# THE TRANSPORT, TRANSFORMATION, AND TROPHIC TRANSFER OF BIOACTIVE METALS IN AN URBAN IMPACTED BUOYANT RIVER PLUME

By

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#### ABSTRACT OF THE DISSERTATION

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At the mouth of the Hudson River estuary, one of the most urbanized and pollution impacted estuaries in North America, estuarine water forms a buoyant plume which transports nutrients and contaminants into the Mid-Atlantic Bight. As part of the LaGrangian Transport and Transformation Experiment (LaTTE), the transport, transformation, and zooplankton bioaccumulation of contaminant and terrestrial metals (Ag, Al, Cd, Cu, Fe, Hg, Mn, Pb, Zn) in the plume were examined in May 2004, April 2005, and May 2006. In order to determine the low level concentrations of dissolved metals in plume waters, an improved method for determining metals in seawater by online column preconcentration, isotope dilution HR-ICP-MS was developed. Within the plume, metal concentrations generally decreased as plume waters were diluted with low metal shelf water. Within the plume, particle sinking was an important loss mechanism for metals. The formation of a narrow coastal current resulted in rapid down shelf (southward) transport of plume constituents, while the formation of a large recirculating eddy delayed down shelf transport, resulted in increased particle sinking, and may result in cross shelf (eastward) transport if shifting winds advect plume waters offshore. Results suggest that while plume particulate matter was composed of a mixture of biogenic and

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terrigenous material, metals were primarily (54-100%) associated with terrigenous particles. Hg in the plume was largely associated with particulate matter (median 61%) and dissolved Hg had similar concentrations as those in North Atlantic surface waters. Water-particle distribution coefficients (K<sub>D</sub>) for Hg were relatively constant in 2004 and 2005, but decreased within the plume within the phytoplankton bloom at mid salinity in 2006, suggesting that plume phytoplankton may release Hg binding ligands in response to metal stress. With the exception of Cd, metals in plume copepods were elevated relative to oceanic copepods. Modeling results show that trophic transfer was an important bioaccumulation pathway for Cd, Cu, and Zn, while the importance of this pathway for Ag was less clear. Comparison with toxicity data suggests that plume zooplankton may experience sub-lethal toxic effects from Ag and Zn, however future work will be required to confirm or refute this hypothesis.

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#### **Chapter 1: Introduction**

The Hudson River estuary, located in the heart of the New York/New Jersey metropolitan area, is one of the most urbanized estuaries in North America. It is heavily impacted by industrial discharge, historic contamination, and wastewater discharge (Feng et al, 1998; Williams et al, 1978; Brown, 1985) which accounts for roughly 10% of the Hudson River's mean flow.

Within the estuary, contaminant metals have accumulated in sediments to high, even potentially toxic levels (Heyes et al, 2004; Menon et al, 1998). This has resulted in elevated levels of Cu, Hg, Ni, Pb, Sn, and Zn in benthic mussels within the Hudson Raritan estuary (Kimbrough et al, 2008), an important indicator species due to its widespread distribution and direct exposure to local sediments. Unlike many organic contaminates, metals concentrations within these mussel populations are generally not decreasing significantly with time. This suggests that despite the decrease in dissolved metal concentrations in the estuary (Sanudo-Wilhelmy and Gill, 1999), their persistence in the sediments continues to affect species within the estuary.

At the mouth of the estuary, water from the Hudson River forms a buoyant plume (Fig. 1) that has the potential to transport nutrient and contaminant-laden water into the Mid-Atlantic Bight. The ultimate fate of the material within the plume is dependant primarily on physical transport processes. The formation of a narrow coastal current results in rapid down shelf transport of plume constituents, while the formation of a recirculating bulge (as observed in April 2005, see Fig. 2), delays down shelf transport, and may result in cross shelf transport if shifting winds advect the bulge waters offshore.

The LaGrangian Transport and Transformation Experiment (LaTTE) is unique in several ways when compared to most studies of trace metals in the estuarine and coastal systems. Few studies have examined the biogeochemical cycling of contaminant metals in estuarine river plumes, and I am not aware of any others which have done so in a LaGrangian manner. Another unique feature of LaTTE is the interdisciplinary nature of the research, its location within a coastal ocean observatory, and the integration of the results in sophisticated numerical models. This provides a rich framework for interpreting field results, which is rarely available within a single set of experiments.

(LaTTE) utilized a combination of traditional field sampling techniques and numerical modeling to assess the rates that chemical and biological processes transform metals, nutrients, organic contaminants, and organic carbon within the Hudson River buoyant plume. One goal of LaTTE was to try to bring the time scale of the chemical sampling closer to the time scales of the physical and biological processes. While there is still much progress to be made on this front, progress was made in some areas using continuous underway sampling, and semi-continuous measurement of chemical species such as dissolved gaseous mercury (DGM).

Within the context of the LaTTE project, the objectives of my dissertation are to (Fig. 3):

- Estimate advective fluxes of metals associated with the HR plume to the shelf
- Quantify the vertical fluxes of metals into and out of the HR plume
- Quantify the transformation (ex dissolusion/adsorption) of metals within the HR plume
- Evaluate the bioavailability and trophic transfer of metals in the plume

LaTTE cruises were conducted in May 2004, April 2005, and May 2006. During each cruise, injection of Rhodamine dye allowed a water mass to be traced for 2-3 days. 2 injections were performed in 2004 and 2005, and one in 2006 for a total of 5 experiments. In 2004 and 2006, sampling was carried out under moderate discharge conditions that generally resulted in a characteristic southward flowing coastal current, with the exception of the first experiment in 2004, which was forced northeast, along Long Island. In contrast, April 2005 sampling was carried out immediately following a 10-year high discharge rate which resulted in the formation of a large recirculation zone that occupied the entire New York Bight. These contrasting discharge regimes and circulation patterns will allow the above objectives to be evaluated over a range of conditions.

#### **Overview of the Dissertation**

This dissertation is divided into three chapters of original research (Chapters 2-4), followed by final chapter (Chapter 5) detailing the major research findings of this dissertation, and outlining the major unanswered questions that will provide a framework for future research.

Chapter 2, The fate and transport of trace metals in the Hudson River Plume, is divided into two parts. The first part discusses the analysis of Fe, Cu, Ni, Zn, Cd, and Pb in coastal seawater by online pre-concentration and isotope dilution HR-ICP-MS. This portion details the development of a method for the automated analysis of trace metals for the purpose of its application to Hudson River plume waters. The second portion of this chapter combines this data with particulate metal data to evaluate the fate and transport of metals within the Hudson River plume. A simple box model is used to examine the effect of physical processes on the particle export, down shelf and cross shelf transport of metals by the plume.

Chapter 3 discusses the fate and transport of Hg in the Hudson River plume. Speciation and partitioning are discussed, and a simple box model is used to examine the effect of physical processes on the volatilization, particle export, down shelf and cross shelf transport of Hg by the plume.

Chapter 4 examines the bioaccumulation and trophic transfer of metals in plume zooplankton. Bioaccumulation and biomagnification factors are calculated, and kinetic modeling is utilized to estimate the relative contributions of dissolved uptake and trophic transfer to zooplankton body burdens. Spatial patterns of metal accumulation are examined, and interannual variations are discussed. Additionally, the potential for plume zooplankton to experience sublethal toxic effects from the observed body are examined.

Chapter 5 reviews the major findings of the dissertation, and discusses the future research needs.

Personal contribution to the data presented in the dissertation. – Numerous individuals assisted with the generation of data and data analysis presented here. Assistance in field sampling was provided by Lora Smith, Kristie Ellikson, and John Reinfelder. Shiptime prior to LaTTE fieldwork, and assistance in developing the sampling system was provided by Robert Chen. Under my supervision, the following undergraduate students assisted with the preparation (acid cleaning) of bottles and sampling equipment: Karan Bhandari, David Loeffler, and assistance from others. Ancillary and physical data used here were provided by LaTTE PI Robert Chant and Research Computing Specialist Eli Hunter. Contributions of others to material in chapter 2 were as follows. During much of the development of the analytical method for the determination of metals in seawater, I worked closely with Marina Chong. M. Paul Field supervised the method development throughout, providing considerable advice and technical assistance. Elemental Scientific Inc. (Omaha, NE) provided us with much of the equipment used by the method, and provided us with product and programming support. Research Computing Specialist Eli Hunter developed the peak integration software used to process the data generated by the analytical method. Under my supervision, the following undergraduate students assisted with digestion of particulate material for trace element analysis (including weighing filters for mass determinations): David Loeffler, Rebecka Spaul, Jennilynn Kos, Kristen Meistrell, and Jennifer Quinones. Advice and assistance with physical plume modeling (box models) was provided by John Reinfelder and Robert Chant, with additional physical parameters provided by Robert Houghton.

Contributions to chapter 3 were as follows. Contributions to plume modeling were as in chapter 2. DGM (dissolved gaseous mercury) data processing and flux calculations were performed by John Reinfelder. Methylmercury analysis and zooplankton Hg speciation were performed by Quicksilver Scientific (Lafayette, CO).

Contributions to chapter 4 were as follows. Samples for zooplankton metal analysis were collected and size fractionated by Tom Frazer. Zooplankton samples were then cleaned and digested by Frank Reig under the supervision of John Reinfelder, who also assisted in the determination of non-Hg trace metals by ICP-OES. Assistance with the kinetic modeling was provided by John Reinfelder. Throughout this project, M. Paul Field provided important technical assistance with the ICP-MS and ICP-OES instruments used to generate all of the non-Hg metal data. Valuable advice on sample collection and handling was provided by Robert Sherrell.

My personal contributions to the production and analysis of data presented here were primarily in the areas of method development, preparations for field sampling, field work, analytical determinations, data analysis, and interpretation. Prior to initial LaTTE fieldwork I improved our laboratory facilities and protocols for the trace determination of Hg in seawater, including the construction of a heated 4N HCl bath for bottle cleaning, the construction of a larger class 100 clean bench to improve workspace for Hg determinations, a HEPA filtered hotplate for sample digestion, and the improvement of Hg method detection limits by nearly an order of magnitude (due primarily to the use of larger bubblers and improved blank control). I also assisted in development of the sampling system, and development of sampling protocols used throughout.

In preparation for field sampling in 2004, 2005, and 2006, I assisted with the development of the sampling plan, and had primary responsibility for the preparation of the trace metal clean sampling system, bottles, filters etc. I personally performed >50% of the bottle cleaning etc., while the remainder was completed under my supervision by undergraduate students as detailed above.

In chapter 2, I personally performed the following work: I led the development of the dissolved metals in seawater method as applied to the analysis of the transition row/contaminant metals. I prepared and analyzed the dissolved metal samples, and performed the data analysis. I supervised and assisted with the digestion of particulate matter, and analyzed the particulate metal digests. I calculated Total Suspended Solids

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(TSS) based on filtere3d particulate matter, and corrected them for salt content based on ICP-OES analysis of the digests. I also calculated distribution coefficients, performed spatial analysis, and performed model calculations with assistance detailed above.

In chapter 3, I performed all dissolved and total Hg analysis, calculated distribution coefficients, performed spatial analysis, and performed model calculations with assistance detailed above.

In chapter 4, I analyzed zooplankton digests, as detailed above, performed spatial analysis, and with assistance, performed kinetic modeling analysis.

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Fig. 1. Salinity field of the Hudson River plume in May 2004, showing the formation of a narrow coastal current. Black arrows are surface currents (indicating direction with length indicating relative velocity) from CODAR data.



Fig. 2. Satellite image of the Hudosn River plume in April, 2005, showing a bulge formation and surface currents (red arrows indicate direction and length indicates relative velocity) from CODAR data.



Fig. 3. Biogeochemical cycling of trace metals in the Hudson River plume.  $M_{part}$  = metals in the particulate phase,  $M_{diss}$  = dissolved metals, Cu` = the sum of the inorganic copper complexes (which are typically more bioavailable than organic Cu complexes). Dissolved metals may be transformed by changes in redox speciation and organic complexation. Elemental mercury (Hg<sup>0</sup>) is typically supersaturated, and volatilizes to the atmosphere.

Chapter 2 – The determination of dissolved metals in the coastal seawater, and its application to the investigation of trace metal transport and fate in the Hudson River buoyant plume.

Part I. Analysis of Fe, Ni, Cu, Zn, Cd, and Pb in coastal seawater.

#### Introduction

Accurately quantifying ambient concentrations of trace metals in seawater is a significant analytical challenge. The extremely low levels of the trace metals (ppb to ppg) combined with the high salt concentrations ( $\sim 3.5\%$ ), preclude the direct determination of metals in seawater using traditional methods. To overcome this difficulty, several approaches have been developed. The classic approach is to preconcentrate the metals of interest using a chelating agent, extract them with a solvent, and back extract them into a small volume of acid, achieving a concentration of 100x or more (Bruland et al, 1979). The large preconcentration factors make these methods attractive, but they are time consuming and prone to contamination during the multiple handling steps. Other approaches include direct injection techniques ICP-MS which use various strategies to limit matrix loading to the plasma (Field et al, 1999; Chapple and Byrne, 1996; Louie et al, 2002), and coprecipitation techniques (Bloom and Crecelius, 1984; Wu and Boyle, 1997). Unfortunately, direct analysis methods generally require significant operator expertise, and do not readily lend themselves to routine use. Coprecipitation methods are effective and yield low detection limits, but do not lend themselves to automation, limiting sample throughput. Low sample throughput is considerable limitation for projects such as the LaGrangian Transport and Transformation Experiment (LaTTE), which generate large sample loads.

An alternative is to use a chelating ion exchange resin to preconcentrate the analyte, while reducing problematic matrix components (ex Na, Ca, Mg, Cl). Chelating resins generally consist of a metal binding ligand immobilized on an inert support (ex quartz beads, or various polymers). The resin works by binding the analyte(s) and subsequently allowing their quantitative and/or reproducible recovery, usually achieved by using a low pH eluent. This alternative has the advantage of large preconcentration factors, and efficient matrix separation. It also readily lends itself to automation, making the processing of large numbers of samples possible. For these reasons, we elected to develop an automated method for trace element determination in coastal seawater based on column preconcentration, isotope dilution HR-ICP-MS, which would have sufficiently low detection limits to routinely determine the analytes of interest in coastal seawater.

#### Methods

For this work, the instrument used was either an Element or Element XR (Thermo Finnigan) High Resolution (HR) ICP-MS. Typical operating parameters are shown in Table 1. The standard Ni cones were replaced with Al cones in order to reduce the Ni blank. The standard torch and injector were replaced with a precision torch and an O ring free quartz injector (Elemental Scientific Inc, ESI; Omaha NE). An Apex high sensitivity inlet system (ESI) was used to maximize sensitivity at a low nebulizer flow rate of ~100  $\mu$ l min<sup>-1</sup>). In order to sufficiently reduce oxide interferences on <sup>110</sup>Cd and <sup>111</sup>Cd, an additional prototype desolvating unit was added between the Apex and injector. This desolvating unit, which removes residual water vapor from the sample stream, consists of

5 parallel Nafion membranes within an outer shell. A counter current Ar flow is then passed through the outer shell, selectively removing water vapor without loss of analytes.

In order to achieve the necessary scan speed for the measurement of transient signals, the instrument method was optimized for rapid scanning (~1.5 s) as follows. All isotopes were measured in medium resolution ( $M/\Delta M = 4300$ ), which is sufficient to separate all significant spectral interferences from the measured isotopes of the first row transition elements (<sup>56</sup>Fe, <sup>57</sup>Fe, <sup>60</sup>Ni, <sup>62</sup>Ni, <sup>63</sup>Cu <sup>65</sup>Cu, <sup>66</sup>Zn, and <sup>68</sup>Zn). Measuring all isotopes in one resolution setting eliminates the time consuming step of changing resolutions, which would otherwise severely hamper the ability of the instrument to measure transient signals. In medium resolution, molybdenum oxide interferes on both measured Cd isotopes (<sup>110</sup>Cd and <sup>111</sup>Cd), however, as a resolution of >17,000 is required to resolve this interference, it is not advantageous to analyze Cd at the instruments highest resolution (R=10,000). For each isotope, method settings were: mass window = 100, sample time = .003s, search window = 50, integration window = 60.

Tuning was conducted by adding Y and U to the elution acid and tuning for maximum possible sensitivity (generally >2 million cps for 1ppb U) while maintaining low oxides (<0.5% UO<sup>+</sup>/U<sup>+</sup>).

*Reagents* - Ultrapure water (>18.2 Mohm cm<sup>-1</sup>) was provided by a Milli-Q Academic water system. The ultrapure water used for the probe rinse and column washing solutions was replaced daily. Acetate buffer was prepared by pouring 35 mL Baseline Acetic Acid and 45 ml of Baseline Ammonia solution (Seastar Chemicals) into a 2L PFA bottle containing 0.5L of Ultrahigh purity water and diluting to 1L. The pH was then adjusted to ~5.5 using high purity Acetic Acid or Ammonia. The elution acid was prepared by diluting concentrated Optima nitric acid (Fisher Scientific) to 1 N with ultrapure water in a 2L PFA bottle. The elution acid was then transferred to a 10L HDPE bottle, and 1ppb of Y and U were added for tuning.

*Calibration* – Calibration of seawater samples was performed by spiking each acidified seawater sample with an enriched isotope spike, and calculating the concentration of each element in the original sample using the isotope dilution technique. Isotope dilution is a robust calibration technique whose advantages include the internal standardization of each sample, and insensitivity to instrument drift or changes in column performance within a run. Each element was quanitified based on the ratio of the unspiked isotope (<sup>56</sup>Fe, <sup>60</sup>Ni, <sup>63</sup>Cu, <sup>66</sup>Zn, <sup>111</sup>Cd, and <sup>208</sup>Pb) and the enriched isotope (<sup>57</sup>Fe, <sup>62</sup>Ni, <sup>65</sup>Cu, <sup>68</sup>Zn, <sup>110</sup>Cd, and <sup>204</sup>Pb).

The enriched isotopes were obtained from Oak Ridge National Laboratory (Oak Ridge TN), solubilized, and diluted with 3% HNO<sub>3</sub>. Element standards at natural abundances were purchased from High Purity Standards (Charleston, SC). Spike solutions of individual elements were then combined into a multielement spike, which was then calibrated by reverse isotope dilution ICP-MS as follows. The instrument mass bias correction was determined for each element by measuring the difference in the determined isotopic ratio in a natural abundance standard, and the accepted natural abundance. All subsequent element ratio determinations were corrected for instrument mass bias using these correction factors. Following the mass bias determination, the isotopic ratios were determined for each element in the multielement spike solution, and a mixture of the multielement spike and an unenriched multielement standard. These ratios

determined ratios were then used to calculate the concentration of each element in the multielemet spike.

Prior to analysis, acidified seawater samples were spiked with enriched isotopes, which were allowed to equilibrate for a minimum of 36 hrs.

Analytical system - The sample uptake/column loading was achieved using a SC Fast integrated autosampler and programmable 6 port flow injection valve (ESI), with the column inserted into the sample loop as shown in Fig. 1. In order to minimize the blank and achieve the lowest possible detection limits, we eliminated the use of peristaltic pump tubing from the system, as it has been shown to be a significant source of blank for some elements (Beck et. al., 2002). The SC fast typically uses a vacuum to load the sample loop of its 6 port flow injection valve. By replacing the sample loop with the column, the vacuum can then be used to load the column with buffered sample, eliminating this potential source of contamination. Also, by inserting the buffer line and a mixing tee into the sample uptake line just before the valve, the samples and blanks are automatically buffered in the correct ratio when the vacuum pump is activated, eliminating pump tubing from the buffer line. Additionally, the peristaltic pump tubing was eliminated from the eluent line by pressurizing the eluent bottle with 10-20psi of 0.2µm filtered nitrogen. The elution rate can be optimized by simply adjusting the inside diameter and/or length of the elution line, and adjusting the pressure on the bottle.

The column was prepared by pipeting the commercially available IDA resin Toyopearl AF chelate 650 (Tosoh Bioscience) into a 2 cm all plastic minicolumn with non metal frits (MC-2CNME, Global FIA). The uptake tubing consisted of a 1.1m length of teflon PFA, ESI yellow tubing with an integrated PFA uptake probe that utilized an encapsulated carbon fiber support and a flanged end for connection to the mixing tee. A second uptake tube (0.5m of ESI green tubing), is fixed in a 250ml FEP bottle containing the acetate buffer. This tube connects via a flanged end to the mixing tee such that when the vacuum is applied, the sample and buffer are automatically taken up at a 2:1 ratio and mixed within the mixing tee. The small flow rates involved make it difficult to quantitatively assess whether complete mixing of sample and buffer is occuring within the mixing T, however it is assumed that samples must be sufficiently buffered based on the observed reproducibility of pH sensitive elements such as Zn.

Valve switching was performed automatically by the SC Fast software using the program in Appendix 1. Briefly, the program contains four primary phases (Table 2): 1) sample loading, 2) column washing/matrix removal, 3) elution, and 4) column conditioning. During the sample loading step, the valve switches to the load position, and the autosampler sends the probe to the first sample container. The vacuum is then activated, and  $\sim 1.5$  mL of sample (automatically buffered to pH  $\sim 5.5$  immediately before entering the valve), is loaded onto the column. Following completion of sample loading, the column washing step is performed in order to significantly reduce the major ions retained by the column. Column washing is performed by first moving the autosampler probe to an ultrapure water rinse to remove residual sample drops from the probe exterior, followed by immediately moving the probe to a second bottle of ultrapure water. Upon entering the second bottle of ultrapure water, the vacuum is activated for 100s, and ultrapure water is taken up, automatically buffered, and drawn through the column. Following the completion of column washing, the valve is switched to the inject position, allowing the elution acid (1N HNO<sub>3</sub>, Optima) to pass through the column for 2 min in the opposite direction of loading, and carry the analyte metals to the nebulizer. While the column is eluting, the uptake probe moves to the two stage autosampler rinse station and rinses with 3% nitric acid and flushes for 60 s, then moves to the two stage ultrapure water rinse and flushes with ultrapure water for 30 s. Following the completion of the elution step, the valve is then returned to the load position, the probe is rinsed in the ultrapure water rinse, and then returned to the ultrapure water reservoir. The vacuum is then activated, and the column is conditioned with buffered ultrapure water for 2min.

*Data Processing* – Data was processes using custom peak integration software written for Matlab version 7 (Appendix 2). One advantage of this software over commercially available software packages is that it includes a high degree of user control over the integration parameters that control various operations such as peak identification, peak smoothing (including choice of multiple filter types), background subtraction etc. Another advantage is that is automatically compiles the individual chromatograms from each run into a single Excell spreadsheet which includes a copy of the input parameters used to generate the data. For this work, the data was smoothed using a cosine type filter, the background was subtracted, and the peak was identified by slope and integrated to +/- 10% of the peak height. Where no peak could be identified (such as with Cd blanks, which generally do not contain any measured counts), the blank subtracted background was integrated based on a user input integration range.

#### **Results and Discussion**

*Matrix removal* – An experiment was performed to determine the minimal column washing time in order to remove sufficient matrix elements (Na, Ca, and Mg)

from the column. The nebulizer was removed from the Apex system, and the elution aerosol was collected in 15ml polypropylene centrifuge tubes and the matrix elements Na, Ca, and Mg were determined by ICP-OES (Varian, Vista Pro Radial). Based on this experiment, a 75s washing time is sufficient for a >500 fold decrease in these matrix elements using a 0.33M acetate buffer wash solution (Fig. 2). This matrix reduction should be sufficient to prevent variations in sensitivity due to the large variations in salinity frequently encountered in estuarine and near coastal waters. It also is sufficient to prevent the accumulation of salt in the Apex, membrane desolvation unit, and on the ICP-MS cones. This is important, as the accumulation of salt degrades sensitivity, causes spiking, and, may clog the pores of the desolvating membrane. Note that the washing time reported here is the length of time that the software activates the pump to deliver the washing solution. Due to the delay between the probe entering the washing solution and it reaching the column, the reported column washing times (ie the time input into the software control) exceeds the actual washing time by ~10s.

*Co-elution of peaks* – Fig 3. demonstrates the co-elution of peaks using this method. This method produces sharp peaks, which elute reproducibly, and elute rapidly (95% of the peak area within ~30s) and quantitatively within 120s using 1N HNO<sub>3</sub>. These features are important for producing high quality, reproducible data, and accurate baseline correction.

Interferences – When analysis is performed in medium resolution (M/ $\Delta$ M = 4300), the only significant interference on the isotopes measured is that of molybdenum oxide on <sup>110</sup>Cd and <sup>111</sup>Cd. Using the Apex alone, this interference accounts for approximately 50% of the measured <sup>111</sup>Cd signal. While this interference could be

corrected for mathematically, it is detrimental to accuracy and precision to make such a large correction on the isotopes in question. Therefore, we added a prototype desolvating system that utilized 5 concentric nafion tubes purged by a countercurrent Ar flow into the analytical stream between the Apex and the injector. This desolvating system selectively removes water vapor without decreasing analyte sensitivity, resulting in significantly improved oxide performace (**Fig. 4**). This results in an interference correction of <5% of the analyte signal in NASS-5, minimizing the effects on accuracy and precision.

*Detection Limits* - To determine the method detection limits 10 bottles were filled with 0.2% nitric acid, spiked with the stable isotope solution, and analyzed in succession. Detection limits were then calculated as 3 times the standard deviation of the blanks (Table 3). Blanks were generally 2-5% of CASS-4, and 3-10% of NASS-5 for elements other than Cd, where the blank was generally <1% of the peak area in both reference materials. The detection limits of this method are generally better than or comparable to similar preconcentration methods. The reported detection limits are sufficiently low to allow for quantification of each of these elements in estuarine and coastal waters. Due to improvements in the cleanliness of the uptake system used in this method, the primary limitation to detection limits is the blank associated with the pH buffer. While we made every effort to make the buffer as clean as possible (purchasing the cleanest available reagents, pouring reagents directly into the storage bottle with no pippetting or intermediate transfer bottles), the buffer blank still limits our ability to determine most elements in open ocean surface sea water.

*Precision and Accuracy* - Precision and accuracy were evaluated by analyzing replicates of CASS-4 and NASS-5 (Table 4) certified reference material (National

Research Council, Canada) on three separate occasions. Determined values were typically within the certified range, with the exception of Cu, which was consistently below the certified value in CASS-4, and low, but generally within the certified range in NASS-5.  $2\sigma$  relative standard deviations were typically less than 20%, and were less the  $2\sigma$  ranges for CASS-4 and NASS-5 certified values.

While our data demonstrate good agreement with reference materials for most elements, the difficulty of obtaining reliable copper data with this method is perplexing. When we initially observed the low bias in our copper results, we hypothesized that this was due to incomplete spike equilibration due to residual organic complexation in acidified samples. In order to test this hypothesis, we UV oxidized the May 2008 samples in 30mL FEP sample vials (Nalgene) using a custom built UV oxidation chamber, consisting of an aluminum foil lined box with 2 UV lights running the length of the interior. The 10 ml samples were oxidized in this manner for 48 hours prior to the addition of the isotope spike, which was subsequently allowed to equilibrate for 1 week. Suprisingly, the copper results from this experiment are even lower than in previous experiments, suggesting that either 1) during this experiment, the analytical system was not well controlled and was behaving in an anomalous fashion, or 2) that the difficulty is unrelated to organic ligands in the samples.

*Conclusions* - The newly developed analytical method performs well for elements other than Cu, which exhibits variable low recoveries. An important advantage of this method over many is that all components used here are commercially available. Many methods employ resins which must be synthesized by the analyst, as there is no commercial vender. Under the conditions employed here, and the commercially available IDA resin utilized in this method achieves a high degree of matrix separation.

Detection limits for this method are generally better than or comparable to other similar published methods, and it is automated and relatively simple to operate. This suggests that this method may find use for both trace metal research and routine regulatory monitoring in estuarine and coastal systems.

Operating conditions						
Instrument						
Forward power	1450 w					
Cool Gas	16 L min <sup>-1</sup>					
Aux Gas	1.0 L min <sup>-1</sup>					
Sample Gas	0.8 L min <sup>-1</sup>					
Additional Gas (Ar)	$\sim 20 \text{ ml min}^{-1}$					
Additional Gas (N <sub>2</sub> )	~10 ml min <sup>-1</sup>					
Autosampler / FIA system						
Elution acid pressure	15 psi					
Elution acid flow	$\sim 0.100 \text{ ml min}^{-1}$					
Column loading	$\sim_{1}^{2}$ 0.450 ml min <sup>-</sup>					

Table 1. Typical instrument and modified flow injection system (SC Fast) operating conditions. Typical operating parameters are given hereThe elution acid flow rate is pressure dependant.

Table 2. A simplified description of the column loading and elution Program. The full program is in Appendix 1.

Step	Time	Valve Position	Purpose
Load column	180 s	Load	Preconcentrate metals
Wash colum	100 s	Load	Matrix removal
Elute column <sup>1</sup>	120 s	Inject	Peak elution/measuement
Condition column	120 s	Load	Prepare to load next sample

<sup>1</sup>During column elution, the uptake probe is rinsed in 3% HNO<sup>3</sup> and water

	This					
Element	paper	1	2	3	4	5
Fe	23	ND	36	2000	ND	ND
Ni	4	28	18	100	29	14
Cu	7	17	ND	50	99	14
Zn	11	46	2200	ND	76	50
Cd	2	1.7	12	30	10	3
Pb	1	ND	3.6	80	7	17

Table 3. Detection limits in ng  $L^{-1}$  determined for this method and comparable published methods (ie automated column preconcentration methods).

ND = Not Determined

1 Beck et. al 2002

2 Sohrin et. al. 1998

3 Heithmar et. al. 1990

4 Hirata et. al. 2001

5 Hirata et. al. 2003

Cass 4		Cert	2σ RSD	Feb 2008	2σ RSD	May 2008	2σ RSD		
	Cd	0.026	12%	NR	10%	0.023	15%		
	Cu	0.592	9%	0.52	22%	0.179	21%		
	Fe	0.713	8%	0.707	7%	0.741	7%		
	Ni	0.314	10%	0.0311	15%	0.302	8%		
	Pb	0.010	37%	0.008	13%	0.009	20%		
	Zn	0.381	15%	0.328	12%	0.379	7%		
				n=10		n=4			
Nass 5		Cert	2σ RSD	Jan 2008	2σ RSD	Feb 2008	2σ RSD	May 2008	2σ RSD
	Cd	0.023	13%	NR	18%	NR	12%	0.022	13%
	Cu	0.297	15%	0.273	12%	0.288	13%	0.112	7%
	Fe	0.207	17%	0.237	6%	0.194	5%	0.215	17%
	Ni	0.253	11%	0.261	4%	0.260	5%	0.263	7%
	Pb	0.008	63%	0.01	12%	0.007	12%	0.008	7%
	Zn	0.102	38%	0.103	14%	0.095	15%	0.080	$34\%^{1}$
				n=10		n=10		n=4	

Table 4: Accuracy and precision results for seawater reference materials. In the left column are certified values and  $2\sigma$  uncertainties. The remaining columns contain values determined by this method on separate analytical dates. Determined and certified values are in  $\mu$ g L<sup>-1</sup>. NR = Not reported.

<sup>1</sup>Note: the high Zn variability for these samples is related to high Zn in the buffer solution on this date
the SC East quotem (ESI, Omaha NE)

Fig. 1. Method schematic. The FIA valve is the SC Fast system (ESI, Omaha NE), with the sample loop replaced by the IDA column. Liquid is drawn through the waste line by vacuum from the SC-2 autosampler (ESI, Omaha, NE)





Fig. 2. Removal of matrix ions during column washing with 0.3 M acetate buffer.



Fig. 3. Co-elution of smooth peaks using the developed method. Data in this figure is unsmoothed.

Fig. 4. Elution profile of <sup>111</sup>Cd in CASS-4 CRM and the interference peak from a 10 ppb Mo solution. Elution peaks are unsmoothed.



# Part II. Fate and transport of trace metals in the Hudson River buoyant plume: Distributions and modeling results.

#### Introducton

The Hudson River estuary is a highly urbanized estuary, which has been heavily contaminated with metals from industrial discharges, urban runoff, and inputs from wastewater treatment plants. Within the estuary, sediments are highly enriched in metals, frequently exceeding federal toxicity guidelines (Feng et al, 1998; Menon et al, 1998). Sediment resuspension events within the estuary mix contaminated sediments into the water column, and constitute a significant source of metals to estuarine waters (Sanudo-Wilhelmy and Gill, 1999; Menon et al, 1998). Additionally, inputs from wastewater treatment plants, industrial sources, and urban runoff, and atmospheric deposition to the watershed also contribute to elevated metal concentrations within the estuary (Hirschberg et al, 1996; Sanudo-Wilhelmy and Gill, 1999). Ultimately, the fraction of metals that is maintained within the water column is transported to the New York Bight within a buoyant river plume.

*Plume Dynamincs* - The Hudson River plume is a relatively thin (2-10 m) surface advected buoyant plume which extends seaward from the lower New York estuary, typically flowing down shelf (southward), along the New Jersey Coast. To the north, its flow is constrained by Long Island, which extends ~150 km to the East. Significant inputs of nutrients from the estuary (Garside et. al., 1976), result in the formation of a large diatom dominated phytoplankton bloom (Fan, 2002), where biological production rates exceed those in the estuary by a factor of 3 (Malone et. al., 1996).

The ultimate fate of trace metals within the Hudson River plume is highly dependant on the circulation and mixing within the plume, as well as its position and physical dimensions. These in turn, are primarily controlled by physical forcing from winds, and river discharge. Fieldwork in May 2004, April 2005, and May 2006 suggests that two basic scenarios control the fate and transport of plume constituents (Chant et. al., 2008): Under the first scenario, low to moderate discharge conditions and downwelling favorable winds promote the formation of a narrow (2-4 km) coastal current. Under the second scenario, high discharge conditions and the absence of downwelling favorable winds promote the formation of a recirculating bulge feature, which retains >50% of the fresh water flux (Chant et. al., 2008), preventing it from entering the coastal current. Due to the retention of fresh water within this feature, it will increase in size until the winds shift, typically within 3-5 days. The fate of material retained within the bulge then depends on the nature of the wind forcing. If the winds shift to downwelling favorable conditions, the plume will be compressed against the shore forcing the bulk of the fresh water flux back into the coastal current. Conversely, winds may also force the bulge to become detached from the coast, advecting the plume water offshore onto the shelf. These differing discharge scenarios have important implications for the transport and biogeochemical cycling of metals within the Hudson River plume. The formation of a narrow coastal current will tend to promote the downshelf transport of metals, while the formation of a recirculating bulge could potentially result in cross shelf transport. In this paper, field data and modeling results will be used to evaluate the transport, biogeochemical cycling of trace metals in the Hudson River buoyant plume. Specifically, I will evaluate the hypothesis that wind driven physical dynamics have a significant

impact on metal transport processes within the plume, and that 1) Formation of a coastal current results in significant down shelf transport of metals, and 2) Formation of a recirculating bulge retains material within the plume, increasing export of particulate and volatile forms, and providing an opportunity for cross shelf transport

Additionally, the composition of plume particulate matter, its metal enrichment, and the partitioning of metals on various types of particles will be examined in order to evaluate the relative importance of physical vs. chemical and biological processes on the ultimate fate of metals within the plume.

## Methods

In May 2004, April 2005, and May 2006, surface water sampling was performed via a trace metal clean pumping system mounted to the R/V Cape Hatteras' over the side pole. Surface water was collected via a Teflon pipe attached to a 1.25 cm OD teflon tube, that was attached to the seaward side of a stainless steel pole with an aluminum mount (Fig. 1). The pipe was mounted such that it extended in front of the aluminum mount, approximately 1.5 m from the ship's hull. All sampling occurred while the ship was travelling at 6-8 knots, with samples typically collected every 2-4 hours while underway.

During underway sampling, water was pumped onboard and into a HEPA clean bench at 3-4 L min<sup>-1</sup> with a Teflon/polypropylene bellows pump. All wetted parts of the uptake system were leached by pumping 10% HCl through the system for a minimum of 72 hrs, and rinsed copiously with ultra high purity water. Additionally, prior to sampling, the uptake system was flushed extensively with seawater.

Within the shipboard lab, trace metal clean techniques were used at all phases of sample collection and manipulation in order to minimize the potential for contamination.

Samples for dissolved metals were filtered in-line with a high capacity  $0.2 \,\mu m$ polypropylene cartridge filter, and collected in rigorously acid cleaned polyethylene bottles. In 2004-2006, whole water samples for particulate metals were collected in either a 4 or 8 L acid cleaned polycarbonate carboy, homogenized, and vacuum filtered on acid cleaned 47 mm polycarbonate filters (>2  $\mu$ m, and >20 $\mu$ m size fractions; Whatman, Nucleopore filters) or Supor filters (>0.2 µm size fractions; Pall Corporation, East Hills NY) housed in an acid cleaned all Teflon filter apparatus (Savillex, Minnetonka MN). Samples were separated into size fractions (0.2-20  $\mu$ m, 2-20  $\mu$ M, >20 μM) by serial filtration in 2004. In 2005 and 2006 parallel filtration was used instead  $(>0.2 \mu m, >2 \mu m, and >20 \mu m)$  in order to increase the mass of particles on each filter. In order to maximize the material collected on each filter, filters were loaded until the flow of filtrate was significantly reduced due to clogging. In all cases, samples were filtered using a vacuum of < 130 mm Hg to avoid breaking cells. Following collection, filters were immediately frozen and stored at -20°C until immediately prior to mass determination and analysis.

Upon returning to shore, dissolved metals were determined as described in Part I of this chapter and particulate metal concentrations were determined as follows. Filters for particulate metal analysis were digested in quartz crucibles using 5mL hot aqua regia (3:2 Optima grade HCl and HNO<sub>3</sub>, Thermo Fisher Scientific). Following digestion, undigested filter pieces were removed with an acid cleaned Tefzel forceps. Filter digests were then evaporated just to dryness (with care to avoid overheating), and metals were resolubilized in 1N HNO<sub>3</sub>. Digests were centrifuged to remove particles, diluted with ~ 3% HNO<sub>3</sub> to a final volume of 1.5-3 mL, and analyzed by HR-ICP-MS using calibration

by standard additions and In as an internal standard to monitor for drift in instrument sensitivity. A detailed description of filter blanks is given in Appendix 3.

Mass of particulate matter for each sample was determined as follows: filters were dried to constant mass in a laminar flow bench, and weighed in triplicate to  $\pm 0.1$  mg prior to digestion, with care taken not to contaminate the filters. All filters and filter blanks for mass specific particulate metals determination were weighed in triplicate prior to sample collection on an analytical balance ( $\pm 0.1$  mg). The mass on each filter was determined by difference, and corrected based on the mean difference in the mass of the filter blanks before and after sampling (< 0.2 mg). Following digestion in aqua regia, a sub sample of each digestion was retained for sodium analysis by ICP-OES, and filter weights were corrected for salt content based on those results. Mean salt corrections ( $\pm 1$ standard deviation) were 1.1 mg ( $\pm 0.5$ ) for 2 µm filters, and 1.7 mg ( $\pm 0.5$ ) for 20 µm filters. Following salt correction, total particulate mass on the filters ranged from 0.8-6.1 mg for 2 µm filters.

*Modeling of trace metal fate and transport within the Hudson River plume* – In order to evaluate the relative importance of various physical processes on the fate and transport of Metals in the Hudson River plume, a simple box model (Fig. 2) was created to evaluate four basic scenarios: 1) conditions leading to the formation of a coastal current at moderate discharge (CC 1) and at high discharge (CC 2), and conditions leading to the formation of a recirculating bulge feature with 50% of the water flux entering the coastal current (Bulge 1) and 33% of the water flux entering the coastal current (Bulge 2). In the model, the plume was assumed to be a single box, with instantaneous mixing. The following terms were input: Initial plume dimensions,

fraction of water diverted to the coastal current, concentrations of dissolved and particulate Metals in the estuary and bottom waters, vertical eddy diffusivity  $(K_z)$ , River discharge (Q), and the rate constant for particulate metal loss. Hudson River discharges (Q) were estimated from the combined flow of all USGS gauges in the watershed. The moderate discharge condition was based on the approximate Hudson River discharge at the initiation of sampling in May 2006, and the high discharge condition was the approximate average discharge during a large discharge event from March 29, 2005 until the initiation of sampling on April 10, 2005. Estuarine input concentrations were estimated from data points collected near Sandy Hook, NJ. Bottom water (shelf water) metal concentrations were estimated based on offshore surface samples. Vertical eddy diffusivity for the plume was estimated as  $K_z = dS/dt * H / dS/dz$  (Houghton et al, in preparation). Plume dimensions were approximated based on remote sensing data. Loss of particulate metals due to sinking was modeled as a pseudo first order process, and the rate constant was estimated by plotting ln[Metal<sub>particulate</sub>] vs. plume age, which was estimated based on the sample salinities and the salting rate (dS/dt) from Houghton et. al. (in preparation). Based on these inputs, the model calculates the water fluxes due to bottom water entrainment and in the coastal current, the Metals fluxes in and of the plume, and the change in plume dimensions with time under conditions of bulge growth (water retention within the plume).

In the bulge formation scenarios, the water entering the coastal current was assumed to be fully mixed plume water. Input parameters for each scenario are given in Table 1. A full algebraic description of the model is given in Appendix 4. For the first two scenarios, diverting all of the water into the coastal current (fraction to the coastal current = 1), results in a constant volume of the plume over time. This results in steady state conditions, assuming all other parameters remain constant with time. For the bulge scenarios, the bulge area was allowed to increase with time (fraction to the coastal current < 1), resulting in non-steady state conditions. In the recirculating bulge scenarios (Bulge 1 and Bulge 2), the range of 33 and 50% of the water entering the coastal current represents the upper and lower estimates from the April 2005 experiments.

The general form of the model was as follows:

 $\Delta$ Plume = HRE + BW - PS - CC

where  $\Delta$ Plume is the change in Metals in the plume over time (which is equal to 0 at steady state), HRE is the Metals input from the estuary, BW is the Metals input from the bottom entrainment, PS is the loss from particle sinking, and CC is the export of trace metals into the coastal current. Water fluxes, dissolved metal concentrations, and particulate metal concentrations were estimated from field measurements, and the transfer of each is accounted for independently in the model. Non-steady state solutions were determined numerically, with time steps of 0.1 d. Atmospheric inputs to the plume are not considered by the model, as they are highly episodic in nature, and applying mean fluxes in the model is dubious over the short time scales (0-5 days) being considered here.

### **Results and discussion**

Dissolved concentrations of Fe, Ni, Zn, and Pb in the Hudson River plume and adjacent coastal waters for May 2004, April 2005, and May 2006 are given in Figs. 3-5. A complete tabulation of all dissolved and particulate metal concentrations presented in this chapter is given in Appendix 5. Metal concentrations decreased with salinity, as plume water mixed with low metal shelf water, and metal concentrations were typically of the order Fe > Zn > Ni >Pb. Concentrations of dissolved Fe in the plume ranged from ~5-55 nM, with concentrations in 2005 and 2006 about twice those in 2004. Concentrations of Ni ranged from ~ 5-10 nM and were similar in all three years. Concentrations of Zn in the plume ranged from ~ 2-27 nM, and were lower in 2004 than in 2005 and 2006. Pb concentration in the plume ranged from ~40-280 pM, and was highest in May 2006. Overall, dissolved metal concentrations in 2004 were lower than those observed in 2005 and 2006. This is likely due to lower river discharge in 2004 (3-10x lower than 2005 and 2006), which resulted in increased dilution of estuarine water with shelf water, and higher salinities within the plume.

Measured concentrations of dissolved metals are generally lower than in the Hudson River estuary (Sanudo-Wilhelmy and Gill, 1999), and are consistent with the dilution of estuarine water with low metal shelf water. Concentrations determined within the plume, are also consistent with reported concentrations of dissolved metals off the New Jersey coast (Field et. al., 1999). The dissolved metal concentrations observed within the Hudson River plume are similar in magnitude (generally within a factor of 2) to those reported for the anthropogenically influenced San Francisco Bay plume (Hurst and Bruland, 1998), the Danube River plume (Guieu et al, 1998), and to dissolved Fe concentrations reported within the Mississippi River plume (Powell and Wilson-Finelli, 2003), and the Columbia River Plume (Lohan and Bruland, 2006), though the Columbia River plume receives large inputs of dissolved Fe from entrainment of bottom waters.

Dissolved metals in May 2004 generally showed conservative or near conservative mixing. Mixing curves for Ni and Pb are essentially conservative, while Fe appears to be slightly non conservative, though this interpretation relies strongly on the highest point. This suggests that Fe may be precipitating on particles, which is consistent with its low solubility in oxic seawater, however the evidence for this is not strong based on the salinity profiles alone. The Zn curve is approximately conservative, however it is more variable than other metals. This variability might be caused by biological cycling of Zn in surface plume waters, or alternatively, could be a result of larger analytical variability.

In April 2005 the mixing patterns are more complex, with dissolved Zn showing significant non conservative behavior. The observed dissolved metals profiles suggest that multiple mixing lines were present during the sampling period. likely due to incomplete mixing within a large recirculating bulge feature that was present during that sampling period. Dissolved Ni shows the most conservative behavior, suggesting that the estuarine Ni concentration didn't vary significantly over the sampling period. Fe and Pb profiles show more behavior than Ni, suggesting that their concentrations were more variable over the sampling period. In addition to multiple mixing lines, Fe, Pb, and Zn profiles appear to show non-conservative behavior, though the complex mixing patterns make it difficult to clearly discern the mixing lines. The apparent non-conservative behavior suggests that these metals may be partitioning to particles, or are experiencing significant uptake by phytoplankton.

Mixing patterns in 2006, with the exception of Ni, which is relatively conservative, are also somewhat complex. Dissolved Fe and Zn have numerous data points below the primary mixing line at mid-salinity (S ~26-30), while the Pb data appear to exhibit numerous points above the primary mixing line over the same salinity range,

though this may be the result of analytical variability. The observed mixing profiles of Fe, Pb, and Zn, indicate conservative mixing at high and low salinities, with significant non-conservative behavior at mid salinities ( $\sim$ 26-30). Fe and Zn anomalies lie below the mixing line, while Pb anomalies lie primarily above the mixing line. There are two possible explanations for these observations: 1) the profiles indicate mixing with a second low salinity mass which was not sampled at lower salinities, or 2) the observed deviations from the mixing line are a function of dissolved metal/particle interactions, which have resulted in the removal of dissolved Fe and Zn, and the release of dissolved Pb. In 2006, there is a mid salinity increase in TSS (likely due to an increase in phytoplankton biomass), that coincides with the anomalous behavior of the dissolved metals. This suggests that biological processes might be affecting dissolved metal profiles in the plume in May 2006, however the first possibility can not be ruled out, and may be more likely considering the observed particulate metal salinity profiles from the same sampling period. Tidal forcing results in plume waters being released in discrete pulses, and observations during LaTTE fieldwork have demonstrated that one pulse may overrun another, potentially resulting in complex salinity curves. This mechanism might also explain some of the observed complexity in 2005 profiles.

 $>20 \ \mu m \ particulate \ metals$  – concentrations of particulate metals in the  $>20 \mu m$  size fraction from the plume and adjacent coastal waters for May 2004, April 2005, and May 2006 are given in Figs. 6-8. In 2004, metals in this size fraction displayed non-conservative mixing, while in 2005 and 2006, metals displayed more complex mixing patterns.

The mass specific concentration of metals on >20µm plume particulate matter was determined in April 2005 and May 2006 (Figs. 9 and 10). In 2005, the concentrations decreased slightly with salinity, while in 2006 a much larger gradient was observed. In May 2006, the observed mass specific metal concentrations were initially greater than April 2005, though they decreased rapidly and were lower than 2005 observations at high salinities.

Within this size fraction, it is likely that metal concentrations are dominated by phytoplankton, especially at higher salinities, as large sediment particles would be expected to sink rapidly upon exiting the estuary. The non-conservative behavior of >20 $\mu$ m metals in May 2004 is most likely due primarily to particle sinking, as there is no concurrent increased in dissolved metals which would be expected if dissolution was significant. It is possible that these profiles could indicate a shift of metals to smaller particles, however this is unlikely as filters of 2-20 $\mu$ m particulate material in 2004 failed to yield enough material to quantify, suggesting that the metal concentrations associated with these particles were likely small.

In 2005, a conservative mixing line was observed, with anomalies above and below the line at low to mid salinity (~22-24). These anomalies could be a result of multiple mixing lines, or phytoplankton growth, or a combination of both factors. In 2005 mass-specific particle concentrations decrease with salinity (with the exception of a small number of anomalous points), but have a rather shallow gradient. This suggests that the particle composition of this size fraction is relatively uniform over the sampling period.

In 2006, a clear mixing line was observed, with mid salinity anomalies over the same salinity range (~26-30) as those observed in dissolved metal profiles from 2006.

The mass-specific metal concentrations clearly show multiple particle compositions, suggesting that two low salinity water masses were sampled in May 2006. This is most likely a result of newer plume water mixing into the older plume water during sampling.

>2  $\mu$ m particulate metals – In April 2005, the concentration of metals in the >2  $\mu$ m size fraction were also examined (fig. 11). In general, metal concentration in the >2  $\mu$ m size fraction were approximately twice that of the >20  $\mu$ m size fraction. Median >2  $\mu$ m:>20  $\mu$ m ratios for each metal were as follows: Ag 1.8, Cu 1.9, Fe 2.2, Mn 1.9, and Pb 2.0. Mass specific concentrations (Fig. 12) are slightly elevated (~30% ± 20%) compared to the >20  $\mu$ m size fraction. Median >2  $\mu$ m:>20  $\mu$ m mass specific ratios for each metal were as follows: Ag 1.1, Cu 1.1, Fe 1.5, Mn 1.4, and Pb 1.3.

In April 2005, >  $2\mu m$  metals were relatively conservative, with some anomalies at mid to low salinity, similar to the >  $20\mu m$  size fraction. The similarity in mass specific metal concentrations between the > $2\mu m$  and the > $20\mu m$  size fractions suggests that either the particulate matter composition is relatively uniform across these size fractions, or that metals are primarily associated with a dominant phase that is significant in both size fractions.

 $>0.2 \ \mu m \ particulate \ metals$  – A number difficulties were encountered in the analysis of  $>0.2 \ \mu m$  size fraction samples. Supor filters were selected for the  $>0.2 \ \mu m$  size fraction samples as polycarbonate filters clogged rapidly, and yielded insufficient particulate material for analysis. As Supor filters collect particles internally, as well as on the surface, they are more resistant to clogging. This feature results in difficulties during extraction however, as the filters are not completely dissolved during digestion. This may lead to underestimation of  $>0.2 \ \mu m$  metal concentrations if the metals associated with

small particles trapped within the filter are not fully recovered. Another difficulty with Supor filters is that retain ~ 3-5x more salt than polycarbonate filters, making accurate correction of the mass of these samples unreliable.

As a result of these issues, data for this size fraction should be interpreted cautiously. In order to evaluate the likelihood of incomplete digestion, Al data for the >0.2  $\mu$ m size fraction was compared with the >2.0  $\mu$ m size fraction and found to be significantly lower (on average 88% of the >2.0  $\mu$ m size fraction) using a paired t test (n=19, p= 0.028). The mean ratios of the >2.0:>0.2 size fractions for each metal were as follows: Ag = 0.72, Al = 1.13, Cu = 0.83, Fe = 1.09, Mn = 1.02, Pb = 0.91. A paired t test was also utilized (n=19) to determine if the remaining metals were significantly different in the two size fractions. Cu, Fe, and Mn were not significantly different in the two size fractions, while Ag and Pb were significantly higher (p < 0.001 for both metals) in the >0.2  $\mu$ m size fraction. This suggests that particles less than 2.0  $\mu$ m contain significant amounts of Ag and Pb, with this size fraction likely being relatively less important for other metals, though the actual degree of importance is uncertain.

Composition of Plume Particulate Matter - Biogenic vs. Terrigenous Fractions – In order to provide a first order estimate of the composition of plume particulate matter, we estimated the masses of three fractions, terrigenous crustal material, biogenic particles (phytoplankton), and biogenic silica (diatom frustules) based on its P and Al content. This approach depends on the underlying assumption that essentially all of the particulate Al is associated with terrigenous crustal material, and all of the P is associated with biogenic particles. Under this assumption, the crustal contribution is estimated by multiplying the measured Al content of the particulate matter samples by the average Al content of material from the upper crust (Wedepohl, 1995). The mass of biogenic material can be estimated by multiplying the measured phosphorus by the median C:P ratio for plume particles in April 2005 of 195:1 (Reinfelder, unpublished data) and by a Organic Matter:C ratio (g:g) of 2.4:1. Biogenic silica can then be estimated from a Si:C ratio of 0.13:1 (Brzezinski, 1985), assuming that plume phytoplankton consist primarily of diatoms.

In May 2005, the mean mass fraction (± relative standard deviation) of the measured TSM that can be accounted for by using this method was  $0.46 (\pm 28\%)$  in the >2  $\mu$ m size fraction, and 0.68 (± 47%) in the >20  $\mu$ m. The estimated fractions of crustal material, organic matter, and biogenic silica were 15%, 66%, and 18% respectively for the >2  $\mu$ m size fraction and 9%, 71%, and 20% respectively for the >20  $\mu$ m size fraction. These estimates however significantly underestimate the observed TSM values. As C:P ratios are constrained by field data from the plume, the most likely source of error in the estimates are due to uncertainties in the estimation of the terrigenous crustal component which might be caused by 1) local crustal composition varying significantly from the mean upper crust values used here, or 2) incomplete recovery of Al from silicate particles in the aqua regia digest. Either way, it is likely that the majority of the underestimated material is non-biogenic in nature. For this reason, the particulate matter composition was reestimated, assuming that the previously unaccounted for mass was crustal material. Using this estimate, the fractions of crustal material, organic matter, and biogenic silica were 61%, 30%, and 8% respectively for the >2  $\mu$ m size fraction and 38%, 49%, and 14% respectively for the >20  $\mu$ m size fraction. These estimates are consistent with optical observations indicating that phytoplankton and non phytoplankton particles had

similar absorbance values within the lower salinity plume waters (Schofield et. al., unpublished data). These estimates are also consistent with the high river sediment loads observed during April 2005, and are further anecdotally supported by high sediment loads visible in satellite images, as well as by observations of non biogenic material on filters from 2005 prior to digestion, and observations of undigested particulate matter is the sample digests. Taken as a whole, these lines of evidence strongly suggest that a significant fraction of the plume particles in April 2005 are non-biogenic in nature.

In May 2006, the mean mass fraction ( $\pm$  relative standard deviation) of the measured TSM that can be accounted was 1.4 ( $\pm$  54%) in the >20 µm size fraction, with a median value of 1.1. The estimated fractions of crustal material, organic matter, and biogenic silica in May 2006 were 3%, 88%, and 9% respectively. While there is considerable uncertainty in these estimates, taken as a whole, these data suggest that significantly more non-biogenic particles were present in April 2005 following the large discharge event, than in the >20 µm size fraction in May 2006 under conditions of moderate flow.

*Enrichment of Metals in Plume Particulate Matter* – In order to evaluate the potential enrichment of metals in Hudson River plume particulate matter, enrichment factors were calculated by taking dividing the metal:Al ratios from the plume particulate matter by the average metal:Al from the upper crust (Wedepohl, 1995). For reference, the enrichment factors were similarly calculated by dividing the metal:Al ratios from the plume particulate matter by the average metal:Al from the upper crust (Wedepohl, 1995). For reference, the enrichment factors were similarly calculated by dividing the metal:Al ratios from the plume particulate matter by the average metal:Al from Appalachian watershed riverine suspended particles (Windom, 1990), which is the dominant watershed type in the Hudson River watershed (Table 2).

In general, crustal enrichment factors for plume particulate material follow the order Ag >> Pb > Cu > Mn, Ni > Fe, Co (though Ni and Co are based on only one year of data). Ag in plume particulate material is highly enriched relative to the upper crust. This is likely due to the significant sewage inputs in the Hudson River estuary (~100 m<sup>3</sup> s<sup>-1</sup>; ISC, 1997) which is typically highly enriched in Ag (Smith and Flegal, 1993; Rozan and Benoit, 2001). The remaining metals, while enriched relative to average upper crustal material, are not enriched relative to Appalachian rivers by more than a factor of two, with the exception of Pb. This may partially reflect natural enrichment of metals in Appalachian watersheds due to variations in the composition of source crustal material and natural weathering processes (Windom, 1990; Reiman and De Caritat, 2000). This could also reflect some degree of anthropogenic influence in the reference rivers, though suspended material was collected at high TSM loads to minimize anthropogenic influence (Windom, 1990). In the case of Pb, the enrichment factors relative to Appalachian rivers range from 2.5-6.0, suggesting that enrichment due to anthropogenic activity is likely. This is consistent with suggestions that anthropogenic Pb from the Hudson River watershed is an important source of Pb to the Hudson River estuary (Sañudo Wilhelmy and Gill, 1999).

*Metal Partitioning to Particulate Matter – Biogenic vs. Terrigenous Fractions –* In May 2004, April 2005, and May 2006, a first order estimate of the partitioning of metals to biogenic vs. terrigenous particles was made as follows. For each metal, the concentration (nmol  $L^{-1}$ ) was plotted against the Al concentration (nmol  $L^{-1}$ ), which was used as a tracer of the terrigenous fraction. A line was fit to each plot by lease squares regression, with the intercept giving the concentration of each metal that was associated with biogenic particles, and the slope giving the overall metal to aluminum ratio. Table 3 gives the results of these regression analyses, as well as estimates of the fraction of metals associated with biogenic particles (based on the median particulate metal concentration within the plume), including ranges based on 95% confidence intervals of the intercepts. In some cases where intercepts were close to zero, least squares regression analysis yielded negative intercepts. In these cases, the negative value was replaced with zero, as negative concentrations are not possible. This analysis was not extended to particulate Zn in May 2006, as it showed a complex relationship with Al, exhibiting what appear to be at least two independent correlations, with considerable scatter.

Examining the estimated fractions of metals that are associated with biogenic particles, several observations may be made. First, it is apparent that, despite the considerable uncertainty in the estimates, metals within the plume are primarily associated with non biogenic particles. Of the metals examined, only Cu and Mn have biogenic fractions that may exceed 50% using the maximum value of the 95% confidence interval of the intercept (Table 3). Pb is generally highly correlated with Al ( $r^2 \ge 0.90$ ), as is Fe with the exception of the >2 data in April 2005 ( $r^2 \ge 0.95$ ), as were Co ( $r^2 = 0.98$ ) and Ni ( $r^2 = 0.97$ ), though there were only data from May 2004 and May 2006, respectively for these metals. Ag was also fairly well correlated with Al ( $r^2 = 0.85$ -0.88). This suggests that these metals are strongly associated with biogenic material. In contrast, Mn and Cu were more variably associated with Al, which in the case of Mn in >2 µm samples in April 2005 and >20 µm samples in May 2006, is likely due to a larger biogenic fraction.

Estimated biogenic metal fractions are similar in the >20  $\mu$ m size fraction in May 2004 and May 2006, and, with the exception of Fe, are higher than estimates for April 2005. In April 2005, the estimated biogenic metal fractions in the >2  $\mu$ m size fraction are consistently higher than in the >20  $\mu$ m size fraction. For this result, the test of signs was performed to determine the likelihood of all 5 metals examined having a higher estimated biogenic fraction in the >2  $\mu$ m size fraction. The resulting p value of 0.03 indicates that the estimated biogenic metal fractions in the >2  $\mu$ m particulate matter were significantly higher at the 95% confidence level. This is a surprising result considering that biogenic material was previously estimated to comprise a smaller fraction of the  $>2 \,\mu m$  size fraction than the >20  $\mu$ m size fraction in April 2005. One possible explanation is that in the smaller size fraction, surface adsorption of metals plays an increasingly significantly role, likely in association with authigenic Fe oxyhydroxides on the cell surface. In the >2 $\mu$ m size fraction, Cu, Fe, and Mn correlations with Al are weaker than in the >20  $\mu$ m size fraction (Table 3), suggesting the importance of another phase, however associations with P are also relatively weak (Cu  $r^2 = 0.62$ , Fe  $r^2 = 0.74$ , Mn  $r^2 = 0.67$ ). In contrast, correlations of Cu and Mn with Fe are stronger (Cu  $r^2 = 0.87$ , Mn  $r^2 = 0.87$ ). Further evidence for the importance of surface adsorbed Cu, Fe, and Mn is obtained when biogenic Me:P ratios are examined (Table 4). Biogenic Me:P ratios were estimated by taking the biogenic metal estimates based on the intercepts of the Me:Al plots, and normalizing them to the median particulate P concentrations from the plume. These estimates were compared to values obtained by Ho et. al. (2003) from laboratory cultures of 15 oceanic phytoplankton species representing the major marine phyla. These cultures were grown at moderately low unchelated Fe concentrations (Fe<sup>i</sup> = 0.14 nM), in order to

minimize the formation of Fe oxides on the cell surface, while Mn in these cultures was set at a value typical of coastal settings. Therefore, these data likely represent a good approximation of the intracellular content of these metals under the culture conditions.

When the estimated biogenic metal:P ratios from April 2005 >2  $\mu$ m field data are compared to the culture data (Table 4), they show enrichment in Fe:P and Mn:P relative to the intracellular phytoplankton data, suggesting significant precipitation/adsorption of these metals on the cell surface. In the April 2005 >20  $\mu$ m field data, estimated biogenic Me:P ratios are consistent with intracellular metal:P ratios from culture data, with the exception of Fe, which is still an order of magnitude higher than culture data, suggesting Fe precipitation on the cell surface is still important, but to a lesser degree than in the smaller particles. This supports the notion that higher biogenic fractions of metals other than Fe in the smaller size fractions in April 2005 may be related to surface adsorption on (or coprecipitation with) Fe oxyhydroxides.

Tang and Morel (2006) however, have provide evidence from laboratory cultures, that suggests that Mn and Cu (Ag and Pb were not evaluated) do not strongly adsorb to extracellular Fe oxyhydroxides, though Mn may still precipitate on its own and form hydroxide coatings on coastal marine particles (Balls, 1986). This suggests that the increased metal accumulation in smaller phytoplankton implied by these results alternatively may simply be a function of the increased surface area to volume ratio in smaller phytoplankton. Increased surface area to volume may result in increased internalization (higher uptake rates), adsorption directly to the cell surface that is independent of Fe oxyhydroxide formation, and/or adsorption of inorganic particles on the cell surface. The latter process was invoked to explain metal enrichment in smaller

particulate size fractions in the South China Sea (Ho et. al., 2007). Comparison of the intracellular metal:P of Cu and Co, and possibly Mn with field data in Table 4, is consistant with the internalization hypothesis for these metals.

*Transport and fate of plume metals: Model results* –In order to further evaluate the effects of physical processes on the transport of metals in the Hudson River plume, the transport of two metals, Fe and Ag, were examined using a simple numerical model. Fe and Ag were selected because they represent contrasting scenarios with differing sources within the estuary, and differences in the relative importance of dissolved vs. particulate forms. Fe is an abundant element with primarily natural geological sources. Fe has a low solubility in seawater, and readily precipitates as an oxyhydroxide coating on particles. In the plume, the concentration of particulate Fe is often >2 orders of magnitude greater than the dissolved Fe concentration. In contrast, Ag is a relatively nonabundant element, whose primary source in the Hudson River estuary is wastewater treatment plants (Sañudo-Wilhelmy and Gill, 1999). In contrast to Fe, dissolved Ag in the plume is similar in magnitude to particulate silver concentrations.

The results of Fe modeling are given in Table 3. The largest source of Fe to the plume is the Hudson River estuary, with inputs ranging from 354 - 815 kmol d<sup>-1</sup> under the conditions examined. Fe inputs due to the entrainment of bottom water, which ranged from 5.4 - 43.5 kmol d<sup>-1</sup>, were not a significant source of Fe under the model conditions examined (<6 % of river inputs).

In the model, loss of Fe from the plume occurs from export of particulate Fe to bottom waters, and down shelf transport of Fe by the coastal current. Export of particulate Fe to bottom waters varied from 137 - 402 kmol d<sup>-1</sup> under the conditions

examined, and increased with plume area. Sensitivity of the model to variation of the sinking rate constant was examined, and model results (particle sinking, Fe export in the coastal current, Fe concentration in the coastal current) were affected by up to ~45% when the rate constant was varied by a factor of 2 higher or lower under the conditions examined. Assuming that export of particulate Fe is a first order process, the half life of particulate Fe within the plume can be estimated as  $T(1/2) = \ln(2)/k$ , where T = the half life (d), and k is the first order rate constant. Applying the pseudo first order rate constant of  $0.25d^{-1}$  (estimated from the regression of ln[metal] vs. estimated plume age) yields an estimated half life of 2.8 d. Allowing the rate constant to vary by a factor of 2 (higher or lower), yields a range in the estimated half life of 1.4-5.5 d.

Under the conditions examined here, Fe export to the coastal current (down shelf transport) ranged from 152-493 kmol d<sup>-1</sup>. Entrainment of bottom water is a function of plume area, and increases proportionally with area as water is retained during bulge formation. Due to the increasing flux of low Fe bottom water, when a recirculating bulge is present Fe export to the coastal current and the concentration of Fe within the coastal current steadily decreases as total water flux increases.

For Fe under the conditions examined, down shelf transport is ~60% of the Fe inputs (nearly all particulate Fe from the estuary) in the absence of a bulge formation (CC1 and CC2). Under bulge conditions, the down shelf transport is reduced by the ~ coastal current conditions x (f), the fraction of bulge water entering the coastal current (transport = ~30% for Bulge 1, and 20% for Bulge 2). This suggests that the downshelf transport of Fe (or any other metal dominated by the particulate input from the estuary relative to all other sources) is essentially a function of the fraction of particles that sinks,

the estuary input, and the fraction entering the coastal current, with bottom water entrainment essentially only serving to dilute the estuarine inputs.

The results of Ag modeling are given in Table 6. The largest source of Ag to the plume is the Hudson River estuary, with inputs ranging from  $15.8 - 35.8 \text{ mol d}^{-1}$  under the conditions examined. Ag inputs due to the entrainment of bottom water, which ranged from  $3.67 - 29.6 \text{ mol d}^{-1}$ , were also a significant source of Ag under the model conditions examined. The Ag input from bottom water is proportional to the area, and became increasingly important under conditions of bulge growth.

The export of particulate Ag to bottom waters varied from  $2.97 - 9.40 \text{ mol d}^{-1}$ under the conditions examined, and increased with plume area, but less rapidly than bottom water Ag inputs. Sensitivity of the model to variation of the sinking rate constant was examined, and model results (sinking flux, Ag export in the coastal current) were affected by < 10%, when the rate constant was varied by a factor of 2 higher or lower under the conditions examined. As the estimated sinking rate constant for Ag was the same as for Fe, the estimated half life for Ag (2.8d) is the same as that for Fe.

Under the conditions examined here, Ag export to the coastal current (down shelf transport) ranged from 13.2-39.6 mol d<sup>-1</sup>. In contrast to Fe, when a recirculating bulge is present Ag export to the coastal current steadily increases as total water flux increases. At the same time, the concentration of Ag in the coastal current decreases due to the increasing proportion of lower Ag bottom water. For Ag, under the conditions examined, down shelf transport is ~85% of the total Ag inputs in the absence of a bulge formation (CC1 and CC2). Under bulge conditions, the reduction in down shelf transport is again

given by the ~ coastal current conditions x (f), the fraction of bulge water entering the coastal current (transport =  $\sim$ 42% for Bulge 1, and 28% for Bulge 2).

The Particle sinking rate is potentially an important controlling factor in the ultimate fate of metals in the Hudson River plume. While particles retained within the plume are transported down shelf, or potentially, off shore, particulate metals that sink into the bottom water may potentially be carried back toward Lower New York Bay, as the net bottom water flow is to the north (opposite the flow of the plume). This mechanism may act to retain metals with significant particle fluxes near the moth of the estuary, potentially slowing the recovery of contaminated sediments in this area. This suggests that for metals whose speciation is dominated by particulate inputs from the estuary such as Fe, the fraction of particles that sinks is the key factor determining its retention near the estuary.

Model results also were also used to evaluate the likelihood of significant cross shelf transport of metals. In the bulge formation scenarios, the bulge potentially retains metalsidssolved and particulate phase metals within the plume waters. These metals are potentially available for cross shelf transport, if the winds shift favorably. Model results confirm that for both Ag and Fe, the potential for significant cross shelf transport exists, as the concentrations of both metals in the bulge water remain elevated relative to shelf waters after 3-5 days, the typical lifespan of a recirculating bulge formation.

## Conclusions

The reported concentrations of trace metals in the Hudson River plume, are consistent with previously reported data from the estuary with coastal shelf water, and similar to other plumes from urban estuaries. Metal concentrations in the plume (dissolved + particulate) were generally lower in 2004 than in 2005 and 2006, likely due to the lower river discharge during the 2004 sampling period.

Salinity profiles of dissolved and particulate metals showed complex mixing patterns in April 2005 and May 2006, with the exception of dissolved Ni, which was conservative, or nearly so, across all sampling years. These complex salinity profiles make the traditional interpretations of removal processes difficult, however, based on estimates of the sinking rate, particle sinking appears to be an important loss term for each of the metals examined. Dissolved Fe profiles, particularly in May 2004 and April 2005, show some suggestion of a removal process, suggesting the formation of authigenic Fe oxyhydroxides is likely to be important. Dissolved and particulate Zn profiles are generally more variable and complex than for those of the other metals, which may represent the effects of biological cycling of Zn.

Estimates of the composition of plume particulate matter suggest that significant terrigenous material was present in plume waters in April 2005 in both the >2 and >20  $\mu$ m size fractions, following a high discharge event. In contrast, during May 2006, under moderate discharge conditions, terrigenous material was estimated to be a relatively small fraction of the >20  $\mu$ m size fraction.

Examination of enrichment factors relative to both crustal abundances and Appalachian rivers suggests that plume particles are highly enriched in Ag and Pb, and are also enriched in Cu, Mn, Ni, Co, and Fe relative to the mean crustal values, however the observed values in the plume are similar to those reported for other Appalachian rivers. Within the plume, estimates of the biogenic vs. terrigenous partitioning of metals suggest that most metals are associated with terrigenous rather than biogenic particles, even in May 2006 when the estimated fraction of terrigenous particles in the >20  $\mu$ m size fraction is small. This further suggests that physical particle settling, particularly of non-biogenic particles, is likely to be important in controlling the fate of metals within the plume. In April 2005, larger biogenic fractions were estimated for the >2  $\mu$ m size fraction than the >20  $\mu$ m size fraction, which is consistent with the increased importance of surface area in metal accumulation in smaller phytoplankton. Estimated biogenic metal:P ratios suggest that Fe and in some cases Mn, may be largely associated with the cell surface (consistent with oxyhydroxide formation), while Cu and Co are consistent with previously published data for intracellular concentrations, suggesting that these elements may be largely intracellular. Pb and Ag are also enriched in small phytoplankton, however their cellular location is unknown. It is likely though that both elements are largely associated with the cell surface based on their high particle reactivity.

Modeling results suggest that particle sinking is an important loss term for plume metals, and in the case of metals such as Fe, which are dominated by the particulate phase, is the most important metal sink. This has important implications for the recovery of the lower New York Harbor, as sinking particles are retained near the estuary, and may in fact be recycled back toward the estuary by bottom currents. Modeling results further suggest that wind driven circulation has the potential to significantly affect metal transport to the coastal ocean. While standard coastal current formation results primarily in down shelf transport (southward along the New Jersey shore) of metals, the formation of a recirculating bulge formation may result in significant cross shelf (eastward into the North Atlantic) transport of metals.

	CC 1	CC 2	Bulge 1	Bulge 2
River Input				
Discharge condition	Moderate	High	High	High
Q m3/s	1000	2300	2300	2300
Estuary MeD (nM/pM)*	50/50*	50/50*	50/50*	50/50*
Estuary MeP (nM/pM)*	2000/40*	2000/40*	2000/40*	2000/40*
Plume Characteristics				
Initial length (km)	50	50	50	50
Initial width (km)	5	15	15	15
Plume depth (m)	4	4	4	4
Bottom water mixing				
Eddy diffusivity (Kz) x10 <sup>-4</sup> m <sup>2</sup> s <sup>-1</sup>	0.3	0.3	0.3	0.3
Bottom water MeD (nM/pM)*	5/15*	5/15*	5/15*	5/15*
Bottom water MeP (nM/pM)*	20/2*	20/2*	20/2*	20/2*
Particle sinking				
rate constant (d-1)	0.25	0.25	0.25	0.25
Coastal current				
Fraction to coastal current (f)	1	1	0.5	0.33
Time Step				
$\Box T(d)$	SS	SS	0.1	0.1

Table 1. Model input parameters for the various scenarios considered. SS indicates the model was in steady state conditions and an iterative numerical solution was unnecessary.

\*Concentrations of Fe/Ag

		Ag	Со	Cu	Fe	Mn	Ni	Pb
	crustal metal:Al <sup>1</sup>	1.8E-07	6.9E-05	7.8E-05	1.9E-01	3.3E-03	1.1E-04	2.9E-05
	river metal:Al <sup>2</sup>		6.8E-04	1.1E-03	5.5E-01	5.2E-02	2.3E-03	1.3E-04
	river/crust		9.9	14.2	2.9	15.4	20.8	4.6
May-04	>20							
	HRP/crust	167		25.2	5.7		7.9	27.1
	HRP/river			1.8	2.0		0.4	6.0
A 0.5	. 2							
Apr-05	>2 HRP/crust	61		9.0	36	45		11.2
	HRP/river	01		0.6	1.2	0.3		2.5
Apr-05	>20							
	HRP/crust	81		11.1	3.7	7.7		13.3
	HRP/river			0.8	1.3	0.5		2.9
May 06	> 20							
1v1ay-00	>20 LIDD/4	100	25	10.7	4 4	15 4		25.7
	HKP/crust	109	3.5	12.7	4.4	15.4		25.7
	HRP/river		0.4	0.9	1.6	1.0		5.6

Table 2. Metal enrichment factors (metal:Al/metal:Al) relative to the upper crust<sup>1</sup>, and to Appalahcian rivers<sup>2</sup>. HRP is the Hudson River Plume. >20 indicates the >20 $\mu$ m size fraction from the plume, while >2 indicates the >2  $\mu$ m size fraction from the plume.

<sup>1</sup>Wedepohl, 1995

<sup>2</sup>Windom, 1990

Table 3.Results of regression analysis of metals vs. Al. % Biogenic is calculated by dividing the intercept to the median metal concentration in the plume. Max (95% CI) and Min (95% CI) indicate the maximum and minimum biogenic fractions based on the 95% confidence interval of the slope divided by the median plume metal concentration. >20 indicates the >20 $\mu$ m size fraction from the plume, while >2 indicates the >2  $\mu$ m size fraction from the plume.

May-04	>20	Ag	Со	Cu	Fe	Mn	Ni	Pb
	slope (Me:Al)	3.0E-05		2.0E-03	1.1E+00		8.7E-04	7.8E-04
	r2	0.85		0.92	0.98		0.97	0.94
	Intercept (nmol L-1)	0.0004		0.020	0		0	0.008
	% biogenic	25%		20%	0%		0%	20%
	max (95% CI)	50%		42%	6%		12%	37%
	min (95% CI)	0%		0%	0%		0%	3%
Apr-05	>2	Ag	Со	Cu	Fe	Mn	Ni	Pb
	slope (Me:Al)	1.1E-05		7.0E-04	6.8E-01	1.5E-02		3.2E-04
	r2	0.86		0.54	0.78	0.62		0.92
	Intercept (nmol L-1)	0.0049		0.414	227.2	21.8		0.106
	% biogenic	21%		26%	16%	46%		16%
	max (95% CI)	41%		72%	44%	74%		32%
	min (95% CI)	0%		0%	0%	17%		0%
Apr-05	>20	Ag	Со	Cu	Fe	Mn	Ni	Pb
	slope (Me:Al)	1.4E-05		8.7E-04	7.1E-01	2.6E-02		3.8E-04
	r2	0.85		0.76	0.95	0.87		0.91
	Intercept (nmol L-1)	0.0015		0.140	30.8	2.4		0.027
	% biogenic	10%		15%	5%	9%		7%
	max (95% CI)	33%		43%	20%	31%		24%
	min (95% CI)	0%		0%	0%	0%		0%
May-06	>20	Ag	Со	Cu	Fe	Mn	Ni	Pb
	slope (Me:Al)	1.9E-05	2.4E-04	9.9E-04	8.6E-01	5.2E-02		7.3E-04
	r2	0.88	0.98	0.79	0.99	0.74		0.90
	Intercept (nmol L-1)	0.0009	0.003906	0.047	0.9	3.0		0.016
	% biogenic	23%	11%	29%	1%	37%		20%
	max (95% CI)	41%	21%	59%	8%	73%		48%
	min (95% CI)	5%	2%	0%	0%	0%		0%

Table 4. Estimated biogenic metal:P ratios in comparison to intracellular metal:P ratios<sup>1</sup>. Plume biogenic metal:P ratios were estimated by dividing the estimated biogenic metal concentration by the median plume particulate phosphorus concentration. >20 indicates the >20 $\mu$ m size fraction from the plume, while >2 indicates the >2  $\mu$ m size fraction from the plume.

		Со	Cu	Fe	Mn
Phytoplankton (PP) <sup>1</sup>	Me:P	1.9E-04	3.8E-04	7.5E-03	3.8E-03
May-04	>20	Со	Cu	Fe	Mn
	Me:P		7.0E-04	$N.E.^2$	
	Plume/PP		1.9	$N.E.^2$	
Apr-05	>2	Со	Cu	Fe	Mn
	Me:P		8.2E-04	4.5E-01	4.3E-02
	Plume/PP		2.2	60.4	11.4
· • • •	20	G	G	Б	
Apr-05	>20	Co	Cu	Fe	Mn
	Me:P		3.2E-04	7.0E-02	5.4E-03
	Plume/PP		0.8	9.3	1.4
May-06	>20	Со	Cu	Fe	Mn
	Me:P	3.5E-05	4.2E-04	8.0E-03	2.7E-02
	Plume/PP	0.2	1.1	1.1	7.0

<sup>1</sup>Ho et. Al., 2003

<sup>2</sup>Not estimated due to a negative intercept in the regression

	CC 1	CC 2		Bulge 1	(f = 0.5)			Bulge 2	(f = 0.33)	
	Steady State	Steady State	Day 0	Day 1	Day 3	Day 5	Day 0	Day 1	Day 3	Day 5
River Input							-			
Fe Input (kmol d <sup>-1</sup> )	354	815	815	815	815	815	815	815	815	815
Plume Characteristics										
Fe content (kmol) <sup>a</sup>	573	1420	1420	1470	1570	1660	1420	1490	1620	1720
Area (km <sup>2</sup> )	250	750	750	887	1210	1610	750	935	1398	2013
Bottom water mixing										
Fe Input (kmol d <sup>-1</sup> )	5.4	16.2	16.2	19.2	26.1	34.8	16.2	20.2	30.2	43.5
Particle sinking										
Fe export (kmol d <sup>-1</sup> )	137	337	337	350	372	390	337	354	381	402
Coastal current										
Fe export (kmol d <sup>-1</sup> )	223	493	247	242	234	230	164	160	155	152
Fe Conc. (nM)	573	472	472	415	325	257	472	399	289	213

Table 5. Model results for the fate and transport of Fe in the Hudson River plume.

<sup>a</sup>Metal content after particle sinking

	CC 1 CC 2		Bulge 1 (f = 0.5)				Bulge 2 (f = 0.33)			
	Steady	Steady State	Day 0	Day 1	Day 3	Day 5	Day 0	Day 1	Day 3	Day 5
River Input										
metal Input (mol d <sup>-1</sup> )	15.6	35.8	35.8	35.8	35.8	35.8	35.8	35.8	35.8	35.8
Plume Characteristics										
Ag content (mol) <sup>a</sup>	42	114	114	126	152	182	114	130	166	211
Area (km <sup>2</sup> )	250	750	750	887	1210	1610	750	935	1398	2013
Bottom water mixing										
Ag Input (mol d <sup>-1</sup> )	3.67	11.0	11.0	13.0	17.8	23.7	11.0	13.8	20.5	29.6
Particle sinking										
Ag export (mol $d^{-1}$ )	2.87	7.18	7.18	7.54	8.2	8.85	7.18	7.65	8.52	9.40
Coastal current										
Ag export (mol $d^{-1}$ )	16.4	39.6	19.8	20.6	22.7	25.3	13.2	14.0	15.9	18.6
Ag Conc. (pM)	42.1	37.9	37.9	35.4	31.4	28.3	37.9	34.7	29.8	26.2

Table 6. Model results for the fate and transport of Ag in the Hudson River plume.

<sup>a</sup>Metal content after particle sinking


Fig. 1. Trace metal clean underway sampling system used on the LaTTE project on board the R/V Cape Hatteras. a) shows the pole to which the sampling system was attached, b) shows the HEPA filtered enclosure where samples were collected, and c) shows the Teflon sample uptake at the end of the over the side pole.

# Plume transport model



Fig. 2. A conceptual diagram of the Hudson River plume box model. Inputs to the plume include metals from the Hudson River estuary and bottom water entrainment. Loss terms for metals include particle sinking and down shelf (southward) transport by the coastal current.



Fig. 3: Dissolved (<0.2  $\mu$ m) concentrations of Fe, Ni, Zn, and Pb in the Hudson River plume and adjacent coastal waters in May 2004.



Fig. 4: Dissolved ( $<0.2 \mu m$ ) concentrations of Fe, Ni, Zn, and Pb in the Hudson River plume and adjacent coastal waters in April 2005.



Fig. 5: Dissolved (<0.2  $\mu$ m) concentrations of Fe, Ni, Zn, and Pb in the Hudson River plume and adjacent coastal waters in May 2006.



Fig. 6: Particulate (>20  $\mu$ m) concentrations of Fe, Ni, Ag, Pb and Cu in the Hudson River plume and adjacent coastal waters in May 2004.



Fig. 7: Particulate (>20  $\mu$ m) concentrations of Fe, Mn, Ag, Pb and Cu in the Hudson River plume and adjacent coastal waters in April 2005.



Fig. 8: Particulate (>20  $\mu$ m) concentrations of Fe, Co, Ag, Pb and Cu in the Hudson River plume and adjacent coastal waters in May 2006.



Fig. 9: Mass specific particulate (>20  $\mu$ m) concentrations of Fe, Mn, Ag, Pb and Cu in the Hudson River plume and adjacent coastal waters in April 2005.



Fig. 10: Mass specific particulate (>20  $\mu$ m) concentrations of Fe, Co, Ag, Pb and Cu in the Hudson River plume and adjacent coastal waters in May 2006.



Fig. 11: Particulate (>2  $\mu$ m) concentrations of Fe, Mn, Ag, Pb and Cu in the Hudson River plume and adjacent coastal waters in April 2005.



Fig. 12: Mass specific particulate (>2  $\mu$ m) concentrations of Fe, Mn, Ag, Pb and Cu in the Hudson River plume and adjacent coastal waters in April 2005.

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**Chapter 3:** Fate and transport of mercury in the Hudson River buoyant plume: Distributions and modeling results.

#### Introduction

The highly urbanized Hudson River estuary is home to the New York metropolitan area (~15 million residents), one of the most densely populated regions in North America. Intense human activity in and around the Hudson River estuary, has resulted in heavy contamination with nutrients, metals, and persistent organic pollutants, (Feng et al, 1998; Fisher et al, 1988) which may potentially be transported out to the adjacent coastal ocean.

Historically, the estuary has been heavily impacted by pollution from industrial sources, wastewater treatment facilities, and urban runoff (Williams et al, 1978; Klinkhammer and Bender, 1981). Despite decreases in industrial inputs and advancements in sewage treatment since the 1970's, water quality within the estuary continues to be impaired (Sañudo-Wilhelmy and Gill, 1999). In particular, legacy pollution associated with sediments continues to be a concern, as there is a high degree of sediment resuspension and redistribution within the estuary that prevents rapid burial of contaminated sediments (Bero and Gibbs, 1990). This mechanism maintains contaminated sediments within the biologically active zone at the sediment water interface, where they have the potential to be taken up and enter the food web.

One of the pollutants of greatest concern within the Hudson River estuary is Hg, due to its propensity to bioaccumulate within aquatic food webs, often exceeding levels that are toxic to humans (Adams and Ononrato, 2005; Trasande et al, 2005) and pisciverous predators (Scheuhammer, 2007). The primary form of Hg that accumulates in higher trophic levels is monomethlymercury (MeHg; Bloom, 1992: Storelli et al, 2005), which, in estuarine systems, is primarily formed in anoxic sediments by sulfate reducing bacteria (Compeau and Bartha, 1985; Gilmour and Henry, 1991) where it enters pore waters and partitions to sediment particles. Sediment resuspension events within the estuary allow both MeHg and inorganic Hg associated with estuarine sediments and pore waters to be mixed into the water column (Heyes et al, 2004), where it may be subsequently transported with the estuarine discharge.

*Plume Dynamics* - The ultimate fate of Hg within the Hudson River plume is highly dependant on plume morphology and its intrinsic physical dynamics. These in turn, are primarily controlled by physical forcing from winds, and river discharge.

Fieldwork in May 2004, April 2005, and May 2006 suggests that two basic scenarios control the fate and transport of plume constituents (Chant et al, 2008): Under the first scenario, low to moderate discharge conditions and downwelling favorable winds promote the formation of a narrow (2-4 km) coastal current, which propogates downshelf (southward). Under the second scenario, high discharge conditions and the absence of downwelling favorable winds promote the formation of a recirculating bulge feature, which retains >50% of the fresh water flux (Chant et. al., 2008), preventing it from entering the coastal current. Due to the retention of fresh water within this feature, it will increase in size until the winds shift, typically within 3-5 days. The fate of material retained within the bulge then depends on the nature of the wind forcing. If the winds shift to downwelling favorable conditions, the plume will be compressed against the

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shore forcing the bulk of the fresh water flux back into the coastal current. Conversely, winds may also force the bulge to become detached from the coast, advecting the plume water offshore (eastward) onto the shelf. These differing discharge scenarios have important implications for the transport and biogeochemical cycling of mercury within the Hudson River plume. The formation of a narrow coastal current will tend to promote the downshelf transport of Hg, while the formation of a recirculating bulge could potentially result in cross shelf transport of Hg. In this chapter, field data and modeling results will be used to evaluate the transport, biogeochemical cycling, and ultimate fate of Hg in the Hudson River buoyant plume. Specifically, I will evaluate the hypothesis that wind driven physical dynamics have a significant impact on mercury transport processes within the plume, specifically that: 1) Formation of a coastal current results in significant down shelf transport of metals, 2) Formation of a recirculating bulge retains material within the plume, increasing export of particulate and volatile forms, and providing an opportunity for cross shelf transport. I will also evaluate the hypothesis that reduction and subsequent volatilization of mercury is an important loss process for mercury in the plume.

#### Methods

In May 2004, April 2005, and May 2006, surface water sampling was performed via a trace metal clean pumping system mounted to the R/V Cape Hatteras' over the side pole. Surface water was collected via a Teflon pipe attached to a 1.25 cm OD teflon tube, that was attached to the seaward side of a stainless steel pole with an aluminum mount. The pipe was mounted such that it extended in front of the aluminum mount, approximately 1.5 m from the ship's hull. Samples were pumped onboard and into a HEPA clean bench at 3-4 L min<sup>-1</sup> with a Teflon/polypropylene bellows pump. All wetted parts of the uptake system were leached by pumping 10% HCl through the system for a minimum of 72 hrs, and rinsed copiously with ultra high purity water. Additionally, prior to sampling, the uptake system was flushed extensively with seawater.

Within the shipboard lab, trace metal clean techniques were used at all phases of sample collection and manipulation in order to minimize the potential for contamination. Samples for dissolved Hg were filtered in-line with a high capacity 0.2  $\mu$ m polypropylene cartridge filter, and collected in rigorously acid cleaned Teflon bottles. In 2004, whole water samples for particulate Hg were collected in a 4 L polycarbonate carboy, homogenized, and vacuum filtered on acid cleaned 47 mm polycarbonate filters housed in an all Teflon filter apparatus. Samples were filtered under gentle vacuum (< 130 mm Hg) minimizing cell damage and potential cell lysis. In 2005, and 2006, particulate Hg was not measured directly, but was instead estimated as the difference between total (unfiltered) Hg and dissolved (<0.2  $\mu$ m filtered) Hg. All water samples were preserved with 0.3% v/v BrCl immediately following sample collection, double bagged in clean polyethylene bags, and stored in clean plastic bins until analysis (within 3 months of collection).

Upon returning to shore, filters for particulate Hg analysis were digested in aqua regia and ~3% BrCl. Filter digests were then analyzed by SnCl<sub>2</sub> reduction, gold amalgamation, and Cold Vapor Atomic Fluorescence Spectroscopy (Fitzgerald and Gill,

1979; Bloom and Crecelius, 1983). Water samples were monitored to be sure that excess BrCl remained in each sample, as indicated by the persistent yellow color.

Samples for particulate MeHg were collected on 120 mm GF/F filters, which had been previously baked in a muffle furnace at 500°C for 12 hrs prior to use. Filters were sealed in a PTFE filter housing and 10-40 L of unfiltered seawater were slowly pumped through the filter. Loaded filters were then folded and placed in acid cleaned polystyrene filter holders and immediately frozen until analysis. MeHg analysis was performed by Quicksilver Scientific by leaching with acidic thiourea, followed by Hg-thiourea complex ion-chromatography with on-line cold vapor generation and atomic fluorescence spectrometric detection (Shade and Hudson, 2005).

Dissolved gaseous mercury (DGM) was determined using a continuous flow bubbler similar to (O'Driscoll et al, 2003). Briefly, uncontaminated seawater from the underway sampling system was continuously pumped into a 500ml custom glass flow through bubbler at a rate of ~ 29 ml min<sup>-1</sup>. DGM was continuously stripped from solution by bubbling with Hg free air at a rate of  $1.5 \text{ L} \text{ min}^{-1}$ , and measured at 5 min intervals with a Tekran 2537A Mercury Vapour Analyzer (Tekran Instruments, Toronto Ontario, Canada).

Mercury volatilization fluxes were estimated as described in Cardona-Marek et. al. (2007). Breifly, fluxes were estimated from DGM and total gaseous mercury (TGM) measurements using the two-layer model of air–water exchange assuming that diffusion through the water-side microlayer dominates the resistance to gas exchange (Poissant et. al., 2000). In this model, the volatilization flux (F) is given by:  $F = k_w(DGM - TGM/K^{\circ})$ , where  $k_w$  is the water-side mass transfer coefficient (cm h<sup>-1</sup>), DGM is the dissolved

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gaseous mercury concentration in the water, TGM is the total gaseous mercury concentration in the air, and K` is the temperature corrected dimensionless Henry's law constant for Hg<sup>0</sup>. The Henry's law constant was temperature corrected using K` = 0.0074T + 0.1551 (Sanemasa, 1975). The water-side mass transfer coefficient was estimated according to (Wanninkohf, 1985) where k<sub>w</sub> =  $(0.45u^{1.64})[Sc_{w(Hg)}/Sc_{w(CO2)}]^{-0.5}$ , where u is the average wind speed (m s<sup>-1</sup>) and Sc<sub>w(X)</sub> are the Schmidt numbers for CO<sub>2</sub> and Hg in water (Poissant et. al., 2000).

Total Suspended Solids (TSS) were estimated based on filtration of whole seawater on weighed 2.0 µm polycarbonate filters, which were folded and frozen immediately following collection. In the laboratory, filters were dried, weighed, and digested in aqua regia for metals analysis. A subsample of each digestion was retained for sodium analysis by ICP-OES, and filter weights were corrected for salt content based on those results.

*Modeling of Hg transport within the Hudson River plume* – To evaluate the relative importance of various physical processes on the fate and transport of Hg in the Hudson River plume, a simple box model (Fig. 1) was created to evaluate four basic scenarios: conditions leading to the formation of a coastal current at moderate discharge (CC 1) and at high discharge (CC 2), and conditions leading to the formation of a recirculating bulge feature with 50% of the water flux entering the coastal current (Bulge 1) and 33% of the water flux entering the coastal current (Bulge 2). In the model, the plume was assumed to be a single box, with instantaneous mixing. The following terms were input: Initial plume dimensions, fraction of water diverted to the coastal current, concentrations of dissolved and particulate Hg in the estuary and bottom waters, vertical

eddy diffusivity  $(K_z)$ , River discharge (Q), the rate constant for particle loss, and the mean Hg volatilization flux. Hudson River discharges (Q) were estimated from USGS gauges in the estuary. The moderate discharge condition was based on the approximate Hudson River discharge at the initiation of sampling in May 2006, and the high discharge condition was the approximate average discharge during a large discharge event from March 29, 2005 until the initiation of sampling on April 10, 2005. Estuarine input concentrations were estimated from data points collected near Sandy Hook, NJ. Bottom water (shelf water) Hg concentrations were estimated based on offshore samples collected as part of this project. Vertical eddy diffusivity for the plume was estimated as  $K_z = dS/dt * H / dS/dz$  (Houghton et al, in preparation). Plume dimensions were approximated based on remote sensing data obtained from the Rutgers Coastal Ocean Observation Lab. Loss of particulate Hg due to sinking was modeled as a first order process, and the rate constant was estimated by plotting ln[HgP] vs. plume age, which was estimated based on the sample salinities and the salting rate (dS/dt) (Houghton et. al., in preparation). Hg volatilization flux was the mean daily flux. Based on these input parameters, the model calculates the water fluxes due to bottom water entrainment and in the coastal current, the Hg fluxes in and out of the plume, and the change in plume dimensions with time under conditions of bulge growth (water retention within the plume).

In the bulge formation scenarios, the water entering the coastal current was assumed to be fully mixed plume water. Input parameters for each scenario are given in Table 1. For the first two scenarios, diverting all of the water into the coastal current (fraction to the coastal current = 1), results in a constant volume of the plume over time. This results in steady state conditions, assuming all other parameters remain constant with time. For the bulge scenarios, the bulge area was allowed to increase with time (fraction to the coastal current < 1), resulting in non-steady state conditions. In the recirculating bulge scenarios (Bulge 1 and Bulge 2), the range of 33 and 50% of the water entering the coastal current represents the upper and lower estimates from the April 2005 experiments.

The general form of the model was as follows:

 $\Delta Plume = HRE + BW - PS - DGM - CC$ 

where ΔPlume is the change in Hg in the plume over time (which is equal to 0 at steady state), HRE is the Hg input from the estuary, BW is the Hg input from the bottom entrainment, PS is the loss from particle sinking, DGM is the evasion of dissolved gaseous mercury, and CC is the export of Hg into the coastal current. Water fluxes, dissolved Hg fluxes, and particulate Hg fluxes were estimated from field measurements, and are accounted for independently in the model. Non-steady state solutions were determined numerically, with time steps of 0.1 d.

## Results

*Distribution of Hg Species* – Total Hg (unfiltered) concentrations within the study area ranged from 1.0 pM to 19.8 pM (Table 2), with the highest concentrations located closest to the estuary, and the lowest concentrations further offshore, in high salinity areas that were the least impacted by the plume. Total Hg concentrations within the plume were generally highest in 2006, and were lower in 2004 and 2005. Total Hg in

2004 and 2006 showed mixing either in a conservative or near-conservative pattern, while total Hg in 2005 showed a complex mixing pattern (Fig. 2) indicative of multiple low salinity water masses, at least one of which was depleted in particulate Hg. Total Hg in 2004 and 2005 were correlated with TSS, while total Hg in 2006 was not (Fig.3). Dissolved Hg (<0.2  $\mu$ m) in the sampling area ranged from 0.8 to 3.6 pM, with the largest gradient observed in 2006, and little or no gradient observed in 2004 and 2005.

DGM concentrations within the plume (3 hr running averages) ranged from 75 to 607 fM (7% - 48% of the dissolved Hg pool). Average DGM concentrations ( $\pm$  1 S.D) were 204 fM ( $\pm$  51) in 2004, 233 fM ( $\pm$  116) in 2005, and 342 fM ( $\pm$  174) in 2006, while the mean fraction of the dissolved pool that was present as DGM (%DGM) was similar for each year (14% in May 2004, 12% in April 2005, and 15% in May 2006).

Particulate MeHg concentrations were determined in seven samples each from 2005 and 2006, and ranged from 6-64 fM in 2005 and 10-84 fM in 2006. Particle mass specific concentrations for these samples ranged from 3.8 - 13 pmol g<sup>-1</sup> in 2005 to 5.7 - 42.3 pmol g<sup>-1</sup> in 2006. Particulate Hg in the plume was generally lower than values reported for the lower Hudson River estuary (70-520 pM; Balcom et al, 2008), but on a mass specific basis were similar to those in the estuary (2.0 - 41.3 pmol g<sup>-1</sup>).

The log of the Hg distribution coefficients,  $K_D$  (L kg<sup>-1</sup>), ranged from 4.4-6.6, and showed no trend with salinity. Log  $K_D$ 's were similar in 2004 (mean 5.3) and 2005 (mean 5.2) and showed no trend with Total Suspended Solids, TSS (Fig. 4). Log  $K_D$ 's were higher in 2006 (mean 6.1), and showed a decreasing trend with increasing TSS.

*Hg transport in the Hudson River plume: Model predictions* - Results of the plume Hg model are presented in Table 3. The largest source of Hg to the plume is the

Hudson River estuary, with inputs ranging from  $1.3 - 3.0 \text{ mol d}^{-1}$  under the conditions examined. Hg inputs due to the entrainment of bottom water, which ranged from  $0.32 - 2.61 \text{ mol d}^{-1}$ , were also a significant source of Hg under the model conditions examined. The Hg input from bottom water is proportional to the area, and became increasingly important under conditions of bulge growth.

In the model, loss of Hg occurs from evasion of DGM, export of particulate Hg to bottom waters, and down shelf transport of Hg by the coastal current. Evasion of plume DGM to the atmosphere ranged from 0.078 to 0.628 mol d<sup>-1</sup> (5-11% of the Hg inputs), under the various model conditions examined. Both total Hg evasion, and Hg evasion as % of Hg input, increased with increasing plume area. Sensitivity of the model to variation of the Hg evasion flux was examined, and while the estimation of evasion of Hg to the atmosphere is strongly dependant on the flux value, the estimation of Hg export in the coastal current was affected by  $\leq 20\%$ , when the volatilization flux rate was varied by a factor of 2 higher or lower under the conditions examined.

Export of particulate Hg to bottom waters varied from  $0.53 - 1.58 \text{ mol d}^{-1}$  under the conditions examined, and also increased with plume area, but to a lesser degree than DGM evasion or bottom water Hg inputs. Sensitivity of the model to variation of the sinking rate constant was examined, and model results (sinking flux, Hg export in the coastal current) were affected by  $\leq 20\%$ , when the rate constant was varied by a factor of 2 higher or lower under the conditions examined. Assuming that export of particulate Hg is a first order process, the half life of particulate Hg within the plume can be estimated as  $T(1/2) = \ln(2)/k$ , where T = the half life (d), and k is the first order rate constant. Applying the estimated rate constant of 0.55 d<sup>-1</sup> yields an estimated half life of 1.26 d. Allowing the rate constant to vary by a factor of 2 (higher or lower), yields a range in the estimated half life of 0.63–2.52 d.

Under the conditions examined here, Hg export to the coastal current (down shelf transport) ranged from 0.81-2.42 mol d<sup>-1</sup>. Entrainment of bottom water is a function of plume area, and increases proportionally with area as water is retained during bulge formation. As a result, when a recirculating bulge is present, Hg export to the coastal current steadily increases as total water flux increases. Though the total transport of Hg increases, the concentration of Hg in the coastal current decreases, as it is diluted by the increasing proportion of lower Hg bottom water. As time approaches  $\infty$ , the concentration of Hg in the coastal current spreaches  $\infty$ , the concentration of Hg in the coastal current provides a value approximately given by:

 $[Hg]CC = (DHg_{bottom} - DGM) / Water_{bottom}$ 

Where [Hg]CC is the concentration of Hg in the coastal current (pmol  $m^{-3}$ ),

DHg<sub>bottom</sub> is the input of dissolved Hg from bottom water entrainment (pmol d<sup>-1</sup>), DGM is the Hg evasion to the atmosphere (pmol d<sup>-1</sup>), and Water<sub>bottom</sub> is the entrainment of bottom water (m<sup>3</sup> d<sup>-1</sup>). In this approximation, the contribution of particulate Hg can be neglected, as it is efficiently removed at longer residence times.

# Discussion

*Enrichment of Hg in plume waters* – The waters of the Hudson River plume were typically highly enriched in particulate Hg relative to the surrounding coastal waters in 2005 and 2006 during this study ( $0.3 \pm 0.4$  pM, n=4), and relative to the North Atlantic ( $0.035 \pm 0.02$ , n=8; Mason et al, 1998). This enrichment however, is not observed in several samples collected in April 2005 at relatively low salinities (s =23.7-25.1),

indicating multiple water masses. This is consistent with particulate concentrations of other metals (data not shown), and has several possible explanations. One explanation is that the export of particulate Hg from the estuary fluctuated dramatically prior to or during sampling, and a low particle water mass was sampled. A second explanation is that a large discharge of fresh water occurred prior to sampling, and that it was retained within the sampling area long enough for most of its particulate matter to sink to the bottom waters. Considering the river discharge history (a large peak occurred several days prior to sampling) and that winds in 2005 created a large bulge, it seems most likely that the second scenario created the observed mixing patterns.

In 2006, concentrations of particulate Hg in the plume were ~2x those observed in 2004 or 2005, while TSS values in 2006 were ~ half those in 2004 and 2005. Coupled with the observed mid salinity peak in TSS in 2006 and the absence of a correlation between TSS and particulate Hg, this suggests an estuarine source of small Hg enriched particles in 2006. This is supported by the Hg concentration of the particles, which in 2006 averaged  $3.1 \pm 3$  nmol g<sup>-1</sup>, nearly an order of magnitude higher than in 2004 and 2005 ( $0.371 \pm 0.23$  nmol g<sup>-1</sup>), but similar to concentrations in the lower harbor ( $3.2 \pm 1.8$  nmol g<sup>-1</sup>).

In contrast to particulate Hg, the small gradients in dissolved Hg observed over the three sampling periods suggest that the Hudson River plume is only slightly enriched in dissolved Hg relative to the underlying shelf water. The dissolved Hg concentrations observed in the plume are similar to those in the North Atlantic ( $2.4 \pm 1.6$  pM; Mason et al, 1998), but somewhat higher than those measured outside the plume in 2005 and 2006 of this study ( $1.1 \pm 0.3$  pM, n=4), and offshore in Hudson Canyon in June 2003 (0.6 pM;

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Wright and Reinfelder, unpublished data) indicating that while dissolved Hg concentrations in the plume are slightly elevated above the local background, they are similar to concentrations found in oceanic waters.

It is interesting that dissolved Hg concentrations in 2005 (median, 2.2) are higher than those in 2004 (median 1.5), and similar to those in 2006 (median 2.3), despite significantly larger river discharge in 2005 than in 2004 or 2006. This observation suggests that the primary source of dissolved Hg is from the watershed, as estuarine sources would likely be diluted by the higher fresh water input. This conclusion is consistent with Hg mass balance estimates for the Hudson River estuary (Balcom et al, 2008).

Dissolved Gaseous Mercury concentrations in the plume (~78-607 fM; Reinfelder and Wright, unpublished data), were highly variable, but were higher than those in the Hudson River Estuary (typically <50 fM; Reinfelder and Wright, unpublished data), and similar to or lower than those in the North Atlantic ( $480 \pm 310$  fM; Mason et al, 1998).

*Hg Partitioning* – Log K<sub>D</sub>s for mercury within the plume in 2004 and 2005 (5.2  $\pm$  0.3) were significantly lower than in the Hudson River estuary (6.1  $\pm$  0.4; Balcom et al, 2008). In 2006, however, Hg partitioning in the plume (Log K<sub>D</sub> 6.1  $\pm$  0.4) exhibited a particle concentration effect, which has also been observed within the Hudson River estuary (Balcom et. al., 2008). The particle concentration effect is observed when the K<sub>D</sub> decreases with increasing TSS, usually due to binding by colloids. The observed particle concentration effect suggests that Hg binding to colloids is important in 2006. As TSS in 2006 does not show an inverse relationship with salinity (salinity range of 26.3-32.3, maximum TSS at S ~ 29), this further suggests that the source of the Hg binding

particles/colloids is within the plume. This likely implicates phytoplankton as the source of the Hg binding colloids, as high phytoplankton biomass is the most likely source of increased TSS at mid salinities within the plume. It is important to note that using the >2 $\mu$ m size fraction to estimate TSS, could cause an overestimation of K<sub>D</sub>. Based on comparison of observed K<sub>D</sub> with published values for the estuary, it appears unlikely that this fraction has a large enough mass to bias the K<sub>D</sub>s significantly, as values reported here are similar or lower.

*Fate of Hg in the Hudson River plume* – Model results suggest that the input of particulate Hg from the Hudson River estuary, which accounts for ~70-85% of total Hg input from the estuary, is largely depleted within 50 km of lower New York Bay, with very little Hg transported farther down shelf in the coastal current. Particulate Hg that sinks into the bottom water may potentially be carried back toward Lower New York Bay, as the net bottom water flow is to the north (opposite the flow of the plume; Chant, personal communication). This mechanism may act to retain Hg and other contaminants near the mouth of the estuary, potentially slowing the recovery of contaminated sediments in this area.

Dissolved Hg inputs from the estuary, however, are transported to the coastal current far more efficiently. Under moderate discharge conditions in the absence of bulge formation (CC1), nearly all (~95%) of the dissolved Hg in the plume is transported downshelf, following dilution with bottom water. Under high discharge conditions with bulge formation and 67% retention within the bulge (Bulge 2), ~90% of the estuary dissolved Hg inputs were transported to the coastal current after dilution. This suggests that, to first order, the eventual fate of Hg in the estuary outflow is determined by

partitioning to particulate mater, with particulate mercury being retained locally, and dissolved Hg being transported to the coastal ocean.

An important aspect of Hg transport in the plume is the fate of Hg retained within the recirculating bulge when winds shift. Model results demonstrate that while total Hg retention within the bulge increases with time, the concentration of Hg decreases, as it approaches a balance of dissolved Hg inputs from the bottom water and depletion from air water exchange. In the bulge formation scenarios (bulge 1 and bulge 2), by day 5 the Hg concentration entering the coastal current (which is equivalent to the mean concentration in the plume after air water exchange and particle sinking) is 1.7 pM and 1.6 pM, respectively, approaching the model concentration of 1.5 pM in the bottom water. This suggests that significant cross shelf transport of Hg enriched waters will only occur under conditions of high water discharge, low bottom water mixing, and a shift of wind conditions within 2-3 days to force the bulge offshore before mixing dominates.

#### Conclusions

Hg inputs to the Hudson River plume are dominated by particulate forms of Hg, which likely come from sources within the estuary such as phytoplankton, detritus, and suspended sediments. Conversely, dissolved Hg appears to come primarily from the watershed, and from the entrainment of bottom water.

Within the plume, modeling results predict that particulate Hg is rapidly transferred to the bottom waters by sinking particles, which may subsequently be transported back toward the estuary by bottom currents, suggesting that particulate Hg is retained locally. Conversely, model results predict that dissolved Hg is transported

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efficiently down shelf by the coastal current, and only a small fraction is lost to volatilization to the atmosphere.

During bulge formation, the potential for cross shelf transport of Hg exists, but model results suggest that in many cases, rapid dilution of dissolved Hg by bottom water may limit the impact of this process.

Finally, in May 2006, a particle concentration effect was observed within the plume during bloom conditions, raising the possibility that phytoplankton growth may be correlated with increased colloidal Hg binding, possibly as a result of metal stress in plume phytoplkankton species.

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	CC 1	CC 2	Bulge 1	Bulge 2
River Input				
Discharge condition	Moderate	High	High	High
$Q m3 s^{-1}$	1000	2300	2300	2300
Estuary HgD (pM)	2.5	2.5	2.5	2.5
Estuary HgP (pM)	5	5	5	5
Plume Characteristics				
Initial length (km)	50	50	50	50
Initial width (km)	5	15	15	15
Plume depth (m)	4	4	4	4
Bottom water mixing				
Vert. eddy diffusivity (K <sub>z</sub> ) $x10^{-4}$ m <sup>2</sup> s <sup>-1*</sup>	0.3	0.3	0.3	0.3
Bottom water HgD (pM)	1.3	1.3	1.3	1.3
Bottom water HgP (pM)	0.2	0.2	0.2	0.2
DGM				
Median flux pmol/m2/hr	13	13	13	13
Particle sinking				
rate constant $(d^{-1})$	0.55	0.55	0.55	0.55
Coastal current				
Fraction to coastal current (f)	1	1	0.5	0.33
Time Step				
$\Box T (d)$	SS	SS	0.1	0.1

Table 1. Input parameters for the Hudson River plume box model. SS indicates the model was at steady state and an iterative numerical solution was not required.

\* Houghton et. al., unpublished data

Table 2. Hg speciation in the Hudson River plume and adjacent coastal waters in May 2004, April 2005, and May 2006. Time is local time, S=salinity, TSS is total suspended solids, HgP is particulate Hg, HgD is dissolved Hg, DGM is dissolved gaseous mercury (elemental Hg), and  $K_D$  is the distribution coefficient in L Kg<sup>-1</sup>.
2004	Sample ID	Time	S	TSS	HgP	HgD	HgT	DGM	Particle Hg	log Kn
	I I			mσ L <sup>-1</sup>	nM	nM	nM	fM	nmol g <sup>-1</sup>	-8 b
	050404-2	10.40	29 79	11.5	57	16	7.4	123	0.498	5 5
	050404-3	13.00	31.10	11.2	19	1.5	3.5	204	0.174	5.1
	050404-4	15:00	29.55	10.8	4.4	1.4	5.8	238	0.407	5.5
	050404-6	19:00	29.82	7.1	2.6	1.6	4.2	238	0.365	5.3
	050504-3	10.00	31.10	3.2	1.0	1.5	2.6	220	0.327	5.3
	050504-5	15:00	30.97	3.9	1.0	1.5	3.1	234	0.454	5.5
	050604-1	2.28	31.65	69	1.0	1.1	2.2	213	0.141	5.5
	050604-2	2.20 7.00	31.33	5.6	1.0	1.2	2.3	nd	0.174	5.1
	Mean	,,,,,,,	30.57	75	2.4	1.5	3.9	211	0.325	53
2005	Sample ID	Time	S	TSS	ΗσΡ	HøD	НоТ	DGM	Particle Hø	log Kr
2000	Sumple ID	Time	5	mg I <sup>-1</sup>	nM	nM	nM	fM	nmol a <sup>-1</sup>	iog iip
	041005-1	15.54	25.60	97	56	2.4	8.0	nd	0.572	54
	041105-2	6.58	23.00	79	5.0	2.1	0.0 7 7	nd	0.680	5.5
	041105-3	16.43	23.00	79	3.6	2.3	59	nd	0.460	5.3
	041305-5	5.10	25.00	11.2	3.0	2.5	6.1	162	0.348	5.2
	041305-6	11.00	24 50	53	0.9	2.2	3.1	224	0.173	49
	041305-7	13.00	29.70	1.0	0.1	17	1.8	167	0.145	49
	041305-8	13.37	27.40	2.1	0.2	19	2.1	144	0.073	4.6
	041305-9	15:07	29.33	1.6	0.2	1.5	1.4	75	0.036	4.4
	041405-10	0.24	27.33	1.0	0.1	1.5	2.6	126	0.520	5 5
	041805-11	7.39	23.10	7.2	4.8	24	7.2	349	0.662	5.4
	041805-12	8.25	26.80	7.2	3.8	2.1	6.1	382	0.524	5.4
	041905-13	5.07	23.70	24	0.1	2.5	2.5	503	0.057	4.4
	042005-15	4.00	27.00	2.1	13	1.9	3.2	340	0.657	5 5
	042005-16	12.38	26.40	3.5	2.9	1.9	4.8	nd	0.826	5.6
	042005-18	22.50	25.10	3.1	0.8	1.7	2.5	nd	0.256	5.0
	Mean	22.31	25.10	5.4	2.3	2.0	43	247	0.426	5.2
2006	Sample ID	Time	S	TSS	HaD	HaD	НаТ	DCM	Dorticlo Ha	log K
2000	Sample ID	Thic	5	155 ma I ·1	nM	nM	ng i	fM	n article Hg	log Kj
	050206 1	15.45	22.45	2 A	0.2	0.8	1.0	nd	0.071	4.0
	050200-1	15.45	52.45 27.69	2.4	12.9	0.8	1.0	222	0.071	4.9
	050300-2	15.10	27.08	1.0	15.0	2.2	10.0	244	0.872	6.5
	050300-3	0.00	26.26	2.0	0.0	2.0	12.0	244	9.675	6.2
	050406-5	9.00	26.20	2.0	9.0 7.8	2.0	12.0	412	4.525	6.5
	050406-5	14.30	20.97	2.0	6.8	2.9	10.7	412 261	3.431	6.0
	050406-7	21.23	26.78	2.0	3.0	2.5	6.4	168	1 555	5.8
	050406-8	21.25	20.91	2.5	5.9 67	2.5	0.4	274	2 308	5.0
	050506-9	25.50 8·21	27.21	2.9	5.4	2.0	9.5 8.0	274	1.498	5.9
	050506-10	0.21	27.95	3.0	7.0	2.7	0.0	202 nd	2 332	5.0 6.0
	050506-11	13.48	27.22	2.6	5.6	2.5	9.5 7.8	504	2.552	6.0
	050506-11	17.13	20.10	2.0 4 0	5.0	2.2 2.1	7.0	607	1 208	5.8
	050606-12	8.25	27.07 28.16	<del>1</del> .0 5 3	2.2 2.8	2.1	5.0	320	0.531	5.0 5.4
	050606-14	0.25 23.50	20.10	3.5	2.0 2.0	2.2 1.5	5.0 4 A	433	0.331	5. <del>4</del> 5.7
	050706-16	25.59	30.02	1.2	2.9	0.8	 	371	2 106	5.7 6.4
	050806-17	2.31 12.07	30.02	1.2	2.5	0.0	5.5 1.5	nd	0.430	5. <del>4</del>
	Mean	12.07	28.08	2.6	5.1	2.3	7.3	332	3.084	6.1

Table 3: Results of the box model under 4 conditions. CC1 and CC2 represent the formation of a coastal current, while Bulge 1 and Bulge 2 represent the formation of a recirculating bulge feature with differing fractions of water diversion into the coastal current (f). Initial conditions in Bulge 1 and Bulge 2 assume instantaneous establishment of the water flux into the coastal current at the fraction (f).

	CC 1	CC 2		Bulge 1	(f = 0.5)			Bulge 2	(f = 0.33)	
	Steady State	<b>Steady State</b>	Day 0	Day 1	Day 3	Day 5	Day 0	Day 1	Day 3	Day 5
River Input										
Hg Input (mol d <sup>-1</sup> )	1.3	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Plume Characteristics										
Hg content (mol) <sup>a</sup>	2.6	7.0	7.0	7.7	9.2	11.0	7.0	7.9	10.0	12.8
Area (km <sup>2</sup> )	250	750	750	887	1210	1610	750	935	1398	2013
Bottom water mixing										
Hg Input (mol $d^{-1}$ )	0.32	0.97	0.97	1.15	1.57	2.09	0.97	1.21	1.81	2.61
DGM										
Hg evasion (mol d <sup>-1</sup> )	0.078	0.234	0.234	0.277	0.378	0.502	0.234	0.292	0.436	0.628
Particle sinking										
Hg export (mol $d^{-1}$ )	0.53	1.30	1.30	1.34	1.42	1.51	1.30	1.36	1.46	1.58
Coastal current										
Hg export (mol $d^{-1}$ )	1.01	2.42	1.21	1.26	1.37	1.53	0.81	0.85	0.96	1.13
Hg Conc. (pM)	2.6	2.3	2.3	2.2	1.9	1.7	2.3	2.1	1.8	1.6

<sup>a</sup>Hg content after DGM evasion and particle sinking



Fig. 1: A conceptual box model for the fate and transport of Hg within the Hudson River plume. Arrows represent major transport processes into or out of the plume.



Fig. 2. Mixing curves of total and dissolved Hg in the Hudson River plume for a) May 2004, b) April 2005, and c) May 2006 and d) total Hg in the Hudson River estuary and plume, April 2005.



Fig. 3: Relationship between Total Hg and Total Suspended Solids (TSS) in May 2004, April 2005, and May 2006.



Fig. 4: Distribution coefficients vs. salinity for May 2004, April 2005, and May 2006. The regression line is for May 2006 data, excluding the circled data point.

# Chapter 4: – Trace metal bioaccumulation and trophic transfer in the Hudson River buoyant plume

### Introduction

As one of the most urbanized estuaries in the world, the lower Hudson River and its seaward extension, the Hudson River buoyant plume, have been significantly influenced by anthropogenic sources of inorganic and organic contaminants from sewage, urban runoff, elevated atmospheric deposition, and historically contaminated industrial sites (Sañudo-Wilhelmy and Gill, 1999; Brown et. al., 1985). The discharge of Hudson River water as a buoyant plume to the New York Bight has the potential to transport these contaminants directly to the coastal ocean where they may enter the benthic and pelagic food webs of the continental shelf. One of the goals of the LaGrangian Transport and Transformation Experiment (LaTTE) project was to examine the fate of contaminant trace metals in the Hudson River buoyant plume including their potential for bioaccumulation into the coastal food web.

The accumulation of trace metals by marine zooplankton has primarily been examined with laboratory experiments, with few field studies. Based on laboratory data, the key factors that control metal accumulation by zooplankton have been identified: aqueous speciation, phytoplankton accumulation and intracellular partitioning, zooplankton grazing and metal efflux rates (Wang and Fisher, 1998). Aqueous speciation controls zooplankton metal uptake from the dissolved phase, as well uptake rate of the phytoplankton community - the primary food source of mesozooplankton in most systems. Partitioning within the phytoplankton cells is also relevant, as higher assimilation efficiencies (greater bioavailability) are associated with higher fractions of metal in the cytoplasm of the phytoplankton cells (Reinfelder and Fisher, 1991; Hutchins et. al., 1995). Metals associated with phytoplankton cell walls and other detritus may still be assimilated however, in some cases with assimilation efficiencies comparable to intracellular metals (Xu and Wang, 2002). The zooplankton grazing rate controls the influx of material into the cell, and may influence the assimilation efficiencies of ingested metals (Xu and Wang, 2001), while the metal efflux rates represent the metal lost from the cell.

These factors have been incorporated into a kinetic model of zooplankton metal accumulation (Wang and Fisher, 1998) that successfully predicts the patterns of metal accumulation observed under controlled experimental conditions. Limited field data (Fisher et. al., 2000) suggest that this model is applicable to zooplankton in natural settings, however, natural systems are highly complex, and additional studies will be required before we understand the range of conditions under which the model can be successfully applied.

When considering the accumulation of metals in zooplankton, it is important to note that the metal exposure route (i.e. dietary vs. dissolved uptake) has a significant effect on metal accumulation and toxicity. Metals delivered directly to internal tissues from trophic transfer may be significantly more toxic than metals taken up from the dissolved phase (Hook and Fisher 2001b). Zn, for instance, has been shown to cause toxic effects at body burdens similar to natural levels, in copepods fed with Zn enriched phytoplankton (Hook and Fisher, 2002). In natural systems, the Zn may be largely associated with the exoskeleton (Wang and Fisher, 1998) without inducing toxic effects. In laboratory experiments, toxicity was induced at approximately the same body burden by directly delivering Zn to more sensitive intracellular tissues via trophic transfer (Hook and Fisher, 2002). This example illustrates the importance of considering the uptake pathway as well as the metal body burden when evaluating the potential for metal toxicity in natural systems.

To assess the bioaccumulation of contaminant trace metals at the base of the Hudson River buoyant plume pelagic ecosystem, the concentrations of several trace metals (Ag, Cd, Cu, Hg, Pb, and Zn) were measured in plume phytoplankton and zooplankton (>90% calanoid copepods) as well as dissolved surface waters in April 2005 and May 2006. Results from field efforts have then been applied to evaluate the following hypotheses 1) Zooplankton within the plume are enriched in metals relative to oceanic zooplankton,. 2) Plume zooplankton closest to the estuary will accumulate more metals due to higher dissolved and particulate metal concentrations, 3) Significant trophic transfer of metals will result in biomagnification of metals in zooplankton, and 4) Metal accumulation by zooplankton may result in sub-lethal toxic effects.

#### Methods

*Field sampling* - The April 2005 experiments were conducted following a major discharge event which resulted in the formation of a large rotating gyre in the New York Bight (Chant et al., 2008). In contrast, the May 2006 experiments were conducted under moderate discharge conditions resulting in a southerly coastal current modified by recirculation features south of the New York Bight.

*Sample collection and analysis.* Zooplankton samples were collected within the Hudson River Plume in April 2005 and May 2006 onboard the R/V Oceanus as part

of the Lagrangian Transport and Transformation Experiments (LaTTE).

Mesozooplankton were collected with a 1-m ring net (202  $\mu$ m mesh fitted with a nonfiltering cod end) towed vertically (~ 25 m min<sup>-1</sup>) through the upper, mixed layer (< 10 m) at each discrete sampling station (Table 1). Any zooplankton adhering to the mesh upon retrieval, were gently washed down into the cod end prior to processing on the deck. On deck, the contents of the cod end were poured into a small plastic tub and the > 202  $\mu$ m fraction of the sample further concentrated by gently passing the entire sample through a 202  $\mu$ m plastic sieve. To obtain size-fractionated samples for metal analysis, the concentrated samples were passed through a series of nylon sieves (4000, 2000, 1000, 500 and 200  $\mu$ m mesh). Material retained on each of the sieves was transferred via a clean plastic spatula to acid-cleaned cryovials and stored frozen.

Filtered seawater and suspended particles were collected with an underway sampling system during the same time period on a second ship, the R/V Cape Hatteras. Surface water was collected via a Teflon pipe attached to a 1.25cm OD teflon tube, that was mounted on the seaward side of a stainless steel pole with an aluminum mount. The pipe was mounted such that it extended in front of the aluminum mount, approximately 1.5m from the ships hull. Samples were pumped onboard and into a HEPA clean bench at 3-4 L min-1 with a Teflon/polypropylene bellows pump. All wetted parts of the uptake system were leached in 10% HCl for a minimum of 72 hrs, and rinsed copiously with ultra high purity water. Additionally, prior to sampling, the uptake system was flushed extensively with seawater.

Within the shipboard lab, trace metal clean techniques were used at all phases of sample collection and manipulation in order to minimize the potential for contamination. Seawater was pumped directly into a hepa filtered clean bench (class 100) and whole water samples were transferred to a second class 100 clean bench for filtering. Samples for dissolved metals were filtered in-line with a high capacity 0.2 μm polypropylene cartridge filter, and collected in rigorously acid cleaned polyethylene bottles. Samples for particulate metals were collected in a 4 L polycarbonate carboy, homogenized, and vacuum filtered on acid cleaned 47mm polycarbonate filters housed in an all Teflon filter apparatus. Samples were filtered under gentel vacuum (< 130 mm Hg) to avoid cell lysis. Dissolved metals were analyzed by dilution/direct injection HR-ICP-MS or IDA column pre-concentration/matrix separation HR-ICP-MS. Particulate metals were digested in aqua regia and analyzed by HR-ICP-MS.

Prior to analysis, thawed zooplankton samples were rinsed with ultra-pure water on a 160 µm nitex mesh to remove residual phytoplankton and salt. Samples were then transferred to acid-cleaned pre weighed polypropylene microcentrifuge tubes for digestion. Samples for determination of (non Hg) trace element composition were then dried at 40°C to constant mass in a drying oven. Once dry, digestion vials (with sample) were weighed to +/- 0.1 mg on an analytical balance and the mass of sample determined by difference. Samples for determination of (non Hg) trace element composition were digested for ~12 hrs in hot 4 N nitric acid (60°C). Following digestion, samples were transferred to acid cleaned 15 ml centrifuge tubes and diluted to 5% acidity. Samples were then analyzed by radial ICP-OES (Varian Vista-Pro, Rutgers Inorganic Analytical Laboratory, New Brunswick NJ). To enhance the capabilities of radial ICP-OES to accurately quantify low ppb concentrations of some metals (esp. Ag, Cd, and Pb) in diluted samples, an APEX E high sensitivity desolvating spray chamber (Elemental Scientific Inc.) was employed, resulting in a  $\sim 10x$  improvement in sensitivity and detection limits. Y was added to all samples, standards and blanks as an internal standard to correct for variations in sensitivity (all corrections were < 10%). Appropriate analytical wavelengths were selected for each element based on sensitivity and likelihood of spectral interferences as follows: Ag 328.068 nm, Ag 338.289 nm, Cd 214.439 nm, Cd 228.802 nm, Cu 213.598 nm, Cu 324.754 nm, Cu 327.395 nm, Pb 217.000 nm, Pb 220.353 nm, Pb 283.305 nm, Zn 202.548 nm, Zn 206.200 nm, Zn 213.857 nm, Zn 334.502 nm. Whenever possible, multiple spectral lines were used to determine the concentration of each element to minimize the potential influence of spectral interferences. Where multiple wavelengths could be used for calibration of a given metal, good agreement (within 10%) was generally obtained between the values determined by calibration at each wavelength. Digestion blanks were performed for each set of samples, diluted as the samples, and analyzed with each sample run. Blanks generally did not contain detectible concentrations of metals, by this technique. Due to the limited biomass available, duplicate analyses could not be performed for the majority of samples, however for the limited duplicate analysis (n=2) performed, good agreement (<8%) was found between the independent digestions for Fe, Cd, Cu, and Ag. Greater variability however, was observed for Zn (24%), Pb (58%), and Cu (65%), which can most likely be attributed to the contamination of one of the replicates during digestion and/or sample preparation.

For Hg speciation analysis, samples were freeze dried to minimize losses of volatile forms. Following freeze drying, digestion vials (with sample) were shipped to Quicksilver Scientific (Lafayette, CO) for analysis. Zooplankton were leached with

acidic thiourea, and analyzed for methylmercury (MeHg) and inorganic mercury (Hg(II)) by Hg-thiourea complex ion-chromatography with on-line cold vapor generation and atomic fluorescence spectrometric detection (Shade and Hudson, 2005). Total Hg was calculated as the sum of the MeHg and Hg(II).

Stastical analysis - Metal concentrations in zooplankton from April 2005 and May 2006 were compared to each other and to oceanic copepods using the nonparametric Komolgorov-Smirnoff test (95% confindence). A non-parametric test was selected because the distributions of most of the data sets analyzed were found to depart significantly (p > 0.05) from the normal and log-normal distributions using the Komolgorov-Smirnoff test for normality.

*Copepod bioaccumulation model* - The potential impact of trophic transfer on zooplankton metals was assessed using the copepod bioaccumulation model developed by Wang and Fisher (1998). In this model, the steady state concentration ( $C_{ss}$ ) of a given metal in zooplankton is described as:

$$C_{ss} = \frac{AE \cdot IR \cdot C_p}{k_e + G} + \frac{k_u \cdot C_w}{k_e + G}$$

where  $k_u$  is the uptake rate constant of the metal from the dissolved phase (l g<sup>-1</sup> d<sup>-1</sup>), C<sub>w</sub> is the concentration of the metal in the dissolved phase (nmol l<sup>-1</sup>), AE is the assimilation efficiency (%) of the metal from the ingested food particles, C<sub>f</sub> is the concentration of the metal in the food (nmol g<sup>-1</sup>),  $k_{ew}$  is the efflux rate constant following uptake from water (d<sup>-1</sup>),  $k_{ef}$  is the efflux rate constant following uptake from food (d<sup>-1</sup>), and g is the copepod growth rate constant (d<sup>-1</sup>).

# Results

Enrichment of metals in copepods of the Hudson River plume. The

concentrations of Ag, Cd, Cu, MeHg, Hg, Pb, and Zn in zooplankton collected in April 2005 (n=19) and May 2006 (n=48) are given in Table 2. In both April 2005, and May 2006, the mesozooplankton population was composed primarily of calanoid copepods (>90%). In order to assess the accumulation of metals in plume copepods relative to the water and their food sources, metal bioconcentration and biomagnification factors were calculated for each metal based on the median metal concentrations in copepods, dissolved metal concentrations in the plume, and particulate metal concentrations in the 2-20µm size fraction. Copepod bioconcentration factors (L kg<sup>-1</sup>), which describe the metal concentration in plume copepods relative to that in the water column, decreased as follows: Zn  $(2.1 \times 10^5) > Hg (1.8 \times 10^5) > Ag (9.5 \times 10^4) > Pb (5.2 \times 10^4) > Cd (3.7 \times 10^4) > Cu (3.6 \times 10^4)$ . Copepod biomagnification factors, which relate the metal concentration in plume copepods relative to the particulate matter that they feed on decreased as follows: Zn (3.0) > Ag, Cu (2.5) > Hg (1.3) > Cd (0.59) >> Pb (0.068).

To evaluate potential metal enrichment of Hudson River plume zooplankton, metal concentration in zooplankton from each plume sampling event were compared with those for oceanic copepods (Stern and MacDonald, 2005; Fisher et. al, 2000; Zauke and Schmalenbach, 2006) as well as each other (Fig. 1). In 2005, plume copepods were significantly (p < 0.05) enriched in Ag, Cu, Pb, Zn and MeHg, while showing no significant enrichment in total Hg, and depletion in inorganic mercury (Table 3). In 2006, plume copepods showed enrichment in Ag, Pb, Cu, Zn, inorganic mercury, total Hg and MeHg. In both April 2005 and May 2006, plume zooplankton were slightly depleted in Cd relative to oceanic copepods, however, this depletion was not significant at the 95% confidence level, though in May 2006, the depletion was significant at the 94.8% confidence level.

Hudson River plume zooplankton collected in 2006 were enriched in Ag and total Hg relative to those collected in 2005, while Cu was enriched in the 2005 samples. Zooplankton concentrations of Pb, Zn, and MeHg were not significantly different in 2005 and 2006.

The spatial distributions of metals in plume zooplankton showed multiple patterns of enrichment (i.e. patchiness). In April 2005, Pb, Zn, Fe, MeHg, and Cu were primarily enriched in zooplankton from lower salinity waters closer to the mouth of the Hudson River Estuary, which correlated spatially with elevated concentrations of particulate and dissolved metals. For example, in 2005, Cu in plume zooplankton increased linearly with Cu in particulate metals (2-20  $\mu$ m, r<sup>2</sup>=0.68; >20  $\mu$ m, r<sup>2</sup>=0.82). While most metals showed a decreasing trend with salinity, Ag and Hg(II) showed elevated concentrations in zooplankton at higher salinities in 2005 (Fig. 2). These patterns were also apparent in May 2006 for all metals except Cu, which showed enrichment in zooplankton from both lower salinity and higher salinity feature that formed in-shore of the plume as the southern portion became detached and propagated offshore (see Fig. 3). As the plume advected offshore, a mixture of high salinity shelf water and aged plume water rotated clockwise around the southern end of the plume and formed the high salinity intrusion feature. This intrusion was relatively stable, and was not impacted by upwelling during the sampling period.

Copepod bioaccumulation pathways - For the May 2005 data, the predictive power of the model was evaluated by comparing the plume copepod metal concentration predicted by the model to the median measured concentrations of Ag, Cd, Cu, and Zn in zooplankton from the HR Plume. The model was not used to predict bioaccumulation of Pb and Hg, as appropriate model parameters could not be located in the literature. The mean concentrations of each metal in suspended particulate matter and in the dissolved (<  $0.2\mu m$ ) fraction were used for C<sub>f</sub> and C<sub>w</sub> respectively, while the other model parameters were estimated based on literature values (Table 4). The model results were generally comparable with the field observations in 2005, with all model predictions within a factor of  $\sim 2$  or less of field observations (Table 5). Based on the model predictions, we can evaluate the relative importance of trophic transfer vs. dissolved uptake on the metal body burdens in plume zooplankton. In April 2005, the model estimated fraction of the body burden due to trophic transfer decreased as follows: Cd (83%) > Zn (79%) >> Cu (33%) >> Ag (9%). Additionally, the model was used to predict the likelihood of biomagnification for each element. The predicted biomagnification factors were Cu (5.3) > Zn (1.7) > Ag (1.5) > Cd (0.50).

### Discussion

*Metal accumulation in plume zooplankton* – Hudson River plume zooplankton accumulate significant body burdens of trace metals relative to the surrounding waters, with the greatest degree of accumulation (largest bioaccumulation factors) observed for Zn and Hg. The high Zn concentration factor is not surprising as Zn is an essential nutrient for both phytoplankton and zooplankton, and is readily assimilated by copepods (Wang and Fisher, 1998). Mercury would also be expected to exhibit significant bioconcentration as Hg has been shown to accumulate in aquatic foodwebs, largely in the form of MeHg at higher trophic levels.

Within the Hudson River plume, Zn, Ag, Cu, and Hg all exhibit biomagnification factors greater than 1, indicating that copepod body burdens of these metals exceed phytoplankton concentrations. Biomagnification of each of these elements (excluding Hg, which was not evaluated), and biodiminuation of Cd were successfully predicted by the copepod bioaccumulation model, suggesting its utility for evaluating the likelihood for biomagnification between phytoplankton and zooplankton in coastal ecosystems.

*Metal enrichment in plume zooplankton* – Hudson River plume zooplankton were generally enriched in metals relative to oceanic zooplankton. In both April 2005 and May 2006, all metals in zooplankton were enriched relative to oceanic copepods with the exception of total and inorganic mercury in 2005, and Cd in both 2005 and 2006. Enrichment of metals in zooplankton is not surprising considering that both dissolved and particulate phase metals are highly enriched in the Hudson River Estuary which forms the Hudson River plume and it does suggest that a significant fraction of the metals within the plume are in a bioavailable form.

In 2006, Ag, total Hg, and Hg(II) in zooplankton were significantly higher than in 2005. In 2006, these same metals showed significant enrichment in the high salinity intrusion that separated the offshore extension of the plume from the coastal current, and in the case of Hg, in the higher salinity portions within the plume. This pattern is not observed in the particulate metal samples from May 2006, however, the high salinity intrusion was not sampled for particulate metals as the R/V Cape Hatteras focused primarily on sampling the plume itself. It should be noted however that particulate Hg concnetrations in the offshore extension of the plume do not correlate with the observed increase in zooplankton Hg(II) in this region. A number of possible scenarios could potentially explain the observed pattern: 1) A second source of metals that is enriched in Hg(II) and Ag is influencing zooplankton in these areas, 2) The flux of Hg and Ag from the estuary was significantly higher prior to the field observations in 2006, 3) increased bioavailability of Ag and Hg due to oxidation of organic ligands or 4) Changes in plankton community structure which resulted in increased bioavailability of phytoplankton and/or microzooplankton associated Hg(II) and Ag to mesozooplankton.

With the regard to the first possibility, we evaluated the likelihood of Ag and Hg inputs from two potential sources: offshore sewage outfalls and contaminated sediments. Neither of the first two sources should affect the plume directly, as they are likely entrained within the bottom waters where a strong density gradient prevents them from rapidly mixing with the surface plume waters. Dye studies in the Shark River sewage outfall, near Belmar NJ, show that discharges from that outfall primarily travel along a north south line parallel to the shore, and remain at the bottom of the water column (Obropta and Hires, 2007). Metals from these sources are therefore, not likely to accumulate in surface phytoplankton or adsorb to the particles within the plume. Mesozooplankton, however, vertically migrate, and may potentially feed within the bottom waters which are susceptible to influence from these sources. The sewage

outfalls however, appear to be too far inshore (>10 km from the center of the intrusion) to directly influence zooplankton over the entire area of observed Hg and Ag enrichment, as their combined discharge and estimated metal fluxes are relatively small in comparison. Contaminated sediments also appear to be an unlikely explanation for the observed enrichment as there are no known sites of contamination or potential contamination large enough to influence zooplankton over such a large area. It is further unlikely that an additional input source alone could explain the observed enrichment patterns as the Hg(II) enrichment in plume zooplankton is observed to begin at a lower salinity and in a different geographic location from the zooplankton Ag enrichment.

A second potential explanation was that the flux of Hg and Ag from the estuary was significantly higher prior to the field observations in 2006, resulting in higher dissolved and particulate metal concentrations in the older plume water of the intrusion. Hg and Ag are both highly enriched in the Hudson River estuary, and variations in river discharge, as well as anthropogenic inputs such as sewage can affect the supply of metals entering the plume. This variability has the potential to create discrete water masses with the plume that contain relatively higher concentrations of metals which would be expected to result in higher body burdens of metals within these water masses. As with the previous explanation however, it seems unlikely that this scenario fully explains the observed metal accumulation patterns, as the maximum Hg and Ag enrichment occurs in different water masses.

The third potential explanation I considered was the possibility that the bioavailability of Ag and Hg(II) increased, possibly due to the oxidation/degradation of an organic ligand, or an inorganic reduced sulfur species. Hg forms strong complexes

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with organic molecules that contain reduced sulfur functional groups such as thiols that can reduce bioavailability and toxicity to phytoplankton (Gorski et al, 2008; Mason et al, 1996). For Ag, the importance of organic complexation is less clear. It has been suggested that organic Ag complexes are relatively unimportant in marine systems (Miller and Bruland 1995), however, Ndund'u et al (2006) and Wen et al (2002) have noted significant interferences on silver preconcentration techniques which they have attributed to organic complexation based on their to absence following UV oxidation. If organic complexes dominate the dissolved speciation of Hg(II) and Ag within the Hudson River Estuary, it is possible that oxidation of these ligands within the plume could gradually increase the bioavailability of these species causing increased levels of biomagnification in older plume waters.

It is also possible that the same effect could be achieved by complexation with inorganic reduced sulfur ligands if the dissociation kinetics are sufficiently slow. Leal et al. (1999) have demonstrated the production of thiols and Walsh et al (1994) observed production of dissolved sulfide and acid volatile sulfide by phytoplankton in response to increasing free metal ions. This suggests that complexation by either organic thiols or inorganic sulfide complexes, either of which would be subject to oxidation within the plume, could potentially affect the bioavaility of Ag and Hg. This hypothesis does not appear to adequately explain the observed Hg(II) enrichment, however, as there is no observed enrichment in particulate (which includes phytoplankton) Hg(II) in the offshore extension of the plume, which would be expected if the bioavailability increased due to a decrease in reduced sulfur complexes. As we have no dissolved or particulate Ag data

from the area of Ag enrichment, we can not rule out this possibility for Ag, however, we expect that a similar process is controlling both the Hg(II) and Ag observations.

A fourth possibility is that changes in plankton community structure which resulted in increased bioavailability of Hg(II) and Ag to mesozooplankton. Fessenden and Cowles (1994) observed that copepods consumed phagotrophic ciliates preferentially to phytoplankton, except during bloom conditions when large phytoplankton were dominant. It has also been shown that mesozooplankton assimilate Ag and Hg significantly more efficiently from certain microzooplankton species than from phytoplankton, likely due to the larger fraction of those metals present in the cytoplasm (Twining and Fisher, 2004). Therefore, a shift from bloom conditions within the lower salinity portions of the plume, to post bloom conditions in the high salinity portions of the plume, could result in higher concentrations of metals in mesozooplankton. This scenario results in higher metal body burdens in mesozooplankton, without a proportional increase in the measured concentration of particulate metals.

*Copepod bioaccumulation pathways* – The copepod bioaccumulation model suggests that trophic transfer was an important bioaccumulation pathway for copepods within the Hudson River plume in April 2005 for all metals except Ag. Trophic transfer was the dominant pathway by which Cd, Zn, and Pb, accumulated in mesozooplankton, and accounted for about half of the body burden of Cu. The relative unimportance of trophic transfer to Ag accumulation in 2005, is due to a combination of its low assimilation efficiency from phytoplankton (10-18%; Wang and Fisher, 1998; Reinfelder and Fisher, 1991) and its relative stability in the dissolved phase in seawater. Variations in dissolved speciation and prey composition, however have the potential to affect the

bioavailability and trophic transfer of Ag, such that it may be an important accumulation pathway in mesozooplankton under certain conditions.

*Potential for zooplankton toxicity* – The potential of Ag, Cd, Cu, Hg, and Zn to exhibit toxic effects on the mesozooplankton of the Hudson River Plume was evaluated based on laboratory toxicity tests conducted by Hook and Fisher (2001b and 2002) on marine copepods. The potential for Pb toxicity was excluded from this analysis due to a lack appropriate toxicity data.

In April 2005, the median zooplankton concentrations of Ag and Zn exceeded the threshold for sub-lethal toxicity by a factor of ~2, while Cd, Cu, and Hg were generally below the toxicity threshold. In May 2006, median Ag and Zn concentrations again exceeded the potential toxicity threshold by a factor of ~8 and ~2 respectively, while Cd, Cu and Hg were generally below the toxicity threshold. It is important to note however, that the toxicity of a given metal depends not only on its concentration within the organism, but on its route of exposure (dietary vs. dissolved uptake), and whether an organism has had sufficient time to adapt to elevated metal exposure.

In the case of Ag, it is necessary to closely examine the relative contributions of dietary sources and dissolved uptake in order to evaluate the likelihood of sublethal toxicity, as copepods are much more sensitive to Ag accumulated from food than that accumulated from direct uptake from the dissolved phase (Hook and Fisher, 2001b). In April 2005, model estimates predict that ~90% of the zooplankton Ag was a result of uptake from the dissolved phase. If this result is accurate, then it is unlikely that zooplankton experienced significant toxicity during this time period. In May 2006 however, silver accumulation showed a significantly different pattern. Silver levels in

2006 samples were significantly higher than in 2005 (~3.5-5x), particularly in the high salinity intrusion. As salinity increased from 29 to 30, the zooplankton body burden increased by ~40 nmol g<sup>-1</sup> to a maximum of 77 nmol g<sup>-1</sup>. Hook and Fisher (2002), noted a sub-lethal toxic effect, manifested as reduced egg viability, with an increased body burden of 3 nmol g<sup>-1</sup> when Ag was added from enriched phytoplankton. Although, as discussed earlier, the mechanism responsible for the observed enrichment is unknown, it is likely that trophic transfer plays a significant role in the higher Ag concentrations observed. If this is the case, zooplankton from the high salinity intrusion are very likely to be Ag stressed.

In addition to potential Ag toxicity, mesozooplankton in the Hudson River Plume are also likely to be experiencing sublethal toxic effects due to elevated Zn body burdens. Within the cell, Zn is complexed by metalliothionein and glutathione, which mitigates its toxicity (Engel and Brower, 1991 and 1993). This mechanism allows a cell to adjust to high Zn exposures, however, the response rate is such that dietary influx rates >25 nmol  $g^{-1}h^{-1}$  exceed its capacity and result in toxic effects (Hook and Fisher, 2002). Based on model estimates, Zn influx from suspended particles in the Hudson River plume is in the range of ~200-7500 nmol  $g^{-1}h^{-1}$ , which suggests that mesozooplankton are unlikely to be able to fully mitigate the effects of Zn ingestion by this mechanism.

*Conclusions* – This study provides strong evidence for the importance of trophic transfer in the bioaccumulation of metals in mesozooplankton of the Hudson River plume. All metals within the plume mesozooplankton are significantly bioconcentrated relative to the plume waters, and Ag, Cu Hg, and Zn have been observed to biomagnify relative to phytoplankton. Mesozooplankton within the plume are generally enriched in

metals relative to oceanic copepods, with the exception of Cd, which was slightly depleted in plume zooplankton, though the result was not significant at the 95% confidence level. The greatest degree of enrichment was for Ag in May 2006 zooplankton, which had body burdens ~25-30x higher than oceanic copepods. The observed metal enrichments were compared to predicted concentrations from kinetic modeling and generally good agreement was found, confirming the validity of the modeling approach.

Zooplankton generally showed greatest metal enrichment in the low salinity regions of the plume near the moth of the estuary. Ag and Hg(II) however, showed the opposite pattern, with zooplankton body burdens generally increasing at higher salinities, with the greatest enrichment in the high salinity intrusion of May 2006. Though the mechanism(s) leading to the observed patterns of Ag and Hg(II) enrichment are unclear, in this paper we present several testable hypotheses for future research.

Within the plume, and the nearby coastal waters, plankton are exposed to high concentrations of metals which leads to the accumulation of potentially sub-lethal toxic body burdens of Ag and Zn in mesozooplankton. As this study was not designed to directly evaluate the toxicity of these metals, additional studies will be necessary to either confirm or refute potential toxicity, as this has important implications for the management of the Hudson River Estuary, including the sewage treatment strategies of the New York metropolitan area.

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					Depth	Temp	
ID	Date	Time	Lat	Lon	( <b>m</b> )	(°C)	Salinity
Apr-05							
B1	10-Apr-05	19:52	40.348	73.922	0-12	7.0	23.55
B2	10-Apr-05	20:20	40.350	73.915	0-16	8.7	22.50
C2	11-Apr-05	18:30	40.389	73.908	0-19.2	7.6	23.49
B2	12-Apr-05	17:32	40.350	73.943	0-7	7.7	23.71
A1	13-Apr-05	13:50	40.230	73.882	0-23	7.2	26.11
A2	13-Apr-05	13:59	40.230	73.882	0-23	7.2	26.67
A1	14-Apr-05	10:23	40.206	73.001	0-45	5.7	31.55
A2	14-Apr-05	13:20	40.208	73.001	0-45	5.8	31.50
A3	14-Apr-05	13:30	40.208	73.001	0-45	5.8	31.50
J1	17-Apr-05	20:26	40.342	73.887	0-22	10.3	23.03
J2	17-Apr-05	20:55	40.342	73.887	0-22	9.7	24.36
H1	18-Apr-05	17:08	40.166	73.978	0-18.7	11.2	24.01
H2	18-Apr-05	17:43	40.167	73.977	0-18.5	9.8	24.66
A1	19-Apr-05	13:12	39.999	74.034	0-18.6	8.0	27.47
May-06							
04A-1	4-May-06	13:30	40.243	73.958	0-6	13.1	26.10
06A-1	6-May-06	12:33	39.982	73.754	0-3	14.5	27.70
07A-1	7-May-06	12:28	39.978	73.612	10-15	10.2	32.09
06B-1	6-May-06	18:43	39.982	73.755	0-6	15.5	27.95
07B-1	7-May-06	15:21	40.021	73.570	0-20	10.2	32.17
04C-1	4-May-06	18:56	40.285	73.945	0-6	12.8	27.02
05C-1	5-May-06	14:48	40.000	73.918	0-6	12.6	29.08
07C-1	7-May-06	17:04	40.024	73.644	0-20	10.4	32.04
04D-1	4-May-06	20:09	40.268	73.958	0-6	12.9	27.14
05D-1	5-May-06	17:02	39.860	73.854	0-6	13.8	29.46
07D-1	7-May-06	18:47	40.020	73.761	0-30	11.2	31.51
04E-1	4-May-06	21:45	40.246	73.963	0-6	15.6	25.38
05E-1	5-May-06	18:42	40.005	73.858	0-6	13.0	29.02
03F-1	3-May-06	23:08	40.253	73.963	0-6	12.8	26.23
04F-1	4-May-06	22:29	40.202	73.962	0-6	14.1	26.69
05F-1	5-May-06	20:31	40.067	73.782	0-6	14.6	28.58
07F-1	7-May-06	20:48	40.020	73.870	0-20	13.3	30.05
05G-1	6-May-06	0:02	40.048	73.770	0-3	14.3	27.70
07G-1	7-May-06	22:36	40.021	73.911	0-20	13.1	29.86
07H-1	7-May-06	23:47	40.018	73.939	0-15	12.7	29.98
07I-1	7-May-06	0:55	40.018	73.969	0-15	12.6	30.42

Table 1. Zooplankton sample locations and sampling data for April 2005 and May 2006. Temperature and salinity data are for the surface water.

Station ID	Size	Ag	Cd	Cu	Pb	Zn	MeHg	Hg(II)	Total Hg
	□m	nmol g <sup>-1</sup>	nmol g <sup>-1</sup>	nmol g <sup>-1</sup>	nmol g <sup>-1</sup>	µmol g <sup>-1</sup>	pmol g <sup>-1</sup>	pmol g <sup>-1</sup>	pmol g <sup>-1</sup>
Apr-05						1 0	1 0	1 0	1 0
10B	202	3.3	17.0	2273	8.9	17.3	197	248	445
	500	12.1	10.9	681	3.4	6.2	ND	ND	ND
11C	202	< 1.1	0.3	482	ND	5.7	ND	ND	ND
	500	< 1.1	12.4	419	ND	5.5	171	149	320
12B	202	< 1.1	15.3	486	42.4	31.7	ND	ND	ND
	500	< 1.1	8.1	553	3.1	6.1	ND	ND	ND
13A	202	15.5	22.9	420	28.0	6.5	162	188	350
	500	9.5	15.8	504	1.3	3.3	ND	ND	ND
14 <b>G</b>	202	9.8	16.8	252	13.2	3.0	141	212	354
	500	11.7	15.8	312	8.7	2.9	118	150	268
	1000	< 1.1	2.4	192	17.0	2.5	ND	ND	ND
14K	202	9.1	14.2	403	36.7	4.8	204	221	425
	500	10.7	11.5	584	14.5	3.5	128	136	264
17J	202	16.9	20.9	549	ND	5.4	39	59	98
	500	< 1.1	15.2	570	ND	4.7	ND	ND	ND
18H	202	11.0	16.9	540	5.7	4.2	115	144	259
	500	13.3	9.9	351	1.2	2.4	88	105	193
19A	202	4.3	3.5	128	0.6	0.8	223	215	438
	500	15.1	14.1	481	3.6	4.8	ND	ND	ND
<b>May-06</b>									
04A-1	202	28	14.4	578	30.3	16.8	ND	ND	ND
	500	42	13.6	707	24.5	7.2	ND	ND	ND
06A-1	202	34	11.6	175	10.4	12.4	294	365	659
	500	43	10.1	395	18.8	17.9	124	304	428
07A-1	202	50	25.4	383	19.4	4.8	102	446	549
	500	38	21.4	491	20.5	3.8	157	282	439
	1000	15	13.9	224	6.7	2.7	102	276	378
06B-1	202	35	20.3	391	8.1	4.9	ND	ND	ND
	500	38	16.4	388	13.2	5.7	ND	ND	ND
07B-1	202	30	60.1	285	10.6	4.9	96	214	310
	500	14	26.5	213	3.4	2.7	233	224	456
	1000	8	9.6	173	22.0	3.1	99	182	281
04C-1	202	24	11.2	328	16.4	4.2	ND	ND	ND
	500	29	12.7	505	14.6	5.1	ND	ND	ND
05C-1	202	29	34.0	317	9.3	5.3	ND	ND	ND
	500	51	10.5	1236	8.8	7.4	ND	ND	ND
07C-1	202	22	27.8	255	15.3	10.2	182	349	531
	500	16	13.6	167	5.8	3.7	238	311	550
	1000	8	7.6	145	5.9	3.6	118	155	272
04D-1	202	26	15.9	699	87.2	17.6	260	343	603
	500	31	7.8	496	20.1	5.7	276	311	586
05D-1	202	43	31.4	307	19.9	10.1	159	439	598

Table 2. Zooplankton metal concentrations from the Hudson River plume in April 2005 and May 2006. Samples were size fractioned into 202-500 $\mu$ m, 500-1000 $\mu$ m, and >1000 $\mu$ m size classes. Samples from the >1000  $\mu$ m size class were not collected at sites where there was insufficient biomass. ND = not determined.

	500	65	12.1	326	12.9	6.6	121	482	602
07D-1	202	20	10.3	209	7.0	4.2	ND	ND	ND
	500	67	11.9	521	7.0	3.9	ND	ND	ND
	1000	22	5.6	210	7.6	3.7	ND	ND	ND
04E-1	202	28	8.4	463	62.8	4.7	285	294	579
	500	38	7.2	470	11.4	4.9	150	313	463
05E-1	202	47	10.5	399	9.2	5.9	ND	ND	ND
	500	40	8.2	740	19.0	6.8	ND	ND	ND
03F-1	202	35	10.3	386	11.9	4.2	241	240	481
	500	42	7.8	527	11.1	5.4	159	320	479
04F-1	202	32	9.2	338	34.1	5.1	224	340	563
	500	31	9.8	341	15.6	5.0	236	344	580
05F-1	202	32	18.4	333	24.1	5.3	181	370	551
	500	37	34.4	297	23.3	6.9	153	440	593
07F-1	202	57	12.2	304	19.6	4.7	107	350	457
	500	68	7.8	333	11.0	3.8	122	321	443
	1000	53	5.6	252	10.4	4.5	110	334	444
05G-1	202	33	16.0	218	8.7	4.8	ND	ND	ND
	500	30	10.4	263	5.1	3.9	ND	ND	ND
	1000	15	8.3	210	10.7	3.9	ND	ND	ND
07G-1	202	70	11.4	268	11.4	6.3	155	355	510
	500	74	35.6	324	10.3	7.4	119	449	568
07H-1	202	74	15.4	291	14.1	4.6	93	321	415
	500	73	12.6	332	19.4	5.1	122	488	610
07I-1	202	77	11.2	288	10.1	4.8	128	290	419
	500	77	11.7	348	11.3	4.3	96	388	484

Table 3: Metal enrichment in Hudson River plume zooplankton from April 2005 and May 2006 relative to oceanic mesozooplankton. The + symbol indicates significant enrichment relative to oceanic zooplankton, while the - symbol indicates a given metal is less enriched in the plume zooplankton than in oceanic zooplankton from the reference data set. On the right hand side, the degree of metal enrichment in zooplankton from May 2006 are given relative to zooplankton from April 2005, where a + symbol indicates a greater degree of enrichment in 2006 than in 2005. NS indicates that the relative metal enrichments are not significantly different at the 95% confidence level.

	Plu	ime vs Oce	2005 vs 2006			
	2005	р	2006	р	2006	р
Ag	+	0.002	+	< 0.001	+	< 0.001
Cd	NS	0.116	NS	0.052	NS	0.318
Cu	+	< 0.001	+	< 0.001	-	0.001
Hg(II)	-	0.026	+	0.002	+	< 0.001
HgT	NS	0.680	+	< 0.001	+	< 0.001
MeHg	+	< 0.001	+	< 0.001	NS	0.466
Pb	+	0.013	+	< 0.001	NS	0.144
Zn	+	0.004	+	< 0.001	NS	0.198

	Cp	AE	IR	k <sub>ef</sub>	G	C <sub>w</sub>	k <sub>u</sub>	k <sub>ew</sub>
	(nmol g <sup>-1</sup> )	(%)	( <b>d</b> <sup>-1</sup> )	( <b>d</b> <sup>-1</sup> )	( <b>d</b> <sup>-1</sup> )	(nmol L <sup>-1</sup> )	$(L g^{-1} d^{-1})$	( <b>d</b> <sup>-1</sup> )
Ag	3.8	$10^{1}$	0.44 6	0.3 1	0.026	0.043	10.42 1	0.173 1
Cd	24	30 <sup>2</sup>	0.44 6	0.3 1	0.02 6	0.39	0.6661	0.108 1
Cu	195	40 <sup>3</sup>	0.44 6	$0.08^{4}$	0.02 6	13	5.1 4	$0.08^{4}$
Zn	1600	30 <sup>2</sup>	0.44 6	0.078 1	0.02 6	23	2.678 1	0.108 1

Table 4. Copepod bioaccumulation model parameters. Cw values are median dissolved metal concentrations and Cp values are median particulate metal concentrations from the 2-20  $\mu$ m size fraction, during the April 2005 sampling event.

<sup>1</sup> Wang and Fisher, 1998

<sup>2</sup> Reinfelder and Fisher, 1991

<sup>3</sup> Chang and Reinfelder, 2000

<sup>4</sup>Chang and Reinfelder, 2002

<sup>5</sup> Wang and Fisher, 2001

<sup>6</sup>Londsdale et. al., 1996

	Predicted	Observed	% Dissolved	% Trophic
	$(nmol g^{-1})$	$(nmol g^{-1})$	Uptake	Transfer
Ag	5.9	9.5	91	9
Cd	12	14	17	83
Cu	1029	482	67	33
Zn	2713	4754	21	79

Table 5. Predicted and observed copepod metal body burdens for April 2005, based on kinetic modeling, as well as predicted contributions from dissolved uptake and trophic transfer.



Fig. 1. Comparison of metal concentrations in zooplankton of the Hudson River plume in April 2005 (a), and May 2006 and oceanic copepods. For each sampling event, the median and range of samples from the plume are plotted against a 1:1 line, representing the median metal concentrations from the reference data sets.



Fig. 2. Zooplankton Ag (a) and Hg(II) (b) body burdens in the Hudson River Plume and adjacent waters during May, 2006.


Fig. 3. Zooplankton metal concentrations in samples collected from May 1-May 6, 2006. The dark blue line represents the approximate location of the Hudson River plume during the sampling period, as delineated by satellite sea surface temperature, and confirmed by shipboard salinity and temperature measurements. Symbol shapes represent the various size classes of mesozooplankton as follows: circles, 202-500  $\mu$ m; triangles, 500-1000  $\mu$ m; and stars, >1000  $\mu$ m. In order to reduce symbol overlap, 500-1000  $\mu$ m samples are offset by lat. 0.02 and lon. 0.02, and > 1000  $\mu$ m samples are offset by lat. 0.04 and lon. 0.04. For Pb and Zn, samples greater than the maximum scale are plotted as the maximum value (see Table 2).

#### **Chapter 5 - Summary of findings**

This Chapter reviews the major research findings of this dissertation, which are presented by chapter, below. Following the presentation of research findings is a discussion on future research needs.

Chapter 2, Part I – The first part of Chapter 2 details the results of an improved method for the determination of trace metals in coastal seawater. Strengths of the method include low detection limits for all elements examined, good accuracy and precision for all elements except copper, and the use of commercially available products throughout. This is an important advance, because many previously published methods for trace metal determinations in seawater have only been appropriate for estuarine waters, which are significantly higher than the levels determined here for Hudson River plume waters. In order for a method to be appropriate for research projects with large sample loads, or for use in routine monitoring by regulatory agencies, it should use commercially available components (with appropriate technical support), and should not require significant operator expertise beyond what is typically necessary for low level trace element analysis. This method accomplishes these goals for all elements studied except for copper. Research is currently ongoing to determine the source of the difficulties in determining copper by this method. If these difficulties can be fully resolved, the method can be considered fully successful.

*Chapter 2, Part II* – The second part of Chapter 2 details the distributions and mixing patterns of dissolved and particulate trace metals in the Hudson River plume. Within the plume, levels of trace metals are similar to other anthropogenically influenced river plumes. Salinity profiles suggest that most dissolved metals experience

conservative or near conservative mixing, with non-conservative deviations primarily indicating transfer to the particulate phase. Particulate metal profiles generally indicate loss of particulate matter, primarily by particle sinking. In April 2005, >2  $\mu$ m metal concentration were approximately twice the >20  $\mu$ m metal concentrations, indicating similar concentrations of metals in the 2-20 and >20 size fractions.

Modeling results suggest that the fate and transport of metals within the plume are dependant on circulation and physical transport processes. When the plume is directed primarily into the coastal current, there are significant fluxes of metals to bottom waters through particle sinking, and down shelf transport of dissolved metals. When the plume forms a recirculating bulge formation, the sinking flux of metals increases and the down shelf transport is significantly reduced. Under this scenario, the potential for cross shelf transport of metals exists if changing wind conditions advect the bulge water offshore. In both scenarios, particulate metals that sink to bottom waters may be carried northward back toward the estuary, as the mean flow of bottom currents is in this direction. This implies that particulate metals may be recycled in this area, slowing the recovery of contaminated sediments.

*Chapter 3* - The second part of Chapter 2 details the distributions and mixing patterns of dissolved and particulate trace metals in the Hudson River plume. Salinity profiles suggest that most dissolved metals experience conservative or near conservative mixing. Small gradients suggest that dissolved Hg is not highly enriched relative to surrounding coastal waters, and measured concentrations are within the range measured in oceanic waters. Particulate metal profiles generally indicate loss of particulate matter, primarily by particle sinking.

Modeling results suggest that the fate and transport of Hg within the plume are dependant on circulation and physical transport processes. In contrast to other metals considered, Hg is volatile and typically supersaturated in surface seawater. On average, the model predicts that 5-11% of the Hg in the plume is lost to the atmosphere, with greater evasion during bulge formation. In the scenarios considered, particulate Hg is efficiently removed from plume waters, and transport to the coastal current is primarily in the dissolved phase. When the plume is directed primarily into the coastal current, there are significant fluxes of metals to bottom waters through particle sinking, and down shelf transport of dissolved metals. When the plume forms a recirculating bulge formation, the sinking flux of metals increases and the down shelf transport is significantly reduced. Under this scenario, the potential for cross shelf transport of metals exists if changing wind conditions advect the bulge water offshore, however, this potential is more limited than for other metals due to the small difference between the dissolved Hg in the plume and in bottom waters, and efficient particle removal. In both scenarios, particulate Hg that sinks to bottom waters may be carried northward back toward the estuary, as the mean flow of bottom currents is in this direction. This implies that particulate Hg may be recycled in this area, slowing the recovery of contaminated sediments. In May 2006, the particle concentration effect was observed within the plume during bloom conditions, raising the possibility that phytoplankton growth may be correlated with increased colloidal Hg binding.

*Chapter 4* – Chapter 4 details investigations into the accumulation, enrichment, potential for trophic transfer, and potential toxicity in plume zooplankton. Within the plume, zooplankton were observed to bioconcentrate metals, and several metals (Ag, Cu,

Hg, and Zn) were biomagnified relative to plume phytoplankton. Plume zooplankton were generally enriched in metals relative to oceanic zooplankton, with the exception of Cd. Kinetic modeling was used to predict the relative importance of trophic transfer vs. dissolved uptake in plume zooplankton. The model predicts that trophic transfer is the dominant uptake route for Cd and Zn, while dissolved uptake is more important for Ag and Cu. The validity of the model was tested by comparing predicted metal body burdens with field observation, which agreed approximately within a factor of two for the metals examined. In the May 2006 experiment, zooplankton from a high salinity region inshore of the plume were highly enriched in Ag and Hg. Several possibilities for the observed enrichment are discussed, with the most likely explanations involving changes in bioavailability due to metal complexation or shifts in community composition. Finally, high body burdens in Ag and Zn in plume zooplankton may result in sub-lethal toxic effects, though additional studies will be required to confirm or refute this possibility.

*Future research* – The results presented in this dissertation, while providing important insight on trace metal fate, transport, and bioavailability in the Hudson River plume, leave a number of questions unanswered, providing opportunities for future research.

In Chapter 2 - Part 1, results for Cu were consistently lower than accepted values in certified reference materials. This may be related to complexation with organic ligands, which may cause incomplete equilibration of the isotope spike, and reduced retention on the column. Ongoing work will attempt to address these issues. Future work with regards to this method should focus on two issues. The first are of focus

should be on reducing blanks so that lower levels of metals can be determined by this method. On possible way to accomplish this is by using the NTA Superflow resin, which retains Fe(III) and Cu at pH < 2.0 (Lohan et al, 2004). This would eliminate the need to add a pH buffer, which is typically the primary source of blank for these elements in the current method. This might allow the determination of open ocean concentrations of these elements, which in the case of Fe, may be on the order of 100 pM (Landing and Bruland, 1987). The second area for future development is in the determination of dissolved Ag, which in not retained on the resin currently used in this method. Possible approaches for Ag determination include modifying the existing method using either a thiol based resin or online coprecipitation.

In Chapter 2 - Part 2, further work needs to be done on estimating the relative contributions from the biogenic and terrigenous fractions to the determined particulate metal concentrations. Optical data from April 2005, suggest that particles within the plume are primarily biogenic in nature. This could be tested using a combination of crustal tracer elements and sequential extraction techniques on remaining samples and or sample digests from this cruise.

Another area that needs to be looked at in more detail is the possibility of separating water masses based on tjeir trace element signatures. Many of the dissolved and particulate salinity profiles suggest the presence of multiple low salinity water masses, however these are difficult to separate due to the temporal and spatial variability while sampling. It is possible that advanced numerical modeling techniques may be able to assist in separating these water masses using their trace element signatures. A third area for future research is in the area of dissolved speciation and metal binding ligands. Phytoplankton have been shown to release thiols sulfides under metal stress, both of which may complex metals and potentially reduce their bioavailability. Thiol concentrations could potentially be investigated using existing samples from the plume that were collected in April 2005 and May 2006, and have been stored frozen in our lab. In future work, the thiol concentration, sulfide concentration, and the metal binding ligand concentration could be measured simultaneously in a phytoplankton bloom and in deck incubations, to help determine the nature of metal binding ligands, and the response of the plume phytoplankton community to metal stress.

With regard to Chapter 3, several aspects of Hg within the plume need to be examined in greater detail. Due to the fact that traditional methods generally yield non detectable concentrations of MeHg in surface seawater (Mason et al, 1998), dissolved MeHg dynamics in the plume were not studied here. However, MeHg may be detectable using large volume distillations (effectively a preconcnertation technique) of by Hgthiourea complex ion-chromatography with on-line cold vapor generation and atomic fluorescence spectrometric detection (Shade and Hudson, 2005), both of which yield detectable Hg concentrations ~5-6 x lower than by the traditional distillation techniques.

Another potential area of investigation includes the potential release of Hg binding ligands by phytoplankton. Thiols and sulfide, which may be relaeased due to metal stress from other trace metals (e.g. Cu or Zn), may also form strong complexes with Hg. In future work, the thiol concentration, sulfide concentration, and the Hg binding ligand concentration could be measured simultaneously in a phytoplankton

bloom and in deck incubations, to determine the nature of Hg binding ligands, and the response of the phytoplankton community to metal stress.

In Chapter 4, there are several potential areas for future work. A kinetic modeling approach was used to estimate the potential for trophic transfer for Ag, Cd, Cu, and Zn, with comparison with field observations confirming the utility of the modeling approach. Unfortunately, it was not possible to utilize the model for MeHg, Hg(II), or Pb, as the dissolved uptake rate constant for these metals in marine copepods has not been measured. Completing these measurements would allow trophic transfer of these metals to be evaluated in this and other systems. This is particularly important for modeling Hg trophic transfer, as trophic transfer of MeHg is primarily responsible for effects on human and ecosystem health (Trasande et al, 2005; Scheuhammer, 2007).

Another area for future work in chapter 3 is to more closely examine the factors that affect Ag and Hg uptake and trophic transfer in the plume and adjacent coastal waters. Dissolved speciation and shifts in community composition both have the potential to impact body burdens of metals in zooplankton, so the relative importance of each must be systematically examined. This is particularly important for Ag, as toxicity data suggests that plume zooplankton egg production may be affected at observed Ag body burdens, if dietary uptake is significant. In the May 2006 experiment, the trophic transfer of Ag for the ZP with the highest body burdens could not be evaluated due to gaps in sample coverage. Therefore additional field study will be required to further evaluate potential toxicity in this system.

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# Appendices:

Event	Action	Para.	Par. Units	Comment
On Probe Down	Load			Move valve to Load Position prior to sample uptake
On Probe Down	Timer A	180	seconds	Sample uptake time
Probe In Sample	Vacuum On			begin sample uptake
Timer A Expires	Vacuum Off			end sample uptake
Timer A Expires	Timer G	45	seconds	rest period to allow residual vacuum to dissipate
Timer G Expires	Move Into(rrvv)	3	rrvv	move to Milli-Q Rinse (rinse exterior of probe)
Timer G Expires	Timer H	5	seconds	Milli-Q rinse time (dip)
Timer H Expires	Move Into(rrvv)	1	rrvv	Move to Milli-Q blank (wash/conditioning solution)
Timer H Expires	Timer B	10	seconds	allow time for the autosampler arm to move prior to turning vacuum on
Timer B Expires	Vacuum On			begin column washing step (salt removal)
Timer B Expires	Timer C	40	seconds	end column washing step
Timer C Expires	Move rinse			begin rinsing of the probe/uptake tubing with 3% HNO3 from rinse station
Timer C Expires	Inject			Move valve to inject position for column elution
Timer C Expires	Timer F	60	seconds	3% HNO3 rinse time
Timer C Expires	Timer D	120	seconds	Column elution time
Timer F expires	Move Into(rrvv)	3		Move from 3%HNO3 rinse station to Milli-Q rinse
Timer F expires	Timer J	5	seconds	Milli-Q rinse time (dip)
Timer J expires	Move Into(rrvv)	1	rrvv	Move to Milli-Q blank (wash/conditioning solution)
Timer F expires	Timer I	30	seconds	Milli-Q Blank rinse time
Timer I expires	Vacuum off			End probe/uptake tubing rinse
Timer D Expires	Load			Move to Load position for column conditioning
Timer D Expires	Vacuum On			Begin column conditioning
Timer D Expires	Timer E	120	seconds	Column conditioning time
Timer E Expires	Vacuum Off			End Column conditioning
Timer E Expires	Move Next	1		Move to the next sample in the sequence

# Appendix 1: Program sequence for the SC Fast flow injection integrated with the SC-2 autosampler.

Appendix 2 – Matlab code for peak integration software. Written by research computing specialist Elias Hunter (2008). Explanation of the software parameters code follows (by Christine Theodore, 2008)

## 1) create\_param\_file

function create\_param\_file(file,data)

```
nparam=12;

out{1,1}='Parameter';

out{2,1}='Base_line_len';defaults{1}=10;

out{3,1}='Slope_cut_a';defaults{2}=500;

out{4,1}='Slope_cut_b';defaults{3}=100;

out{5,1}='Slope_width';defaults{4}=2;

out{6,1}='N_fit_points';defaults{5}=2;

out{7,1}='Percent_height';defaults{6}=0.1;

out{8,1}='Filter_width';defaults{7}=3;

out{9,1}='Filter_Cutoff';defaults{8}=2;

out{10,1}='Filter_type';defaults{9}=1;

out{11,1}='Polyfit';defaults{10}=1;

out{12,1}='Start_integrate';defaults{10}=120;
```

```
names=fieldnames(data);
for i=1:length(names)
    out{1,i+1}=names{i};
    for j=1:nparam
        out{j+1,i+1}=defaults{j};
    end
    oud
```

## end

```
[SUCCESS,MESSAGE]=xlswrite(file,out,'sheet1');
```

# 2) read\_metals\_file

function [data,n\_iso]=read\_metals\_file(file)

```
if ~exist(file)
disp('File does not exist')
return
end
```

```
fid=fopen(file,'r');
```

```
%Get Iso. names and the number of Iso.
mass_str=fgetl(fid);
%Just getting rid of some header lines, these may be useful later on
res_ln=fgetl(fid);
blk_ln=fgetl(fid);
desc_ln=fgetl(fid);
units_ln=fgetl(fid);
blk_ln=fgetl(fid);
```

```
%Parse the first header line
```

```
[tmp]=textscan(mass_str,'%s');
iso_names=tmp{1};
n_iso=length(iso_names)-3;
```

```
%get the data
fdata=[];
while ~feof(fid)
ln=fgetl(fid);
[tmp]=textscan(ln,'%f');
fdata=[fdata;tmp{1}'];
end
%Store the data in a structured array.
for i=1:n_iso
    data.(iso_names{i+3}(1:end-4)).name=iso_names{i+3}(1:end-4);
    data.(iso_names{i+3}(1:end-4)).intensity=fdata(:,i+1);
    data.(iso_names{i+3}(1:end-4)).time=fdata(:,1);
end
```

```
fclose(fid);
```

# 3) read\_param\_file

```
function [params,n_iso]=read_param_file(file)
```

```
[n,t,raw]=xlsread(file);
dims=size(raw);
n_iso=dims(2)-1;
for i=1:n_iso
    for j=1:dims(1)-1
        params.(t{1,i+1}).(t{j+1,1})=n(j,i);
    end
end
```

## 4) process\_metals\_data\_v3

function [data,params,outdata]=process\_metals\_data\_v3(direc,of,slope\_flag)

```
%direc='c:\latte\derek\data\';
disp(['Searching Directory ' direc])
files=dir([direc '*.TXT']);
nfiles=length(files);
disp(['Found ' sprintf('%d',length(files)) ' files in directory: ' direc])
```

```
if ~exist([direc 'params.xls'])
  disp('params.xls does not exist: creating')
  [data,n_iso]=read_metals_file([direc files(1).name]);
  create_param_file([direc 'params.xls'],data);
end
```

```
disp('Reading parameters file')
```

```
[params,n_iso_param]=read_param_file([direc 'params.xls']);
names=fieldnames(params);
```

for i=1:nfiles

```
disp(['Reading and Processing file: ' files(i).name])
[data,n_iso]=read_metals_file([direc files(i).name]);
```

```
if n_iso~= n_iso_param
   disp('Number of Isotopes in data file and parameter file do not match')
   disp([n_iso n_iso_param])
   return
end
```

for j=1:length(names)

```
Itmp=data.(names{j}).intensity;
Ttmp=data.(names{j}).time;
fname=strtok(files(i).name,'.');
try
```

%Filter Data if set in parameter file

```
st filt='none';
switch params.(names{j}).Filter_type
  case 1 % FIR lowpass filter with cutoff
    uf_Ttmp=Ttmp;
    uf_Itmp=Itmp;
    %disp('Using a Low Pass Filter')
    N=params.(names{j}).Filter_width;
    fcut=params.(names{j}).Filter_Cutoff;
    Wn=0.5*fcut;
    B1=fir1(N,Wn);
    fItmp=filter(B1,1,Itmp);
    Itmp=fItmp(N:end);
    Ttmp=Ttmp(N/2:end-N/2);
    st_filt='Lowpass';
  case 2 % Boxcar Smoothing filter
    % disp('Using a Boxcar Filter')
    uf_Ttmp=Ttmp;
    uf Itmp=Itmp;
    N=params.(names{j}).Filter_width;
    B1=boxcar(N)/N;
    fItmp=filter(B1,1,Itmp);
    Itmp=fItmp(N:end);
    Ttmp=Ttmp(N/2:end-N/2);
    st filt='Boxcar';
  case 3 % SG
    % disp('Using a Savitzky-Golay Filter')
    uf_Ttmp=Ttmp;
    uf Itmp=Itmp;
    N=params.(names{j}).Filter_width;
    rem(N,2)
    if rem(N,2) == 0
       N=N+1;
    end
    fItmp=sgolayfilt(Itmp,2,N);
    Itmp=fItmp(N:end);
    Ttmp=Ttmp(N:end);
    st_filt='Savitzky-Golay';
```

#### %Get background Information and subtract

data.(names{j}).back\_mean=mean(Itmp(1:params.(names{j}).Base\_line\_len)); data.(names{j}).back\_std=std(Itmp(1:params.(names{j}).Base\_line\_len)); data.(names{j}).intensity\_filt=Itmp; data.(names{j}).intensity\_nb=Itmp-data.(names{j}).back\_mean; Itmp=data.(names{j}).intensity\_nb;

back\_mean=sprintf('%0.5g',data.(names{j}).back\_mean); back\_std=sprintf('%0.5g',data.(names{j}).back\_std);

%Calculate running Slope

```
w=params.(names{j}).Slope_width;
js=1;
for is=w+1:length(Itmp)-w
    xt=Ttmp(is-w:is+w);
    yt=Itmp(is-w:is+w);
    res=polyfit(xt,yt,1);
    slp_tmp(js)=res(1);
    t_slp(js)=Ttmp(is);
    js=js+1;
end
```

- % % Find Start of peak byt starting at the beginning of the
- % run an check each point to find a slope manitude gt
- % Slope\_cut\_a

```
for is=1:length(slp_tmp)
  if abs(slp_tmp(is)) > params.(names{j}).Slope_cut_a
     start_peak=is+w;
     break
  else
     start_peak=1;
  end
end
```

- % End of peak byt starting at the end of the
- % run an check each point to find a slope magnitude gt
- % Slope\_cut\_b

```
for is=length(slp_tmp):-1:1
  if abs(slp_tmp(is)) > params.(names{j}).Slope_cut_b
    end_peak=is+w;
    break
  else
    end_peak=1;
  end
end
```

if end\_peak ==1 | start\_peak ==1 | start\_peak==end\_peak

```
disp('No Peak Detected')
data.(names{j}).pk_height=-999;
data.(names{j}).pk_area=-999;
data.(names{j}).pk_area_wb=-999;
data.(names{j}).pk_area_slope=-999;
data.(names{j}).pk_start_slp=-999;
data.(names{j}).pk_stop_slp=-999;
data.(names{j}).pk_start_ph=-999;
data.(names{j}).pk_stop_ph=-999;
```

%Peak Area by start/stop integration using filtered data and %no background removed

Int\_times=[params.(names{j}).Start\_integrate:0.01:params.(names{j}).Stop\_integrate]; Int\_intensity=interp1(Ttmp,data.(names{j}).intensity\_filt,Int\_times); pk\_area\_wb\_int\_lims=trapz(Int\_times,Int\_intensity);

%Peak Area by start/stop integration

```
Int_times=[params.(names{j}).Start_integrate:0.01:params.(names{j}).Stop_integrate];
Int_intensity=interp1(Ttmp,Itmp,Int_times);
```

pk\_area\_int\_lims=trapz(Int\_times,Int\_intensity); data.(names{j}).pk\_area\_int\_lims=pk\_area\_int\_lims; data.(names{j}).pk\_area\_wb\_int\_lims=pk\_area\_wb\_int\_lims;

```
Int_times=[Int_times(1) Int_times Int_times(end)];
Int_intensity=[0 Int_intensity 0];
figure(1)
plot(Ttmp,Itmp,'r+-',uf Ttmp,uf Itmp,'m+-')
legend('Filtered Intensity', 'Unfiltered Intensity')
grid on
title([files(i).name ' (' names{j} ') - No peak Detected'])
set(gca,'xlim',[50 250])
       hold on
  hf=fill(Int_times, Int_intensity,[.80.80.80]);
  set(hf,'edgecolor','none')
  hold off
print(gcf,'-dpng',[direc fname '_' names{j} '_' of ])
if slope_flag
  figure(10)
  plot(t_slp,slp_tmp,'r+-',t_slp,abs(slp_tmp),'ko-',...
     t_slp,params.(names{j}).Slope_cut_a*ones(size(t_slp)),'g',...
     t_slp,params.(names{j}).Slope_cut_b*ones(size(t_slp)),'b')
  title([files(i).name ' (' names{j} ') - Slope Time Series'])
  xlabel('Elapsed Time')
  ylabel('Slope')
  legend('Slope','Slope Magnitude','Slope_cut_a','Slope_cut_b')
```

pause

## end continue end

- % Try and Locate the Peak center by applying a polynomial fit,
- % if desired

peak=[start\_peak:end\_peak];

```
[Imax,Imx]=max(Itmp(peak));
Ic=peak(Imx);
Tmax=Ttmp(Ic);
if params.(names{j}).Polyfit
    disp('Using Polynominal fit to find Maximum peak height')
    w2=params.(names{j}).N_fit_points;
```

```
Iw2=find(peak>=Ic-w2 & peak<=Ic+w2);
P=polyfit(Ttmp(peak(Iw2)),Itmp(peak(Iw2)),2);
nTtmp=[Ttmp(min(peak(Iw2))):0.01:Ttmp(max(peak(Iw2)))];
nItmp=polyval(P,nTtmp);
Tmax=-P(2)/(2*P(1));%ALgebra
Imax=polyval(P,Tmax);
else
nTtmp=Ttmp;
nItmp=Itmp;
```

#### end

Icut=Imax\*params.(names{j}).Percent\_height; data.(names{j}).pk\_height=Imax; pk\_height\_str=sprintf('%0.5g',Imax);

% Now lets get the peak intersections with our cutoff

% This needs to be fixed to account for a start\_peak > Icut

```
get_start=1;
```

for is=start\_peak:length(Itmp)

```
if Itmp(is) > Icut & get_start==1
    if Itmp(is-1)< Icut
        Int_start_t=interp1(Itmp(is-1:is),Ttmp(is-1:is),Icut);
    else
        Int_start_t=Ttmp(start_peak);
    end
    get_start=0;
end

if Itmp(is) < Icut & get_start==0
    Int_end_t=interp1(Itmp(is-1:is),Ttmp(is-1:is),Icut);
    get_start=2;
end</pre>
```

```
end
```

% This is the whole point, calculate a peak area.

#### %Peak area by slope

```
data.(names{j}).pk_start_slp=Ttmp(start_peak);
data.(names{j}).pk_stop_slp=Ttmp(end_peak);
Int_times_slp=[Ttmp(start_peak):0.01:Ttmp(end_peak)];
Int_intensity_slp=interp1(Ttmp,Itmp,Int_times_slp);
pk_area_slope=trapz(Int_times_slp,Int_intensity_slp);
```

%Peak Area by peak Height cutoff data.(names{j}).pk\_start\_ph=Int\_start\_t; data.(names{j}).pk\_stop\_ph=Int\_end\_t; Int\_times=[Int\_start\_t:0.01:Int\_end\_t]; Int\_intensity=interp1(Ttmp,Itmp,Int\_times);
pk\_area=trapz(Int\_times,Int\_intensity);

#### %Peak Area by start/stop integration

Int\_times\_lims=[params.(names{j}).Start\_integrate:0.01:params.(names{j}).Stop\_integra
te];

Int\_intensity\_lims=interp1(Ttmp,Itmp,Int\_times\_lims);
pk\_area\_int\_lims=trapz(Int\_times\_lims,Int\_intensity\_lims);

%Peak Area by peak Height cutoff using filtered data and no %background removed Int\_times\_wb=[Int\_start\_t:0.01:Int\_end\_t]; Int\_intensity\_wb=interp1(Ttmp,data.(names{j}).intensity\_filt,Int\_times\_wb); pk\_area\_wb=trapz(Int\_times\_wb,Int\_intensity\_wb);

%Peak Area by start/stop integration using filtered data and no %background removed

Int\_times\_wb\_lims=[params.(names{j}).Start\_integrate:0.01:params.(names{j}).Stop\_int egrate];

pk\_area\_str=sprintf('%0.5g',pk\_area); pk\_area\_slp\_str=sprintf('%0.5g',pk\_area\_slope); Int\_times=[Int\_times(1) Int\_times Int\_times(end)]; Int\_intensity=[0 Int\_intensity 0]; data.(names{j}).pk\_area=pk\_area; data.(names{j}).pk\_area\_int\_lims=pk\_area\_int\_lims; data.(names{j}).pk\_area\_wb=pk\_area\_wb; data.(names{j}).pk\_area\_wb\_int\_lims=pk\_area\_wb\_int\_lims; data.(names{j}).pk\_area\_slope=pk\_area\_slope;

## % This plots everything

if params.(names{j}).Polyfit
 figure(1)

```
hp=plot(Ttmp,data.(names{j}).intensity_nb,'r+-',...
            [Ttmp(start_peak)*ones(1,2) nan Ttmp(end_peak)*ones(1,2)],[0 max(Itmp)
nan 0 max(Itmp)],'k',...
            nTtmp,nItmp,'k-',...
            Tmax,Imax,'b^',...
            Ttmp(Ic),Itmp(Ic),'go',...
            [Int_start_t*ones(1,2) nan Int_end_t*ones(1,2)],[0 max(Itmp) nan 0
max(Itmp)],'b',...
            Ttmp,Icut*ones(size(Ttmp)),'k--',...
            uf_Ttmp,uf_Itmp,'m+-');
          set(hp(3),'linewidth',1.5)
          set(hp(6),'linewidth',1.5)
          legend('Intensity (Back. rem.)',...
            'Peak Range (by Slope)',...
            'Poly. Curve Fit',...
            'Poly Fit Max.',...
            'Peak Absolute Max.',...
            'Integration Range',...
            'Cutoff',...
            'Raw Data'....
            'location', 'NorthEast')
          hold on
          hf=fill(Int_times, Int_intensity,[.80.80.80]);
          set(hf,'edgecolor','none')
          hold off
          ch=get(gca,'children');
          grid on
          set(gca,'children',[ch(2:end);ch(1)])
          set(gca,'xlim',[50 250])
          abs_max_time=sprintf('%0.5g',Ttmp(Ic));
          fit_max_time=sprintf('%0.5g',Tmax);
          yl=get(gca,'ylim');
          dy=0.02;
          ytext=yl(2)*dy
          xtext=145;
          text(xtext,ytext+yl(2)*0.25,strvcat(['Background Mean(cps): ' back_mean],...
            ['Background St. Dev.(cps): ' back_std],...
            ['Pk. Area (Counts): ' pk_area_str],...
            ['Pk. Area by slope (Counts): ' pk_area_slp_str],...
            ['Pk. Height (cps): ' pk_height_str],...
            ['Abs. Peak Time (Sec): ' abs_max_time],...
            ['Fitted Peak Time(Sec): ' fit_max_time],...
```

[' '],... ['Background Length: ' sprintf('%0.5g',params.(names{j}).Base\_line\_len)],... ['Slope cutoff (peak start): ' sprintf('%0.5g',params.(names{j}).Slope cut a)],... ['Slope cutoff (peak end):' sprintf('%0.5g',params.(names{j}).Slope\_cut\_b)],... ['Slope half Window: ' sprintf('%0.5g',params.(names{j}).Slope\_width)],... 'Poly. Fit half Window: sprintf('%0.5g',params.(names{j}).N\_fit\_points)],... ['Peak Height Cutoff Fraction:' sprintf('%0.5g',params.(names{j}).Percent\_height)],... ['Filter Type:' st filt],... ['Filter Width:' sprintf('%0.5g',params.(names{j}).Filter\_width)],... ['Filter Cutoff:' sprintf('%0.5g',params.(names{j}).Filter\_Cutoff)],... ['Poly. Fit: Used for Max. Peak Height']));

```
title([files(i).name ' - ' names{j}])
fname=strtok(files(i).name,'.')
print(gcf,'-dpng',[direc fname '_' names{j} '_' of ])
```

```
hold on
plot(uf_Ttmp,uf_Itmp,'m+-')
hold off
else
```

```
figure(1)
         hp=plot(Ttmp,data.(names{j}).intensity_nb,'r+-',...
            [Ttmp(start peak)*ones(1,2) nan Ttmp(end peak)*ones(1,2)],[0 max(Itmp)
nan 0 max(Itmp)],'k',...
            Ttmp(Ic),Itmp(Ic),'go',...
            [Int_start_t*ones(1,2) nan Int_end_t*ones(1,2)],[0 max(Itmp) nan 0
max(Itmp)], b', ...
            Ttmp,Icut*ones(size(Ttmp)),'k--',...
            uf Ttmp, uf Itmp, 'm+-');
          set(hp(3),'linewidth',1.5)
          legend('Intensity (Back. rem.)',...
            'Peak Range (by Slope)',...
            'Peak Absolute Max.',...
            'Integration Range',...
            'Cutoff'....
            'Raw Data',...
            'location', 'NorthEast')
```

hold on hf=fill(Int\_times, Int\_intensity, [.80.80.80]); set(hf,'edgecolor','none') hold off ch=get(gca,'children'); grid on set(gca,'children',[ch(2:end);ch(1)]) set(gca,'xlim',[50 250]) abs\_max\_time=sprintf('%0.5g',Ttmp(Ic)); fit\_max\_time=sprintf('%0.5g',Tmax); yl=get(gca,'ylim'); dy=0.02; ytext=yl(2)\*dy;xtext=145; text(xtext,ytext+yl(2)\*0.25,strvcat(['Background Mean(cps): ' back\_mean],... ['Background St. Dev.(cps): ' back\_std],... ['Pk. Area (Counts): ' pk\_area\_str],... ['Pk. Area by slope (Counts): ' pk\_area\_slp\_str],... ['Pk. Height (cps): ' pk\_height\_str],... ['Abs. Peak Time (Sec): ' abs\_max\_time],... ['Fitted Peak Time(Sec): ' fit\_max\_time],... [' '],...

```
['Background Length: '
sprintf('%0.5g',params.(names{j}).Base_line_len)],...
['Slope cutoff (peak start): '
sprintf('%0.5g',params.(names{j}).Slope_cut_a)],...
['Slope cutoff (peak end):'
sprintf('%0.5g',params.(names{j}).Slope_cut_b)],...
['Slope half Window: ' sprintf('%0.5g',params.(names{j}).Slope_width)],...
['Poly. Fit half Window: '
sprintf('%0.5g',params.(names{j}).N_fit_points)],...
['Peak Height Cutoff Fraction:'
sprintf('%0.5g',params.(names{j}).Percent_height)],...
['Filter Type:' st_filt],...
['Filter Width:' sprintf('%0.5g',params.(names{j}).Filter_width)],...
```

```
['Filter Cutoff:' sprintf('%0.5g',params.(names{j}).Filter_Cutoff)],...
```

['Poly. Fit: Not Used']));

title([files(i).name ' - ' names{j}])

```
print(gcf,'-dpng',[direc fname '_' names{j} '_' of ])
```

```
hold on
plot(uf_Ttmp,uf_Itmp,'m+-')
hold off
```

## end

```
catch
errfile=[direc of '_error.log'];
efid=fopen(errfile,'a');
disp(['ERROR: On isotope ' names{j} ' in file ' fname])
fprintf(efid,'\n%s\n',datestr(now));
fprintf(efid,'%s\n',['ERROR: On Isotope ' names{j} ' in file ' fname]);
err=lasterror;
fprintf(efid,'%s\n',err.message);
fprintf(efid,'%s\n',['On line ' num2str(err.stack.line) ' of ' err.stack.name]);
```

```
disp(['ERROR:WRITING ERROR TO FILE ' errfile])
```

```
disp(['ERROR:Setting output values to -888'])
```

```
\label{eq:start_slp=-888;} \\ data.(names{j}).pk_start_slp=-888; \\ data.(names{j}).pk_stop_slp=-888; \\ data.(names{j}).pk_stop_ph=-888; \\ data.(names{j}).pk_area=-888; \\ data.(names{j}).pk_area_wb=-888; \\ data.(names{j}).pk_area_int_lims=-888; \\ data.(names{j}).pk_area_wb_int_lims=-888; \\ data.(names{j}).pk_height=-888; \\ data.(names{j}).back_mean=-888; \\ data.(names{j}).back_std=-888; \\ data.(names{j}).pk_area_slope=-888; \\ data.(names{j}).pk_a
```

fclose(efid);

end

## end

```
outdata(i).data=data;
outdata(i).fname=fname;
```

## end

nfiles=length(outdata);

pk\_start\_slp\_cell=cell(nfiles+1,n\_iso\_param+1); pk\_stop\_slp\_cell=cell(nfiles+1,n\_iso\_param+1); pk\_start\_ph\_cell=cell(nfiles+1,n\_iso\_param+1); pk\_stop\_ph\_cell=cell(nfiles+1,n\_iso\_param+1);

pk\_area\_cell=cell(nfiles+1,n\_iso\_param+1); pk\_area\_wb\_cell=cell(nfiles+1,n\_iso\_param+1); pk\_area\_int\_lims\_cell=cell(nfiles+1,n\_iso\_param+1); pk\_area\_wb\_int\_lims\_cell=cell(nfiles+1,n\_iso\_param+1); pk\_area\_slp\_cell=cell(nfiles+1,n\_iso\_param+1); pk\_height\_cell=cell(nfiles+1,n\_iso\_param+1); back\_mean\_cell=cell(nfiles+1,n\_iso\_param+1); back\_std\_cell=cell(nfiles+1,n\_iso\_param+1);

for i=1:nfiles

pk\_start\_slp\_cell{i+1,1}=outdata(i).fname; pk\_stop\_slp\_cell{i+1,1}=outdata(i).fname; pk\_start\_ph\_cell{i+1,1}=outdata(i).fname; pk\_stop\_ph\_cell{i+1,1}=outdata(i).fname;

pk\_area\_cell{i+1,1}=outdata(i).fname; pk\_area\_wb\_cell{i+1,1}=outdata(i).fname; pk\_area\_wb\_int\_lims\_cell{i+1,1}=outdata(i).fname; pk\_area\_slp\_cell{i+1,1}=outdata(i).fname; pk\_height\_cell{i+1,1}=outdata(i).fname; back\_mean\_cell{i+1,1}=outdata(i).fname; back\_std\_cell{i+1,1}=outdata(i).fname;

#### end

```
for i=1:n_iso_param
    pk_start_slp_cell{1,i+1}=names{i};
    pk_stop_slp_cell{1,i+1}=names{i};
    pk_start_ph_cell{1,i+1}=names{i};
    pk_stop_ph_cell{1,i+1}=names{i};
```

```
pk_area_cell{1,i+1}=names{i};
pk_area_wb_cell{1,i+1}=names{i};
pk_area_wb_int_lims_cell{1,i+1}=names{i};
pk_area_int_lims_cell{1,i+1}=names{i};
pk_area_slp_cell{1,i+1}=names{i};
pk_height_cell{1,i+1}=names{i};
back_mean_cell{1,i+1}=names{i};
end
```

```
data=outdata(i).data;
  for j=1:n_iso_param
    pk_start_slp_cell{i+1,j+1}=data.(names{j}).pk_start_slp;
    pk_stop_slp_cell{i+1,j+1}=data.(names{j}).pk_stop_slp;
    pk_start_ph_cell{i+1,j+1}=data.(names{j}).pk_start_ph;
    pk_stop_ph_cell{i+1,j+1}=data.(names{j}).pk_stop_ph;
    pk_area_cell{i+1,j+1}=data.(names{j}).pk_area;
    pk_area_wb_cell{i+1,j+1}=data.(names{j}).pk_area_wb;
    pk area int lims cell{i+1,j+1}=data.(names{j}).pk area int lims;
    pk_area_wb_int_lims_cell{i+1,j+1}=data.(names{j}).pk_area_wb_int_lims;
    pk_height_cell{i+1,j+1}=data.(names{j}).pk_height;
    back_mean_cell{i+1,j+1}=data.(names{j}).back_mean;
    back_std_cell{i+1,j+1}=data.(names{j}).back_std;
    pk area slp cell{i+1,j+1}=data.(names{i}).pk area slope;
  end
end
nparam=12;
oparam{1,1}='Parameter';
oparam{2,1}='Base line len';
oparam{3,1}='Slope cut a';
oparam{4,1}='Slope_cut_b';
oparam{5,1}='Slope width';
oparam{6,1}='N_fit_points';
oparam{7,1}='Percent height';
oparam{8,1}='Filter_width';
oparam{9,1}='Filter_Cutoff';
oparam{10,1}='Filter type';
oparam{11,1}='Polyfit';
oparam{12,1}='Start_integrate';
oparam{13,1}='Stop integrate';
names=fieldnames(params);
for i=1:length(names)
  oparam{1,i+1}=names{i};
  for j=1:nparam
    oparam{j+1,i+1}=params.(names{i}).(oparam{j+1,1});
  end
end
```

[SUCCESS,MESSAGE]=xlswrite([direc of '\_data.xls'],pk\_area\_cell,'Peak Area (cutoff)no back.');

[SUCCESS,MESSAGE]=xlswrite([direc of '\_data.xls'],pk\_area\_wb\_cell,'Peak Area (cutoff)-with back.');

[SUCCESS,MESSAGE]=xlswrite([direc of '\_data.xls'],pk\_area\_int\_lims\_cell,'Peak Area (IL)-no back.');

[SUCCESS,MESSAGE]=xlswrite([direc of '\_data.xls'],pk\_area\_wb\_int\_lims\_cell,'Peak Area (IL)-with back.');

[SUCCESS,MESSAGE]=xlswrite([direc of '\_data.xls'],pk\_height\_cell,'Peak Height'); [SUCCESS,MESSAGE]=xlswrite([direc of '\_data.xls'],back\_mean\_cell,'Background Mean');

[SUCCESS,MESSAGE]=xlswrite([direc of '\_data.xls'],back\_std\_cell,'Back Std. Dev.'); [SUCCESS,MESSAGE]=xlswrite([direc of '\_data.xls'],pk\_area\_slp\_cell,'Peak Area (slope)');

[SUCCESS,MESSAGE]=xlswrite([direc of '\_data.xls'],pk\_start\_slp\_cell,'Peak Start(slope)');

[SUCCESS,MESSAGE]=xlswrite([direc of '\_data.xls'],pk\_stop\_slp\_cell,'Peak Stop(slope)');

[SUCCESS,MESSAGE]=xlswrite([direc of '\_data.xls'],pk\_start\_ph\_cell,'Peak Start(Cutoff)');

[SUCCESS,MESSAGE]=xlswrite([direc of '\_data.xls'],pk\_stop\_ph\_cell,'Peak Stop(Cutoff)');

[SUCCESS,MESSAGE]=xlswrite([direc of '\_data.xls'],oparam,'parameters');

**5) Params.xls** (note: this is a Microsoft Excel file – a column must be added to the right of the parameters column on the left for each isotope of interest – an example is shown below).

Parameter	Fe56	Fe57	Ni60	Ni62	Cu63	Cu65
Base_line_len	10	10	10	10	10	10
Slope_cut_a	100	100	100	100	100	100
Slope_cut_b	100	100	100	100	100	100
Slope_width	2	2	2	2	2	2
N_fit_points	2	2	2	2	2	2

Percent_height	0.1	0.1	0.1	0.1	0.1	0.1
Filter_width	10	10	10	10	10	10
Filter_Cutoff	1	1	1	1	1	1
Filter_type	1	1	1	1	1	1
Polyfit	0	0	0	0	0	0
Start_integrate	80	80	80	80	80	80
Stop_integrate	120	120	120	120	120	120

## 6) Instructions for using the software (by Christine Theodore, 1998).

To start:

All my matlab files are in a folder in "my documents" called "matlab". This is where all the programs are saved. I'm not entirely sure if you have to keep everything in a similarly named folder.

To start using matlab:

- 1. Have a folder ready that has your sample data as .txt files and a copy of the parameters file in it.
- 2. you have to tell matlab where your files are. You did this by typing:

direc='filename/'

and then pressing enter.

note that the file name is in single quotes ' ' and that there is a slash at the end of the file name and inside the quotes

After defining the directory, you need to tell matlab what program to run. This is done by typing:

[data,params,outdata]=process\_metals\_data\_v3(direc,'filename',#)

and then pressing enter.

note that the filename in ' ' can be anything, but will be put at the end of the original .txt file name, so I usually give it a letter or number.

The # needs to be a 0 or a 1.

If you put in a 0, it will run straight through

If you put in a 1, it will stop when the program can not find a peak and will display a graph of the slope vs time so you can look at it and determine how to change your parameters. To continue with the run, press any key.

The data will be saved in the same folder that the original .txt files are. It will output images of all peaks as well as an excel sheet with the data.

#### Parameters:

Parameter Base\_line\_len Slope\_cut\_a Slope\_cut\_b Slope\_width N\_fit\_points Percent\_height Filter\_width Filter\_Cutoff Filter\_type Polyfit Start\_integrate Stop\_integrate

Base line length: how many points from the beginning of the data to use to determine the baseline

Slope cut a and b: the value that the slope has to be for matlab to define a peak. A is the beginning and b is the end. This is an absolute value, so you do not have to put in a negative number of the tail end of the peak

Slope width: the amount of points on either side of a single point used to determine the slope

N fit points: how many points on either side of the max point to determine max. height

Percent height: how much you want to integrate. This number should be entered as a percent of the max height, as a decimal.

Filter width: decreasing this number will include more of the noise, increasing will smooth the peak more, should be about 10-30

Filter cutoff: I can't really remember exactly what this does, but I know that decreasing it will smooth the data more. Is should be no higher than 2 I think, maybe less. (I know Eli has previously told me it can go up to 4, but I get an error when I try, so it might not work) I've decreased it down to .5 before. I'm not sure how low you can make that number. I usually keep it at 1 unless I'm trying to integrate blanks

Filter type: should be 1, 2 or 3

Filter\_type 1 is a cosine type lowpass filter. It requires Filter\_width and Filter\_Cutoff to be set. Filter\_width should be in the range 10-30 for this filter. Filter cutoff should be 1-4.

Filter\_type 2 is a boxcar filter (running average) It only needs Filter\_width to be set. Filter\_width should be in the range 1-5 for this filter.

Filter\_type 3 is a Savitzky-Golay filter. It only needs Filter\_width to be set. Filter\_width should be in the range 3-5 for this filter.

Polyfit: should be either a 0 or 1.

If it is set to 0, polyfit is turned off

If it is set to 1, it will force the top of the peak into a parabola to determine the peak height only. It will still use the actual peak shape for integration. It is parabolic shape to determine peak height and use that peak height to determine how much of the peak to interate.

Start integrate and stop integrate

These are parameters set in seconds on where to start and stop the integration. Matlab will first try to integrate a peak using the parameters. If it can not find a peak ( usually in blanks) it will look at these numbers and just integrate everything in this range as a peak.

In the print out in excel, however, it will give you the peak area of all the peaks in this integration range as a separate sheet, as comparison.

Data output:

Data is outputted to an excel workbook with multiple sheets. They are described as follows:

Peak Area (cutoff)-no back : Peak area calculated using the Peak Height Cutoff. Background is subtracted.

Peak Area (cutoff)-with back. : Peak area calculated using the Peak Height Cutoff. Background is NOT subtracted.

Peak Area (IL)-no back. : Peak area calculated using the Integration

limits Background is subtracted.

Peak Area (IL)-with back.: Peak area calculated using the Integration limits Background is NOT subtracted.

Peak Height : Peak Height

Background Mean: Mean of the first N (filtered if using a filter) points specified in Base\_line\_len.

Back Std. Dev.: Standard deviation of the first N (filtered if using a filter) points specified in Base\_line\_len.

Peak Area (slope) : Peak area calculated using the Slope limits. Background is subtracted.

Peak Start(slope) : Start of the peak a s determined by slope cutoffs

Peak Stop(slope) : End of the peak as determined by slope cutoffs

Peak Start(Cutoff): Start of the peak a s determined by peak height cutoff;

Peak Stop(Cutoff): End of the peak a s determined by peak height cutoff;

parameters : Copy of the parameters file.

#### **Appendix 3: Digestion Filter Blanks**

2004		20 µm			
		mean (ppb)	%RSD		
	Ag107(LR)	0.0080	19%		
	Pb208(LR)	0.077	25%		
	Al27(MR)	3.5	71%		
	P31(MR)	50	15%		
	Fe56(MR)	40	12%		
	Ni60(MR)	0.22	11%		

	Cu63(MR)	0.10	36%				
2005		20 µm		2 µm		0.2 µm	
				mean		mean	
		mean (ppb)	%RSD	(ppb)	%RSD	(ppb)	%RSD
	Ag107(LR)	0.026	26%	0.026	18%	0.029	26%
	Pb208(LR)	0.30	32%	0.33	88%	0.22	66%
	Al27(MR)	114	80%	71	59%	34	36%
	P31(MR)	15	44%	12	11%	15	59%
	Mn55(MR)	14	96%	7	68%	2.0	75%
	Fe56(MR)	683	95%	324	72%	51	55%
	Cu63(MR)	2.2	73%	1.3	21%	2.1	39%
2006		20 µn	n				
		mean (ppb)	%RSD				
	Ag109(LR)	0.0010	31%				
	Pb208(LR)	0.026	48%				
	P31(MR)	1.2	9%				
	Mn55(MR)	0.058	47%				
	Fe56(MR)	2.9	39%				
	Co59(MR)	0.0058	53%				

57%

29%

54%

## Appendix 4: Hudson River Plume Box Model – Algebraic Description

 $\Delta$ Plume = HRE + BW - DGM - PS - CC

0.11

1.1

3.1

Cu63(MR)

Zn66(MR) Al27(MR)

## **Plume Dimensions (Box Size):**

User Input: L, W, H, f

Calculations:

- Initial Conditions A = L \* W, V = A \* H.
- Numerical solution  $V = Vi + (1-f)^*(BWwater + HRwater)$

L = Length (m), W = Width (m), H = Height (m), f = the fraction of the Water inputs directed to the coastal current, A = Area (m<sup>2</sup>), V = Volume (m<sup>3</sup>), Vi = Volume at previous time step (m<sup>3</sup>), BW water = water input from bottom water entrainment(m<sup>3</sup> d<sup>-1</sup>), and HR water = water input from the estuary (m<sup>3</sup> d<sup>-1</sup>).

# **Estuary Input (HRE):**

User Input: HRwater, MetDiss, MetPart

Calculations: HRmetal = HRwater\*1000\*(HRMetDiss + HRMetPart)

HRmetal = Hudson River estuary metal input (pmol  $d^{-1}$ ), MetDiss = Estuary dissolved metal concentration (pM), MetPart = Estuary particulate metal concentration (pM)

## **Bottom Water Entrainment (BW):**

User Input: Kz, Hm, BWMetDiss, BWMetPart

Calculations:

BWwater =  $Kz^{*}Hm^{-1}*86400^{*}A$ ,

BWmetal = BWwater\*1000\*(BWMetDiss+ BWMetPart)

Kz = Vertical eddy diffusivity (m<sup>2</sup> s<sup>-1</sup>), Hm = vertical mixing height, BWwater is the water input from bottom water entrainment, BWMetDiss = the dissolved metal concentration in bottom water (pM), and BWMetPart = the particulate metal concentration in bottom water (pM).

# Volatilization (DGM, Hg only):

User Input: Vf

Calculation: Vout = Vf \* A

Vout = the loss of Hg to the atmosphere (pmol  $d^{-1}$ ), Vf = the mean volatilization flux (pmol  $m^{-2} d^{-1}$ )

# **Particle Sinking (PS):**

User Input: ks

Calculations:

MetPartSink = MetPartIn – MetPartOut,

MetPartIn = BWMetPart + HRMetPart,

MeD = (fHRMetPart + fBWMetPart)/(((BWwater+HRwater)/V) + ks)

MetPartOut = MeD\*(BWwater+HRwater)

fHRMetPart = HRMetPart \*  $V^{-1}$ , fBWMetPart = BWMetPart \*  $V^{-1}$ 

ks = the pseudo first order rate constant for particle sinking, MetPartSink = particle sinking (pmol  $d^{-1}$ ), MetPartIn = the particulate metals entering the plume (pmol  $d^{-1}$ ), MetPartOut = the particulate metals exiting the plume in the coastal current (pmol  $d^{-1}$ )

## **Coastal Current (CC):**

Calculations:

 $CCwater = f^*(HRwater + BWwater)$ 

MetCC = f((HRmetal +BWmetal)-(Vout + MetPartSink))

CC water = the export of water to the coastal current (pmol  $d^{-1}$ ), MetCC = the metal export in the coastal current (pmol  $d^{-1}$ ).

Appendix 5: Trace Metal Data from the Hudson River buoyant plume

	memou,	Chapter 2, p	<i>(a</i> 1 <i>t</i> 1 <i>)</i>	Tomn	F۵	Ni	Dh	
Year	Latitide	Longitude	Salinity	°C	nM	nM	nM	Zn nM
2006	40.16499	-73.9279	28.72	12.47	22.1	6.6	ND	5.4
2006	40.09234	-73.973	30.24	14.73	7.9	5.6	0.13	7.7
2006	40.46009	-73.9473	26.74	12.76	14.5	6.3	0.16	9.3
2006	40.04103	-73.8589	28.70	14.19	17.0	6.0	0.16	7.4
2006	39.97603	-73.7554	27.90	14.34	21.9	7.9	0.16	8.2
2006	40.00891	-73.7545	27.98	14.43	24.1	6.9	0.18	10.2
2006	40.48407	-73.9984	23.94	12.64	54.1	9.6	0.27	26.5
2006	40.17182	-73.9628	26.89	13.78	24.6	8.1	0.19	8.6
2006	40.04177	-73.7715	27.85	14.54	24.9	7.2	0.19	14.1
2006	40.13263	-73.8933	27.24	13.34	23.2	7.8	0.18	7.6
2006	40.15668	-73.9183	28.98	12.44	7.8	6.5	0.13	9.1
2006	40.0565	-73.7771	31.75	10.04	ND	5.0	ND	5.0
2006	40.08476	-73.959	27.93	13.44	20.5	7.0	0.16	7.1
2006	40.17447	-73.9146	27.21	13.42	ND	8.2	0.22	9.2
2006	39.76232	-73.2237	32.46	9.24	2.5	4.5	0.03	1.2
2006	39.91831	-73.7195	30.34	11.04	8.2	6.2	0.09	7.9
2006	40.17911	-73.9569	26.42	14.83	23.3	8.2	0.20	18.2
2006	39.7892	-73.7616	29.27	13.67	18.0	6.1	0.18	6.5
2006	40.06858	-73.8486	28.12	13.03	15.1	6.7	0.14	10.5
2006	39.70779	-73.7807	30.00	12.36	10.4	5.5	0.12	6.1
2006	40.25158	-73.9588	26.73	12.66	36.7	8.1	0.22	9.8
2006	39.87578	-73.892	30.24	13.11	7.4	5.3	0.13	7.6
2006	39.75704	-73.0809	32.44	9.25	3.6	4.1	ND	1.8
2006	40.15808	-73.9199	28.94	12.40	26.1	5.8	0.11	6.6
2006	40.02187	-73.8011	27.77	14.82	18.6	7.4	0.16	10.3
2006	40.10418	-73.8084	28.03	14.40	19.9	7.0	0.15	8.0
2005	40.28334	-73.7122	29.53	7.62	6.3	5.8	0.08	6.6
2005	40.07401	-73.6564	29.39	9.01	5.8	5.6	0.06	6.8
2005	40.29993	-73.9351	23.08	10.59	30.6	6.9	0.12	5.6
2005	40.30067	-73.8542	23.01	9.60	30.5	6.7	0.13	6.4
2005	40.28334	-73.7122	29.53	7.62	6.8	5.8	0.08	5.9
2005	40.12594	-73.3948	31.29	6.22	4.7	5.1	0.07	6.6
2005	40.24633	-73.9124	27.28	7.63	21.9	6.7	0.08	8.4
2005	40.36795	-73.9298	23.72	7.35	33.5	7.4	0.11	13.5
2005	40.36622	-73.9297	23.74	7.34	34.0	7.4	0.11	ND
2005	40.31684	-73.9434	23.62	7.15	37.7	8.9	0.10	10.0
2005	40.27371	-73.9273	23.91	7.89	31.9	8.6	0.11	8.4
2005	40.34506	-73.8533	22.04	7.35	52.6	8.9	0.13	19.6
2005	40.34975	-73.9228	22.57	8.34	41.3	8.4	0.12	14.6
2005	40.28334	-73.7122	29.53	7.62	13.5	5.6	0.06	6.8
2005	40.07401	-73.6564	29.39	9.01	6.4	5.7	0.08	5.4
2005	40.30624	-73.8576	25.79	9.55	19.0	6.3	0.10	9.5
2005	40.31003	-73.869	26.33	9.23	19.5	6.9	0.08	8.1
------	----------	----------	-------	-------	------	------	------	------
2005	40.12594	-73.3948	31.29	6.22	13.7	5.2	0.08	8.0
2005	40.36622	-73.9297	23.74	7.34	29.6	7.9	0.09	15.7
2005	40.08143	-73.5987	29.44	7.03	13.8	5.5	0.07	6.8
2005	40.25688	-73.9331	28.15	6.60	11.5	6.3	0.08	7.8
2005	40.28334	-73.7122	29.53	7.62	11.8	6.1	0.06	7.8
2005	40.34768	-73.9256	22.56	8.25	40.4	7.7	0.11	11.6
2005	40.34305	-73.9077	24.11	7.45	42.2	7.7	0.11	11.9
2005	40.07381	-73.6545	29.40	9.03	6.6	5.7	0.06	7.8
2005	40.32235	-73.9322	24.39	7.00	25.0	6.8	0.11	7.6
2005	40.34873	-73.9242	22.57	8.31	41.7	7.9	0.11	16.0
2005	40.33467	-73.955	23.17	7.43	30.0	7.0	0.12	7.6
2005	40.31602	-73.9593	24.22	7.07	31.5	7.9	0.10	9.4
2005	40.31376	-73.9078	24.85	6.86	24.6	7.6	0.09	14.2
2005	40.27357	-73.9257	24.00	7.81	27.5	7.8	0.08	8.6
2005	40.32902	-73.7885	24.72	7.21	27.2	5.4	0.07	7.5
2005	40.33467	-73.955	23.17	7.43	28.6	7.8	0.10	15.7
2005	40.3173	-73.9078	24.81	6.83	28.8	8.0	0.10	9.3
2005	40.34513	-73.8558	22.05	7.40	45.9	9.0	0.12	12.9
2005	40.25549	-73.9461	29.22	6.55	9.1	6.3	0.09	8.9
2005	40.00014	-73.9779	28.28	6.95	20.8	5.7	0.11	ND
2005	40.27935	-73.8311	26.15	6.87	18.5	6.7	0.09	7.2
2005	40.31873	-73.9322	24.49	6.99	25.3	7.7	0.11	9.5
2005	40.33467	-73.955	23.17	7.43	33.0	8.1	0.13	ND
2005	40.38824	-73.9114	22.22	7.60	36.7	8.8	0.12	14.0
2005	40.32505	-73.8885	20.92	9.10	41.3	7.9	0.20	5.9
2005	40.26365	-73.9666	25.86	7.38	18.8	7.2	0.08	7.3
2005	40.2645	-73.8342	27.53	8.77	12.8	6.5	0.09	6.7
2005	40.46975	-73.9253	19.41	9.20	49.0	10.6	0.14	8.0
2005	40.14696	-73.9488	29.79	7.20	10.2	6.1	0.09	ND
2005	40.13882	-73.5895	29.31	7.21	6.2	5.4	0.06	5.5
2005	40.31826	-73.9297	22.89	11.14	23.0	8.4	0.09	6.2
2005	40.38824	-73.9114	22.22	7.60	39.6	9.4	0.16	14.6
2005	40.13885	-73.6245	29.38	7.22	7.2	5.9	0.05	6.6
2005	40.30025	-73.8442	25.45	9.57	23.6	7.0	0.08	6.3
2005	40.13862	-73.6621	29.44	7.21	6.7	5.8	0.06	4.5
2005	40.13891	-73.7785	30.39	6.99	4.4	5.7	0.07	5.7
2004	40.34392	-73.9115	29.71	8.87	21.7	7.4	0.15	ND
2004	40.21717	-73.89	31.92	8.83	5.2	4.9	0.08	7.1
2004	40.19917	-73.9648	30.10	9.37	14.6	6.1	0.12	13.5
2004	40.20017	-73.9482	29.87	9.26	16.6	7.0	0.15	11.2
2004	40.37517	-73.8339	30.23	9.15	11.3	5.9	0.12	9.0
2004	40.30411	-73.9332	29.70	9.41	16.9	6.3	0.14	10.7
2004	40.29283	-73.8315	31.12	8.87	9.1	5.6	0.09	9.6
2004	40.243	-73.9623	31.50	7.96	ND	6.0	0.10	7.5
2004	40.07967	-73.9702	30.81	9.25	9.1	6.3	0.10	5.8
2004	40.12963	-73.9608	30.50	8.94	11.8	6.2	0.11	ND
2004	40.1495	-73.9947	30.47	8.83	ND	6.7	ND	8.0
2004	40.14024	-74.0074	30.74	9.07	ND	6.4	0.10	9.1

Additional dissolved metals data determined by	10 fold dilution a	and direct analysi	is by desolvation	(Apex Q, Elemental
Scientific Inc, Omaha NE) HR-ICP-MS.				

Date	5/5/2004	5/4/2004	5/6/2004	5/4/2004	5/5/2004	5/4/2004				
Time(EDT)	15:00	11:20	2:28	9:00	8:00	19:00				
Ag	ND	0.0054	0.0026	0.0041	0.0057	ND				
Pb	0.037	0.103	0.029	0.060	0.039	0.072				
Р	11.5	15.9	9.8	16.1	9.7	11.8				
Mn	3.5	6.5	1.5	7.0	3.3	6.6				
Fe	0.78	1.28	0.32	1.31	0.55	0.79				
Cu	0.23	0.64	0.13	0.55	ND	ND				
Zn	1.3	3.1	1.6	1.6	1.5	ND				
Date	4/13/2005	4/20/2005	4/20/2005	4/10/2005	4/19/2005	4/13/2005	4/12/2005	4/11/2005	4/11/2005	4/12/2005
Time(EDT)	15:02	3:53	9:26	15:51	14:50	5:06	22:25	6:52	23:49	6:52
Ag	0.011	0.002	0.007	0.003	0.006	0.004	0.004	0.005	0.005	0.003
Pb	0.043	0.034	0.038	0.077	0.047	0.054	0.039	0.135	0.082	0.058
Р	10.9	8.1	8.5	17.8	8.2	7.4	5.5	16.1	11.5	10.0
Mn										
IVIII	2.7	5.6	8.6	18.1	9.9	12.6	10.9	29.6	20.6	7.4
Fe	2.7 0.9	5.6 1.0	8.6 1.7	18.1 3.1	9.9 1.3	12.6 1.9	10.9 1.4	29.6 4.5	20.6 2.9	7.4 1.1
Fe Cu	2.7 0.9 0.10	5.6 1.0 0.6	8.6 1.7 1.0	18.1 3.1 1.4	9.9 1.3 0.9	12.6 1.9 0.8	10.9 1.4 0.4	29.6 4.5 1.8	20.6 2.9 1.3	7.4 1.1 0.5

2004 trace metal particulate data (n	mass:vol of	' water)	i.
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Sample ID	Ag ppt	Pb ppt	AI dqq	P dqq	Cr ppt	Mn daa	Fe ppb	Ni ppt	Cu ppt
PPM050204-	1-1	1-1	1-1	1-1	1-1	1-1	1-1	1-1	1-1
1(20) PPM050204-	0.16	9	1.07	0.95	5	0.28	2.63	2.7	6.1
2(20) PPM050204-	0.19	11	1.47	0.85	6	0.30	3.14	2.8	6.1
3(20) PPM050204-	0.14	8	1.04	0.86	5	0.30	2.40	2.3	6.1
4(20) PPM050304-	0.05	3	0.35	0.28	2	0.07	0.77	0.6	2.2
1(20) PPM050304-	0.18	7	0.76	0.48	4	0.28	1.77	1.7	4.5
2(20) PPM050304-	0.36	21	3.90	1.50	21	0.46	9.22	6.7	15.6
3(20) PPM050304-	0.18	8	0.92	1.01	7	0.21	2.03	1.7	6.1
4(20) PPM050404-	0.31	18	3.02	1.29	15	0.20	6.30	5.7	12.3
2(20) PPM050404-	0.43	16	2.69	0.87	15	0.41	5.26	5.2	12.8
3(20) PPM050404-	0.41	16	2.69	1.06	16	0.28	6.04	4.7	15.0
4(20) PPM050404-	0.47	25	3.41	1.81	24	0.58	8.35	6.3	19.8
5(20) PPM050404-	0.16	8	1.26	0.50	5	0.11	2.57	1.9	5.9
6(20) PPM050504-	0.19	9	1.15	0.50	5	0.26	2.26	1.7	5.9
3(20) PPM050504-	0.27	13	1.45	1.32	10	0.36	2.96	2.7	8.7
5(20) PPM050504-	0.11	6	1.22	0.93	6	0.00	2.84	1.8	7.6
6(20) PPM050604-	0.12	6	0.80	0.91	4	0.21	1.33	1.0	4.8
1(20) PPM050604-	0.13	3	0.18	0.84	3	0.34	0.25	0.1	3.7
2(20)	0.10	4	0.42	0.68	3	0.08	0.60	0.6	3.5

# 2005 particulate metal data

Date	>0.2 um			oentiuti	ons (ug/L)		
Time(EDT)	Ag	Pb	AI	Р	Mn	Fe	Cu
4/10/05 15:58	0.0053	0.235	68.5	24.3	3.42	106.2	0.179
4/10/05 18:35 4/11/05	0.0043	0.195	44.5	22.8	2.58	81.3	0.127
12:53 4/11/05	0.0038	0.193	57.5	23.0	3.03	100.2	0.133
16:44 4/11/05	0.0026	0.100	20.0	7.2	1.65	35.0	0.070
23:53 4/12/05	0.0037	0.167	49.0	20.0	2.75	78.4	0.156
6:11 4/12/05	0.0025	0.107	27.9	12.4	1.83	46.6	0.074
6:47 4/12/05	0.0036	0.070	17.5	10.1	1.27	25.5	0.062
10:32 4/12/05	0.0028	0.145	38.5	18.9	2.67	61.4	0.107
14:16 4/12/05	0.0042	0.190	44.2	20.7	3.26	84.9	0.151
16:36 4/12/05 22:34	0.0135	0.857	249.9	56.1	18.77	420.6	0.986
4/13/05 5:17 4/13/05	0.0013	0.048	15.2	6.8	1.10	25.3	0.042
10:45 4/13/05	0.0016	0.064	18.1	9.4	1.58	31.6	0.045
13:03 4/13/05	0.0005	0.014	2.5	6.1	0.64	3.9	0.018
13:35 4/13/05	0.0011	0.020	6.4	4.7	0.43	8.2	0.011
14:51 4/14/05	0.0000	0.009	2.6	3.5	0.20	3.8	0.021
1:26 4/14/05	0.0007	0.040	10.0	7.2	0.99	55.7	0.047
11:11 4/14/05	0.0043	0.208	65.8	20.1	3.16	107.6	0.149
13:32 4/14/05	0.0009	0.034	8.0	4.6	0.97	12.6	0.119
15:50 4/14/05	0.0033	0.160	55.3	19.2	3.27	84.8	0.134
18:06	0.0048 > <b>2 um</b>	0.241	69.2	24.8	3.76	130.9	0.199
	Ag	Pb	AI	Р	Mn	Fe	Cu
4/10/05 15:58 4/10/05	0.0039	0.216	89.5	22.5	3.6	116.8	0.159
18:35	0.0034	0.164	59.9	17.4	3.4	113.9	0.147
12:53	0.0031	0.176	53.6	18.7	2.6	89.2	0.106

LaTTE-2005 particulate metal concentrations (ug/L)

4/11/05							
4/11/05 16·44	0 0021	0.091	26.7	37	22	59 5	0 096
4/11/05	0.0021	0.001	20.7	0.7	<i>L.L</i>	00.0	0.000
23:53	0.0026	0.139	44.9	17.5	2.4	75.4	0.094
4/12/05							
6:11	0.0017	0.095	32.7	10.4	1.9	55.0	0.069
4/12/05	0 0010	0.000	04.0	44.0	0.4		0.050
6:47 4/12/05	0.0016	0.090	31.9	11.2	2.1	41.5	0.052
4/12/05	0 0023	0 1 2 6	43.0	15 5	22	65.3	0 080
4/12/05	0.0020	0.120	40.0	10.0	<i>L.L</i>	00.0	0.000
14:16	0.0030	0.151	49.8	14.5	2.7	80.2	0.102
4/12/05							
16:36							
4/12/05		0.4.40	40.0	10.0	<b>0</b> 4		0.440
22:34	0.0028	0.149	43.6	18.8	3.1	81.4	0.116
4/13/05 5·17	0 0024	0 1 1 0	42.6	15.2	37	101 3	0 175
4/13/05	0.0024	0.110	42.0	10.2	0.7	101.0	0.170
10:45	0.0008	0.054	18.0	5.9	1.3	24.9	0.032
4/13/05							
13:03	0.0002	0.012	2.7	2.1	0.4	5.4	0.008
4/13/05	0 0001	0.047			0.0	7.0	0.007
13:35	0.0001	0.017	5.5	2.0	0.3	7.2	0.007
4/13/05 14·51	0 0001	0.008	25	17	0.1	32	0.003
4/14/05	0.0001	0.000	2.0	1.7	0.1	0.2	0.000
1:26	0.0002	0.017	5.5	1.7	0.4	7.6	0.007
4/14/05							
11:11	0.0032	0.188	65.2	15.9	3.1	102.1	0.113
4/14/05	0.0004	0 0 2 2	0.6	2.4	1.0	24 5	0 0 2 2
13.32	0.0004	0.032	0.0	2.4	1.0	24.5	0.033
15:50	0.0023	0.140	48.2	14.4	2.3	74.7	0.084
4/14/05			-		-		
18:06	0.0038	0.212	71.5	20.9	3.5	131.5	0.163
	>20 um						
	Ag	Pb	AI	Р	Mn	Fe	Cu
4/10/05	0 0000	0.400	00.4	10.0	4 7	<b>54 5</b>	0.075
15:58	0.0023	0.102	30.4	16.8	1.7	51.5	0.075
4/10/05	0.0013	0.057	19.0	9.6	0.8	30.6	0.037
4/11/05	0.0010	0.007	10.0	0.0	0.0	00.0	0.007
12:53	0.0022	0.112	37.5	16.1	1.9	55.0	0.080
4/11/05							
16:44	0.0002	0.011	3.3	1.7	0.2	3.9	0.006
4/11/05	0.0014	0.071	01 7	107		00.0	0 000
23:53	0.0014	0.071	21.7	13.7	1.1	29.2	0.039
6.11	0 0008	0.037	12.8	89	10	27 2	0.053
4/12/05	0.0000	0.007	. 2.0	0.0		_/	0.000
6:47	0.0004	0.017	5.3	5.1	0.4	9.2	0.017
4/12/05						<i>a</i> -	
10:32	0.0012	0.070	23.1	13.4	1.3	33.2	0.052
4/12/05 14:16	0 0020	0.096	25 F	15 1	10	100	0.065
14.10	0.0020	0.000	20.0	10.1	1.0	42.2	0.000

4/12/05	0.0000	0.400	00.7	17.0	0.0	477	0.000
16:36 4/12/05	0.0023	0.108	29.7	17.8	2.0	47.7	0.083
22:34	0.0018	0.081	22.5	17.2	1.7	37.7	0.060
4/13/05 5:17	0.0040	0.170	50.7	35.5	3.9	86.0	0.158
4/13/05	0 0005	0.004		4.0	<u> </u>	0.7	0.040
10:45 4/13/05	0.0005	0.024	6.8	4.3	0.4	8.7	0.016
13:03	0.0001	0.003	0.7	1.6	0.0	0.6	0.001
4/13/05 13:35	0.0001	0.004	0.9	1.2	0.1	3.1	0.007
4/13/05	0.0000	0.004					0.004
14:51 4/14/05	0.0000	0.001	0.3	0.9	0.0	0.0	0.001
1:26	0.0000	0.002	0.5	0.9	0.0	0.2	0.001
4/14/05 11:11	0.0017	0.084	37.1	15.5	1.7	47.9	0.064
4/14/05	0.0001						
13:32 4/14/05	0.0001	0.006	1.2	1.2	0.1	1.8	0.003
15:50	0.0016	0.079	22.5	13.0	1.4	35.3	0.083
4/14/05 18:06	0.0022	0.116	36.5	20.1	2.2	58.9	0.087

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Month	day	Year	Âg	Pb	Р	Mn	Fe	Со	Cu	Zn	Al
5	2	2006	0.000	0.0	343	1	17	0.02	0.0	0	15
5	2	2006	0.223	6.2	2364	105	3567	1.05	4.8	47	1904
5	3	2006	0.476	8.6	4031	180	2963	0.99	17.0	150	2135
5	3	2006	0.132	3.9	966	36	1111	0.41	9.0	101	499
5	3	2006	0.461	20.2	3441	424	7422	2.11	8.9	93	4092
5	3	2006	0.908	57.3	4566	968	20163	5.82	29.3	188	10519
5	3	2006	0.492	32.3	3091	478	11636	3.50	16.5	64	6203
5	3	2006	1.697	85.7	5044	1495	32239	9.33	47.8	175	17455
5	4	2006	0.940	73.4	6841	1494	22792	6.84	31.7	424	14004
5	4	2006	0.896	69.3	6547	1207	18907	5.65	21.8	232	10726
5	4	2006	ND	40.5	4020	822	12150	3.32	14.0	139	6226
5	4	2006	0.217	9.0	2541	185	3884	1.18	8.3	53	2117
5	5	2006	0.826	67.9	8063	1541	17131	5.92	33.9	ND	9718
5	5	2006	0.421	14.5	1912	392	5807	2.01	10.0	169	2885
5	5	2006	0.660	49.4	6030	1367	13925	4.21	10.7	82	7645
5	5	2006	0.410	23.2	3553	768	6582	2.48	14.6	261	3372
5	5	2006	0.813	78.2	7390	1535	13445	5.73	26.3	523	8778
5	6	2006	0.256	12.5	2966	389	3198	0.90	5.5	447	1886
5	6	2006	0.762	44.1	9042	1461	9307	3.45	14.0	303	5508
5	6	2006	0.107	6.4	1538	276	1921	0.67	0.9	31	1064
5	6	2006	0.593	34.6	4888	985	7813	3.03	29.4	293	4130
5	6	2006	0.233	14.7	2736	514	3807	1.45	8.7	108	2236
5	6	2006	0.081	5.2	1676	125	1010	0.53	1.0	11	592
5	6	2006	0.320	7.1	3806	199	1259	0.72	9.5	141	798
5	7	2006	0.122	6.6	2142	103	937	0.69	4.0	107	521
5	7	2006	0.132	7.6	2531	247	2039	0.78	3.4	60	1142
5	7	2006	0.481	53.9	5887	1180	10350	3.41	11.4	97	5789
5	8	2006	0.078	8.5	2528	11	175	0.00	0.0	60	156

2006 Particulate metal data in ng/L

ND = Not determined

#### **Curriculum Vita**

## **Derek David Wright**

## Education

- 2008 Ph.D. Environmental Sciences Rutgers University, New Brunswick NJ.
- 2001 **B.S. Environmental Chemistry (magna cum laude)** Lake Superior State University (LSSU), Sault Ste. Marie, MI.

## **Principle Occupations and Positions Held**

2008-Current – Assistant. Professor of Chemistry and Environmental Science, Lake Superior State University

2007-2008 - GAANN Fellow, Dept. of Environmental Sciences, Rutgers University.

2003-2007 - Graduate Assistant, Dept. of Environmental Sciences, Rutgers University.

2002-2003 - GAANN Fellow, Dept. of Environmental Sciences, Rutgers University.

2001-2002 – Environmental Sanitarian, LMAS Dist. Health Dept., St. Ignace, MI.