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ECOSYSTEM RESPONSE

Biological Responses in a Dynamic Buoyant River Plume

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ABSTRACT. Buoyant river plumes are highly dynamic and often characterized by marked physical and chemical gradients that interact to drive biological responses. For example, interactions among factors resulting in algal growth (e.g., nutrient and light availability) and algal loss (e.g., sinking and zooplankton grazing) vary with spatiotemporal changes in physics and chemistry. The nature of these interactions profoundly influences the transfer and transformation of materials carried by the plume, including nutrients and metals. In April 2005, during the Lagrangian Transport and Transformation Experiment (LaTTE), water from the Hudson River recirculated in a nearshore eddy before moving southward to mix with relatively saline water along the New Jersey coast. Within the recirculating eddy, phytoplankton rapidly assimilated nutrients, resulting in extremely high rates of productivity  $(> 10 \text{ mg C m}^{-3} \text{ h}^{-1})$ , with approximately 75% of carbon fixed by large, chain-forming diatoms. Sampling of phytoplankton and mesozooplankton, along with experimental estimates of microzooplankton and mesozooplankton grazing rates, indicated that these large phytoplankton escaped grazing and sank. The subsequent decomposition of this carbon contributed to decreased oxygen concentrations in bottom waters along the edges of the buoyant plume. In contrast to carbon, particulate metal concentrations derived from the smaller size class of phytoplankton were twice as high as those derived from larger phytoplankton. Relatively efficient grazing on the smaller size class led to bioaccumulation of metals in mesozooplankton. The interactions among chemistry, physics, and biology in the dynamic Hudson River plume serve as an example of how anthropogenic activities in urbanized watersheds can influence and potentially alter coastal food webs.

### INTRODUCTION

Estuaries, shallow coastal waters, and continental shelves comprise only 10% of Earth's total ocean area; however, they account for at least 25% of global primary productivity and support over 90% of marine fisheries (Agardy et al., 2005). The bulk of this productivity is fueled by elements delivered by two main sources: upwelling and riverine inputs—the focus of this article. In particular, major rivers deliver critical quantities of macronutrients, trace metals, and other elements that support the growth of planktonic autotrophs, which, in turn, support higher trophic levels.

Access to high productivity and other ecosystem services, including aesthetic appeal, draws people to the watersheds of major rivers and the coastlines of all countries. In turn, people exert pressures on the same characteristics that attracted them by extracting water, fish, and other resources; disturbing habitats; introducing nonnative species; and increasing inputs of nutrients and metals to rivers and coasts. These increased loads interact with the rates and limits of biological processing to create a conundrum. At what point do loads of nutrients and metals from large rivers, especially anthropogenic loads, compromise sustainability of coastal ecosystems?

Macronutrients stimulate biological production, but overenrichment can lead to eutrophication and an array of undesirable changes. Eutrophication can alter the dynamics of microbial assemblages, impacting both the chemistry and biology of coastal systems (Scavia and Bricker, 2006). If left unchecked, synergy among these alterations can generate catastrophic consequences, including zones with chronic hypoxia and anoxia, changes in energy flow that disrupt trophic webs, loss of biodiversity, loss of economically important fisheries, and production of extremely potent greenhouse gases (Pacyna and Manø, 2006). For example, in the 1970s, signs of nutrient overenrichment, increased production of organic matter, higher rates of decomposition, and consequent hypoxia/anoxia became obvious in some coastal systems. By the early 1990s, the problem was known to be widespread and recurrent (Welsh, 1991), with one highly publicized example being the recurring, seasonal "dead zone" in the Gulf of Mexico that has been linked

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better understanding of the fate of terrestrial nutrient inputs into coastal regions.

The development and changes in land use that increase anthropogenic loads of macronutrients to the coastal ocean often increase loads of chemical contaminants and trace metals. For example, over the last 20 years, levels of potentially toxic trace metals have increased significantly along the Gulf of Mexico and the northeastern United States (Kimbrough et al., 2008). In addition, data from National Estuary Programs identified contamination of fish in 23% of estuaries sampled (US Environmental Protection Agency, 2007). At concentrations found in the open ocean (< 100 nM), trace metals promote biological productivity by functioning as enzymatic cofactors and supporting protein structure (Morel and Price, 2003). However, at higher levels, metals and other contaminants begin to reduce productivity either directly through lethal effects on key organisms or indirectly through uptake and trophic links, leading to accumulation of sublethal body burdens that make fish and shellfish unsuitable for human consumption. Accumulation of metals and other contaminants is a complex process. Aqueous speciation, accumulation, and intracellular partitioning by phytoplankton; grazing rates; and excretion rates have been shown to influence accumulation of metals in a range of marine consumers (Reinfelder et al., 1998; Wang and Fisher, 1998; Wang, 2002).

Overall, economic and ecological impacts from nutrients and metals are influenced by proximity to urban areas, discharges from major watersheds, local trophic webs, physical processes that influence the dynamics of water masses, chemical transformations, and biological interactions along coastal margins and over broad continental shelves (see Schofield et al., this issue). At this point, efforts to address the conundrum of sustainable coastal management in the face of increased loadings will benefit from detailed, multidisciplinary case studies of coastal systems that ultimately yield a predictive capacity.

# LaTTE: A CASE STUDY OF BIOLOGICAL INTERACTIONS IN A BUOYANT PLUME

The Lagrangian Transport and Transformation Experiment (LaTTE) was a multiyear, multidisciplinary study of the complex interactions among nutrient and contaminant loadings, biological processes, and physical dynamics in a buoyant river plume. LaTTE was conducted as part of the Coastal Ocean Processes (CoOP) program, which was founded on the principle that most continental margins experience a reasonably compact set of fundamental processes, such as air-sea interactions, wind-driven currents and mixing, buoyancy effects, episodic events, western boundary currents, tidal exchange, benthic processes, and biogeochemical transformations. Spatial and temporal differences in conditions along coastal margins were predicted to arise from differences in the relative strength of these processes. LaTTE focused on processes that controlled the transport, transformation, and ultimate fate of nutrients and trace metals delivered to the coastal margin in the plume of the Hudson River, which drains a highly urbanized watershed.

The Hudson River, its associated estuary, and adjacent coastal waters represent a valuable model of interactions among anthropogenic loadings of nutrients and

contaminants, buoyant plumes, and biological processes because anthropogenic influences provide strong nutrient and contaminant signals, and seasonal river flow reliably generates a buoyant plume. The Hudson's watershed is home to over 20 million people, and it has been highly urbanized for more than 100 years- the population of Los Angeles has only recently equaled the population of New York City in 1900 (Gibson, 1998). Due to sustained anthropogenic pressures, the river is arguably the most polluted on the east coast (Adams et al., 1998). Sewage that primarily is subject to secondary treatment flows into the lower estuary at approximately 100 m<sup>3</sup> s<sup>-1</sup> (Bronson et al., 2006). This input contributes to a nutrient loading per unit area or volume that ranks highest among large estuaries in the United States (Nixon and Pilson, 1983; National Research Council, 1993). In addition, the Hudson River had higher than average concentrations of 58 of the 59 chemicals monitored by the US Environmental Protection Agency, and it yielded 90% and 69% of the sediment samples that exceeded that agency's standards for total polychlorinated biphenyls and mercury, although it accounted for only 4% of the area sampled from Cape Cod through Chesapeake Bay (Adams et al., 1998). During spring, the Hudson River forms a buoyant plume, with discharge in April averaging 1000 m3 s-1 (Chant et al., 2007, 2008). During these flow regimes, approximately 90% of the inorganic nitrogen load remains unassimilated in the river and estuary, and it is transferred directly to the coastal ocean (Garside et al., 1976).

Previous work on nutrient dynamics in the system showed the importance

and complexity of biological processing in the buoyant plume. The nutrient load from the Hudson River supported high productivity (370–480 g C m<sup>-2</sup> yr<sup>-1</sup>; Malone, 1977a, b; Malone et al., 1983; Lonsdale et al., 1996) that accounted for 70-80% of the particulate organic carbon measured within the plume (Garside et al., 1976; Segar and Berberian, 1976; Garside and Malone, 1978). Productivity of phytoplankton size classes differed among seasons, with the winter plume dominated by large, chain-forming diatoms (> 20  $\mu$ m) and smaller, solitary chlorophytes and microflagellates dominating in summer months after the onset of thermal stratification (Malone and Chervin, 1979). Malone et al. (1977a) found no seasonal differences in the rates of chlorophyll *a* (chl-*a*) specific photosynthesis or light-saturation rates, which led them to attribute the seasonal succession of phytoplankton size classes to differences in sinking, grazing, advection, or dilution. Examination of sinking and grazing within the Hudson's plume revealed that only 1% of phytoplankton biomass was assimilated by adult copepods during a winter bloom as compared to 26% during a summer bloom (Malone and Chervin, 1979). Sinking was suggested as the likely fate for the larger phytoplankton due to an observed decline of chl-a in downstream surface waters. Earlier studies also acknowledged that local wind events, storms, river discharge, and current patterns had profound effects on spatial and temporal variability in primary producers (Malone et al., 1983), with changes occurring within days (Small and Menzies, 1981; Dagg et al., 2004) and cascading impacts on higher trophic levels (Walsh et al., 1978).

The dynamics of trace metal processing in the Hudson River plume are less well known, and predicting accumulation of metals remains a complex challenge. Uptake by phytoplankton has been shown to play a critical role in the transport and transformation of trace metals in the ocean (Morel and Price, 2003). The work in LaTTE was based on the premise that the same processes driving nutrient uptake, production of phytoplankton biomass, and transfer of carbon to zooplankton also will drive biological accumulation of metals (Luoma et al., 1998). Thus, loadings that will create undesirable consequences depend on interactions among numerous components and processes in coastal systems.

This article focuses on one 13-day campaign conducted in April 2005 as a case study highlighting interactions among nutrients, metals, phytoplankton, and zooplankton in the dynamic, buoyant, coastal plume of the Hudson River. This field effort was conducted toward the end of a 10-year flood event created by the spring thaw of a significant snowpack and several periods of rainfall (Chant et al., 2008). The experimental area, including the Hudson River estuary and a 120-km<sup>2</sup> region along the New Jersey coastline, was sampled from R/V Cape Hatteras and R/V Oceanus. Sampling from R/V Cape Hatteras mapped physical and chemical parameters and characterized zooplankton biomass and size structure with a laser optical plankton counter (LOPC). Sampling from R/V Oceanus focused on optical measurements and discrete sampling that characterized assemblage composition and productivity for phytoplankton, grazing for zooplankton, and concentrations of dissolved metals, particulate metals,

and metals in zooplankton. Sampling off both vessels was adaptive, with guidance derived from data collected by gliders, satellites, and high-frequency radar as part of the New Jersey Shelf Observing System (Schofield et al., 2002). Additional details of the sampling approach are highlighted in Chant et al. (this issue).

## PHYSICAL AND CHEMICAL SETTING

The LaTTE experiment was conducted between April 9 and 21, 2005, which was 4-16 days after outflow from the Hudson River peaked at over 7000 m<sup>3</sup> s<sup>-1</sup> (Chant et al., 2008). During the field effort, winds were variable, and they altered the dynamics of the river plume. For about five days before sampling began, strong winds, predominantly from the south, drove the freshwater plume to the east along the Long Island coast and created upwelling of saline water along New Jersey. Subsequently, winds weakened, blew from the north for approximately one day, and then became dominated by diurnal reversals, with amplitudes of 10 m s<sup>-1</sup> and a mean wind speed near zero. In response to these combined winds, the river plume formed a distinct bulge of turbid freshwater at the estuary's mouth. During this period, Chant et al. (2008) found that no more than half of the outflow from the Hudson River was accounted for in the current flowing south along the New Jersey coast, with the remaining outflow contributing to growth of the recirculating eddy. Because the form of this plume was clearly distinct from earlier settings, we were able to observe its evolution and the associated biological responses.

The increasing volume and residence time of the recirculating eddy intensified

the near-surface density gradient and stability of the water column (Figure 1). The intensity of stratification in the eddy was twice that found in the coastal current. Temperatures in the plume water (~ 11°C) were higher than in the adjacent shelf water ( $\sim 6^{\circ}$ C), and salinities ranged from 22 in the plume to 32 over the shelf. Nitrate concentrations in water exiting the mouth of the estuary remained at 15-20 µM from the initiation of the eddy to the end of the experiment, which indicated that the input of nutrients to the recirculating water was related to river discharge. Relatively constant salinities within the recirculating eddy indicated a stable influx of freshwater, but nitrate concentrations in the eddy decreased to  $5-10 \,\mu\text{M}$  over the same period, which suggested rapid uptake and assimilation by phytoplankton (Figure 1). At the start of the campaign, nitrate concentrations in the coastal current exceeded 5 µM due to previous upwelling. These concentrations rapidly decreased to  $< 0.1 \mu$ M, and

they remained constant throughout the experiment, which indicated that most dissolved nitrate had been stripped from the water leaving the recirculating eddy. The light climate in the Hudson River was determined by high concentrations of sediment, chromophoric dissolved organic matter, and detritus, with absorption by phytoplankton becoming a dominant factor as water recirculated in the eddy (Frazer et al., 2006). Light absorption decreased by an order of magnitude in buoyant waters that flowed out of the eddy to continue southward along the New Jersey coast.

The clearly distinct form of the Hudson River plume during the April 2005 campaign allowed us to address a series of interrelated hypotheses. We hypothesized that phytoplankton production would increase in the recirculating eddy, with its relatively stable water column and high nutrient concentrations. Increased zooplankton abundance and grazing pressure were hypothesized to track increases in phytoplankton, with a potential respite from grazing pressure for larger phytoplankton. Finally, the dynamics of trace metals were predicted to parallel the dynamics of nutrient uptake and carbon fixation by phytoplankton, with transfer to zooplankton via trophic links.

## RESPONSES OF PHYTOPLANKTON

The recirculating eddy acted much like a chemostat used for controlled-growth experiments. Increases in the volume and residence time of water in the eddy as compared to shelf waters and the coastal current produced two major consequences for phytoplankton. Firstly, phytoplankton biomass, as estimated by concentrations of chl-a, increased due to the combination of a stable and stratified water column and a nearly constant supply of nutrients (Figure 2). The ratio of carbon to chl-a remained relatively constant throughout the study  $(r^2 = 0.65; n = 73)$ , so chl-*a* served as a reliable proxy for carbon biomass. In



Figure 1. Three-dimensional view of the sampling locations occupied by R/V Cape Hatteras and R/V Oceanus during the LaTTE study from April 9-12, 2005. Here, we illustrate the impact of buoyancy of the Hudson River plume on the accumulation of phytoplankton biomass. Vertical profiles of density (red) are overlain by surface chlorophyll a concentrations (green). Less-dense plume water is indicated by larger and darker red spheres, and increased chlorophyll *a* concentrations are indicated by larger circles. Densities ranged from 11 to 26  $\sigma$ , and chlorophyll concentrations ranged from 1 to 100 mg m<sup>-3</sup>. The inset is a visible MODIS-Aqua satellite image showing the LaTTE study area, the Hudson River plume, and the associated coastal current to the south on April 13, 2005. The red box indicates the view rendered in the larger image. Larger image produced by C. Malzone using Eonfusion by Myriax

the eddy, maximum concentrations of chl-a approached 100 mg m<sup>-3</sup> and concentrations averaged 65 mg m<sup>-3</sup> at the surface. Higher phytoplankton biomass was restricted to the surface waters of the recirculating eddy, with offshore concentrations remaining below 5 mg m<sup>-3</sup>. Phytoplankton biomass in the surface waters decreased rapidly at the transition to the coastal current, and concentrations remained low as water was transported south. In the transition zone, chl-*a* concentrations became relatively high in subsurface waters. Secondly, the structure of the phytoplankton assemblage differed among

the adjacent physical and chemical settings (Figure 2). Within the recirculating eddy, over 70% of the chl-a resided in the largest size class measured  $(> 20 \ \mu m)$ . This size class was dominated  $(> 4.5 \text{ x } 10^4 \text{ cells ml}^{-1})$  by the chainforming diatoms Skeletonema costatum and Thalassiosira nordenskioldii, which are known to dominate spring blooms in the region (Malone and Chervin, 1979). Contributions of these diatoms decreased significantly at the transition into the coastal current. Dinoflagellates, cryptophytes, and other flagellates increased in number as the plume water traveled along the coast and aged. These



Figure 2. Pie charts representing chlorophyll *a* concentrations in discrete samples of phytoplankton overlain on an Ocean Color Monitor (OCM) satellite image showing the distribution of chlorophyll *a* around the LaTTE study area on April 12, 2005. The size of each pie represents a chlorophyll *a* concentration class, and the sizes of the sections in each pie represent the relative proportions of the chlorophyll *a* contained in the > 20  $\mu$ m fraction (blue) and < 20  $\mu$ m fraction (red). Additionally, the white circles around selected samples indicate that the < 20  $\mu$ m fractions of those samples were dominated by diatoms. The > 20  $\mu$ m fractions were always dominated by diatoms. Phytoplankton biomass, especially in the > 20  $\mu$ m size class, was greater in the recirculating eddy.

taxa became major contributors to concentrations of total chl-*a* in the southern portion of the coastal current. Although these general patterns were observed for broad taxonomic groups, individual species within these groups often responded differently to localized environmental conditions (Yost et al., 2007).

Whole water samples incubated at in situ light levels revealed that volumetric productivity rates mirrored biomass accumulation, with highest rates measured for the > 20-um fraction within the recirculating eddy and progressively lower rates recorded for the 2-20 µm and 0.2-2 µm size classes (Figure 3). Maximum rates recorded for samples taken in the coastal current were typically 50% lower than those recorded for samples from the eddy, and overall productivity and differences in productivity among size classes decreased as the water flowed southward and aged (Figure 3). Productivity rates standardized to chl-a content yielded quite different patterns, with no significant differences across the size fractions within the recirculating eddy (Figure 3). The chl*a*-specific rates in the coastal current were approximately half those within the eddy, and they did not differ among size classes (Figure 3). All size fractions of phytoplankton were operating at  $\sim$  10–30% of their saturating irradiance according to productivity-irradiance (P vs. E) curves, with the highest efficiencies seen in surface samples. Further evidence for a relatively high degree of acclimation to low light was provided by the accumulation of the relevant xanthophyll-cycle pigments (Moline, 1998). The maximum chl-a-specific photosynthetic rates and light utilization efficiencies were recorded in the surface



Figure 3. Size-fractionated, primary productivity per unit volume (mg C m<sup>-3</sup> h<sup>-1</sup>; A and B) and sizefractionated primary productivity standardized to chlorophyll a concentrations (mg C mg chl a h<sup>-1</sup>; C and D) for seven locations sampled during LaTTE. Panels A and C contain results from samples taken within the recirculating eddy of the buoyant Hudson River plume on dates shown, and panels B and D contain results from samples taken progressively further south within the coastal jet on dates shown (see text). Volumetric productivity was highest in the largest size class in the recirculating eddy, but biomass-specific productivity was nearly equal among all size classes and stations. Note the difference in y-axes representing volumetric and biomassspecific measures of productivity.

waters of the recirculating eddy, and they had decreased by tenfold below the pycnocline (~ 5 m) and by half in the older water flowing southward in the coastal current (data not shown). These results were consistent with optical properties measured throughout the study area.

Large diatoms reportedly dominate the phytoplankton assemblage in the Hudson River plume during February and March, with small flagellates dominating in the summer months (Malone and Chervin, 1979). Our results indicated that phytoplankton assemblage composition, size structure, and volumetric productivity also varied within a two-week period across distinct physical and chemical gradients created by river discharge and atmospheric forcing. Such gradients can lead to the observed patterns by influencing an individual cell's nutrient requirements and its responses to light, temperature, and nutrient availability. However, nutrient requirements

for algae of different sizes do not appear to vary sufficiently to account for the observed discrepancy between biomassspecific and volumetric productivity rates (Figure 3) or the massive accumulation of biomass within the recirculating eddy (Figure 2). High nutrient loads in newly discharged water could contribute to differential growth across size classes if larger phytoplankton exploit available nitrate more rapidly (Hecky and Kilham, 1974; Parsons and Takahashi, 1973, 1974). However, our data on chl-a-specific productivity suggested that carbon assimilation and associated nutrient drawdown did not differ among size classes (Figure 3). In fact, nutrient concentrations decreased as water moved down the coast and aged, and these decreases drove decreases in the biomass-specific rates of productivity across all size classes, with little evidence of a differential effect. Thus, the observed differences in volumetric productivity

rates and biomass among size classes must have been due to other processes.

The most dramatic decrease in the biomass and volumetric productivity of large, chain-forming diatoms occurred in the transition to the coastal current and along the margins of the plume (Figures 2 and 3). In these areas, the density gradient was eroded as plume water mixed with shelf water (Figure 1). High chl-*a* concentrations were found at depth in the transition to the coastal current, which suggested that phytoplankton cells were sinking (Yost et al., 2007). In addition, concentrations of key, xanthophyllcycle pigments in the subsurface waters of this transitional region were elevated above the levels expected for cells adapted to this light climate, which also suggested rapid sinking of cells acclimated to surface conditions (Moline, 1998). In fact, sinking rates estimated from data on pigments were comparable to previous reports of 2-4 m d<sup>-1</sup> (Malone



Figure 4. Results from surveys made with a laser optical plankton counter (LOPC) during the LaTTE campaign. The background shows gradients in zooplankton biovolume concentrations [log(Zooplankton mm<sup>3</sup> m<sup>-3</sup>)], with low concentrations in the recirculating eddy and higher concentrations in the initial portion of the coastal current and further offshore. The inset shows the log(biovolume size spectra) plotted against both log(body volume in mm<sup>3</sup>) and equivalent spherical diameters in mm for stations corresponding to those shown in the background. Larger zooplankton were more numerous in the initial portion of the coastal current and further offshore.

and Chervin, 1979; Moline, 1998). Malone and Chervin (1979) proposed that sinking was the primary factor causing loss of large diatoms from the winter plume based on similar observations of declining chl-*a* concentrations in surface waters, increasing chl-*a* concentrations at depth, and a lack of grazing pressure.

Although the relationship between changes in the distribution of chl-*a* and changes in physical forcing in this study were consistent with sinking as the primary force shaping the phytoplankton assemblage, these results do not rule out a role for differential grazing. In particular, sinking does not explain why relatively equal chl-*a*-specific productivity rates across all size classes in the eddy gave rise to higher biomass and more rapid volumetric productivity in the largest size class (Figure 3). It is likely that zooplanktonic grazers responded to the physical, chemical, and biological gradients established during LaTTE (Dagg and Turner, 1982; Smith and Lane, 1988; Lonsdale et al., 1996).

#### **RESPONSES OF ZOOPLANKTON**

Data on zooplankton biovolumes generated by the LOPC indicated that fewer zooplankton from 100  $\mu$ m to 3.5 mm in equivalent spherical diameter were present in the recirculating eddy than in the transition to the coastal current, the initial portion of the coastal current, and a patch of shelf water slightly further offshore (Figure 4). Furthermore, biovolume spectra indicated that the size distribution of zooplankton followed a similar pattern, with larger zooplankton being more numerous in the coastal current than in the eddy. Using appropriate conversion factors, the minimum biomass was estimated to be 4 x 10<sup>3</sup> mg wet weight m<sup>-3</sup> or 1 x 10<sup>2</sup> mg C m<sup>-3</sup>, and the maximum biomass was estimated to be 4 x 10<sup>4</sup> mg wet weight m<sup>-3</sup> and 1 x 10<sup>3</sup> mg C m<sup>-3</sup>.

To translate data on biovolumes to estimates of grazing pressure, dilution experiments were used to estimate instantaneous microzooplankton grazing rates (g; Box 1) and addition experiments were used to estimate instantaneous mesozooplankton grazing rates (z). Samples for these experiments were taken at stations in the eddy, the transition zone, and the coastal current. Grazing rates were estimated for multiple photosynthetic and accessory pigments across three size classes of phytoplankton, 0.2–2 µm, 2–20 µm, and > 20 µm.

The results indicated that instantaneous microzooplankton grazing rates were highest in the eddy, with decreasing rates recorded in the transition to the coastal current and beyond (Figure 5). In the eddy, microzooplankton grazed primarily on diatoms in the < 20-µm size classes, as shown by the grazing rates calculated from changes in fucoxanthin. In the transition zone, microzooplankton grazed on 2–20-µm cells, with the highest rates derived from changes in alloxanthin, which indicated grazing on cryptophytes. In the coastal current, diatoms and cryptophytes in the > 20-µm size class were grazed at a relatively low rate.

By Thomas K. Frazer

Grazing plays a major role in determining the fate of materials delivered to coastal regions by riverine plumes. Classical food webs emphasize photosynthetic production by net phytoplankton, grazing by mesozooplankton (200–500  $\mu$ m), and predation by larger zooplankton and fish. Improved estimates of abundances and turnover rates for smaller organisms indicate that, on average, up to half of all oceanic primary production channels through bacteria (Azam, 1998) and significant amounts of production are consumed by a diverse array of zooplanktonic grazers smaller than 200  $\mu$ m (microzooplankton; Calbet and Landry, 2004). New insights into the pathways and rates comprising these trophic interactions arise continually, and an understanding of their full importance awaits further research.

A full understanding of microbial food webs is hampered by the sizes of the players and their varied and variable trophic strategies, including autotrophy, heterotrophy, and mixotrophy. Dilution experiments provide an alternative to determining grazing rates for microzooplankton by indirect, labor-intensive, and taxonomically selective techniques (Riley, 1956; Beers and Stewart, 1971; Heinbokel, 1978a, b; Heinbokel and Beers, 1979; Capriulo and Carpenter, 1980; Landry and Hassett, 1982).

In dilution experiments, filtering removes macrozooplankton and mesozooplankton from whole seawater, and a finer filter removes microzooplankton from a portion of this filtrate. The





two types of water are combined to create replicate treatments across a range of dilutions, and nutrients are added in excess to eliminate limitation. Concentrations of chlorophyll *a* or accessory pigments are measured at the start of an experiment ( $P_o$ ), treatments are incubated for a given time (*t*), and final pigment concentrations ( $P_t$ ) are determined at the end of the incubation period. It is assumed that any changes in pigment concentrations are related to apparent phytoplankton growth rates (*k*) and instantaneous microzooplankton grazing rates (*g* in d<sup>-1</sup>) according to the formula:

$$P_t = P_0 e^{(k-g)t}$$

Estimation of grazing rates depends on two other assumptions: (1) the density of phytoplankton cells does not affect their growth rates and (2) grazing is not saturated so the consumption of a phytoplankton cell is solely a function of the rate at which it is encountered, which should decrease as phytoplankton and microzooplankton grazers are diluted. If all three assumptions hold, then the grazing rate equals the slope of a least squares linear regression through estimates of apparent phytoplankton growth rates, k (Figure 1). These values are calculated by rearranging the formula above and including the proportion of water containing microzooplankton (D):

$$\frac{1}{t} \ln \frac{P_t}{P_0} = k - Dg$$

Dilution experiments have become a common tool for estimating the impacts of microzooplankton grazing on natural assemblages of phytoplankton. However, interpretations can be complicated by: (1) nonlinear results, which may reflect saturated grazing in less dilute treatments (Redden et al., 2002); (2) positive regressions, which may indicate a stimulation of phytoplankton growth rates; and (3) nonsignificant regressions, which may or may not reflect a lack of grazing. Continued research on microbial food webs and techniques to understand them will improve our ability to manage the effects of human inputs on coastal regions.

**Thomas K. Frazer** (*frazer@ufl.edu*) is Research Foundation Professor, Department of Fisheries and Aquatic Sciences, University of Florida, Gainesville, FL, USA. As expected, some experiments yielded no evidence of grazing (Box 1).

Instantaneous mesozooplankton grazing rates were lower than the rates observed for microzooplankton (Figure 5). In addition, some experiments indicated increases rather than decreases in phytoplankton pigments, which were translated into negative grazing rates. Mesozooplankton grazing rates in the eddy were low, and grazing was heaviest on the two smaller cryptophyte size classes. Mesozooplankton grazed on cryptophytes in all size classes in the transition zone. Grazing on diatoms in the > 20-µm size class was observed in the coastal current.

The results of grazing experiments were consistent with data on phytoplankton and zooplankton. The relatively small zooplankton found in the recirculating eddy would not be expected to graze heavily on phytoplankton in the >  $20-\mu m$ size class, which primarily was comprised of chain-forming diatoms. In fact, the most common zooplankters in the





eddy were copepodite stages of *Arcartia hudsonica*, and the adults of this species grow to be no more than twice as long as the chains formed by the most common diatoms, *Thalassiosira nordenskioldii* and *Skeletonema costatum*.

# BIOLOGICAL PROCESSING OF METALS

Concentrations of metals were determined in samples of water, particles, and zooplankton taken within and outside the recirculating eddy. To parallel sampling of phytoplankton, concentrations of particulate metals were determined separately for two size classes of particles, 2–20 µm and > 20 µm.

Dissolved metal concentrations within the eddy typically were ranked iron (Fe) > copper (Cu) and zinc (Zn) > nickel (Ni) > cadmium (Cd) > lead (Pb) > silver (Ag) > mercury (Hg), and all concentrations decreased as salinities increased in water that exited the eddy and mixed with more saline shelf water that had lower metal concentrations. In addition to illustrating dilution of Hudson River plume water with shelf water, the concentration of some particulate metals, including Ag, Cu, Fe, and Pb exhibited more complex, nonconservative changes in the heart of the recirculating eddy (salinities of 22 to 24) indicative of the uptake by suspended particles, including phytoplankton (Figure 6). The mixing pattern of total Hg was fairly conservative throughout the salinity range, while monomethylmercury showed a more complex pattern in the plume.

Concentrations of particulate metals in samples from within the eddy were higher than concentrations in samples from surface waters on the shelf, as predicted by phytoplankton biomass accumulation in this region. On a volumetric basis, particulate metals were roughly evenly divided between the two size classes, in contrast to particulate phosphorus (64% in the > 20-µm size class) and phytoplankton biomass (70% in the > 20-µm size class). However, particulate metals were correlated with particulate phosphorus within each size class, suggesting that scavenging of particle metals was controlled by biogenic material. Mass-specific metal concentrations in both particle size classes decreased only slightly with salinity, which indicated that binding of metals and particle composition remained relatively uniform across the observed spatial gradients and were consistent throughout the plume's lifetime.

Results also indicated that metals were transferred to zooplankton. Zooplankton from lower-salinity waters closer to the mouth of the Hudson River estuary were enriched in most metals, which correlated spatially with elevated concentrations of particulate and dissolved fractions. In comparison to oceanic copepods, zooplankton from the recirculating eddy were significantly enriched in Ag, Cu, Pb, Zn, and monomethylmercury (the form of mercury that biomagnifies in aquatic trophic webs), but not enriched in Cd (Table 1). For example, copper concentrations in zooplankton were higher in the heart of the recirculating eddy than at its perimeter (Figure 7), and concentrations in zooplankton were positively correlated with concentrations in both small and large phytoplankton (Figure 8). In contrast to copper, the concentrations of Ag and inorganic Hg were enriched in zooplankton taken from higher-salinity water near the edges of the plume.



Figure 6. Concentrations of particle-bound trace metals vs. salinity (S) in the recirculating eddy of the Hudson River plume (S = 22–25), coastal current (S = 25–29), and adjacent shelf waters (S > 29) during April 2005. For Ag, Cu, Fe, and Pb, concentrations on particles > 2  $\mu$ m are represented by orange squares, and concentrations on particles > 20  $\mu$ m are represented by blue squares. Concentrations of particulate total mercury (Hg<sub>T</sub>) and monomethylmercury (MeHg) are for particles > 0.2  $\mu$ m and > 0.7  $\mu$ m, respectively.

Table 1. Metal enrichment in zooplankton from the Hudson River plume during April 2005 relative to oceanic, crustacean mesozooplankton. The + symbol indicates significant enrichment, and the significance levels indicate the results of nonparametric Kolmogorov-Smirnoff tests. NS indicates that metal concentrations in the two types of mesozooplankton were not significantly different at the 95% level.

Element	Enrichment	Significance Level
Ag	+	p = 0.002
Cu	+	p < 0.001
HgT	NS	p = 0.680
MeHg	+	p < 0.001
Pb	+	p = 0.013
Zn	+	p = 0.004



Figure 7. Copper concentrations in zooplankton from the Mid-Atlantic Bight (primarily the calanoid copepod *Acartia hudsonica*) during April 2005, with higher concentrations in organisms from the recirculating eddy of the Hudson River plume. Data relate to three size classes of zooplankton: 200–500  $\mu$ m (circles), 500–1000  $\mu$ m (triangles), and > 1000  $\mu$ m (star).

Copper concentrations in zooplankton were higher than those in both size classes of phytoplankton, indicating Cu biomagnification at this trophic level. In addition, assuming that accumulation of dissolved Cu by zooplankton was relatively constant across our sampling range and less important than trophic uptake, the accumulation of Cu from smaller phytoplankton appears to be more influential when differences in biomass and grazing pressure between the two sizes are considered (Figure 8).

# BROADER IMPLICATIONS OF COASTAL BUOYANT RIVER PLUMES

The results of sampling and experiments conducted during the April 2005 LaTTE campaign yielded three important implications regarding the functioning of the Hudson River estuary related to carbon flow, dissolved oxygen concentrations



Figure 8. Relationships between Cu concentrations in zooplankton (> 500  $\mu$ m) and two size classes of phytoplankton (2–20  $\mu$ m and > 20  $\mu$ m) in the Hudson River plume during April 2005. Copper enrichment in zooplankton was found in all samples, and it was strongly dependent on phytoplankton concentrations for both size classes. Copper concentrations were twice as high in the 2–20  $\mu$ m fraction; however, the biomass represented by this size class was half that of the > 20  $\mu$ m fraction, indicating that Cu availability was equal between the phytoplankton size classes. This result combined with the low rates of grazing on the larger size class (see Figure 5) suggested that the majority of the Cu enrichment in zooplankton was derived from the 2–20  $\mu$ m fraction.

in bottom waters, and metal bioaccumulation (Figure 9). These results also contrast with and serve to enhance our understanding of these processes in other coastal regions influenced by major rivers.

### **Carbon Flow**

Patterns in chl-*a* concentrations attributed to large and small phytoplankton highlighted the main pathways for nutrient uptake and carbon fixation during the LaTTE campaign (Figure 9). In contrast to Lonsdale et al. (1996) who proposed that phytoplankton size structure in the lower Hudson River estuary resulted from differential growth rates, our data suggested that phytoplankton of all sizes were growing efficiently. Our



Figure 9. Conceptual model of processes observed during LaTTE 2005. The relative sizes of boxes with the same color indicate their relative contributions to biomass or concentrations, as appropriate. The relative sizes of arrows with the same color indicate their relative contributions to various fluxes. Micro = microzooplankton grazing; Meso = mesozooplankton grazing;  $< 2 \mu$ m,  $2-20 \mu$ m, and  $> 20 \mu$ m = size classes for phytoplankton; Nutrients = concentrations of macronutrients; Metals = concentrations of metals; Plume water and recirculating eddy = the key physical feature observed during LaTTE; Shelf water = water beyond the plume and outside the coastal current; Coastal current = the flow of water southward along the coastline of New Jersey. Within the eddy, phytoplankton rapidly assimilated nutrients, resulting in extremely high productivity rates, especially for large, chain-forming diatoms. As water exited the eddy and became entrained in a southward flowing coastal current, the taxonomic composition of the phytoplankton assemblage changed, and the size distribution shifted toward smaller size classes. In addition, larger mesozooplankton became more abundant in the coastal current. Size-specific and pigment-specific grazing rates for microzooplankton were higher than those for mesozooplankton, especially in the eddy, and combined grazing on larger phytoplankton was highest in the coastal current. Grazing pressure affected carbon transfer, with evidence that large phytoplankton escaped grazing, sank, contributed to carbon flux to the bottom waters, and increased the likelihood of low dissolved oxygen concentrations. In contrast to nutrients, metals were equally distributed between small and large phytoplankton cells, and they were transferred to zooplankton. Ultimately, metals that entered the trophic web could accumulate in higher trophic levels. Overall, the nature of interactions among physical, chemical, and biological processes had a profound influence on the transfer, transformation, and ultimate

results also indicated that the observed patterns would have been influenced by differences in grazing pressure. In particular, grazing by microzooplankton may have restricted the accumulation of small cells within the recirculating eddy. The relatively low numbers and small sizes of mesozooplankton in the eddy reduced the grazing pressure on large, chain-forming diatoms, allowing their biomass to increase rapidly. In the southerly flowing coastal current, increased numbers of mesozooplankton, especially larger animals, and a decrease in the abundance of diatom chains probably resulted in higher instantaneous mesozooplankton grazing rates on diatoms in the > 20- $\mu$ m size class. These results were similar to those of past studies of grazing in the Hudson River plume, which found that only 1% of the biomass present during a bloom of large chain-forming diatoms was incorporated into zooplankton as opposed to 26% when small flagellates dominated (Malone, 1971; Malone and Chervin, 1979; Chervin et al., 1981).

The size structure of phytoplankton assemblages and the timing of coastal blooms significantly influence the transfer of carbon to higher trophic levels; thus, the trophic interactions observed here served as an excellent example of a mismatch between food availability and grazing capacity. Although the match/ mismatch hypothesis was originally applied to fisheries biology (Cushing, 1969, 1990), it is now recognized as a more general concept governing most predator-prev interactions (Durant et al., 2007; Grémillet et al., 2008). Here, the record spring runoff led to a phytoplankton bloom that outpaced the response of the coastal zooplankton assemblage, resulting in the loss of the majority

of phytoplankton carbon to higher trophic levels due to sinking. Similarly, along the Belgian coast, Rousseau et al. (2000) encountered a trophic mismatch between the zooplankton assemblage and a rapid accumulation of *Phaeocystis* colonies, resulting in over 90% of the carbon generated during the spring escaping higher trophic levels to support bacterial production and remineralization. Changes in temporal matches and mismatches among components of coastal zooplankton assemblages also have been tied to climate change, with climate-induced changes in physical and chemical forcing combining with changes in biological interactions to alter coastal ecosystems (Costello et al., 2006; Harley et al., 2006).

### Oxygen Availability

Carbon flux to the benthos represents a key determinant of oxygen availability in bottom waters. For example, in 1976, a combination of factors (larger than normal river discharge, an excessively hot summer, and a lack of storms) resulted in early stratification of the Mid-Atlantic Bight, a large phytoplankton bloom, significant export of organic carbon to bottom waters, and subsequent decomposition that caused hypoxic/anoxic conditions across the shelf (Figley et al., 1979; Falkowski et al., 1980; Stoddard et al., 1986). This large-scale event and associated economic losses prompted the initiation of long-term monitoring of dissolved oxygen concentrations in the New York Bight (Atwood et al., 1979). Monitoring and recent work revealed that the initial hypothesis linking low dissolved-oxygen concentrations to anthropogenic loadings may not fully explain the phenomenon (Steimle, 1978). Ancient river deltas off the southern coast of New Jersey promote centers of recurrent upwelling along the shore (Song et al., 2001). Several centers are collocated with historical regions of low dissolved oxygen, and the upwelling may provide sufficient organic matter to cause hypoxia/anoxia (Glenn et al., 2004). However, this mechanism does not explain the zone of low dissolved oxygen at the junction of the Hudson River and the ocean, which is not collocated with a center of upwelling. The results from LaTTE suggest that high algal productivity near the mouth of the Hudson River could account for observations of low oxygen in this region.

During LaTTE, the breakdown of the density gradient in the coastal current and along the margins of the recirculating eddy appeared to promote sinking of chain-forming diatoms (Figure 9). Frazer et al. (2006) found that this flux may have led to a 40% decrease in dissolved oxygen concentrations in deeper water at stations south of the transition from the plume to the coastal current. Oxygen concentrations remained supersaturated in the recirculating eddy, with a linear decrease in absolute concentration paralleling an increase in salinity from 18 to 29, but oxygen concentrations decreased exponentially in the highersalinity bottom waters to less than 70% saturation. The increased rate of oxygen decline and the lack of conservative mixing at salinities greater than 30 suggested that oxygen consumption was related to processing of particulate organic carbon, such as sinking diatom cells, rather than a response to conservative mixing of dissolved organic carbon in upwelled water (Kowalczuk et al., 2003).

Rapid deposition of carbon and

subsequent decreases in dissolved oxygen are increasing in frequency and intensity near the mouths of many of the world's river systems (Cloern, 2001). These situations likely arise from both an overall increase in phytoplankton carbon due to eutrophication and changes in phytoplankton assemblages, leading to mismatches between grazers and producers that result in higher fluxes of carbon to the benthos (Rousseau et al., 2000; this study). Coastal systems support a disproportionate amount of the world's fisheries and recreation, so the economic and social costs of these hypoxic/anoxic events are amplified, especially in regions undergoing rapid development (Cloern, 2001; Gray et al., 2002). For example, China has seen unparalleled growth in the last decade, and with this economic expansion has come documented increases in nutrient inputs and significant declines in dissolved oxygen in the coastal estuaries of the Yangtze River (Li et al., 2002), the Pearl River (Yin et al., 2004), and the Yellow River (Liu et al., 2003). These systems resemble the Hudson River estuary, with strong two-layered stratification in a buoyant plume and a high flux of phytoplankton to the benthos, especially at the edge of the plume (Yin et al., 2004).

### Accumulation of Metals

If accumulation of metals followed the same pattern as accumulation of nutrients and carbon, metals would have concentrated initially in larger phytoplankton cells because, on average, 64% of the phytoplankton biomass was contained in the largest size class measured and only 36% was contained in the smaller size classes. Larger cells would have escaped grazing and been subject to sinking, which would have reduced the transfer of metals through the trophic web to zooplankton and beyond. However, particulate metals were nearly equally distributed among cells in the > 20- $\mu$ m and 2–20- $\mu$ m size classes, which indicated a lower effective rate of uptake in larger cells (Figure 9). Thus, metals remained vulnerable to grazing and available for transfer through the trophic web as the enrichment in zooplankton showed (Table 1, Figure 8).

Results from a simple box model of metal cycling in the plume indicated that particulate metals were largely depleted within 50 km of Lower New York Bay, with very little transport further downshelf in the coastal current. A potentially important implication of this result is that particulate metals sinking below the plume may be carried back toward Lower New York Bay because the net flow of bottom water is to the north (opposite to the flow of the plume). 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. Our model also showed that delayed but significant cross-shelf transport of metals was possible because dissolved and particulate metal concentrations in the recirculating eddy remained elevated relative to shelf waters for up to five days, the typical lifespan of an eddy.

In parallel to nutrients, metal concentrations often exceed water-quality standards in buoyant river plumes. Although the concentrations of metals measured in this study were relatively high and bioaccumulation was evident, these potentially detrimental results pale in comparison to reports from other regions of the world. Liu et al. (2003),

for example, documented the impact of industrialization in the watershed feeding Bohai Bay, China, and they consistently recorded concentrations of Pb, Ag, Cu, and Zn that were four orders of magnitude higher than values in this study. Gagnon and Saulnier (2003) also recorded high metal concentrations in wastewater discharged to the St. Lawrence Seaway, Canada. Of particular note in this study was variation in the partitioning of metals between dissolved and particulate phases as a function of distance from the discharge point, which suggests that the potential for bioaccumulation also would vary on scales of 5-10 km. Accumulation of metals in food webs ultimately depends on the background concentrations, the phases of the metals, accumulation rates, retention rates, and tolerance ranges of relevant organisms. Recent studies highlight the pervasiveness of metals in coastal food webs. Benthic macrofauna in the Adour estuary, France, accumulated metals according to feeding guilds, with higher bioaccumulation observed in deposit feeders as compared to suspension feeders and predators (Monperrus et al., 2005). Durrieu et al. (2005) recorded metal contamination in eight fish species from the Gironde estuary, France, with the highest concentrations found in species that resided in the estuary throughout much of their life histories. Endo et al. (2007b, 2008) found accumulation of Hg, Cd, Fe, Mn, Zn, and Cu to be age-dependent in killer whales and tiger sharks. Total Hg concentrations in most samples of muscle and liver tissue from 12 apex predators sold in Korean markets, including whales, porpoises, and dolphins, exceeded safe limits for human consumption (Endo et

al., 2007a). In one of the first attempts at assessing bioaccumulation of metals in a complete food web, Ruelas-Inzunza and Páez-Osuna (2008) found that the most prevalent metal in the food web of the Altata-Ensenada del Pabellón lagoon in the Gulf of California was Zn, followed by Pb and Cd. Almost 65% of trophic links showed evidence of biomagnification, with Pb being the most pervasive in higher trophic levels, and Cd and Zn commonly found in primary producers and primary consumers. Although these studies clearly demonstrate the capacity for bioaccumulation of metals in coastal and estuarine food webs, the physiological and life history effects of chronic body loads in most organisms remains unknown.

### SUMMARY

The Hudson River plume was highly dynamic and characterized by marked gradients in physical and chemical characteristics that drove biological responses. During the April 2005 LaTTE campaign, nutrient-laden, low salinity water from the Hudson River recirculated in a nearshore eddy before dispersing south and across the shelf to mix with the relatively saline waters of the New York Bight. Within the eddy, phytoplankton rapidly assimilated nutrients, resulting in extremely high rates of productivity, with over 70% of carbon fixation attributed to large, chain-forming diatoms. As water exited the eddy and became entrained in a southward flowing coastal current, the taxonomic composition of the phytoplankton assemblage changed, and the size distribution shifted toward smaller size classes. In addition, larger mesozooplankton became more

abundant outside the recirculating eddy and in the coastal current. Size-specific and pigment-specific grazing rates for microzooplankton were higher than those for mesozooplankton, especially in the eddy, and combined grazing on larger phytoplankton was highest in the coastal current. Grazing pressure affected carbon transfer, with evidence that large phytoplankton escaped grazing, sank, contributed to carbon flux to the bottom waters, and increased the likelihood of low dissolved oxygen concentrations. In contrast to nutrients, metals were equally distributed between small and large phytoplankton cells, and the metals were transferred to zooplankton, with maximum transfer in the buoyant plume. This transfer made accumulation in higher trophic levels possible. The nature of interactions among physical, chemical, and biological process profoundly influenced the transfer, transformation, and ultimate fate of nutrients, metals, and organic carbon in the Hudson River plume. These findings serve to enhance our understanding and management of other coastal regions influenced by inputs from major rivers.

Formation of recirculating eddies in the plumes of major rivers has been predicted and modeled but seldom documented (Fong and Geyer, 2002; Avicola and Huq, 2003; Horner–Devine et al., 2006; Chant et al., this volume). If similar combinations of forcing factors create recirculating eddies in the discharge plumes of other major rivers, then we would predict similar dynamics for nutrients and metals and similar potential consequences for the integrity of coastal systems. In particular, a better understanding of the drivers, frequency, and duration of such events would improve predictions of hypoxia and bioaccumulation of metals. Such improved predictions will be of particular value for coastal regions at the mouths of rivers, such as the Changjiang (Yangtze) and Pearl Rivers in China, which have altered river flow due to dams, large nutrient loads due to increasing agricultural use of fertilizers or higher sewage inputs from burgeoning populations, and increased trace metal loads due to expanding industry. If altered flow rates increase the frequency or duration of recirculating eddies, then the dynamics governing the processing of nutrients and metals may lead to further environmental degradation.

Managers of coastal systems and the watersheds of major rivers can derive valuable guidance from LaTTE results. This investigation of a recirculating eddy indicated that a short-term event dramatically altered the fate of nutrients, carbon, and metals from that expected as a response to simple dilution, with potentially serious consequences for the ecological integrity of the Hudson River estuary. The frequency of such shortterm events must be factored into calculations of total maximum daily loads as important deviations from the "average" ability of a system to assimilate inputs. In addition, the possibility that the frequency and duration of such events will be altered under different flow regimes needs to be considered when setting minimum flows for rivers. Continued study of the relationships among coastal processes and efforts to synthesize the results of these studies will enhance sustainability of coastal resources.

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