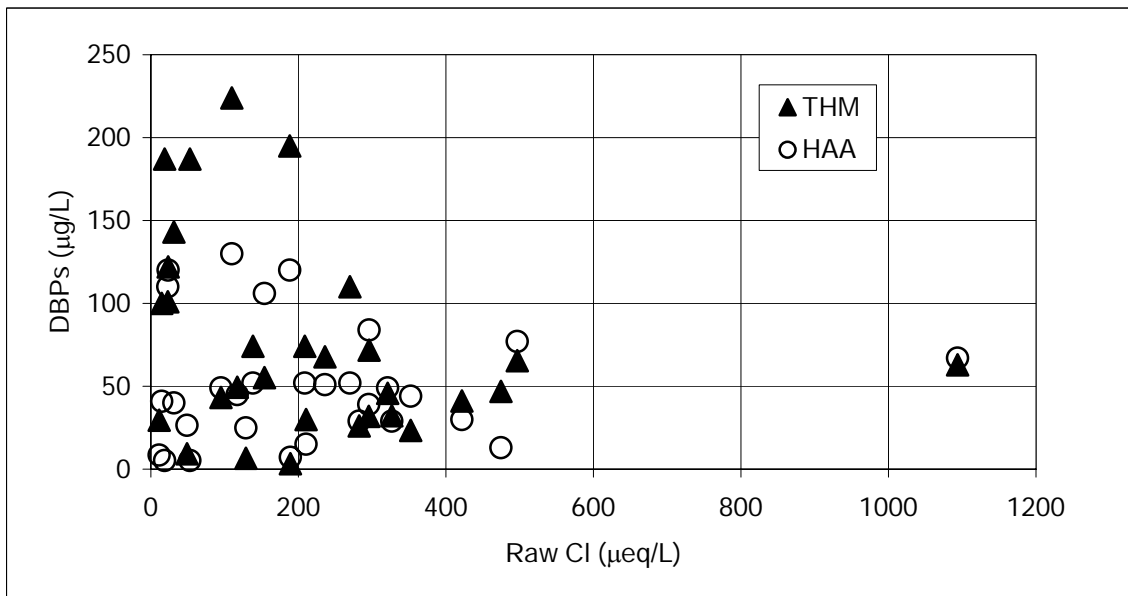
Figure 5. THM and HAA concentrations in finished water versus Cl concentrations in raw water, first-round samples.
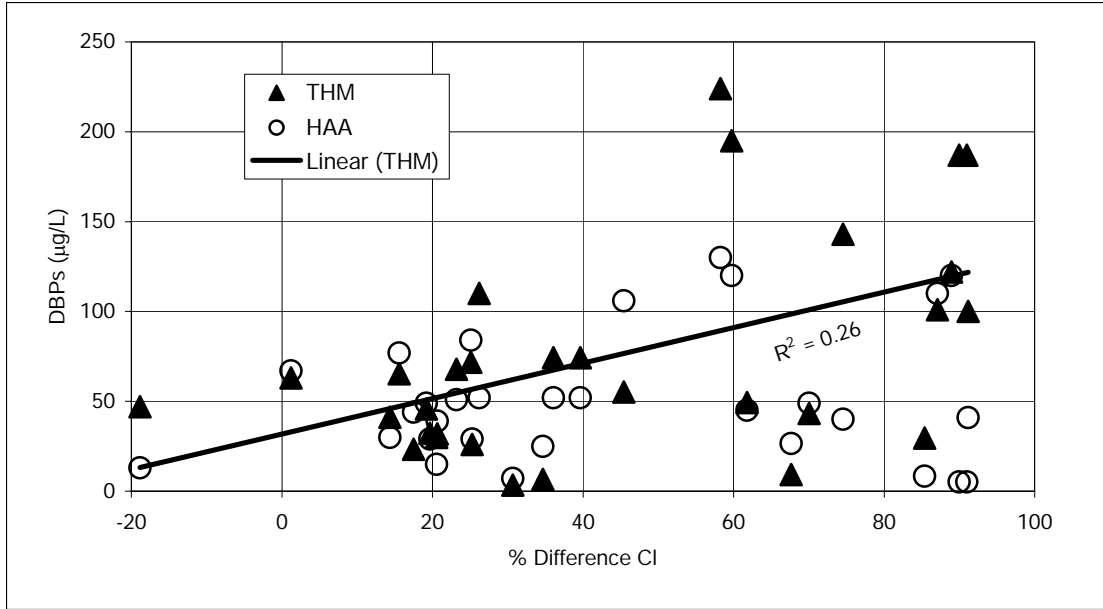
Figure 6. THM and HAA concentrations in finished water versus % difference Cl.
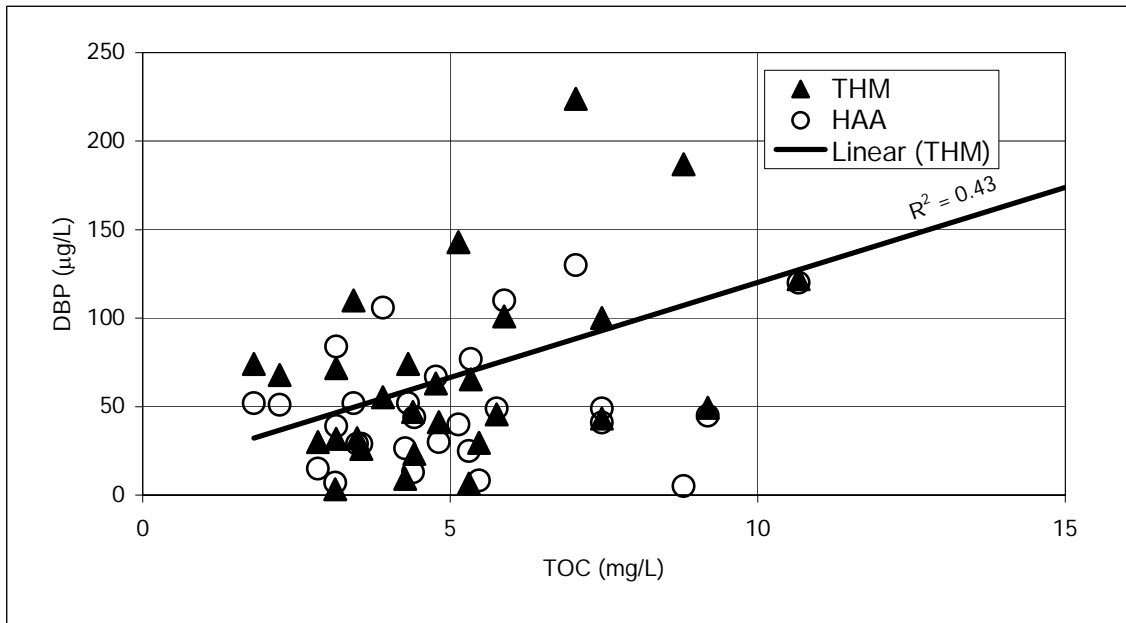
Figure 7. THM and HAA concentrations in finished water versus TOC in raw water, and the trend line for the THM data.
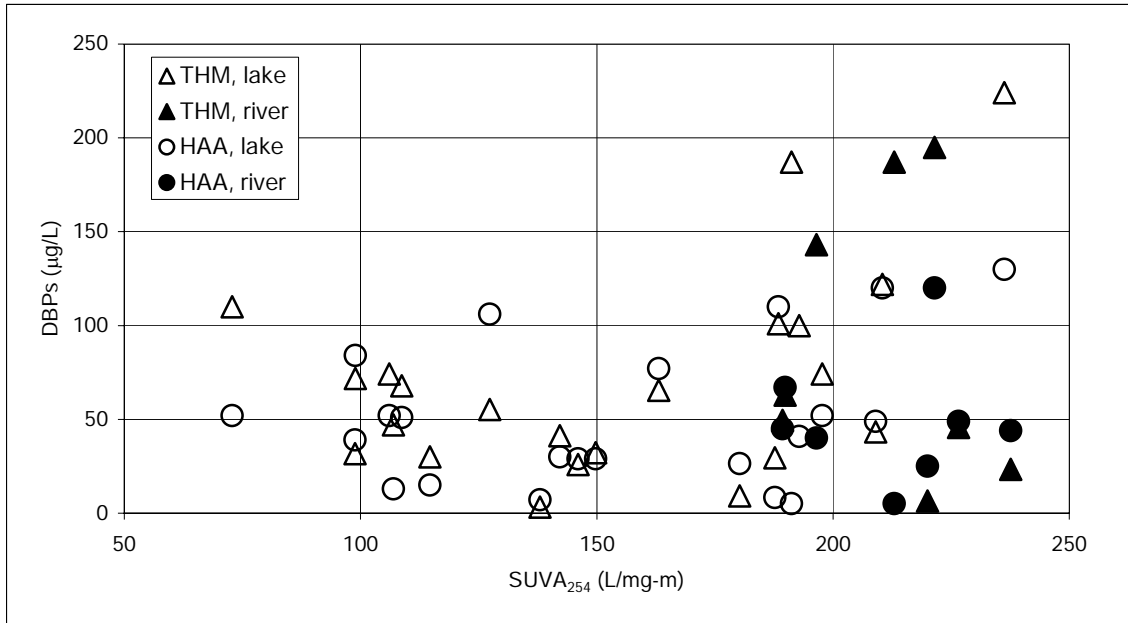
Figure 8. THM and HAA concentrations in finished water versus SUVA in raw water.
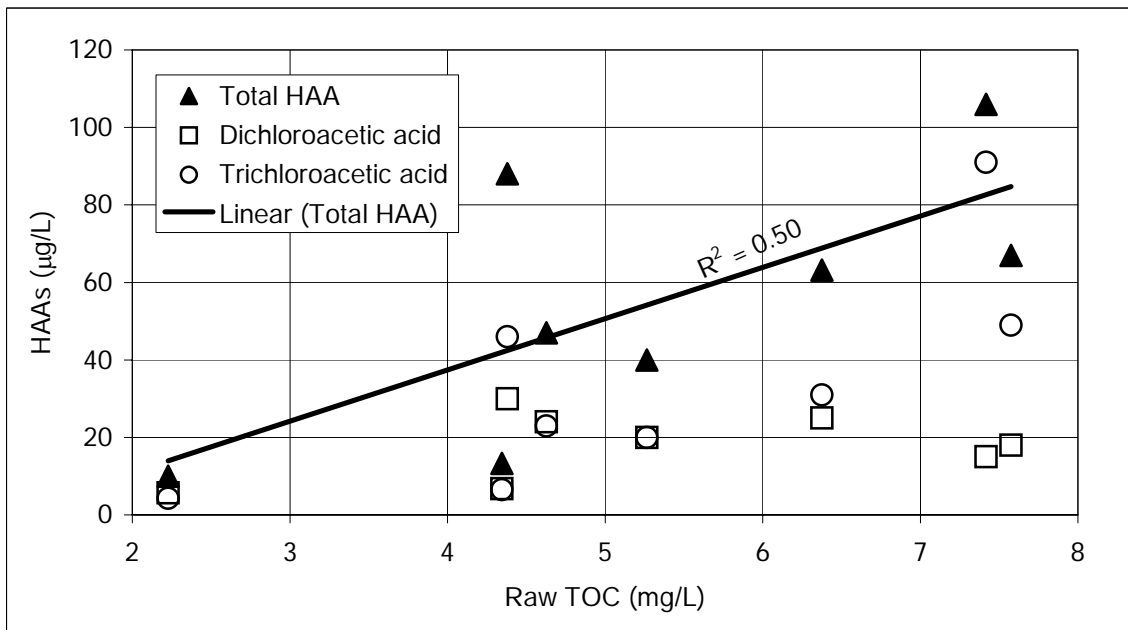
Figure 9. HAA components and total HAA concentration of the finished water versus TOC concentrations of the raw water, second sample round.
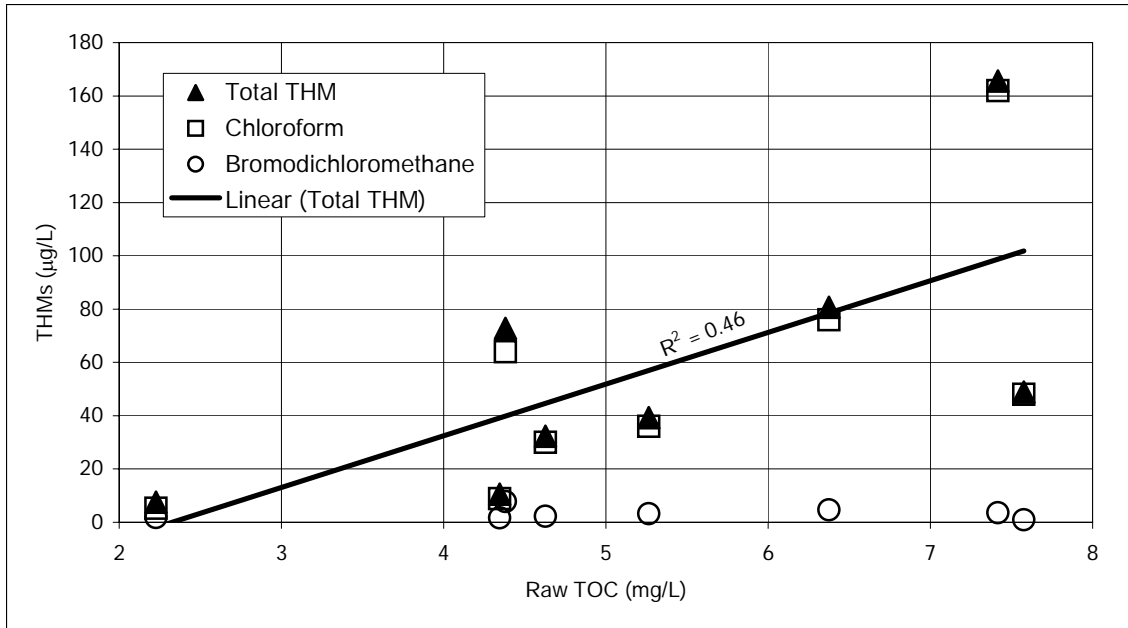
Figure 10. THM components and total THM concentrations of the finished water versus TOC of the raw water, second sample round.
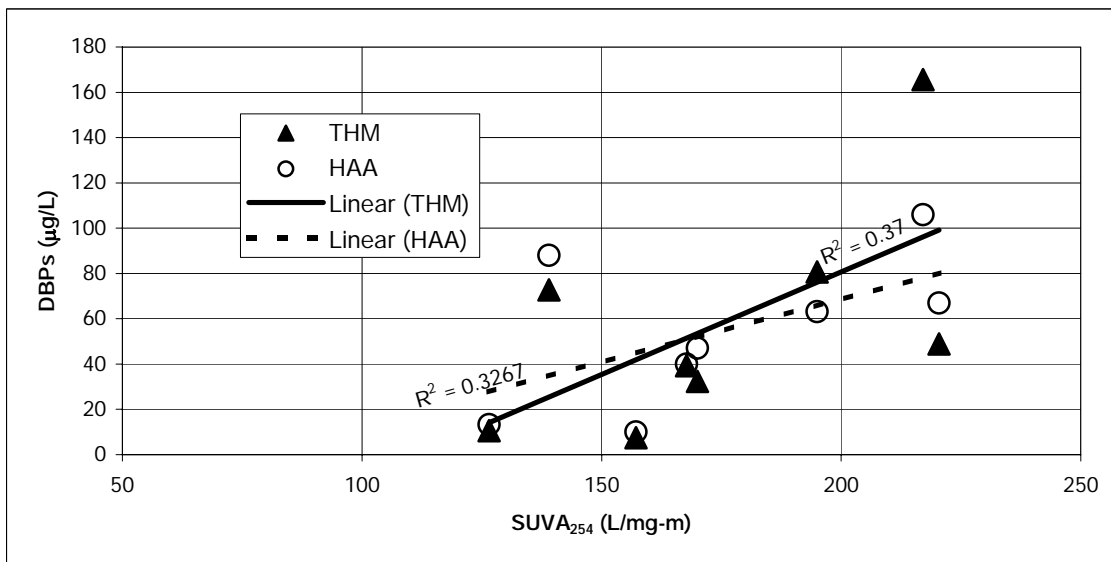
Figure 11. Total THM and HAA concentrations in finished water versus SUVA254 in raw water, and trend lines, second sample round.
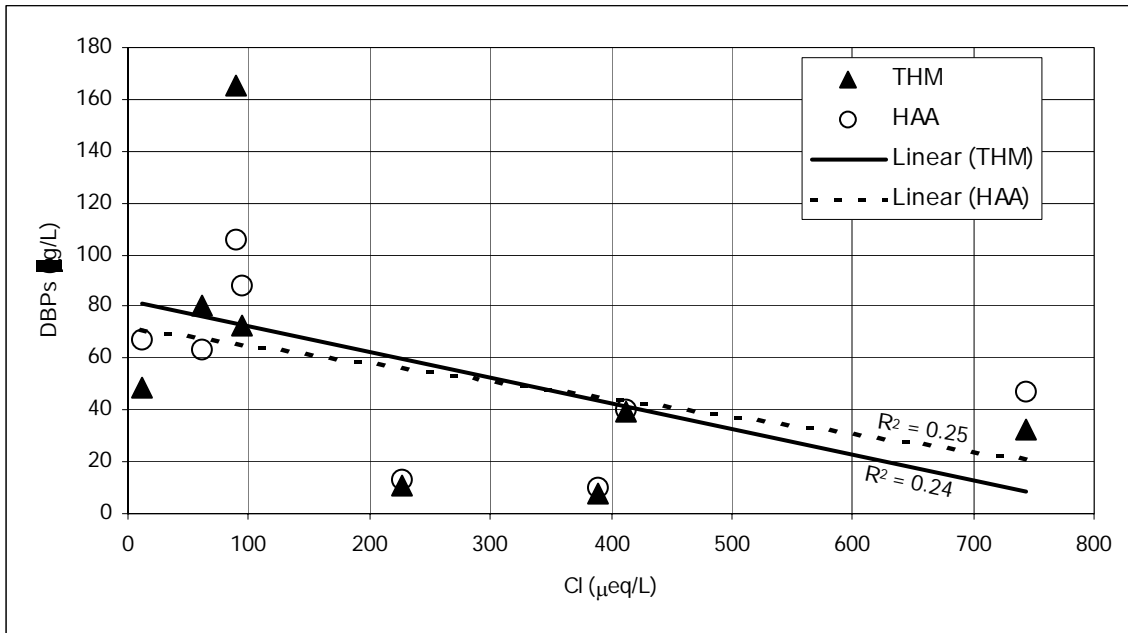
Figure 12. Total THM and HAA concentrations in the finished water versus Cl concentrations and trend lines, second sampling round.

A Pilot Study to Evaluate the Potential for River Water Toxicity to Increase Following Dam Removal

Basic Information

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A Pilot Study to Evaluate the Potential for River Water Toxicity to Increase Following Dam Removal

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Abstract

Precipitous declines in Atlantic salmon (*Salmo salar*) populations have led to the loss of all wild salmon in the United States except Maine where Penobscot River populations have the greatest restoration potential. Dam removal has been identified as the most important restoration strategy, but this can result in the release of contaminants from sediments into overlying waters. To evaluate the toxic potential of Penobscot River sediments, we used a simple laboratory-based, sediment resuspension design and two well-established aquatic toxicology models, fathead minnows (*Pimephales promelas*) and zebrafish (*Danio rerio*). Sediments were collected from Penobscot River sites downstream of the two dams slated for removal and characterized for resuspension-mediated chemical desorption and biological toxicity. Sediment resuspension elevated Penobscot river water concentrations of organic pollutants (PAHs) and several heavy metals, including mercury. Fathead minnow embryo development was delayed in fish exposed to resuspension water, but embryo-larval survival, hatch success, and the incidence of developmental abnormalities were unaffected. Innate immune response was significantly weaker in zebrafish embryos exposed to resuspension water. CYP1A1 gene expression was elevated up to 70 fold in zebrafish embryos exposed to river water, with or without sediment-suspension. There was no evidence of estrogen-active substances in any of the treatments as measured by vitellogenin production by zebrafish embryos and estrogen-sensitive mammalian MVLN cells. Zebrafish carrying a transgene for metal-responsive elements did not respond to any water treatments. Together these results demonstrate that resuspension can release biologically active chemicals from Penobscot River sediments. Studies of resident Penobscot River species, including Atlantic salmon, are needed to evaluate if the biological effects we observed reflect general fish responses to sediment resuspension.

Problem and Research Objectives

There has been a precipitous decline in Atlantic salmon (*Salmo salar*) populations in North America, resulting in extirpation of this species in the US except for 8 Maine rivers whose populations were listed as endangered in 2000. Dam removal has been identified as the most important strategy for restoring salmon populations in Maine (NationalResearchCouncil 2004) and two dams on Penobscot River, Great Works Dam

and Veazie Dam, have been designated for removal. Dam removal can result in release of contaminants from riverine sediments into overlying waters, potentially increasing water toxicity to resident species, including anadromous fish. Because dams will be removed as part of the Penobscot River Restoration Project, there is a need to evaluate the toxic potential of Penobscot River sediments prior to dam removal.

Dam removal in rivers leads to resuspension of sediments, due both to release of sediments behind dams and resuspension of sediments deposited elsewhere in the river. Sediments act as repositories for persistent organic pollutants, including organochlorines, aromatic hydrocarbons, organo-metals and pesticides. Sediment resuspension can release these chemicals to overlying waters (Simpson, Apte and Batley 1998; Latimer, Davis and Keith 1999; Bogdan, Budd, Eadie and Hornbuckle 2002; Martino, Turner, Nimmo and Millward 2002; Hornbuckle, Smith, Miller, Eadie and Lansing 2004), leading to changes in their physico-chemical properties, including potential alterations in toxicity. Aquatic organisms are particularly vulnerable to dam removal, being subjected to the multiple stressors associated with a habitat undergoing dramatic physical, chemical and biological changes (Francisco 2004).

The goal of the proposed study was to determine if resuspension of sediments following dam removal will significantly increase the toxicity of riverine water to early life stage fishes. Physiological responses, including immune function, reproductive success, and embryologic development, are predictive of population level effects and are commonly used as indicators of contaminant stress. The use of transgenic fish that incorporate reporter genes indicative of exposure to metals provide powerful tools for identifying the potential biochemical mechanisms underlying these effects. Understanding underlying mechanisms provides predictive capabilities for extrapolating results to other species.

We used a simple laboratory-based, sediment resuspension design and two well-established aquatic toxicology models, fathead minnows (*Pimephales promelas*) and zebrafish (*Danio rerio*), to evaluate if resuspension of Penobscot River sediment significantly elevates the toxicity of river water as measured by fish survival, hatch success, development, and immune competence, whether bioactive metals and/or endocrine disrupting substances are present, and to provide preliminary information on the types of chemicals likely to desorb during resuspension.

Hypothesis: Release of contaminants bound to Penobscot River sediments during resuspension events will significantly increase the toxicity of river water to early life stage fishes.

Objectives:
- Use a simple laboratory model to simulate resuspension and chemical desorption of Penobscot River sediments
- Quantify persistent organic contaminants released by resuspended sediments
- Use fish models to evaluate lethality and early life stage effects of river water before and after sediment resuspension.
- Use transgenic zebrafish to detect the presence of bioactive metals in river water

- Develop recommendations for management of Penobscot River sediments prior to dam removal

Methodology

Sediment and water collection.
Sediments were collected in August 2005 from two Penobscot River sites, Bowdoin Point and the Marsh River region of Frankfort Flats. These sites, downstream of the former Holtrachem chemical plant and the Veazie dam, contain fine-grained sediments known to have elevated levels of mercury (K. Merritt, pers comm). A composite of three grab samples of the top 5 cm of sediment was taken at each site, homogenized, aliquoted and stored in pre-cleaned, acid-rinsed Teflon bottles at -20 C. River water was collected using pre-cleaned 4-L amber glass bottles, and stored at 4C until resuspended (see 'Desorption' below).

A third sample from Frankfort Flats was collected from the same area as our Marsh River sample in Spring 2003 by K. Merritt (UMaine, Engineering Program), characterized for mercury at that time and stored at -20 C. We used aliquots of this homogenate (Marsh River 03) to determine if any change had occurred, as indicated by the profile and amount of chemicals released during resuspension, during this 2.5 year interval.

Desorption of particle-bound contaminants into overlying waters.
Chemical desorption of sediments was achieved using a simple laboratory method. Wet sediment (equivalent to 20 g dry weight) was weighed into 2L Teflon screw-cap jars and filled with river water. The ratio of dry sediment weight:water (10g:L) was used to represent a maximum sediment loading, as is found during bedload transport (Ogston, Cacchione, Sternberg and Kineke 2000; Campbell, Laycak, Hoppes, Tran and Shi 2005). Pre-cleaned Teflon-coated stir bars were added to each jar, and sediments were stirred continuously on stir plates under refrigeration (4°C) for approximately 72 hours. This timeframe was chosen because in several studies of desorption of semi-volatile hydrophobic contaminants from sediments, maximum desorption of an initial fast-desorbing sorbed phase has been found to occur on the order of hours to a few days (Karickhoff and Morris 1985; Jepsen, Borglin, Lick and Swackhammer 1995; Lick and Rapaka 1996).

After stirring, sediments were allowed to settle for at least 48 hours. Samples were then filtered through pre-combusted glass fiber filters (Whatman GF/F, Maidstone, England), using a Buchner funnel and a vacuum aspirator flask. The filtrate was split into three aliquots for metals, organics, and biological assays and stored in pre-cleaned, acid-rinsed Teflon jars under refrigeration (4°C) until used for biological assays and/or chemical analysis.

Chemical analysis of Penobscot river water and 'resuspension water'.
River water and 'resuspension water' were characterized for general water quality (Table 1), and screened for a variety of organic contaminants, including priority polynuclear

aromatic hydrocarbon (PAH) pollutants, polychlorinated biphenyl (PCB) congeners, organochlorine pesticides, and metals.

Organic analysis
Two methods of organics extraction were utilized and compared using analyte recoveries from matrix spiking experiments. The first method was adapted from Westbom et al. (Westbom, Thorneby, Zorita, Mathiasson and Bjorklund 2004) using C18-impregnated Empore discs (3M Corporation, St. Paul, Mn). One-liter water samples previously filtered through glass fiber filters were extracted through Empore discs using a standard 47 mm Millipore filtration apparatus (Millipore Corporation, Billerica, MA). Prior to extraction, 2000 ng of the PAH surrogate (ortho-terphenyl) and the PCB surrogate (CB-143) standards (dissolved in methanol) were added to the sample to give a final concentration of 2 ng/uL. The discs were allowed to dry for approximately 2 hours in the hood, and then frozen (at -20°C) until analysis.

Samples were eluted from the Empore discs no later than 3 days after extraction. Empore discs were eluted with 3 x 5 mL of methylene chloride, as described (Westbom, Thorneby, Zorita, Mathiasson and Bjorklund 2004). These extracts were then dried over sodium sulfate and reduced in volume to 500 uL using a Zymark Turbovap II sample concentrator (Zymark Corporation, Hopkinton, MA). Internal standard (d_{10}-phenanthrene) was then added and the sample brought to a final volume of 500 uL via evaporation with a stream of nitrogen.

The second method of organic extraction was the more traditional liquid-liquid extraction method. One liter of filtered resuspension water was placed in a 2L separatory funnel and extracted with 3 x 100 mL of methylene chloride. Extracts were combined, dried over sodium sulfate and reduced in volume using a Buchi Rotavor rotary evaporator (Buchi Labortechnik AG, Flawil, Switzerland). Internal standard was added and the final sample volume of 500 uL was achieved via evaporation with a stream of nitrogen.

Instrumental Analysis- Organics
Target analytes included 19 PCB congeners, DDT metabolites and 17 EPA priority pollutant PAHs (Table 2). These compounds were chosen as a preliminary screen targeting the most ubiquitous aquatic pollutants as well as those identified as priority pollutants by the EPA. Samples were quantified from the internal standard added immediately prior to instrumental analysis (d_{10}-phenanthrene) and corrected for surrogate recoveries (ortho-terphenyl for PAH analytes, PCB congener 143 for PCBs and DDT metabolites).

Samples were analyzed on a Hewlett Packard 6000 GC interfaced with a Hewlett-Packard 7200 mass spectrometry system (Agilent Corporation, Palo Alto, CA). Instrumental conditions are listed in Table 3. The instrument was run in selected ion monitoring (SIM) mode, which provided maximum sensitivity for the ions of interest. A five-point calibration curve was analyzed prior to every run.

Instrumental Analysis- Metals
Filtrate was characterized for total mercury by cold-vapor atomic fluorescence (E.P.A.
2002), and for 14 additional metals by high resolution inductively coupled plasma mass
spectrometry (HR-ICP-MS) using a Thermo-Electron Element2 essentially as described
(Osterberg, Handley, Sneed, Mayewski and Kreutz 2006) by the Sawyer Environmental
Research Laboratory (UMaine). Isotopes were measured in low and medium resolutions;
^{107}Ag, ^{111}Cd, ^{133}Cs, ^{138}Ba, ^{208}Pb, ^{238}U were measured in low resolution and ^{27}Al, ^{51}V,
^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni ^{63}Cu, ^{66}Zn were measured in medium resolution. An ApexQ
sample introduction system was used with a 200µL/min self aspirating nebulizer.
Method detection limits for total mercury were 0.04 ng/L (MDL) and 0.2 ng/L (MDL
adjusted for dilution). Detection limits (ng/L) for the additional 14 metals were: Cd
0.03, Cs 0.007, Ba 0.33, Pb 0.15, U 0.006, Ag <10, Al 0.05, V 0.07, Cr 0.14, Mn
0.84, Co 0.41, Ni<10, Zn 10, and Cu 3.5 ng/L.

Quality Assurance and Quality Control- Chemical Analyses
Organics: Prior to sample analysis, matrix spikes, which were river water samples spiked
with the analytes of interest, were processed to compare recoveries from the two
extraction methods above. We found recoveries to be lower and much more variable
using the Empore disc method when compared to liquid-liquid extractions (Tables 4,5)
and so decided to extract the filtered "resuspension water" samples using liquid-liquid
extraction. Duplicate samples from each site were analyzed, along with two procedural
blanks, which consisted of 1L of filtered, deionized water carried through the entire
liquid-liquid extraction procedure.

Average recovery of the ortho terphenyl surrogate was 75 $\pm$ 17 % (mean $\pm$ standard
deviation) and was 96 $\pm$ 24 % for the chlorobiphenyl 143. Procedural blanks revealed no
detectable PCBs, DDTs or PAHs.

Metals: A full suite of quality assurance/quality control samples were run for metals
analysis in accordance with the methods used (E.P.A. 2002; Osterberg, Handley, Sneed,
Mayewski and Kreutz 2006), including filter blanks, calibration standards, standard
reference materials and matrix spike recovery samples. Some of the QA/QC results for
metals appear in Tables 7 and 8.

Sources and maintenance of fathead minnows and zebrafish
Fathead minnows (U.S. Environmental Protection Agency, Cincinnati, OH) and zebrafish
(UMaine Zebrafish Core) were used as first-step, inexpensive screening tools to
determine if resuspension of sediments significantly elevates river water toxicity to fish.
Fathead minnows were housed and spawned at the Aquaculture Research Center,
University of Maine, in flow-through tanks using standard procedures (EPA 1987; ASTM
1992). Water quality conditions in these tanks are listed in Table 6. Zebrafish embryos
(AB strain) and adults were provided by the UM Zebrafish Core Facility.

Fathead minnow spawning
Reproductively mature fathead minnows were held in 25 gallon, flow-through
community tanks at 25 C on a 16/8 L/D cycle, females in one tank, males in another tank.

To obtain embryos, one male was placed into a tank containing 6-8 females. Curved, PVC tiles were placed in each tank and checked daily for embryos. When found, the tile was removed to a separate tank, set against an airstone, and the embryos left to water-harden (3-4 hours) prior to removal by gently rolling them off into a Petri dish containing culture water. Live, healthy embryos of the same developmental stage were selected from the spawn and placed into exposure chambers (beakers or vials, see above). A typical spawn yielded ~ 200-300 embryos per female. A separate spawn was used for each replicate experiment.

Fathead minnow and zebrafish embryo exposures
FHM and ZF embryos were exposed to culture water, river water or 'resuspension water' in static renewal exposure systems for 5 (zebrafish) to 10 (fathead minnows) days. Preliminary studies were run to determine the time course of development from Stage 0 – larval stage 2 (L2) (Devlin, Brammer, Puyear and McKim 1996), to evaluate and identify contaminant-induced developmental abnormalities, and to identify optimal conditions for fathead exposures. For the preliminary studies, fathead embryos were placed in PVC cups with mesh bottoms placed inside 250 mL beakers (25 embryos/125 mL/beaker x 3 beakers) for 12 days. For the Penobscot River experiments, fathead embryos were exposed in 20 mL vials (5 embryos/vial, 5 vials per replicate). Fatheads were held under 16/8 L/D at 25 C for 10 days.

For the respiratory burst assays, zebrafish embryos were exposed to test water at 28C, 14/10 L/D from fertilization through day 5 in 100 mm diameter Petri dishes. All embryos were examined daily and dead individuals removed. For fathead minnow and zebrafish experiments, one spawn was used for each replicate experiment (one spawn=one replicate).

For the estrogen and metal bioassays, zebrafish embryos and MVLN cells were exposed to one of five treatments: distilled water with sodium bicarbonate and sea salt with a constant conductivity of 800μS and pH 6.87 (laboratory water control), Penobscot River water (river water), or 'resuspension water' from one of the three sites. The distilled water with sodium bicarbonate and sea salt is the water in which all zebrafish are maintained at the University of Maine Zebrafish Facility.

MVLN cell exposure conditions
MVLN cells were exposed to the same treatments as described above for zebrafish embryos except that all water samples were sterile filtered, diluted 1:5 or 1:10 in cell media (described below) and the sodium bicarbonate water was replaced with sterile distilled water.

Fathead minnow development: Hatch Success, Mortality and Developmental abnormalities
Mortality, developmental stage, developmental abnormalities, hatch success and days to reach L2 stage were recorded daily. Embryos were examined microscopically for evidence of hatching, death, developmental stage and abnormalities (e.g. tube heart, yolk-sac edema, pericardial edema, skeletal defects). For the Penobscot River studies,

embryos were exposed from developmental stage 13 (set #1, conducted in March/April using one male and 5-6 females) or developmental stage 11 (set#2, conducted in May 2006 using a new male with 6-8 new females), through L2.

Dose-response β–naphthoflavone experiment
A preliminary dose-response study was conducted using a well-studied PAH toxicant, β–naphthoflavone (βNF), to identify developmental abnormalities and to evaluate the effects of a PAH compound similar to those we would expect to find in contaminated river sediments. We also used this experiment to optimize exposure conditions for the Penobscot River experiments. For the βNF study, embryos were aqueously exposed to culture water, vehicle control (0.001% DMSO in culture water), or to a range of βNF doses (0.0001 – 1.0 μM) from developmental stage 13 (7-8 h post-fertilization) through larval stage L2, a stage unambiguously identified by the presence of an inflated swim bladder (Devlin, Brammer, Puyear and McKim 1996). β–naphthoflavone dosing solutions were prepared in culture water by serial dilution of a stock solution (10 μM βNF dissolved in DMSO).

Respiratory burst assay
The respiratory burst of white blood cells, specifically granulocytes, monocytes, and macrophages, in response to a pathogen is a measure of the strength of the innate immune system in an organism. The respiratory burst involves the reduction of molecular oxygen to the anionic radical, superoxide, which can be converted into a number of different reactive oxygen species (ROS). A strong innate immune system reacts to pathogens with a strong respiratory burst. Zebrafish embryos were exposed to river water, 'resuspension water' or laboratory contol water (described above) through 5 days post-fertilization, then transferred to a 96-well plate (one embryo per well), and analyzed for respiratory burst as described (Hermann, Millard, Blake and Kim 2004). Five replicate experiments were conducted, using a different spawn for each replicate. One 96 well plate was run for each replicate, for a total of 5 plates. Additional experiments were run to optimize conditions, these are not reported here.

Zebrafish Embryo Exposures for gene expression endpoints
Zebrafish embryos were exposed to 30mL control laboratory water, river water and 'resuspension water' treatments in polystyrene Petri dishes beginning at the 1-cell stage. Embryos that were exposed to distilled water with sodium bicarbonate/sea salt (control laboratory water), river water or 'resuspension water'. Treatment water was changed every 24 hours. Embryos were exposed for 48-168 hours. At each time point, 25 embryos were pooled per treatment and placed in 200μL lysis buffer. RNA was isolated in triplicate from each pool at each time point and extracted according to Ambion RNAqueous protocol. RNA integrity and concentrations were determined by Agilent RNA Nano 6000 chips.

Zebrafish CYP1A1 and VG mRNA Expression
CYP1A1 primers were designed using Primer3 based upon cDNA sequences attained from GenBank. CYP1A1, vitellogenin, and 18S primer sequences are provided in Table 7. CYP1A1 and vitellogenin expression were determined by fluorescence-based

quantitative real-time polymerase chain reaction (qRT-PCR) using the BioRad iScript SybrGreen qRT-PCR kit and Statagene MX4000. Expression fold change compared to embryos exposed to control laboratory water was determined according to Livak and Schmittgen (Livak and Schmittgen 2001).

Transgenic Zebrafish Embryo Exposure
A transgenic zebrafish line (ZM9) carrying a green fluorescent protein (GFP) reporter driven by the zebrafish metallothionein (MT) promoter was used to detect the presence of metal-active compounds in the treatment waters. Transgenic embryos were exposed to 30mL control and 'resuspension water' treatments in polystyrene Petri dishes beginning at the 1-cell stage for 96 hours. Ninety-six hours had been previously determined as the optimum stage at which to measure fluorescence (data not shown). Fluorescence was determined by a Packard Fusion platereader. Two replicate wells were run per experiment and each experiment was replicated three times (n=3).

MVLN cells
MVLN cells are MCF-7 human breast cancer cells transfected with a luciferase reporter gene downstream of the *Xenopus laevis* vitellogenin promoter. This cell line was developed by Dr. Michael Pons and graciously donated to us by Dr. John P. Giesy. Cells were maintained in 1:1 DMEM and Ham's F-12 media with phenol red and exposed to treatments in 1:1 DMEM and Ham's F-12 media without phenol red to reduce estrogenic interference. The vitellogenin promoter region is characterized by four estrogen responsive elements and exposure to estrogenic compounds provokes luciferase activity with a resulting increase in luminescence. By measuring luminescence after cell exposure, relative vitellogenin expression can be determined. To ensure that estrogen responsive elements were activated by estrogen agonists, the estrogen receptor antagonist, ICI, was used as a negative control. If a chemical is exerting estrogenic activity via the estrogen receptor, co-treatment with ICI will specifically block this effect, thereby confirming the specificity of the chemical's action. Cells were maintained and exposed using sterile techniques. All treatment water was sterile filtered using 0.2μm Acrodisc syringe filters. MVLN cells were exposed to media, three doses of 17β-estradiol (positive control), river water or 'resuspension water' treatments in 96-well polystyrene microplates. Luminescence was determined using the Promega Steady-Glo Luciferase Assay system and measured by the Packard Fusion platereader. Three replicates were run for each treatment.

Statistics
Quantitative RT-PCR data was analyzed using nested one way analysis of variance (ANOVA). All statistical analysis was carried out on raw Ct values, with very stringent standards causing higher likelihood of Type II error (failing to determine significance for a data point that is actually significant). Both equal variance and normality were validated prior to ANOVA. One way ANOVA allowed for analysis between all treatments for a given gene. When statistically significant differences were found between treatment groups, Tukeys HSD was used to determine which treatments were significantly different from unexposed controls at $\alpha=0.05$ for each test. Normalizing genes (18s rRNA) were also analyzed by one way nested ANOVA and $p>0.5$ was used to validate that exposures

did not influence levels of 18s rRNA, the gene against which CYP1A and VG mRNA values are normalized. All statistical analyses were done using SYSAT 11 software (SYSTAT Inc.).

For the fathead minnow development experiments (hatch success, percent survival, percent occurrence of abnormalities) and for the zebrafish respiratory burst experiments, differences among treatments were evaluated by single-factor ANOVA. To statistically evaluate development time (days to reach L2stage), we used 2-way ANOVA (treatment x day). We used a significance level of $P<0.05$ throughout.

Summary of Principle Findings

- Resuspension, even under conditions of high sediment:water ratios for extended periods of time under vigorous stirring, resulted in relatively low contaminant concentrations (ppt) in the river water. This could be due to low levels of contaminants in the sediments, or low contaminant release. To differentiate these possibilities requires measurement of contaminant concentrations in the test sediments, which was too costly to include in this initial pilot study.

- Repeated resuspension of Frankfort flats sediments does not appear to have affected the release of organics or metals; sediments collected from Marsh River in 2003 and 2005 showed no difference in chemical profile or concentration in resuspension water.

- Sediment resuspension provoked delays in fathead minnow development and suppressed the innate immune system of zebrafish. Effects on development were slight, and likely not biologically significant. Suppression of the innate immune response should be followed up with additional studies using fish species resident in the Penobscot River, such as fathead minnows, Atlantic salmon and smallmouth bass.

- Penobscot River water alone elevated gene expression of the pollutant biomarker, CYP1A1, in zebrafish embryos, suggesting that chemical inducers are likely present in the river. Although there was a tendency for sediment resuspension to further elevate CYP1A1 expression, this effect was not statistically significant. These studies should be repeated with other fish species, particularly those resident in the Penobscot river, to determine whether immune suppression is a widespread fish response to sediment resuspension. Further analyses to identify the chemical inducers of CYP1A1 in this system could be used to identify sources and chemicals not yet known in this watershed.

- We found no evidence of endocrine disruption, suggesting that resuspension of sediments from these particular sites is unlikely to provoke adverse estrogenic effects in Penobscot River fish.

Conclusions & Significance

- The multi-pronged approach of this study, chemical analysis coupled with multi-level biological effects, provides a powerful assessment of potential risk useful for any resuspension event, including spring and fall floods, dredging, stream bank remediation (riparian removal) or any event that resuspends significant amounts of sediment in the environment.

- Sediment-bound chemicals from the Frankfort Flats region appear to be fairly recalcitrant to release as evidenced by the finding that repeated tidal and spring/fall flood-mediated resuspension does not appear to reduce sediment release of contaminants over time, including release of mercury. Dam removal in the Penobscot River is not likely to change this.

- Resupsension of Frankfort Flats sediments following dam removal is not likely to be a significant source of contaminants and will likely produce little, if any, adverse biological effects due to released contaminants.

- Whether sediment movement following dam removal will have physical, non-contaminant effects (e.g. smothering) requires further study.

Recommendations

Based on these preliminary findings, we find no reason to recommend management of Frankfort Flats sediments prior to removal of the Veazie and Great Works dams.

Studies of chemical release and biological toxicity should be conducted on other sediments downstream of these dams, particularly the PAH-contaminated sediments in Dunnett's Cove in Bangor (Gagnon 2004), prior to removal of the Veazie and Great Works dams.

Detailed Results and Discussion

This study addresses the relative importance of sediment resuspension as a source of toxicants, provides preliminary information on which chemicals are desorbed and provides recommendations as to whether river sediments should be remediated or removed prior to dam removal.

Chemical release with sediment resuspension.
    a. Metals
Very low concentrations of metals were observed in Penobscot River water alone. Resuspension appeared to elevate total mercury levels (Table 8), and the concentrations of some, but not all, of the 14 other metals analyzed (Tables 9A, 9B). Because this was a pilot study with limited funds, only one sample was analyzed for each site, precluding

statistical analysis. However, differences among water samples are slight and likely statistically insignificant.

        b. Organics

As for the metals, very low concentrations of organic compounds were observed in Penobscot River water alone. Of the 17 priority PAH pollutants analyzed for, only 5 PAHs were detected. Resuspension of Penobscot river sediments elevated levels of these PAHs by 2-50 fold relative to river water alone (Table 10). Of the 209 possible PCB congeners, none were detected. Similarly, the chlorinated pesticides DDT, DDE and DDD, were not detected.

Enhanced release of hydrophobic contaminants from suspended sediments have been demonstrated in a number of studies for organic contaminants (Latimer, Davis and Keith 1999; LeBlanc, Gulnick, Brownawell and Taylor 2006) as well as metals (Cantwell, Burgess and Kester 2002), including mercury (Kim, Mason, Porter and Soulen 2004). The phase associations of these released contaminants range from particulate, colloidally-associated to truly dissolved, depending on a variety of factors, including pH and the degree of oxidation of sediment mineral phases (Eggleton and Thomas 2004). Resistance to desorption has been described in a number of studies (Chen and Mayer 1999; Lamoureux and Brownawell 1999) and so it is possible that PAH compounds present in these sediments are resistant to desorption. The presence of soot carbon has been shown to retard PAH desorption from sediments in a number of studies (see (Gustafsson, Haghseta, Chan, Macfarlane and Gschwend 1997). Also it has been shown that PAHs in highly weathered sediments are resistant to desorption (LeBlanc 2001). Examining desorption kinetics and understanding rate limitations to desorption requires chemical analysis of bioavailable, labile organics present in the sediments themselves, and was beyond the scope of this study.

The aqueous concentrations of total unsubstituted PAH we observed following resuspension of Penobscot sediments into river water (101 – 232 ppt) are in the same range as dissolved concentrations found in moderately impacted coastal areas, such as the Rhone Delta in the Meditteranean Sea (Bouloubassi and Saliot 1991). In contrast, total dissolved PAH concentrations in the heavily impacted Yangtze River in China ranged from 22 – 380 ppm (Huang, Zhang and Yu 2003) while remote lakes in the Pyrenees and Alps had extremely low PAH concentrations (0.7 – 1.1 ppt) (Vilanova, Fernandez, Martinez and Grimalt 2001). The presence of alkylated naphthalene, the only target PAH with an alkyl substituent present in our water samples, suggests that some of the PAH loading may be derived from petroleum sources (NationalResearchCouncil 1985), although more in depth characterization of the PAH distribution would be needed to demonstrate this conclusively.

One conclusion that can be drawn from the organics and metals data is that repeated resuspension of Frankfort flats sediments does not appear to have affected chemical release. Sediments collected from Marsh River in 2003 and 2005 showed no difference in chemical profile or concentration in resuspension water.

Effects in fish:
Overview
We found that resuspension of sediments from Marsh River (Marsh River and Marsh River 03) and Bowdoin Point into Penobscot River water provoked little to no toxic effects on our test organisms.

Specific findings
      a. Preliminary study: Fathead minnow dose-response to β–naphthoflavone
As expected, fathead minnow embryo-larval development was adversely affected by exposure to 1 μM, the highest concentration of β–naphthoflavone we used. Exposure to this dose significantly increased the incidence of developmental deformities (Figure 1) and delayed embryo-larval development relative to controls and to all other βNF doses (Table 11). Similar deformities have been noted in other embryo-larvae exposed to PAHs in this dose range (Arzuaga 2004). Interestingly, survival and hatch success were unchanged relative to controls at any βNF dose.

      b. Fathead minnow development in response to Penobscot River water exposures
Although we found a statistically significant delay in development in fathead minnow embryos exposed to 'resuspension water' relative to 'control water' treatments, this represented a delay of only 1 day, and was only observed in the March-April (Table 12), but not in the May (Table 13), experiments. The main difference between these two sets of experiments was the developmental stage of the embryos when exposures began, the May embryos being in the blastula stage (stage 11) while the March-April embryos had already reached epiboly (stage 13) when exposure began. We also found survival and percent hatch to be considerably lower in the embryos exposed at an earlier age. This may reflect age-specific differences, with the younger life-stage being more sensitive, or it may simply be that the younger embryos were not sufficiently water-hardened prior to removal from the tiles (the latter seems unlikely as the younger embryos appeared to be as resilient to physical removal as the older embryos). In any case, since all other developmental parameters were unaffected (percent hatch, percent survival, percent developmental abnormalities) relative to controls, we consider the one day delay in development to be biologically insignificant.

      c. Zebrafish Respiratory Burst – Immune function
Zebrafish embryos exposed to 'resuspension water' from fertilization to 5 days post-fertilization exhibited a significantly suppressed respiratory burst response relative to embryos exposed to either culture water or river water alone (Figure 2). Suppression of innate immune response in zebrafish embryos using this assay has been reported for other toxicants, including arsenic (Hermann and Kim 2005).   Suppression by arsenic was similar to that observed here, and suggests that this suppression may be biologically meaningful.

      d. Endocrine disruption bioassays
We found no evidence of estrogen-active substances in Penobscot River water either before or after sediment resuspension. Several assays were used to evaluate this,

including vitellogenin gene expression and an estrogen-sensitive mammalian cell line, MVLN cells.

Vitellogenin is a phospholipoprotein whose expression is strongly elevated in oviparous animals exposed to estrogenic compounds. For example, VG levels are high in recrudescing females whose blood levels of estrogens are elevated. However, VG expression in embryos or in male fish is unexpected and inappropriate, and indicates exposure to estrogenic compounds, either through water or diet. We found very low levels of VG gene expression in zebrafish embryos and these were unaffected by exposure to any of the treatments (Figure 3). In contrast, zebrafish embryos exposed to ethinylestradiol, a potent estrogen, exhibit VG induction levels of over 40 fold above unexposed controls (data not shown). Our results suggest that either the concentration of estrogenic compounds present in river sediment released during resuspension was insufficient to provoke an estrogenic response, or that such chemicals were not present in these sediments.

The mammalian cell line, MVLN, which is sensitive to estrogenic compounds, also failed to show any significant response to Penobscot River water samples, either before or after sediment resuspension (Figure 4). This is in direct contrast to the positive control, 17β-estradiol, a potent estrogen which strongly activated the MVLN reporter, a response consistently seen with this cell line (Snyder, Villeneuve, Snyder and Giesy 2001; Furuichi, Kannan, Giesy and Masunaga 2004; Van den Belt, Berckmans, Vangenechten, Verheyen and Witters 2004). The estradiol effect was blocked by the estrogen receptor antagonist, ICI-182,780, confirming that estradiol is exerting its effects directly through the estrogen receptor.

d. CYP1A expression in zebrafish embryos

Expression of the contaminant-inducible enzyme, CYP1A, increased following exposure to Penobscot River water before (River water) and after (Bowdoin Point, Marsh River, Marsh River 03) sediment resuspension, relative to laboratory control water (Figure 5).

The time course of this induction was rapid. By 48 hours post-fertilization (hpf, the first time-point in our study), CYP1A expression was significantly increased in embryos exposed to Marsh River 'resuspension water' relative to laboratory control water (40 fold above control water), reaching peak induction at 96 hours (up to 70 fold above control water) (Figure 5). Thereafter, CYP1A mRNA levels began to fall (Figure 5). The time-course of this induction differs from that reported by others measuring CYP1A mRNA levels in zebrafish embryos exposed to the model CYP1A inducer, TCDD. In those studies, zebrafish CYP1A mRNA transcript levels were elevated in TCDD-treated embryos as early as 15 (Mattingly and Toscano 2001) and 24 hpf (Andreasen, Spitsbergen, Tanguay, Stegeman, Heideman and Peterson 2002), and continued to rise at least until 120 hpf (Andreasen, Spitsbergen, Tanguay, Stegeman, Heideman and Peterson 2002). It is likely that the rapid increase in response to TCDD reflects the high potency of this inducer relative to the compounds present in our treatment water. In contrast to our findings, however, CYP1A mRNA fold-induction was much lower than ours, being no more than 7 fold above controls (Andreasen, Spitsbergen, Tanguay, Stegeman,

Heideman and Peterson 2002).   This may reflect the much shorter exposure time used by Andreasen et al (1 hour exposure) versus our exposures (168 hr).

Although the data suggest sediment resuspension further enhanced CYP1A induction, CYP1A levels in embryos exposed to 'resuspension water' were not significantly different from those in embryos exposed to river water treatments alone.

CYP1A is a biomarker of organic contaminants, including the potent toxicants PAHs, dioxins, and coplanar PCBs (Stegeman and Hahn 1994). Increased CYP1A expression indicates that at least some of these chemicals are likely present and bioavailable in Penobscot River water at levels sufficient to induce a biochemical response (Bucheli and Fent 1995). The PAH levels detected in the treatment water samples (Table 10) are approximately 10 fold lower than concentrations of a model PAH, benzo[a]pyrene, shown to induce CYP1A enzymatic activity in the gills of fish at concentrations as low as 10^{-9}M (250 ng BaP/L) (Jonsson 2003). Taken together, our results suggest that CYP1A inducing chemicals other than those we analyzed for are likely present in the treatment waters.

     e. Bioassay for metal exposure

Transgenic zebrafish embryos were used as biomarkers for the presence and biological activity of metals in the water samples. The metallothionein (MT) reporter, sensitive to metals exposure, in these transgenic zebrafish failed to respond to any of the Penobscot river samples, either before or after sediment resuspension (Figure 6).   Preliminary studies in our laboratory found the lowest concentrations that induce the MT transgenic zebrafish are 25 uM Zn (4,000 ng/L), 2.5 uM Cd (460 ng/L $CdCl_2$) and 25 nM Hg (4 ng/L $HgCl_2$) (Mayer, unpublished data). Cadmium concentrations in Penobscot river water and 'resuspension water' (11-34 ng Cd/L) are 10-40 fold lower than the bioactive Cd concentrations (460 ng/L), and might not be expected to activate the MT reporter in our transgenic fish. However, levels of Zn and Hg in the Penobscot river water and 'resuspension water' (9200-18,000 ng Zn /L; 3-80 ng Hg/L) are far higher than those known to induce the MT gene in our transgenic fish (4,000 ng Zn/L; 4 ng Hg/L) and would be expected to be bioactive in the transgenic fish. One possible explanation for this is loss of metals to the the plastic petri dishes used for the zebrafish exposures. Alternatively, the presence of high DOC (Table 1) may alter bioavailability of these metals to the zebrafish. Analysis of metal-spiked water as well as metal spiked, high DOC Penobscot river water, before and after storage in plastic petri dishes, is needed to determine the nature of metal dynamics in our treatment system.   Based on what the transgenic assay indicates, however, we conclude that metals present in the Penobscot river water, either before or after sediment resuspension, are not likely to exert metal-mediated effects in fish.

Acknowledgements

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Table 1. Water Quality measurements for Penobscot River water before (River Water) and after (Bowdoin Point, Marsh River, Marsh River 03) sediment resuspension. NA = not analyzed

Water	ANC (μe/L)	Conductivity (μS/cm)	pH	Salinity (o/oo)	DOC (mg/L)
River Water	218.96	42.36	7.35	0	8.23
Bowdoin Point	556.13	754	7.34	0	NA
Marsh River	376.5	495.5	7.40	0	25.0
Marsh River 03	434.27	906	7.33	0	NA

Table 2. Analytes and ions monitored for quantitation

Analytes	Quantification[1] Ions m/z[2]	Confirmation[2] Ions m/z	Detection limit[4] ng/L
Clb_1	188	152, 190	10
2ClB_5	222	152, 224	10
3ClB_31	256	258, 186	10
4Cl_44	292	290, 220	10
4Cl_52	292	255, 226	10
4Cl_66	292	290, 220	10
OP_DDE	318	246, 248	10
5ClB_87	326	324, 254	10
5ClB_101	326	291, 256	10
PP_DDE	318	246, 176	10
5ClB_110	326	253, 184	10
OP_DDD	235	165, 199	10
6ClB_138	360	325, 290	10
PP_DDD	235	237, 165	10
6ClB_141	360	362, 290	10
6ClB_151	360	325, 290	10
6Cl_153	360	325, 290	10
7ClB_170	394	359, 324	10
7ClB_180	394	359, 324	10
7ClB_183	394	360, 323	10
7ClB_185	394	360, 323	10
9ClB_206	464	428, 392	10
Naphthalene	128	127, 129	10
2-methylnaphthalene	142	141, 115	10
acenaphthylene	152	151, 153	10
acenaphthene	154	153, 152	10
fluorene	166	165, 167	10
phenanthrene	178	176, 179	10
anthracene	178	176, 179	10
fluoranthene	202	200, 203	10
pyrene	202	200, 203	10
benz[a]anthracene	228	226, 227	10
chrysene	228	226, 227	10
benzo[b]fluoranthene	252	250, 253	10
benzo[k]fluoranthene	252	250, 253	10

Table 2 continued

benzo[a]pyrene	252	250, 253	10
indeno[1,2,3,c,d]pyrene	276	274, 277	10
dibenz[a,h]anthracene	278	279, 279	10
benzo[g,h,i]perylene	276	274, 277	10
d10 phenanthrene (Internal Standard)	188	189, 184	
CB-143 (PCB surrogate standard))	360	325, 290	
o-terphenyl (PAH surrogate standard)	230	229, 215	

[1]Quantification ion used for quantifying each analyte
[2]Mz=mass:charge ratio
[3]Confirmation ions must be present in a specified relative abundance to positively
identify the analyte of interest
[4]Detection limit was determined by spiking river water with each analyte and determining
the concentration that produced a signal three times above the signal:noise ratio. The
detection limit was conservatively chosen to be the same for all analytes, even though
some compounds could be detected at concentrations 4 – 10 times lower.

Table 3. Instrumental conditions for analysis of organic compounds by the Hewlett Packard 6890/5973 GC/MS System

Injection conditions:	splitless injection, injection port Temp = 275°C
GC column	Phenomenex ZB-5 MS (5% phenyl methyl siloxane), 30 m length, 0.25 mm ID, 0.25mm film thickness
Temperature program:	80°C, hold for 2 minutes 80°C - 120°C @ 30°C/minute 120°C - 150°C @ 10°C/minute 150°C - 290°C @ 3°C/minute, 10 minute hold
MS parameters	electron impact ionization, 70eV [1]SIM mode

[1]SIM = selected ion monitoring

Table 4. Comparison of PCB and organochlorine recoveries from Matrix spikes using Empore discs and liquid-liquid extractions

	Empore disc		**Liquid-liquid**	
Compound	Mean[1]	Stdev2	Mean[1]	Stdev[2]
Clb[3]_1	249	21.9	89.2	20.5
2ClB_5	223	65.2	97.7	18.7
3ClB_31	155	41.1	91.7	5.0
4Cl_44	135	23.3	89.7	0.2
4Cl_52	145	20.6	95.7	1.8
4Cl_66	122	12.4	101.2	4.2
5ClB_87	93	6.9	94.5	4.3
5ClB_101	95	5.7	95.8	2.4
PP_DDE	85	4.2	97.7	3.0
5ClB_110	98	8.6	92.6	4.5
6ClB_138	61	1.8	94.8	2.1
PP_DDD	124	13.2	106.5	7.9
6ClB_141	50	7.2	96.2	1.4
6ClB_151	53	6.6	97.2	3.1
6Cl_153	54	6.1	99.1	1.3
7ClB_170	34	4.0	100.1	2.3
7ClB_180	34	5.6	97.3	2.3
7ClB_183	28	8.0	100.5	1.1
7ClB_185	28	6.0	105.4	2.2
9ClB_206	14	8.6	102.5	3.6

[1]Mean of three samples.
[2]Standard deviation
[3]Clb-# =chlorobiphenyl-IUPAC, using the naming convention of Ballschmitter and Zell (Ballschmitter and Zell 1980).
[4]RCl_44=chlorobiphenyl congener 44. The number preceding the Cl indicates the degree of chlorination (here, 4 chlorine atoms). The number following the Cl is the IUPAC designation (Ballschmitter and Zell 1980).

Table 5. Comparison of PAH recoveries from matrix spike samples extracted by empore disc and liquid-liquid extraction

Compound	Empore disc		Liquid-liquid	
	Mean[1]	Stdev2	Mean[1]	Stdev[2]
Naphthalene	61.9	7.4	88.7	20.9
2-methylnaphthalene	68.3	7.2	95.5	16.8
acenaphthylene	50.5	9.8	111.8	21.6
acenaphthene	80.1	9.3	111.3	15.5
fluorene	87.4	10.6	127.0	17.1
phenanthrene	82.6	7.4	126.4	18.3
anthracene	41.8	5.8	114.9	12.7
fluoranthene	65.6	1.3	112.1	9.1
pyrene	66.2	1.4	107.0	7.5
benz[a]anthracene	2.5	0.1	74.9	6.1
chrysene	3.6	0.6	80.9	5.8
benzo[b]fluoranthene	1.4	0.3	56.6	2.0
benzo[k]fluoranthene	1.6	0.5	62.9	3.3
benzo[a]pyrene	0.0	0.0	49.1	0.2
indeno[1,2,3,c,d]pyrene	0.0	0.0	48.7	11.1
dibenz[a,h]anthracene	0.0	0.0	72.5	8.6
benzo[g,h,i]perylene	0.1	0.1	60.0	3.6

[1]Mean of threee samples. [2]stdev = standard deviation

Table 6. Water quality measurements for fathead minnow rearing and spawning water at the Aquaculture Research Center

Parameter	
Temperature (C)	25
pH	7 - 8
Alkalinity (ppm CaCO$_3$)	100
Hardness (ppm CaCO$_3$)	120
Flow rate (mL/min)	160
Dissolved oxygen (mg/L)	6.5
Total Ammonia (ppm NH$_3$-N)	<0.25
Nitrate (ppm NO$_3^{-2}$)	1 – 2
Nitrate (ppm NO^{-2})	0

Table 7. Primer sequences for zebrafish messenger RNA quantification by Q-PCR. See methods for details.

Gene product	5' forward primer	5' reverse primer
cyp1a1	CCTGGGCGGTTGTCTATCTA	TGAGGAATGGTGAAGGGAAG
vitellogenin 1	TTTGAACGAGCAACGAACAG	AGTTCCGTCTGGATTGATGG
18s rRNA	CATGGCCGTTCTTAGTTGGT	CGGACATCTAAGGGCATCAC

Table 8. Total mercury concentrations in Penobscot River water before (River Water) and after (Bowdoin Pt, Marsh River, Marsh River 03) resuspension of Penobscot River sediments. All values in ng/L (ppt). Replicate injections were within 0.6%.

Water Sample	Total Mercury (ng/L)
River Water	3.29
Bowdoin Point	22.5
Marsh River	82.6
Marsh River 03	61.7
Method Blank	0.05
Filter Blank	1.13

Table 9A. Metal concentrations in Penobscot River water before (River Water) and after (Bowdoin Pt, Marsh River, Marsh River 03) resuspension of Penobscot River sediments. All values in ng/L (ppt). SRM = standard reference material. Duplicate injections were all within 5% except for Cd and Al.

Metal Water Sample	Cd (ng/L)	Cs (ng/L)	Ba (ng/L)	Pb (ng/L)	U (ng/L)	Ag (ng/L)	Al (ng/L)
River Water	11	3	19821	73	93	5	63966
Bowdoin Pt	17	17	23219	340	152	18	49599
Marsh River	27	19	30068	429	155	24	87303
Marsh River 03	34	21	54701	1046	89	36	96033
Lab Blank	0.08	0.03	0.89	0.22	2.22	0.06	142.57
SRMcheck	14	7	12483	79	49	4	53625
duplicate inj w/in (%):	10.6%	5.7%	1.7%	1.5%	3.7%	0.0%	28.7%

Table 9B. Metal concentrations in Penobscot River water before (River Water) and after (Bowdoin Pt, Marsh River, Marsh River 03) resuspension of Penobscot River sediments. All values in ng/L (ppt). SRM = standard reference material. Duplicate injections were within 3%.

Metal Water Sample	V (ng/L)	Cr (ng/L)	Mn (ng/L)	Co (ng/L)	Ni (ng/L)	Cu (ng/L)	Zn (ng/L)
River Water	226	228	1914	31	1146	5860	9270
Bowdoin Pt	4136	764	4742	83	1724	5819	13689
Marsh River	4740	805	2107	68	1936	6720	18024
Marsh River 03	1852	753	18672	84	2551	6020	18140
Method Blank	0.78	8.63	9.35	0.40	1.86	1.58	7.13
SRMcheck	346	320	3536	34	682	1696	913
duplicate inj w/in (%):	2.2%	1.7%	0.0%	3.0%	1.8%	1.6%	3.3%

Table 10. Organic analyte concentrations in filtered river water before and after sediment resuspension

Analytes	River water ng/L	Bowdoin Point ng/L	Marsh River ng/L	Marsh River 03 ng/L
Naphthalene	19.8 ± 11.4[1]	45.8 ± 15.1	18.3 ± 8.2	41.0 ± 10.0
2-Methylnaphthalene	2.84 ± 1.3	69.9 ± 0.5	9.4 ± 13.3	70.1 ± 4.8
Phenanthrene	2.72 ± 1.5	21.2 ± 11.5	39.4 ± 29.3	16.9 ± 8.1
Fluoranthene	2.13 ± 1.3	42.3 ± 23.0	74.0 ± 14.0	39.4 ± 24.2
Pyrene	1.80 ± 1.1	40.2 ± 26.1	99.8 ± 26.5	11.7 ± 15.7
Σ PAH	26	150	232	109

[1]Mean +/- SD for 2 replicate analyses

Table 11. Development parameters for fathead minnow embryo-larvae exposed to graded doses of the PAH toxicant, β-naphthoflavone (βNF).

Treatment (μM βNF)	N[a]	Percent Hatch	Percent Survival	Percent Deformities, type	Mean day to reach L2
Culture water[b]	6	100	99.2 (1.9) [c]	5.8 (4.4), PE[d]	8.2 (0.3)
DMSO (0.01%)		100	98.7 (2.3)	8.2 (6.8), PE	7.8 (0.1)
0.0001	3	100	97.0 (5.2)	4.2 (4.0), PE	8.0 (0.1)
0.01	3	100	93.7 (7.3)	10.5 (3.4), PE	7.9 (0.3)
0.1	3	100	96.6 (3.0)	6.8 (2.8), PE	8.4 (0.2)
1.0	3	100	94.7 (9.2)	43.4 (1.0), PE,JM,YS,GA	8.3 (0.2)

[a]number of replicate experiments (each expt: 3 pools, 25 embryos/pool)
[b]water from the Aquaculture Research Center in which adult fathead minnows were maintained and spawned.
[c]Mean (SD)
[d]PE-pericaridal edema, JM- jaw malformations, YS- yolk sac edema, GA-gill abnormalities

Table 12. Development parameters for fathead minnow embryo-larvae exposed to Penobscot River water before (River water) and after (Bowdoin Point, Marsh River, Marsh River 03) resuspension with river sediments. Set #1 – March/April 2006.

Treatment	N[a]	Percent Hatch	Percent Survival	Percent Deformities, type	Mean day to reach L2
Culture water[b]	4	100	100	2.0 (2.3), PE [d]	7.7 (0.1)
River water	4	100	99.0 (2.0)	2.0 (2.3), PE	7.3 (0.1)*
Bowdoin Point	4	100	98.0 (2.3)	4.0 (5.7), PE	7.8 (0.2)#
Marsh River	4	94.0 (9.5)[c]	80.0 (20.4)	4.0 (3.3), PE	8.1 (0.2)#
Marsh River03	4	100	99.0 (2.0)	4.0 (3.3), PE	8.1 (0.2)#

[a]number of replicate experiments (each expt: 5 pools, 5 embryos/pool)
[b]water from the Aquaculture Research Center in which adult fathead minnows were maintained and spawned.
[c]Mean (SD)
[d]PE-pericardial edema
*significantly different from Culture water @ p<0.01
#significantly different from River water @ p<0.001

Table 13. Development parameters for fathead minnow embryo-larvae exposed to Penobscot River water before (River water) and after (Bowdoin Point, Marsh River, Marsh River 03) resuspension with river sediments. Set #2 – May 2006.

	N[a]	Percent Hatch	Percent Survival	Mean day to reach L2
Culture water[b]	3	87.8 (7.1)[b]	85.1 (10.1)	8.1 (0.4)
River water	3	89.3 (2.3)	74.7 (10.1)	8.0 (0.6)
Bowdoin Point	3	90.7 (10.1)	84.0 (6.9)	7.9 (0.5)
Marsh River	3	89.3 (10.1)	78.7 (16.2)	7.9 (0.2)
Marsh River 03	3	94.7 (9.2)	89.3 (8.3)	7.8 (0.2)

[a]number of replicate experiments (each expt: 5 pools, 5 embryos/pool)
[b]water from the Aquaculture Research Center in which adult fathead minnows were maintained and spawned.
[c]Mean (SD)

Figure Legends

Figure 1. Normal and abnormal development in fathead minnows. (a, b) appearance of heart, yolk sac, scales, jaw and gill analgens in normally developing fathead minnows, stages 28 – L2, (c-f) βNF-induced (c) abnormalities in jaw and scales, (d) abnormal jaw, yolk sac edema, pericardial edema, (e) peridcardial edema, (f) gill anlagen and jaw abnormalities.

Figure 2. Innate immune system function, measured by respiratory burst response, of zebrafish embryo-larvae exposed for 5 days to Penobscot River water before (river water) and after (Bowdoin Point, Marsh River, Marsh River 03) sediment resuspension. Values represent mean +/- SEM, n=5 replicate experiments of 6 embryos each. Significantly different from RW at *$P < 0.003$, **$P < 0.001$. CW = culture water, RW=river water, BP=Bowdoin Point, MR=Marsh River, MR03=Marsh River 2003 collection.

Figure 3. Vitellogenin gene expression (mRNA levels) in zebrafish embryos exposed to Penobscot River water before (River water) and after (Bowdoin Point, Marsh River, Marsh River 03) resuspension with river sediments. Values represent means +/ - exponential error of the mean for 3 intrassay replicates. Significantly different from *laboratory control water, # river water, + Marsh River
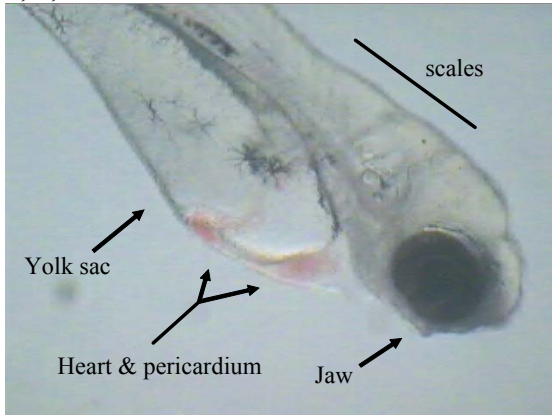
Figure 4. Estrogenic response measured using MVLN cells exposed to Penobscot River water before (River water) and after (Bowdoin Point, Marsh River, Marsh River 03) resuspension with river sediments. Media treatment served as negative control, 17β-estradiol (17β-E2) served as positive control, and ICI was used to confirm chemical specificity for the estrogen receptor. Values represent means +/ SEM, for 3 replicate wells per treatment. *Significantly different from all other treatments at $P < 0.05$.

Figure 5. CYP1A gene expression (mRNA levels) in zebrafish embryos exposed to Penobscot River water before (River water) and after (Bowdoin Point, Marsh River, Marsh River 03) resuspension with river sediments. CW= culture water. Values represent means +/ SEM for 3 intrassay replicates. Significantly different from *laboratory control water, #river water.

Figure 6. Response of zebrafish embryos carrying a transgene for metallothionein to exposure to Penobscot River water before (River water) and after (Bowdoin Point, Marsh River, Marsh River 03) resuspension with river sediments. Values represent means +/ SEM for 3 replicate wells per treatment.

Figure 1.

a, c, e

b, d, f

Figure 2.

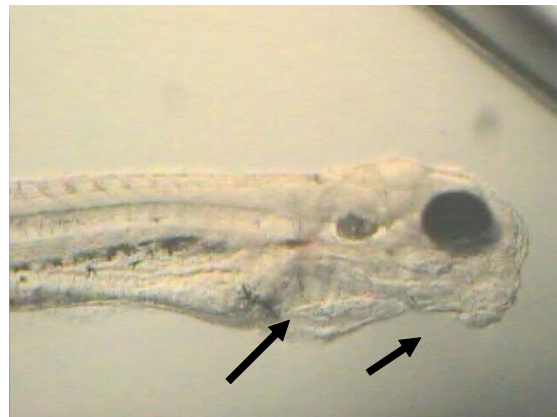**Zebrafish Respiratory Burst Response**

Figure 2.

Figure 3

Zebrafish Vitellogenin Expression
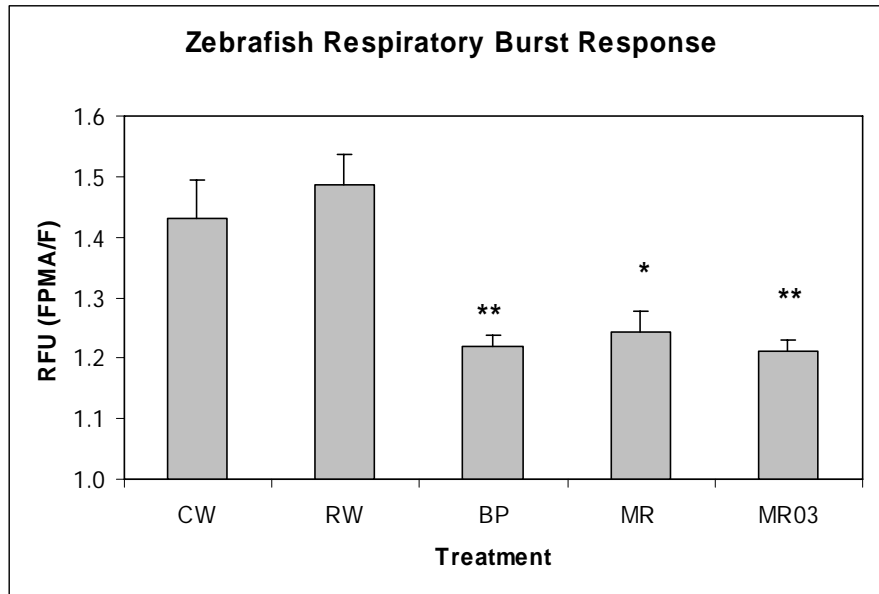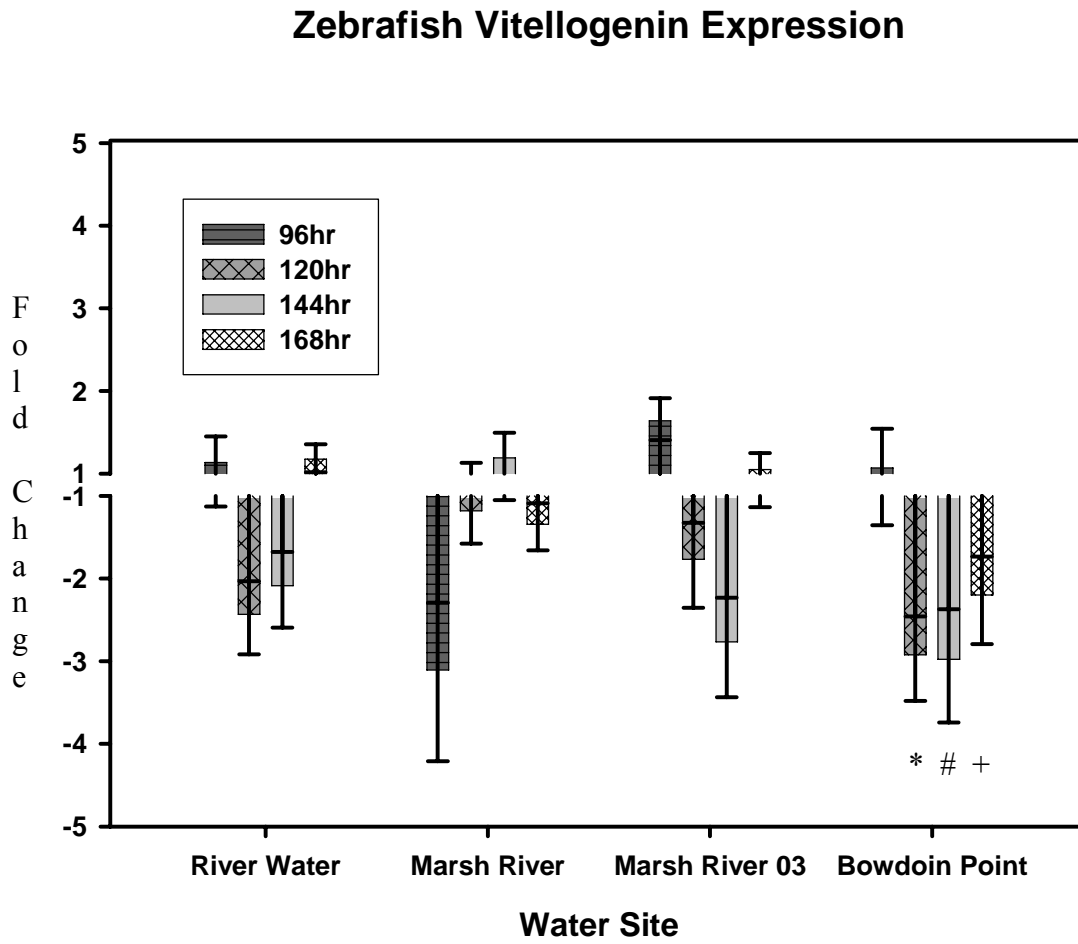
Figure 4.

MVLN Assay for Estrogenicity
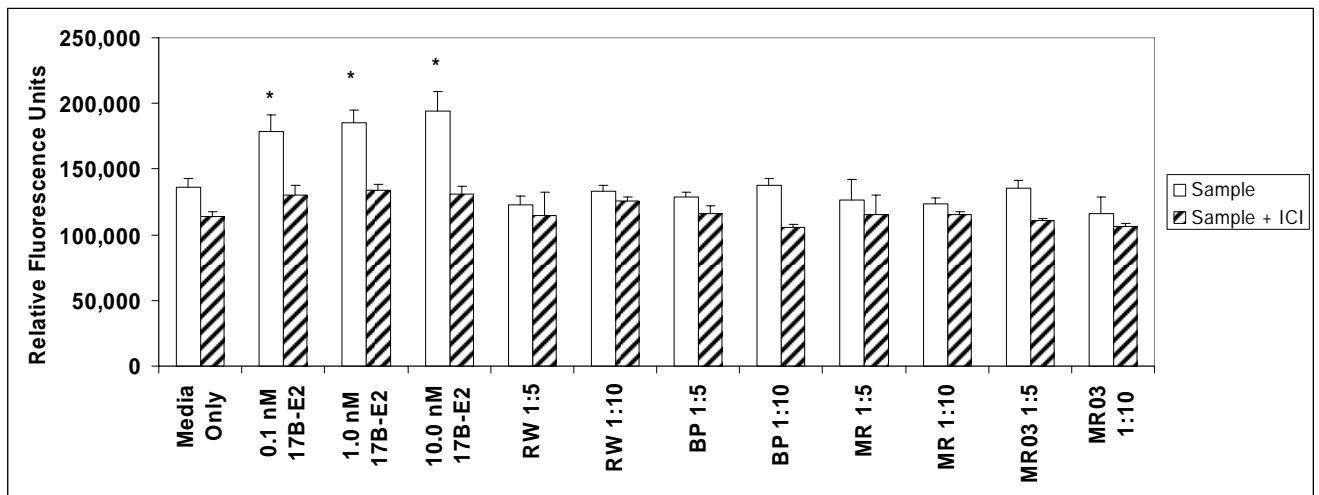
Figure 5

Zebrafish CYP1A1 Expression
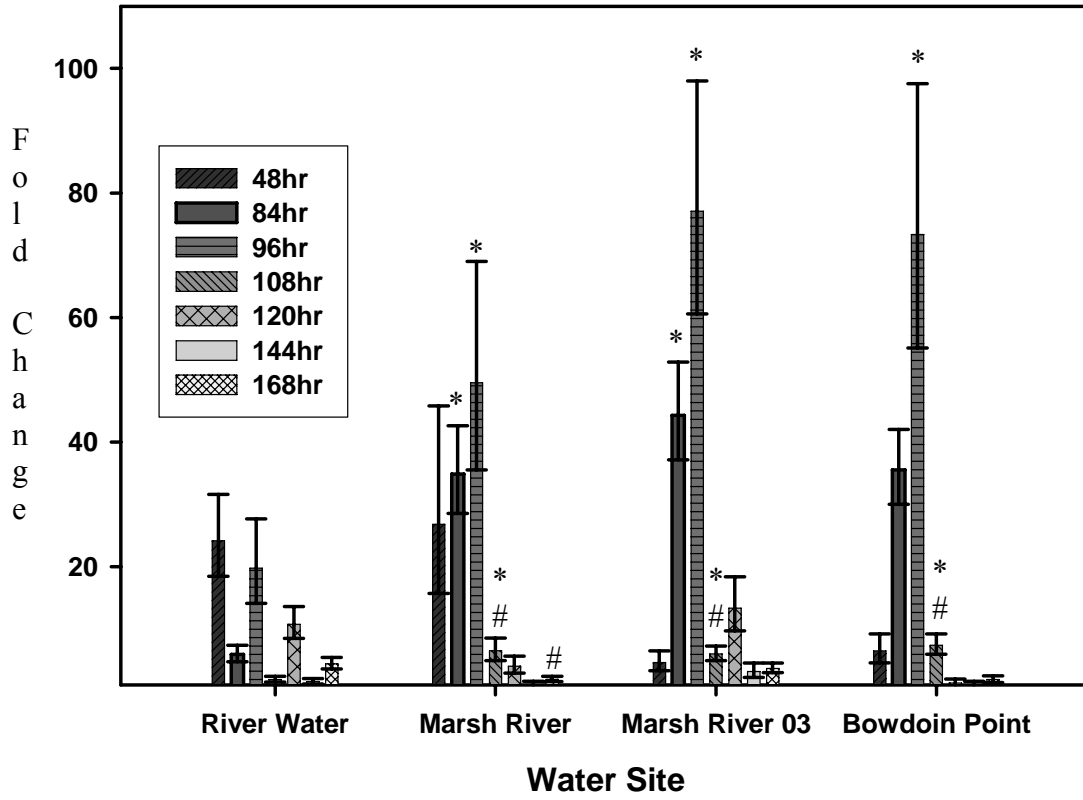
Figure 6.
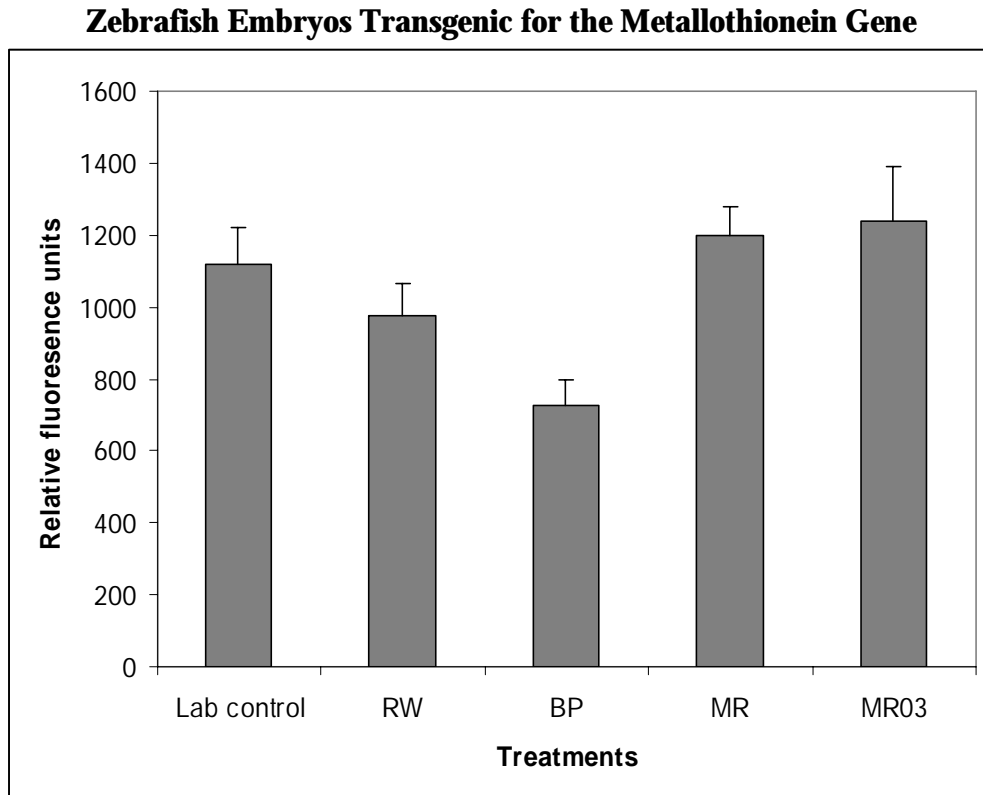
Zebrafish Embryos Transgenic for the Metallothionein Gene

Valuing Environmental Changes for Decision Making: Dam Removal and Restoration on the Penobscot and Kennebec Rivers

Basic Information

Title:	Valuing Environmental Changes for Decision Making: Dam Removal and Restoration on the Penobscot and Kennebec Rivers
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Publication

***Valuing Environmental Changes for Decision Making: Dam Removal and Restoration
on the Penobscot and Kennebec Rivers (Progress Report)***

Lynne Lewis, Bates College
Curtis Bohlen, Trout Unlimited
Laura Rose Day, Penobscot Partners

Introduction
On June 25, 2004, a press conference was held at the Veazie Dam to witness the signing
of the unprecedented restoration agreement on the Penobscot River. Signing the
Penobscot River Restoration Settlement Agreement were Secretary of the Interior Gale
Norton, Governor John Baldacci, Chief of the Penobscot Indian Nation Barry Dana,
Penobscot Partners Project Director Laura Rose Day and Pennsylvania Power and Light
(PPL). The agreement was filed with the Federal Energy and Regulatory Commission
(FERC) the following day. Under the agreement, PPL grants a five-year option to
purchase three of its dams on the Penobscot River to the Penobscot Restoration Trust.
The Penobscot Restoration Trust is made up of a coalition of environmental organizations
including the Natural Resources Council of Maine, Trout Unlimited, Audubon Maine,
American Rivers, Atlantic Salmon Federation and the Penobscot Indian Nation. The
group plans to remove two dams and build a fish bypass at a third, thus freeing up more
than 500 miles of the main-stem river for anadromous fish including the endangered
Atlantic salmon. The agreement gives PPL Corporation the opportunity to maintain more
than 90 percent of its current hydropower generation. The project would be the largest
river restoration effort north of the Everglades.

The Edwards Dam on the Kennebec River, which was breached and removed in 1999,
was the first major dam to be removed in Maine. Since removal of the dam, anadromous
fish, including Atlantic salmon, have returned to the river above the dam site. Aquatic
insect populations have grown dramatically. Recreation on the river in the form of fly
fishing, canoeing and kayaking has also grown. However, little has been done in the way
of post-project research or monitoring. The project has been deemed successful by most
observers, but without formal evaluation, few objective measures of "success" are
possible.

The need for better post-project monitoring and social-economic evaluation of aquatic
restoration projects is widely recognized. The Draft Maine River Restoration User Guide
issued in January 2004[1] emphasized the need for a "comprehensive, accurate method for
evaluating the beneficial and adverse impacts of a dam removal." This report includes a
section highlighting the need for socio-economic valuation. In 2002, the Department of
Interior commissioned the Water, Science and Technology Board (WSTB) to undertake
an assessment of water resources research funded by federal dollars. At the Universities
Council on Water Resources annual conference, in July of this year, Henry Vaux, Chair
of the WSTB Committee, presented a keynote talk on the findings. According to Vaux,

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[1] Maine State Planning Office, January 27, 2004

one of the priority needs is for *ex-post* analysis of projects and for continued monitoring of current projects; social science research is also lacking. These shortcomings will become increasingly apparent as more and more dams outlive their useful lives and come up for relicensing, both in Maine and across the nation.

The removal of the Edwards dam signaled – or partially triggered – a change in thinking about management of Maine rivers. Discussions over river management are taking place among stakeholders and interested groups from York to Fort Kent. Examples include discussions about dissolved oxygen in Gulf Island Pond on the Androscoggin River and about the scheduled demolition of Fort Halifax Dam on the Sebasticook. Other examples abound. Nearly half a dozen smaller dams have recently been removed or are currently being evaluated for removal. Efforts to establish fish passage at other sites have increased as anadromous fish pass downstream dams that have blocked access for most of a century. The Penobscot River Restoration agreement allows for the removal of two major dams north of Bangor and for fish passage to be built at others. Additionally, the removal of Edwards Dam set a national precedent for removing dams of marginal value. All this activity signals a critical need for estimates of the socio-economic benefits of often expensive restoration efforts.

This has been collecting data to refine valuation methods and assess components of value associated with dam removal. The primary effort has been to obtain and categorize value estimates in a manner that can be generalized for other Maine Rivers and to other kinds of aquatic restoration.

Background
In a report submitted to the Federal Energy and Regulatory Commission (FERC), prior to the decision to remove Edwards Dam, Freeman (1996) reviews and critiques FERC's benefit-cost analysis for the Edwards Dam project. In this report, Freeman emphasizes why non-power values must be included in benefit-cost analysis. FERC did not include any non-power values in its study. (Typically these values are excluded from FERC analyses due to the difficulty of estimation.) As Freeman states, "this is a fatal methodological flaw" (Freeman 1996, p.5). By ignoring and excluding these non-power values in its benefit-cost methodology, FERC made it impossible for the dam removal alternative to ever show a net economic benefit to society. Freeman (1995) estimates the present value of benefits to recreational anglers alone would be at least $36.2 - $48.2 million. This estimate is based on a study by Boyle (1991). This, of course, is a lower bound as it does not include other potential economic benefits. For example, whitewater boating benefits were expected to increase with removal. Additionally, there are other nonmarket benefits and costs, such as habitat enhancements and overall water quality improvements that were not estimated. Evidence to date, suggests that these numbers were, in fact, underestimates.

Interestingly, many outcomes of dam removal are not captured by market values and may be in conflict with one another. Naeser and Smith (1995), for example, examine the conflicts between different instream flow users including anglers and rafters. River-based recreation is not necessarily improved by leaving more water in the river. Many times the

timing of flows is important to recreational users, in which case the effects of dam removal would be different for different users.

The difficulty of nonmarket valuation is well established in the literature and much has been written on methods for nonmarket valuation (Freeman 2003 and Mitchell and Carson 1989, for example). Despite the advancements in methodology, reliable estimates are still difficult to obtain.

Few studies have attempted to estimate the total nonmarket value of a dam removal. Loomis (1996) finds a significant willingness to pay to remove dams in the Pacific Northwest in order to restore salmon and steelhead runs. Loomis uses a contingent valuation survey to obtain estimates of willingness to pay for removing dams on the Elwha River. His results suggest that total nonmarket benefits to all U.S. households of these dam removals fall in the range of $3 – 6 billion. He suggests that this type of "valuation information should be used by FERC in relicensing decisions on the east and west coast" (Loomis, p. 446).

Gonzalez-Caban and Loomis (1997) examine willingness to pay to avoid a dam on the Rio Fajardo in Puerto Rico. They find an annual willingness to pay of $28 per household or $13.09 million when expanded to the one million households in Puerto Rico. They also estimate willingness to pay to preserve instream flows for Rio Mameyes and find an annual household willingness to pay of $27 ($11.33 million).

The above studies used survey methods including contingent valuation and travel cost surveys. Another approach to nonmarket valuation, the hedonic property value method, uses market transactions in order to estimate the marginal prices of the various attributes of housing choice, including environmental quality. While the limitations of hedonic models are well known, they are useful because they allow us to determine whether or not environmental variables are reflected in the housing market.

Models that address environmental externalities characterizing locational choice have a strong spatial component. These spatial components may vary within a watershed, but also may be attributed to the health or quality of the watershed. Only recently have hedonic models addressed the spatial components of environmental quality and how these may relate to home prices (Lewis and Acharya 2004, Paterson and Boyle 2002, Acharya and Bennett 2001, Bockstael, 1996 and Geoghegan et al., 1997).

Proximity to water bodies, such as rivers and lakes, may be an asset to home owners but the relative quality of land and water attributes can result in dis-amenities and reduced home prices. Thus, this method is extremely appropriate for evaluating the impacts of dams and dam removal. To our knowledge, hedonic property value models have not yet been utilized in valuation for dam removal.

Interest in spatial analysis with hedonic property models is increasing as evidenced by the growing number of papers that incorporate spatial issues within hedonic property models. For example, Parsons (1992) uses a repeat sales analysis to study the effect of the

distance that houses are from critical areas where new development is not permitted. Michaels and Smith (1990) and Hite et al. (2001) examine the effects of distance from of hazardous waste sites and landfills respectively. Similarly, Palmquist et al. (1997) investigated how non-farm residences were affected by large hog operations. Most recently, a few studies have addressed the question of scale and patterns in land use (Bockstael, 1996, Geoghegan et al., 1997 and Acharya and Bennett, 2001). Leggett and Bockstael (2000) present a hedonic analysis of waterfront property with the *a-priori* expectation that owners of waterfront property care about water quality as they have "essentially self-selected for an interest in water activity." To the best of our knowledge, while studies have utilized distance to rivers as an independent variable, distance to a dam has not been examined as potentially affecting property values.

One drawback of this method is that environmental or ecological data that help identify the quality of a neighborhood are often not accessible to housebuyers or may be highly scientific in nature and, therefore, of little consequence to housebuyers. Additionally, many homebuyers may not be aware of this information until after purchasing the home or the information must be inferred by the purchaser. Extremely few studies have incorporated subjective measures of environmental quality, such as those inferred by the buyer. Poor et al. (2001), examine and compare objective measures of water quality with subjective measures based on survey data on individuals' perceptions of quality. Poor et al. examine the convergent validity of objective and subjective measures of water clarity for lakes in Maine using an hedonic property value study. They utilized property sales data, objective scientific measures of water clarity and data from a household survey designed to elicit perceptions of water clarity. Very few other studies have surveyed the purchasers associated with the property value data. (See Poor et al. (2001) for a summary of the literature).

Project Description
This project addresses a gap in the body of knowledge on valuation of river restoration. Requests are frequently made for information on costs and benefits of restoration that can be used in policymaking. Estimates of nonmarket economic values of environmental benefits related to dam removal are especially crucial. Few such estimates exist. Those that do exist for Maine are dated and restricted to recreational benefits. Additionally, no study has gone back to see if predicted nonmarket values (and disvalues) actually developed following dam removal via *ex-post* analysis. The inclusion of hedonic property value studies add subjective measures of environmental quality captured through surveys of preferences and perceived quality.

The ex-post evaluation of the Edwards Dam removal should be informative to future dam removal evaluations. The linking of survey responses to GIS and hedonic models is an important methodological contribution. The combined results should also inform policy-makers.

The overall goals of this project are as follows:
- Refine a combined approach for estimating environmental values relying on both hedonic and survey methods; Estimate values associated with dam removal using

both predictive (Penobscot River) and *ex-post* (Edwards Dam) methods.
- Create an inventory and GIS-based map of properties, property owners, property values and transactions and land use along the lower Penobscot River;
- Design and implement a pilot survey for anglers, recreationists and property owners along the rivers;

The following information has been collected from diverse sources (and analysis of the data has not yet been completed for publication):
- An ex-post (Edwards removal) survey of anglers modeled on Boyle's (1991) study in order to test the validity of his results and determine recreational values since the dam was removed.
- An *a-priori* (Penobscot dam removal) survey of anglers also modeled on Boyle's study.
- A pilot survey of rafters and kayakers on the Kennebec and Penobscot Rivers aimed at capturing additional recreational value, but also aimed at examining perceptions of values.
- A pilot study linking a hedonic property value study to survey of expressed preferences of local residents using computer-generated simulations of what the Penobscot River will look like after dam removal. The study will explicitly incorporate both distance to the river and distance to the dam variables.

The two angler surveys are based to a significant extent on the methods used previously by Boyle, are being carried out by closely supervised undergraduate researchers, as the cornerstone of senior thesis projects. The two pilot studies are intended to explore theory of nonmarket valuation and to demonstrate the feasibility of novel research methods. Theses are being carried out at a relatively small scale while we work to acquire additional funding for a larger project.

Methods
This project combines survey methods with hedonic property value in an attempt to use pieces of each methodology to capture estimates of economic value attributed to changes in environmental quality such as water quality, recreational or habitat improvements. An innovative component of the project is the use of computer generated images of pre-project river views and projected post-project river views in a revealed preference context to help refine estimates of the value of aesthetic changes in the river. These images have been generated by Penobscot Partners and we have permission from them to use them for this project. The project is applying GIS mapping techniques in association with hedonic and survey methods to better understand the spatial (and thus social) distribution of benefits and costs from river restoration efforts.

Results
This report is a progress report because the collection and analysis of the survey data, property valuations. It would be pre-mature to summarize partially analyzed data. A detailed studied, including student's results, will be included at a future date.

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The functional role of forested seeps in maintaining hydrology, water quality and biological diversity in a New England watershed

Basic Information

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Principal Investigators:	Aram Calhoun, Andrew Reeve, Bryan Dail

Publication

Title

The Function of Forested Seeps in a New England Landscape

Abstract

Headwater streams are important sources of sediment, water, nutrients, and organic matter for downstream systems. Headwater wetlands preferentially contribute to surface flows via their terrestrial-aquatic link. Seeps, a type of headwater wetland, are characterized by relatively concentrated groundwater discharge creating unique ecological environments within a watershed. This research is an interdisciplinary approach identifying connections among hydrology, nutrient dynamics, and the plants and animals they support. From 2003 to 2005 data were collected to quantify the biogeochemical, hydrological and ecological function of forested hillside seeps in a Maine, USA, catchment. Our overarching objectives were to: 1) assess the role of seeps as sources or sinks for nutrients via isotopic analysis of major pools of inorganic nitrogen and transformations of these pools therein, and 2) Identify the role of seeps in maintaining stream hydrology and buffering stream chemistry. During summer low-flow, seeps were the primary source of surface water to the stream with seep flows increasing stream discharge by over 100% in both the spring and fall. Throughout the growing season, seep inflows reduced stream temperatures by an average of 0.5 degrees Celsius. Chemical analysis showed elevated concentrations of beryllium (up to 3.8 µg/L) from seep outflow, yet reduced concentrations (average 0.7 µg/L) at the seep-stream interface.

Progress Report:

Problem and Research Objectives:

Integrated biogeochemical and hydrologic studies assessing the role of nutrient dynamics in forested catchments are needed to quantify seep landscape function (Cirmo and McDonnell 1997). Recent research suggests that springs are an important source for nitrogen loading to streams within the Catskill Mountains of New York (Burns et al. 1998, West et al. 2001). However, the slow or lentic water flow in seeps, as compared to springs, may favor denitrification and N loss to the atmosphere. If denitrification is important in these systems, this would influence water quality and nutrient dynamics in streams that receive seep drainage or recharge. Because seeps and springs may integrate the water quality across large areas within a basin, they may provide a simple and inexpensive way to monitor the overall impacts of human activities and natural processes within a watershed (Manga 2001).

The central Maine landscape affords us an opportunity to evaluate baseline hydrologic, biochemical, and ecological functions of hillside seeps in an environment less influenced by anthropogenic influences. Given this, baseline indices of biological or hydrologic integrity may be developed. We propose to study the biogeochemical, hydrologic, and biological processes of forested hillside seeps and to directly address landscape scale functions.

The objectives of this research are:

1) To establish the extent to which seeps sustain low flow conditions in associated streams and the extent to which seeps buffer stream geochemistry.

2) To determine if saturated aerobic soils reflect nitrogen transformations similar to wetland systems and are in fact distinct from associated upland nitrogen cycling.

3) To augment existing forested seepage community data and to assess floral assemblages in seeps and surrounding uplands.

4) To document seasonal habitat preferences by amphibians in headwater catchments containing seeps.

Methodology:

A primary research catchment has been chosen in northwest Hancock County for intensive sampling of three seeps. Hydrological assessment of seeps were conducted throughout the growing season by bi-monthly groundwater and surface water flow measurements and seasonal collection of groundwater and surface water samples. Groundwater flow and chemistry was ascertained by installation of at least five groundwater well clusters (17 total) at each of three intensively monitored seepage wetlands. Individual well clusters were spaced at depth increments of 0.5 to 1.5 m, to

establish vertical hydraulic and chemical gradients. Seep surface flow were measured using V-notch weirs installed at a point where seep surface flow is constrained and channelized.

Discharge through stream channels were measured at several locations upstream and downstream of the seep to assess the impact of the seep on stream discharge and determine if the stream is gaining or loosing water to the groundwater system. Discharge measurements were compared to stream stage and an empirical relationship will be developed between stage and discharge for the streams. The hydraulic conductivity of the geologic materials was determined by measuring the recovery rates in a well after a volume of water is removed from the well. The porosity of sediment samples was estimated by weight proportion of the split spoon sample when wet and dry, and assuming the volume of water lost is equal to the porosity. Discharge rates and groundwater velocities will be calculated with Darcy's Law using hydraulic head and hydraulic conductivity data.

Water samples were collected from the surface-water and groundwater monitoring stations three times during the growing season. All water samples were lab filtered (0.45 micron) and analyzed at the University of Maine's Environmental Chemistry Laboratory (ECL) for major anions (NO_3, SO_4 and Cl) and cations (Ca, Mg, Na, K, Fe, Mn). Nutrient samples were analyzed at the ECL for inorganic N (NO_2 /NO_3 and NH_4^+), total nitrogen (TDN) and reactive phosphorus. Probes were used to measure pH, dissolved oxygen, water temperature, and specific conductance bi-monthly in the field. Alkalinity was measured in the laboratory using standard titration techniques. Collection of this data set will allow data quality to then be assessed through charge-balance calculations.

Evaluation of selective nitrogen uptake and cycling was completed through concurrent, seasonal collection of: throughfall (19 funnel collectors), soils (18 soil sample locations), vegetation (3 dominant species at each site), and water (17 – groundwater well clusters, 6 – surface water points). The isotopic signature of N forms will be determined in each of the four pools by using solid state Isotope Ratio Mass Spectroscopy (IRMS). This data will also be used to assess the redox conditions within the seeps.

Table 1 – Analytical methods used for water analyses

Water Type	Parameter	Equipment	Analytical Method
Groundwater	Anions	Dionex model DX-500 IC	EPA method 300.0
	Cations	Perkin-Elmer Optimum 3300XL ICP-AES	EPA method 200.15
	inorganic N	Alpkem Flow solution IV Autoanalyzer	Berthelot reaction procedure (NH4) Peroxodisulfate oxidation procedure (NO2/NO3)
	TDN	Alpkem Flow solution IV Autoanalyzer	Peroxodisulfate oxidation procedure
	Alkalinity	Digital titrator	Titration via Gran function
	Ortho-phosphate	Spectrophotometer	EPA method 600/R-93-100
Surface Water	same as GW above, plus:		
	Dissolved Oxygen	YSI Model 55	N/A
	Conductivity	YSI Model 30	N/A
	pH	Hanna HI 9025	N/A
	Temperature	YSI Model 55 & 30	N/A

Soils were classified and described at each of the seep study sites. Near each well cluster, soil profile descriptions, and an analysis of organic and mineral horizons (texture,

percent organic matter, CEC, and pH) were characterized and analyzed for nitrate and ammonium by The Maine Soil Testing Service and Analytical Lab.

Floristic inventories of all the study sites were conducted in spring, mid-summer, and fall along three elevational transects corresponding to seep locations. Data were collected following the protocol used by the Maine Natural Areas Program (nested plots for trees, saplings, shrubs, herbs/forbs, and bryophytes with cover classes recorded for each species) for inclusion in their database. In addition, data was collected on tree basal area, vegetation in adjacent uplands (dominant species in each strata), and a volume measurement of standing and down deadwood (coarse woody debris and fine woody debris) using a method adapted from the US Forest service.

The relative abundance of amphibian assemblages were assessed seasonally using funnel trap arrays, coverboard arrays, and time-constrained searches in all of the seeps and repeated in adjacent uplands along similar elevational gradients. Funnel trap arrays will consist of a series of 10m drift fences arranged in a "T" fashion, within or adjacent to each seep with eight aluminum 0.9x0.2m funnel traps placed near each end of the fence on each side. The traps will contain a sponge (re-wetted upon inspection) and cover objects to reduce amphibian desiccation or mortality. The funnel trap arrays will be opened over two-week intervals throughout the field season. A total of 50 coverboards will be used to identify additional species not apt to be captured by funnel traps. These will be numbered and placed at the wetland/upland boundary along the border of each seep and within vegetation gradients in each seep. The coverboards will be inspected in conjunction with visual encounter surveys conducted following seasonal wet and dry periods concurrent with the sampling periods for soil and water analysis.

Principal Findings:

Stream discharge measurements along Dutton creek above and below wetland outflows were made during the summer of 2005. During the spring, stream flow above seep outflow averaged 5 cm/sec, while flow averaged 12 cm/sec below seep outflow, a 140% increase in discharge. During mid-summer flow above the seep was either non-existent or not sufficient to adequately measure discharge. Stream discharge below seep outflow was 4 cm/sec. Flow returned to the stream above seep outflow during the fall, with stream discharge averaging 4 cm/sec above outflow while below, stream discharge was 9cm/sec, a 125% increase in discharge.

Groundwater flow estimates will be calculated again in 2006 to verify conditions and to obtain more detailed measurements of well characteristics. During 2005, shallow wells recovered at rates faster than expected yielding inadequate relationships to accurately quantify hydraulic conductivity and thus estimates of groundwater discharge.

A charge balance of base cations (Ca, K, Mg, Na) and anions (Cl, HCO_3, SO_4) resulted in differences of less than ±10% for the majority of samples. However, a single sample date (7/27/2004) had seventeen samples (n=21) with greater than +10% charge difference. All of these samples had bicarbonate values an order of magnitude less than those of similar samples from other dates likely causing the charge difference. Fluoride or organic acids were not measured and could contribute to the charge balance discrepancy, however balance errors would be expected on more sample data. Samples not meeting charge balance conditions were left out of subsequent analysis for bicarbonate. However

the samples did reflect typical values for the other constituents and those were included in the results.

Bicarbonate was the dominant anion in surface waters at 6.9 ±3.0 mg/L (mean ± std. dev.) and in deep groundwater wells of 19.3 ±3.2 mg/L (Table 2). Sulfate and chlorine were the second and third dominant anions. Dominant cations were calcium and sodium with average surface water concentration of 2.5± 0.8 mg/L and 2.3± 0.5 mg/L respectively. In deep groundwater wells, concentrations of calcium and sodium were 4.9 ±3.2 mg/L and 4.6 ±2.5 mg/L. Deeper groundwater wells had higher overall concentrations and variability in major ion chemistry while surface waters had the least variability. Sodium was the only exception having highest variability (5±5.8 mg/L) in shallow groundwater wells. Differences in ion concentration did not change significantly through the season (results not shown). The pH did not change significantly from deep groundwater wells to surface waters, both having similar variability.

Metal concentrations were more variable in deeper groundwater wells than in surface water. Maximum concentrations of aluminum, iron, and manganese exceeded 1 mg/L. Two piezometers contributed to the majority of these high concentrations. Beryllium concentrations were elevated in seep wetlands, exhibiting two relationships. First, maximum beryllium concentrations only occurred in surface waters. Second, significantly higher concentrations of beryllium occurred in discharge wetlands (seeps) than in a toe-slope wetland located further downstream.

At two seep outflows, discharge was measured using both pressure transducers (measuring stage at ten minute intervals) and direct discharge measurements (made bi-weekly) into a container of known volume. Transducers allowed passive collection of weir stage. Stage-discharge relationships will be made, but are not included as part of this report. Weirs from both seepage outflows (DNH1 and DNH4) showed similar trends throughout the entire season, however varied in response to seasonal storm events. During spring and fall, storm events increased stage at the DNH4 seep an average of 0.9 cm until full canopy closure in early June. During mid-summer, DNH1 had higher average stage, averaging 0.5 cm higher stage than DNH4. Alternatively in fall, stage at DNH4 was again higher than DNH1 by an average 6.6 cm. This increase in stage is a result of a significantly different storm response to the fall precipitation event in October of 2005. In early spring, DNH4 seep exhibited diurnal stage pulses (Figure 1), while DNH1 stage remained constant.

Manual discharge measurements between seeps indicated similar discharge between the two seeps throughout the year (Figure 2). Average discharge during the spring at DNH1 and DNH4 were 31.4 and 37.5 L/min respectively, similar to the stage data. During mid-summer, DNH1 had higher average discharge (11 L/min), averaging 2.4 L/min more than DNH4 (8.6 L/min), again similar to trends in the stage data. However, during the fall, discharge remained higher in DNH1 (33.6 L/min) than at DNH4 (24.4 L/min). The explanation for the discrepancy is due to the ability of the water level transducers to measure more individual storm responses that could be made by bi-weekly visits. A comparison between a pressure transducer placed in a deep groundwater well at the seepage face and a pressure transducer placed at the weir at seep outflow. Surface water stage showed significant responses to individual storm events, while groundwater levels (measured at percent psi) showed a gradual decrease in groundwater levels after canopy closure (Figure 3). Increases in groundwater levels from storm events were a

subdued reflection of increases in weir stage. These data will be used to analyze recession curves to assist in interpretation of the hydrological properties of the seep and will be included in the final report.

Groundwater hydraulic conductivity measurements were made using a stainless steel slug to displace water within each well. Head changes were then measured at one to ten minute intervals depending on recovery rate. Preliminary data suggest that at the seeps, the hydraulic conductivity at deep groundwater wells (average 1.7 meters below ground surface (bgs)) is approximately 2.4×10^{-7} m/s, while shallow groundwater wells (average 1.1 meters bgs) range from $1.32\text{-}5.0 \times 10^{-6}$ m/s. Slug tests during the 2005 field season will be conducted again in 2006 to verify conditions and to obtain more detailed measurements of head changes. During 2005 shallow wells recovered at rates faster than expected yielding inadequate relationships to accurately quantify hydraulic conductivity at all wells.

Final analysis of natural abundance nitrogen isotopes is awaiting remaining sample data from the University of California –Davis Stable Isotope Facility. Upon receipt and analysis of these data, a complete assessment of isotopic discrimination can be made. Upon completion, these results will be included in the final report.

The ecological assessment including floristic and amphibian assemblage surveys will not be included as part of this report. Analysis of data is still ongoing.

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Table 2 –Summary of ion chemistry by water type.

Water Type		Be µg/L	Fe µg/L	Mn µg/L	Si mg/L	Al µg/L	pH	HCO3 mg/L	Ca mg/L	Cl mg/L	K mg/L	Mg mg/L	Na mg/L	NH4 mg/L	NO3 µg/L	PO4 µg/L	SO4 mg/L	Total N mg/L
Surface	N	36	43	30	36	56	56	44	56	56	56	56	56	56	56	56	56	52
	Min.	0.4	1.9	0.5	2.1	19.9	4.77	1.3	0.9	1.3	0.1	0.2	1.5	ND	1	0.5	0.7	0.1
	Max.	3.8	82.6	16.5	5	224	6.86	11.9	4.2	3.2	1.3	0.9	3.7	0.2	159.0	31	1.7	1.1
	Mean	1.4	13.6	3.9	3.5	67.2	5.62	6.9	2.5	1.6	0.3	0.4	2.3	0.0	41	3	1.2	0.2
	Std. Dev.	1	19	5	0.8	32	0.4	3	0.8	0.2	0.2	0.1	0.5	0.0	47.4	4.2	0.2	0.2
Shallow	N	48	60	43	48	74	53	43	74	74	74	74	74	73	74	73	74	73
(0.6 m bgs)	Min.	0.1	2.5	4.13	2.1	17.2	5.01	1.5	0.7	1	0.2	0.2	1.6	ND	1	0.5	0.1	0.1
	Max.	2.2	1660	468	8.3	1630	6.72	35.5	20.6	17.3	24.2	3.6	39.4	1.8	73	20	4.6	1.8
	Mean	1.0	176.4	135.4	4.7	324.7	5.50	12.1	3.7	2.5	1.1	0.6	5	0.3	10.5	5.8	0.9	0.6
	Std. Dev.	0.5	298	111	1.7	324	0.4	8.7	2.9	2.1	2.9	0.5	5.8	0.5	14.8	4.7	0.7	0.5
Deep	N	28	28	12	28	35	28	19	35	35	35	35	35	35	35	35	35	35
(0.7-2.5m bgs)	Min.	0.02	12	0.5	2.3	23.6	5.06	4.9	1.1	1.4	0.2	0.3	1.7	ND	1	1.1	0.1	0.1
	Max.	2.5	1500	1340	8.9	2010	7.56	55.9	14.6	38.3	48.4	2.6	11.8	1	146	45	8.3	1.9
	Mean	0.9	163.2	198.7	5.3	282.4	5.79	19.3	4.9	3.7	2	1.1	4.6	0.1	17.1	8.1	1.2	0.5
	Std. Dev.	0.8	297	401	2.1	399	0.5	14.5	3.2	6.1	8.1	0.7	2.5	0.2	28.7	9.4	1.4	0.4

N= number of samples taken
Bgs= below ground surface

Figure 1 – Seasonal stage responses by two seepage wetlands (DNH1 and DNH4).

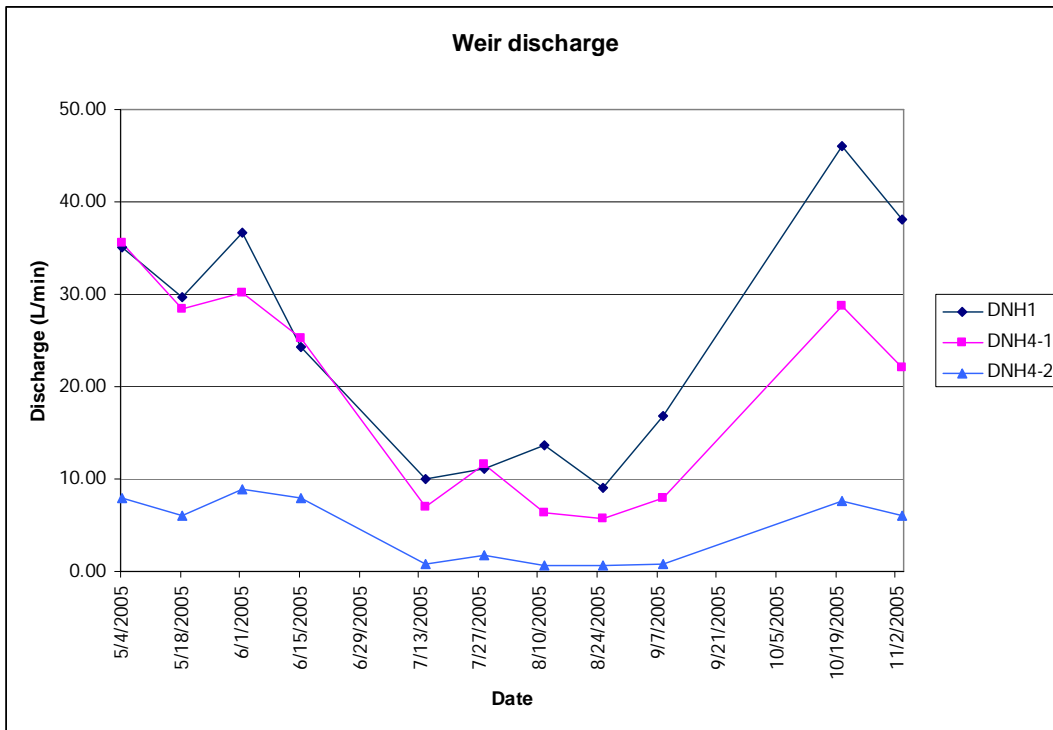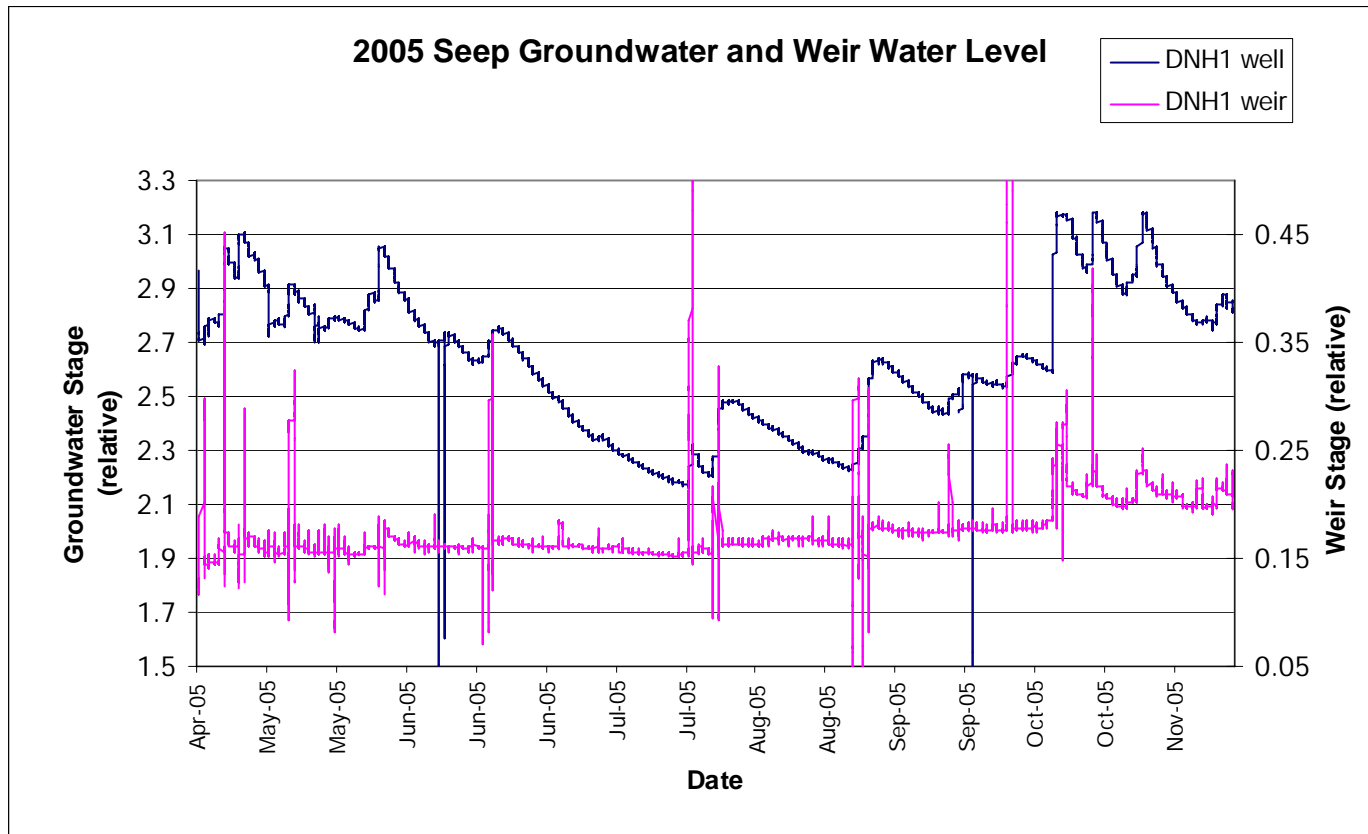Figure 2 – Weir discharge from v-notch weirs at seepage outflows. 2005 data only.

Figure 3 – Groundwater well level measured versus weir stage. Groundwater well measured at seep emanation and weir stage measured at seep outflow. Note - Significant drops in groundwater stage reflect two of the three groundwater collection periods when water was purged from the well.

Information Transfer Program

Penobscot Synthesis

Basic Information

Title:	Penobscot Synthesis
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Focus Category:	Education, Ecology, Water Quality
Descriptors:	None
Principal Investigators:	Peter Vaux, Catherine Schmitt

Publication

1. "Beneath the surface: Uncovering the environmental history of the Penobscot River," Mitchell Center Spring 2006 Lecture Series, University of Maine, January 19, 2006.
2. "Communicating ecosystem restoration: Dam removal as a case study," presented at the 2005 Meeting of Universities Council on Water Resources/National Institutes of Water Resources, Portland, Maine, July 12-14, 2005.
3. "Penobscot River future tied to past," Bangor Daily News, December 26, 2005, p.C1, C3. "Fewer dams let Penobscot River flow," Bangor Daily News, December 27, 2005, p.C4.
4. Peckenham, J.M., C.V. Schmitt, J.L. McNelly, and A.L. Tolman. Linking water quality to the watershed: developing tools for source water protection. Journal AWWA 97:62-69. (September 2005)
5. Schmitt, C., and J. Peckenham. Arsenic in Maine Groundwater. Senator George J. Mitchell Center for Environmental and Watershed Research Digest Series, Orono, ME. (June 2005)
6. "Sampling 143 lakes in 7 states, 8 weeks," UMaine Today, May/June.
7. A Field Guide to Aquatic Phenomena. Senator George J. Mitchell Center for Environmental and Watershed Research, Digest Series. (May 2005) http://www.umaine.edu/WaterResearch/FieldGuide/.
8. "It's in the water," Atlantic Salmon Journal, Spring 2005.
9. "Honoring Mitchell's environmental legacy," Bangor Daily News, April 21, 2005.

Abstract

The Penobscot River Synthesis is a comprehensive bibliography of over 400 scientific references and resources related to the Penobscot River. The Synthesis is designed for use by scientists and educators interested in the Penobscot River Restoration Project, dam removal research, and the environmental history of the Penobscot River. The references were used to write summaries of major river topics: fisheries, pollution, water quality, watershed geography, hydrology, etc. As part of the Synthesis, a canoe journey down the Penobscot from Howland to Bucksport provided the framework for outreach products and publications, some of which are still ongoing and pending future funding. The Synthesis expanded to include an inventory of current research and monitoring efforts related to the Penobscot, which was instrumental in development of a Seminar Series on Penobscot River research and facilitating the formation of the Penobscot River Science Steering Committee. The Penobscot River Synthesis and the George Mitchell Center are being recognized as the virtual hub for the Penobscot River research community.

Problem and Research Objectives

The announcement of the Penobscot River Restoration Project (PRRP) increased awareness of and interest in the Penobscot River. Scientists in Maine and the region, who view the project as an opportunity for ecological research, are coming together to formulate research proposals. As scientists attempt to address the changes that will result from the restoration, they will need baseline information on status and trends in the Penobscot River ecosystem, traditionally obtained by reviewing literature of past research. It is likely that many will be seeking similar references, driving the need for a single, comprehensive bibliography.

It is not just scientists who are interested in the environmental history of the river. People who live in the communities along the river—and across the country—will be paying more attention as the project advances. The general public likewise should have access to the knowledge gained from the literature review. Science results are not fully realized until they are available to the target community, and one way to accomplish this realization is to convey scientific information in a narrative format

Our objectives were to create a literature review of Penobscot River references and place the bibliography on-line, where it would be accessible to the public and searchable by keyword and watershed location. We also wanted to translate the information for a non-scientific audience into newspaper articles, topical summaries, and other publications.

Methodology

We reviewed all relevant scientific and environmental literature on the Penobscot River using online and library resources at the University of Maine. In addition, we visited the offices and libraries of federal and state agencies, local organizations, and historical societies to inventory their references and relevant data sets. The references were organized using ProCite and Microsoft Access into a database containing bibliographic information, a hydrologic code (USGS HUC) linking the reference to its

location in the watershed, and notes on key findings, sample locations, and data. The references are hosted on PEARL, the on-line database for environmental information in Maine. Whenever possible, references are linked to downloadable/PDF documents. Hard copies of references are housed in the Mitchell Center at the University of Maine. A canoe trip down the river will provide the framework for publications and outreach products that will translate the scientific research from the bibliography will be interpreted along the way.

Principal Findings and Significance.

- The Penobscot River Synthesis can be found at http://www.pearl.maine.edu/windows/penobscot/index.htm
- Over 400 references are in the process of being placed on-line. These references are searchable by keyword, title, author, and watershed. Each reference has been coded by its location in the watershed, and contains notes on sample site locations and sampling parameters.
- The references were used to compile summaries of topics relevant to dam removal (pollution, hydrology, fisheries, etc.), which provide background on Penobscot River ecology. These can be found under "River Topics" on the Web site.
- We completed a canoe journey down the Penobscot River from Howland to Bucksport. This trip provided the framework for a series of articles published in the Bangor Daily News in December 2005 and provided background for future publications and presentations.
- The Synthesis expanded beyond past research to include an inventory of current research and monitoring projects to facilitate research networking. This addition to the project has been instrumental in bringing together members of the Penobscot River Science Steering Committee, an outcome of the 2004 Penobscot River Science Forum. Committee members have agreed that Penobscot River data generated from research and monitoring projects should be housed in PEARL, and that the Mitchell Center is the appropriate entity to coordinate the effort.
- The Synthesis is an ongoing project. We are seeking funding to continue the Synthesis by including a Penobscot River data inventory and evaluation, developing several outreach/publications products, and continuing to serve as the virtual hub for the Penobscot River research community.

Maine Information Transfer Project FY05

Basic Information

Title:	Maine Information Transfer Project FY05
Project Number:	2005ME62B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	2
Research Category:	Not Applicable
Focus Category:	Education, Law, Institutions, and Policy, Management and Planning
Descriptors:	None
Principal Investigators:	John M. Peckenham

Publication

1. Peckenham, J. M., C. Schmitt, J. McNelly, and A. Tolman (2005) Linking Water Quality to the Watershed: Developing Tool for Source Water Protection, Journal Amer. Water Works Assoc., 97, pp. 62-69
2. Peckenham, J.M., J. Nadeau and A. Amirbahman (2005) Nitrogen Release from Field Stack Biosolids, BioCycle, 46, pp. 47-52.
3. Caron, H., 2005. Groundwater Hydrology and Chemistry of Fresh Meadow Wetland, Acadia National Park, Maine, USA. M.S. Thesis. University of Maine.
4. Charlestra, L. 2005. The Use of Passive Samplers (SPMS and POCIS) for Monitoring Dioxin and Pesticide Levels in Maine Surface Waters. M.S. Thesis. University of Maine.
5. Hallsworth, R., Schmitt, C., Boothroyd, J., 2005. Waterlines Vol. 11 No. 2. Newsletter, Senator George J. Mitchell Center, August 2005.
6. Hallsworth, R., Schmitt, C., Boothroyd, J., 2005. Waterlines Vol. 12 No. 1. Newsletter, Senator George J. Mitchell Center, February 2006.
7. Johnson, K.B. and J.S. Kahl, 2005. A Systematic Survey of Water Chemistry for Downeast Area Rivers: ASCpH Survey. Technical report to the Maine Atlantic Salmon Commission.
8. Rosfjord, C.H., J.S. Kahl, K. Webster, S. Nelson, I. Fernandez, L. Rustad, R. Stemberger, 2006. Final Report: Acidic deposition-relevant changes in lake chemistry in the EPA Eastern Lake Survey, 1984-2004. Submitted to USDA NSRC.
9. Rosfjord, C. 2005. An Evaluation of 20 Year Changes in Chemistry in the EPA Eastern Lake Survey, a Statistical Population of Lakes in the Northeastern U.S. M.S. Thesis. University of Maine
10. Schmitt, C., and J. Peckenham. Arsenic in Maine Groundwater. Senator George J. Mitchell Center for Environmental and Watershed Research, Digest Series, Orono, ME. (June 2005)

11. Schmitt, C. A Field Guide to Aquatic Phenomena. Senator George J. Mitchell Center for Environmental and Watershed Research, Digest Series. (May 2005) http://www.umaine.edu/WaterResearch/FieldGuide/.

INFORMATION TRANSFER FY05

The Senator George J. Mitchell Center for Environmental and Watershed Research

John Peckenham, WRRI Director & Interim Director Mitchell Center (9/05-2/06)
Dr. Chris Cronan, Interim Director Mitchell Center (3/05-8/05)

Jennifer Boothroyd, Scientific Technician
Ruth Hallsworth, Outreach and Development Manager
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Catherine Schmitt, Research Assistant/Science Writer
Dr. Peter Vaux, PEARL Project Director

Introduction

Linking the academic community with state agencies, environmental organizations, and private companies is a central part of the mission of the Mitchell Center and the Water Resources Research Institute. The Center serves the State of Maine as a point of access to the substantial technical abilities of the University of Maine on issues of water resources. The importance of providing timely and accurate information transfer continues to grow. This mission is being ably served using part-time staff and non-federal funding. In the past year the Center has worked to disseminate research results, organize meetings, participate in statewide forums, serve on committees dealing with water resource issues, work with teachers and conduct special projects.

Summary for 3/05-2/06

Publications

Peer-reviewed articles.

Banaitis M., H. Waldrip-Dail, **M. Diehl**, B. Holmes, J. Hunt, R. Lynch, T. Ohno. Investigating sorption-driven dissolved organic matter fractionation by multi-dimensional fluorescence spectroscopy and PARAFAC. 2006. Journal of Colloid and Interface Science (in review).

Dupont, J., Clair, T.A., Gagnon,C., Jeffries, D.D., Kahl, J.S., **Nelson, S.J.** and **Peckenham, J.M.**, 2005: 'Estimation of critical loads of acidity for lakes in northeastern United States and eastern Canada', Environmental Monitoring and Assessment 109(1-3): pp. 275-291.

Peckenham, J. M., C. Schmitt, J. McNelly, and A. Tolman (2005) Linking Water Quality to the Watershed: Developing Tool for Source Water Protection, Journal Amer. Water Works Assoc., 97, pp. 62-69.

Peckenham, J.M., J. Nadeau and A. Amirbahman (2005) Nitrogen Release from Field Stack Biosolids, BioCycle, 46, pp. 47-52.

Reports and Miscellaneous Publications

Caron, H., 2005. Groundwater Hydrology and Chemistry of Fresh Meadow Wetland, Acadia National Park, Maine, USA. M.S. Thesis. University of Maine.

Charlestra, L. 2005. The Use of Passive Samplers (SPMS and POCIS) for Monitoring Dioxin and Pesticide Levels in Maine Surface Waters. M.S. Thesis. University of Maine.

Hallsworth, R., Schmitt, C., Boothroyd, J., 2005. Waterlines Vol. 11 No. 2. Newsletter, Senator George J. Mitchell Center, August 2005.

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Johnson, K.B. and J.S. Kahl, 2005. Dennys River Survey – 2004 Final Report Technical Report to NOAA-Fisheries and the Maine Atlantic Salmon Commission.

Nelson, S.J., J. S. Kahl, I. J. Fernandez, **K. D. Sheehan, A. Grygo Diamond, K. B. Johnson**, K. C. Weathers, September, 2005. Final Report: Correlating Predictive Contaminant Deposition Maps with Streamwater Chemistry at Acadia National Park. Project PMIS Number: 75017

Nelson, S.J., J.S. Kahl, **K.B. Johnson, J. Boothroyd**, August, 2005. Final Report: Are road de-icing salts a factor in the chemistry of salmon rivers? 2004 Maine Atlantic Salmon Conservation Fund.

Nelson, S., P. Vaux, A. Grygo Diamond, R. Hallsworth, D. Kramar. 2006. Searchable Park Access to Research Catchments (SPARC). Final report submitted to National Park Service. 17 pp.

Peckenham, J.M., J. S. Kahl, and A. Amirbahman (2005) The Impact of Vehicle Traffic and Water Quality in Acadia National Park. Final Report. National Park Service.

Peckenham, J.M. (2005) Beneficial Reuse of Biosolids: A Review, prepared for Maine State Planning Office and the Maine Waste Water Control Association, March 2005, 70 p.

Rosfjord, C.H., J.S. Kahl, K. Webster, **S. Nelson**, I. Fernandez, L. Rustad, R. Stemberger, 2006. Final Report: Acidic deposition-relevant changes in lake chemistry in the EPA Eastern Lake Survey, 1984-2004. Submitted to USDA NSRC.

Rosfjord, C. 2005. An Evaluation of 20 Year Changes in Chemistry in the EPA Eastern Lake Survey, a Statistical Population of Lakes in the Northeastern U.S. M.S. Thesis. University of Maine

Schmitt, C., and **J. Peckenham**. Arsenic in Maine Groundwater. Senator George J. Mitchell Center for Environmental and Watershed Research, Digest Series, Orono, ME. (June 2005)

Schmitt, C. Sampling 143 lakes in 7 states, 8 weeks. UMaine Today, May/June.

Schmitt, C. A Field Guide to Aquatic Phenomena. Senator George J. Mitchell Center for Environmental and Watershed Research, Digest Series. (May 2005) http://www.umaine.edu/WaterResearch/FieldGuide/.

Schmitt, C. It's in the water. Atlantic Salmon Journal, Spring 2005.

Sheehan, K., 2005. Vegetative and Landscape Influences on Forest Litter Mercury at Acadia National Park. M.S. Thesis. University of Maine.

Vaux, P. 2005. PEARL Site Development for Atlantic Salmon Data. Phase 1, Final Report. 31 pp. Submitted to ME Atlantic Salmon Commission.

Vaux, P. 2005. Integrating biological and streams data into PEARL. 42 pp. Submitted to USGS.

Vaux, P. 2005. PEARL site development: progress report. 48 pp. Submitted to ME Dept. Environmental Protection.

Vaux, P. 2005. Freshwater Biodiversity in Maine: an assessment of aquatic systems and their ecological communities. Final report, Maine Aquatic Biodiversity Project. The Nature Conservancy, Maine Department of Environmental Protection, Maine Dept. Inland Fisheries & Wildlife. 299 pp. + app.

Professional Presentations

Diehl, M., K. Webster, I. Fernandez, S. Norton and S. Kahl. Controls on Surface Water Sulfate Concentrations at the Bear Brook Watersheds in Maine. Presented at the Maine Water Conference, March 2005

Diehl, M., K. Webster, I. Fernandez, S. Norton and S. Kahl. Are we there yet? 15 Years of Experimental Acidification at the Bear Brook Watersheds in Maine Presented at the Gordon Research Conference on Catchment Science, July 2005

Fretwell L., D.B. Dail, K.E. Webster, and S.H. Brawley. The relationship between phosphorus and nitrogen concentrations, algal growth, and land use in the Meduxnekeag River watershed. Maine Water Conference, Augusta, ME, March 22, 2005.

Grygo A., K. Webster, C. Loftin, K. Tonnessen, and S. Kahl. A GIS landscape model examining DOC variability among watersheds in National Parks. Maine Water Conference, Augusta, ME, March 22, 2005.

Grygo, A., P. Vaux, S. Nelson, K. Tonnessen, and D. Manski, Sharing the Wealth: Information exchange among research watersheds, George Wright Society Meeting Abstract, March 14-18, 2005, Philadelphia, PA, p. 134.

Johnson, K.B. Multiple formal and informal, public and professional, presentations for National Oceanic and Atmospheric Agency, Maine Atlantic Salmon Commission, and Project SHARE, on water chemistry in Downeast area and other Maine salmon rivers 2003-2006.

Kahl, J.S., **S. Nelson, K. Johnson**, 2005. Perception experiment: paired watershed research at Acadia National Park. Gordon Research Conference field trip, July 20, 2005.

Kramar D. Proximity analysis of the influence of land cover type and loon blood mercury levels using geographic information systems. Maine Water Conference, Augusta, ME, March 22, 2005.

Kramar D., and **P. Vaux.** PEARL: Recent Innovations to the architecture and functionality of the environmental information source for Maine. Maine Water Conference, Augusta, ME, March 22, 2005.

McCabe S., P.Vaux, D. Kramar, and **R. Hallsworth**. Creating and Evaluating Specialized User Interfaces on the PEARL Website. Maine Water Conference, Augusta, ME, March 22, 2005.

Nelson, S.J., K.C. Weathers, **K.B. Johnson**, J.S. Kahl, 2005. Does Vegetation Matter? Mercury Deposition at Acadia National Park, Maine. Maine Water Conference, Augusta, ME, March 22, 2005.

Nelson, S.J., 2005. Invited Lecture: Modeling atmospheric deposition using GIS techniques, INT527. University of Maine, Orono, Maine, November 14, 2005.

Nelson, S.J., K.C. Weathers, C.S. Loftin, **K.B. Johnson**, J.S. Kahl, 2005. Poster and abstract: Pick your season: under-estimation (summer) and over-estimation (winter) of total mercury deposition by MDN collection methods at Acadia National Park, Maine. National Atmospheric Deposition Program 2005 Scientific Symposium and Annual Technical Committee Meeting, Jackson, Wyoming, September 27-30, 2005.

Nelson, S.J., K.C. Weathers, C.S. Loftin, **K.B. Johnson**, J.S. Kahl, 2005. Poster and abstract: Pick your season: under-estimation (summer) and over-estimation (winter) of total mercury deposition by MDN collection methods at Acadia National Park, Maine. North East Regional Air Quality Committee Annual Meeting, Roosevelt Campobello International Park, Campobello Island, Canada, September 7-9, 2005.

Nelson, S.J., C.S. Loftin, J.S. Kahl, I.J. Fernandez, K.C. Weathers, K.E. Webster, 2005. Oral: An empirical model for deposition of atmospheric contaminants and marine aerosols at Acadia National Park. Canon National Parks Science Scholars Program, Ensenada Blanca, Mexico, April 9-13, 2005.

Ness, K. 2005. What are the effects of shoreline development on lakes in Maine? Oral presentation at the Environmental Studies Colloquium, March 2005, Colby College, Waterville, ME.

Ness, K., K.E. Webster, R. Bouchard. 2005. What are the effects of shoreline development on lakes in Maine? Oral presentation at the 7th Annual Association of Graduate Students Research Exposition, April 2005, Augusta, ME.

Ness K., K.E. Webster, and R.J. Bouchard. The effects of shoreline development on habitat complexity of lake littoral zones in Maine. Maine Water Conference, Augusta, ME, March 22, 2005.

Peckenham, J. and **T. Thornton** (2005) The Impact of Gravel Pit Mining on Water Quality, New England Water Works Association Annual Convention, Rockland, Maine, September 19, 2005.

Peckenham, J., C. Schmitt, and **T. Thornton** (2005) Source Water Lakes and Ponds as Water Quality References, Univ. Council Water Res. Annual Conf. July 2005.

Peckenham, J. and A. Tolman (2005) Source Water Protection in Maine: Implementing the Results of the Assessment Process, Ammerican Water Works Assoc. Source Water Protection Symposium, Palm Springs Gardens, FL, January 2005.

Peckenham, J. (2005) Partnerships for Source Water Protection, Keynote Address, New England Water Works Association Annual Convention, Rockland, Maine, September 19, 2005.

Peckenham, J. and **T. Thornton**. The Future of Drinking Water in Maine. Maine Water Conference, Augusta, ME, March 22, 2005.

Peckenham, J. and **T. Thornton** (2005) The Fresh Water Initiative- The Impact of Gravel Pits on Water Quality and Quantity- Lamoine, Hancock, and Ellsworth, Maine, Lamoine, Maine, July 19, 2005.

Rosfjord C., K. Webster, S. Kahl, S.Norton, and I. Fernandez. Are the Clean Air Act Amendments working? A 20 year re-evaluation of biologically relevant chemistry in Northeastern lakes. Maine Water Conference, Augusta, ME, March 22, 2005.

Schmitt, C. Beneath the surface: Uncovering the environmental history of the Penobscot River, Mitchell Center Spring 2006 Lecture Series, University of Maine, January 19, 2006.

Schmitt, C. Communicating ecosystem restoration: Dam removal as a case study, presented at the 2005 Meeting of Universities Council on Water Resources/National Institutes of Water Resources, Portland, Maine, July 12-14, 2005.

Schmitt, C.V., R. Hallsworth, S.J. Nelson, 2005. Map Products: Kenduskeag and Penobscot Watershed GIS Maps. Information Kiosks funded by Sea Grant and NOAA.

Thornton T. and L. Osher. Hexazinone Movement from Upland Soils to Surface Waters via Groundwater. Maine Water Conference, Augusta, ME, March 22, 2005.

Vaux, P. Freshwater Biodiversity in Maine: Status, trends and information gaps. Maine Water Conference, Augusta, ME, March 22, 2005.

Vaux, P. Participation / presentation in Lake classification workshop: Lansing MI, November 2005.

Conferences, Workshops, Annual Meetings

Maine Water Conference 2005
Augusta Civic Center, Augusta, ME. March 22, 2005
The eleventh annual Maine Water Conference took place at the Augusta Civic Center of March 22, 2005. Over 350 water resource professionals, researchers, consultants, citizens, students, regulators, and planners attended the conference. The keynote address was given by The Honorable Tom Allen who spoke on "The Great Policy Abyss: Oceans and Estuaries in the 21st Century". Other plenary speakers included Shippen Bright, Chair of the Federal Invasive Species Advisory Committee, Dave Evers, Executive Director of Biodiversity Research Institute, and John Banks, Director of Natural Resources with the Penobscot Indian Nation. Afternoon sessions topics included: Estuaries – where rivers meet the sea; Mercury, endocrine disruptors and other emerging contaminants; Drinking water planning and conflicts; Connecting the data; State of Maine's environment; and a community roundtable. The conference is run in collaboration with the USGS Maine Water Science Center and the following sponsors: Maine Drinking Water Program, Portland Water District, Aqua Maine, Maine Department of Environmental Protection , Maine Geological Survey, Maine Rural Water Association, Maine Wastewater Control Association, Maine Water Utilities Association, Maine Congress of Lake Associations, Maine Volunteer Lake Monitoring Program, University of Maine Cooperative Extension, Maine Rivers, and Maine Sea Grant.

The session on estuaries at the Maine Water Conference was attended by over 80 people. The session generated such interest that it resulted in a spin-off conference in April 2006 dedicated solely to estuaries.

Maine Stream Summit (MESS)
University of Maine Hutchinson Center, Belfast, ME. April 8, 2005.
Mitchell Center staff and students participated in the planning and coordination of the third annual Maine Stream Summit (MESS) in collaboration with Maine Department of Environmental Protection. MESS is a gathering of citizen and school groups sharing monitoring, research, restoration, and other stewardship work on local streams and rivers. MESS included a wide variety of presentations, including the keynote presentation by Aram Calhoun, Associate Professor of Wetlands Ecology at the University of Maine. Other topics included physical and chemical monitoring in streams and rivers, macroinvertebrate monitoring and identification, access to freshwater data on the internet, managing and presenting water quality data, invasive plants and animals, wetlands, and partnering with local businesses and municipalities.

Exhibits at Conferences and Events
Maine COLA Annual Conference – Mitchell Center and PEARL Exhibits
Maine Water Conference – Mitchell Center and PEARL Exhibits

Public Service

Media/Press
Schmitt, C. "Penobscot River future tied to past," Bangor Daily News, Dec. 26, 2005, p.C1, C3.

Schmitt, C. "Fewer dams let Penobscot River flow," Bangor Daily News, Dec. 27, 2005, p.C4.

Schmitt, C. "Honoring Mitchell's environmental legacy," Bangor Daily News, April 21, 2005.

12/14/2005, Christian Science Monitor, John Peckenham, interview and article on *In selling Maine's fresh waters, does Maine get a cut?*

7/19/05, Bangor Daily News, John Peckenham, interview and article on *Development's impact on aquifers eyed*

Workshops and Other Activities

Mitchell Center Seminar Series
In 2004, the Mitchell Center initiated a seminar series at the University of Maine campus. Seminars are open to all and take place over lunch break to allow for maximum participation. The seminars have become increasingly successful and draw a diverse audience from both on- and off-campus. In 2005, the seminars were moved from the conference room into a classroom setting to accommodate the larger audience. Mitchell Center graduate students are also given the opportunity to participate and present their research.

Speakers for spring 05 included: Arlene Olivero, The Nature Conservancy; Jeff Varrichionne, Maine Department of Environmental Protection; Neil Kamman, Vermont Department of Environmental Conservation; and Dave Courtemanch, Maine Department of Environmental Protection.

The fall 2005 series was based on the theme "Juggling research, policy and management decisions for state, federal and conservation lands". Speakers included representatives from Maine Dept. of Conservation, Moosehorn National Wildlife Refuge, National Park Service, Forest Society of Maine, and Acadia National Park. Representatives from Plum Creek Timber Company, National Resources Council of Maine, and Moosehead Region Futures Committee also spoke on a proposed development plan for the Moosehead Lake region of Maine. Controversy has surrounded this plan, and the Mitchell Center was able to provide an opportunity for people to hear the various sides of the issue.

Guest Lectures

The Mitchell Center hosts occasional guest lecturers as well as its regular seminar series. Dave Krabbenhofft, a Research Scientist with the USGS Mercury Research Lab in Middleton, WI, gave a talk on Mercury Contamination of the Environment: A Wide Spread Problem with an Uncertain Future on February 21, 2006. The talk was cosponsored by the UMaine Program in Ecology and Environmental Science.

PEARL – The Source for Environmental Information in Maine

Live site: www.pearl.maine.edu   Production site: www.pearlmaine.com
With funding from a variety of sources, the new PEARL site went live in summer 2005. Reconstruction of the site was planned to incorporate addition of river, stream and terrestrial data and provide access to various focus topics and educational information – and to make the site more "user-friendly". Information from PEARL is used by a wide audience, from researchers to the general public, and it has become increasingly important to provide access options for the various users.

Funding from Maine Inland Fisheries and Wildlife and USGS allowed integration of stream and river data into the database. This provided the support for the addition of databases from the Maine Aquatic Biodiversity Project and from IF&W. Salmon fisheries data has been added using funding from the Atlantic Salmon Commission. New interfaces for specific user groups provide educational features along with data specific to that particular group.

USGS support allowed integration of the Penobscot River Synthesis into PEARL in 2005. This site compiles a literary review and data inventory of current and past research on the Penobscot River. As the Penobscot River Restoration Project moves, this site continues to expand to meet the needs of researchers involved in studying the Penobscot River ecosystem pre-and post-dam removal.

Maine Department of Environmental Protection continues to provide long-term support for the project.

SPARC – Searchable Park Access to Research Catchments

Website: http://www.umaine.edu/SPARC
SPARC is an on-line forum designed to facilitate access to information about research in catchments of U.S. National Parks. Catchments integrate ecosystem responses to the environment, and to changes in the environment. Following up on the US Environmental Protection Agency/National Park Service PRIMENet initiative, our goal was to create a web-based information network for gauged catchments in National Parks.

The pilot project was completed in late 2005 and is available at the address listed above. The Acadia National Park site section is complete and includes general park information and links along with specific information on the research catchments. The searchable database for Acadia includes research projects compiled from Investigator Annual Reports and other sources, and a bibliography of reports, journal articles, press articles and other materials. A direct link to the PEARL data base provides data for Acadia and the surrounding area.

Penobscot River Restoration Trust
In June 2005, the Penobscot River Restoration Project was announced. The agreement allows removal of the two lower dams on the Penobscot River and decommissioning of a third dam with approval to construct an innovative fish passage. Since the announcement, Mitchell Center staff have been working with members of the Penobscot River Restoration Trust to bring together researchers interested in participating in the project. The Penobscot River Synthesis (see above) has provided additional impetus for this collaborative role for the Mitchell Center.

Cheryl Daigle, the Trust's Community Liaison and Outreach Coordinator, is also housed at the Mitchell Center.

Penobscot River and Bay Institute
May-June 2005: Penobscot River Keepers Expeditions. These day-long canoe expeditions on the Penobscot River provide students in grades 7 to 12 an opportunity to learn about rivers, watersheds, history, and ecology. In 2005 over 450 students took part in the expeditions.

Waterlines
Three issues of our Waterlines newsletter were published in 2005. The newsletter is a hybrid web/hard copy that has decreased paper and mailing costs while simultaneously increasing circulation and content. The main publication of Waterlines is now done online with an accompanying email sent to our subscription list. A printed, one-page "headline" version is still available and is sent to select subscribers including media sources, our congressional delegation, University administration, Board members and others including those without e-mail capabilities. This hard copy version is also used to provide an introduction to organizations and individuals who may not be familiar with the Mitchell Center. Our intent is to reduce costs, increase circulation, and augment the scope of coverage on water issues in Maine. The newsletter continues to contain information on ongoing and upcoming grants, developments at the Center, news releases from the University on water resources related issues, and announcements for our conferences.

Informational Digests and White Papers
Informational digests provide an important outlet for the Mitchell Center to publish research and technical information in a format where it is readily available to the public. New digests are available both in online and hard copy format. Online publications are published as Acrobat and html documents to meet accessibility requirements. Two new digest were published during 2005: Arsenic in Maine Groundwater: Guidance for Small Water Systems and A Field Guide to Aquatic Phenomena (also available on the web at http://www.umaine.edu/waterresearch/FieldGuide/index.htm). These digests were funded by the Maine Drinking Water Program and the USGS respectively.

In March 2005, a white paper entitled "The Use of Biosolids in Maine: A Review" was published by John Peckenham. The goal of the white paper was to review research on the environmental benefits and risks associated with the beneficial reuse of biosolids. The work examined two major questions: 1) Is the beneficial reuse of biosolids, as regulated and practiced in Maine, sufficiently safe and protective of public health and the environment, particularly soil and water quality? 2) Maine public policy since 1988 favors the beneficial use of biosolids over disposal options such as incineration or landfilling; is this beneficial use of biosolids supported by research? Answers to these questions were derived from numerous information sources: peer-reviewed research reports; conference proceedings; National Academy of Science Publications; and state and federal rulemaking documents and regulations. The white paper was intended to be a comprehensive and independent assessment of the beneficial reuse of biosolids as practiced in the state of Maine. The publication is available in hard copy format and on the web at http://www.umaine.edu/waterresearch/outreach/biosolids_white_paper.htm.

Working with Teens on Lake Pollution Problems
Mitchell Center alumna Laura Wilson and graduate student Teresa Thornton spent their summer working with disadvantaged high school students through the University of Maine's Upward Bound program. The students have spent the past month investigating pollution levels in Pushaw Lake, where homeowners have struggled with algae blooms for more than three decades.

Committees and Service:

John Peckenham
- River Flow Advisory Commission- Drought Task Force
- Maine Water Conference Organizing Committee
- Maine Water Utilities Association- Water Resources Committee
- Sustainable Water Withdrawal- Land and Water Resources Council
- Maine Waste Water Control Association- Residuals Management Committee
- Penobscot River and Bay Institute- Board of Directors
- Northern Maine Children's Water Festival
- DEP-Consulting Engineers of Maine Task Force
- Private Well Initiative

Sarah Nelson
- Professional Employees Advisory Council
- Skowhegan High School Environmental Chemistry Water Project mentor
- Maine Water Conference Organizing Committee
- Chair, Planning Board, Town of Clifton, Maine

Peter Vaux
- Development of databases and on-line dataresources with Mount Desert Island Water Quality Coalition
- Development of databases and on-line data resources Union River Watershed

Ken Johnson
- Member of the Atlantic Salmon Federal water quality/quantity working group
- Community outreach for NOAA Liming Committee meeting

- Water chemistry data talk and discussion for the Narraguagus River Watershed Coalition
- Talk and discussion on acid rain for the Union River Watershed Coalition.

Catherine Schmitt
- Co-Chair, 2005 Maine Water Conference

Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	2	0	3	1	6
Masters	8	0	0	1	9
Ph.D.	2	0	0	1	3
Post-Doc.	0	0	0	0	0
Total	12	0	3	3	18

Notable Awards and Achievements

Mitchell Center Graduates Four Mitchell Center students graduated with Masters degrees in Ecology and Environmental Science with an option in Water Resources. Graduating were Lucner Charlestra, Catherine Rosfjord, Kit Sheehan and Heather Caron. Research topics for these students included monitoring pesticide levels in Downeast rivers near blueberry fields, statistical resampling of northeastern lakes to ascertain the results of the Clean Air Act, quantifying mercury flux in forest litter at Acadia National Park, nutrient and groundwater dynamics in Fresh Meadow Estuary.

Researcher receives award to develop citizen-based monitoring plan for mercury at Acadia National Park Sarah Nelson received funding from Acadia Partners for Science and Learning for "How much is enough? Developing a citizen-based monitoring plan for mercury in gauged watershed streams at Acadia National Park." The project will continue the long-term record of mercury data in paired research watersheds at ANP while determining the appropriate timing and frequency of sampling to capture the essential data used to calculate mercury budgets in the watersheds. The project will also develop a long-term monitoring plan for mercury in these watersheds that includes high school students as citizen scientists.

Awards to Mitchell Center Students Graduate student Kirsten Ness received the award for Best Oral Presentation in the Ecology and Marine Sciences category at the Association of Graduate Students Research Exposition. Graduate student Melinda Diehl received the award for Best Graduate Student Poster at the 2005 Maine Water Conference. Melinda also received funding from the Association of Graduate Students to attend the Gordon Research Conference on Catchment Science where she presented.

USGS Mercury Research Lab Provides In-kind Support The USGS research lab worked with Mitchell Center researchers to support the project: Does mercury migrate from soils to snowpack? The lab provided analysis of 50 samples for isotopic and total mercury analysis.

Public Meeting Probes Aquifer Research Findings In July, Mitchell Center Assistant Director John Peckenham and graduate student Teresa Thornton presented their findings at a public meeting from a study which explored the relationship between sand and gravel mining and groundwater resources in the towns of Lamoine, Hancock, and Ellsworth. The results of the research concluded that although the

groundwater was far from polluted, it did show subtle signs of strain.

Special Issue of the Journal Environmental Monitoring and Assessment In February 2006, Sarah Nelson of the Mitchell Center and Steve Kahl, Plymouth State University submitted a group of eleven manuscripts to become a special issue of the journal Environmental Monitoring and Assessment. Nelson and Kahl serve as guest editors for the special issue. Titled Mercury and nitrogen biogeochemistry in paired watershed studies at Acadia National Park, Maine, USA, the special issue is slated for publication in early 2007. The manuscripts report on research at paired gauged watersheds at Acadia National Park, studied by Mitchell Center (Ken Johnson, Sarah Nelson, Steve Kahl) and UMaine (Bruce Wiersma, Molly Schauffler) researchers since 1998. In addition, papers by Mitchell Center researcher John Peckenham and US Geological Survey researcher Martha Nielsen put the small watershed results in an island-wide context; an introduction by Kathy Tonnessen and David Manski of the National Park Service lends a policy and management perspective. A set of papers on mercury in Acadias biota by UMaine researchers Michael Bank and Jerry Longcore (USGS) include a review of previously unpublished results from various UMaine studies, and new information indicating that the mercury problem is Acadia is significant for wildlife there (see also M. Edgecomb, Bangor Daily News, Jan. 5, 2004).

The USGS base grant provided a basis for the Senator George J. Mitchell center to secure other research funding. The following projects were funded in 2005: Title: PEARL Investigator: Vaux Agency: Maine Department of Environmental Protection. Title: Fisheries Data Integration Project Investigator: Vaux Agency: Maine Department of Inland Fisheries and Wildlife Title: Developing PEARL as the Environmental Database for Atlantic Salmon Restoration (on-going) Investigator: Vaux Agency: Atlantic Salmon Commission Title: Water Chemistry Trends in Downeast Salmon Tributaries (on-going) Investigator: Johnson Agency: Atlantic Salmon Commission Title: Biosolids White Paper Investigator: Peckenham Agency: State Planning Office Title: Systematic Chemistry Survey of Salmon Rivers Investigator: Johnson Agency: National Fish and Wildlife Foundation Title: Road Salting Impacts on Atlantic Salmon Investigator: Johnson Agency: National Fish and Wildlife Foundation Title: Do water sampling techniques affect aluminum speciation? (on-going) Investigators: Johnson/Nelson Agency: Atlantic Salmon Commission, 2006 ($15K) Title: Closing the loop on hydrologic and mass balances for a temperate forested park (on-going) Investigator: Nelson Agency: Canon National Parks Science Scholarship (on-going) Title: SPARC Searchable Public Access to Research on Catchments Investigator: Vaux Agency: National Park Service Title: A hydrogeomorphic lake classification system for refining lake assessment at multiple spatial scales (on-going) Investigators: Webster, Vaux, Bell, Bacon Agency: EPA Title: Can Gravel Mining and Water Supply Wells Coexist? (on-going) Investigator: Peckenham Agency: Island Foundation Title: SWWAT Source Water Analysis and Warning Technology (on-going) Investigator: Peckenham Agency: EPA Title: Penobscot River Synthesis (on-going) Investigator: Schmitt Agency: French Foundation Title: The Impact of Vehicle Traffic on Water Quality in Acadia National Park Investigator: Peckenham Agency: National Park Service Title: Acidity partitioning model development Investigator: Johnson Agency: Atlantic Salmon Commission, 2006

Publications from Prior Projects