

## The influence of river plume dynamics on trace metal accumulation in calanoid copepods

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### Abstract

The concentrations of Ag, Cd, Cu, Hg(II), monomethylmercury (MeHg), Pb, and Zn were measured and modeled in calanoid copepods collected from the Hudson River plume in April 2005 and May 2006. Copepods in the buoyant plume were significantly ( $p < 0.05$ ) enriched in Ag, Cu, Pb, Zn, and MeHg (2- to 25-fold), but depleted in Cd (by 25–40%) relative to oceanic copepods. Median burdens of Ag, Cu, and Hg(II) differed in plume copepods collected in April 2005 and May 2006 by factors of 1.5 to 3, reflecting the influence of river discharge and associated physical processes on plankton dynamics and metal bioaccumulation. Only the concentrations of Cu and Zn in plume copepods clearly showed the expected trend of highest levels near the mouth of the Hudson River and lower levels offshore. Spatial trends in concentrations of Ag and Hg(II) in plume copepods were strikingly different from those in suspended particles and the dissolved phase, apparently reflecting differences in metal bioavailability because of shifts in available food types. Modeled concentrations of Cd, Cu, Pb, and Zn in plume copepods were within less than a factor of two of measured values, but model results showed that Hg(II) was less bioavailable, and Ag and MeHg were more bioavailable in the Hudson River plume than laboratory results would predict. Zooplankton from urban river plumes may accumulate potentially toxic levels of trace metals or act as a trophic link between metal contamination in polluted estuaries and pelagic ecosystems.

As one of the most urbanized estuaries in the world, the lower Hudson River and its seaward extension, the buoyant Hudson River plume, receives inorganic and organic contaminants from sewage outfalls, urban runoff, atmospheric deposition, and legacy loads from historically contaminated industrial sites (Brown et al. 1985; Sañudo-Wilhelmy and Gill 1999). The discharge of water from the Hudson River forms a buoyant plume in the New York Bight with potential to transport contaminants directly to the coastal ocean, where they can enter the benthic and pelagic food webs found on the continental shelf. The transport of Hudson River plume water and its associated contaminants depends directly on discharge volume and physical forcing in the coastal ocean. Formation of a coastal current under downwelling favorable winds, for example, could result in rapid alongshore (southward) transport of plume water, whereas the formation of recirculating eddies delays alongshore transport and can result in cross-shelf transport if shifting winds advect surface waters offshore (Chant et al. 2008). How the physical structure and movement of river plumes affect the bioaccumulation of trace metals at the base of coastal food webs is not known.

In fact, few field studies document bioaccumulation of trace metals in estuarine or oceanic zooplankton despite the importance of these organisms in the cycling of metals and their potential value as bioindicators of metal pollution (Miramand et al. 2001; Fang et al. 2006; Zauke and Schmalenbach 2006). Even less is known about metal accumulation in zooplankton within and at the boundaries of river plumes, which represent major sources of metals to the coastal ocean.

The accumulation of trace metals by marine zooplankton has been examined primarily in laboratory experiments, which show that key controlling factors include concentrations and aqueous speciation of dissolved metals, uptake rates for dissolved metals, accumulation and intracellular partitioning of metals in organisms ingested as food (especially phytoplankton), and relative rates of intake through feeding and loss through efflux (Reinfelder et al. 1998; Wang and Fisher 1998). Quantitative models of bioaccumulation in marine zooplankton have the potential to predict total metal accumulation in target organisms (Roditi et al. 2000; Kahle and Zauke 2002; Mathews and Fisher 2008), and they also can be used to apportion bioaccumulation between ingestion and uptake of dissolved forms (Reinfelder et al. 1998; Wang and Fisher 1998). The partitioning of accumulation among uptake pathways is important because metals delivered directly to internal tissues through feeding could be biomagnified (Mathews and Fisher 2008) or exert significantly higher toxicity than metals taken up from the dissolved phase (Hook and Fisher 2001). Bioaccumulation models have been validated with field data only in a limited number of studies (Fisher et al. 2000; Luoma and Rainbow 2005).

In this study, bioaccumulation of trace metals at the base of the trophic web in the buoyant plume of the Hudson River was assessed by measuring concentrations of Ag, Cd, Cu, inorganic Hg, monomethylmercury (MeHg), Pb and Zn in zooplankton (> 90% calanoid copepods), suspended particles, and the dissolved phase of surface water collected during April 2005 and May 2006. All of these metals have histories of industrial point and nonpoint sources to East Coast estuaries (Rozan and Benoit 2001) and are enriched relative to both background concentrations and probable effects levels in Hudson River sediments (Bopp et al. 2005).

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Table 1. Zooplankton net tow locations and depths in the Hudson River plume, April 2005 and May 2006. Temperature (Temp.) and salinity (S) data are for surface water (1.5 m). Lat., latitude; Long., longitude; Sta., station.

Sta.	Date	Time (h)	Lat.	Long.	Depth (m)	Temp. (°C)	S
10B1	10 Apr 05	19:52	40.348	73.922	5	7.0	23.55
11C2	11 Apr 05	18:30	40.389	73.908	7	7.6	23.49
12B2	12 Apr 05	17:32	40.350	73.943	7	7.7	23.71
13A1	13 Apr 05	13:50	40.230	73.882	5	7.2	26.11
14G1	14 Apr 05	19:41	40.304	73.581	10	5.8	31.50
14K1	14 Apr 05	23:57	40.372	73.763	5	5.8	31.50
17J1	17 Apr 05	20:26	40.342	73.887	5	11.2	24.01
18H1	18 Apr 05	17:08	40.166	73.978	5	9.8	24.66
19A1	19 Apr 05	13:12	39.999	74.034	7	8.0	27.47
3F	03 May 06	23:08	40.253	73.963	3	12.8	26.23
4A	04 May 06	13:30	40.243	73.958	3	13.1	26.10
4C	04 May 06	18:56	40.285	73.945	3	12.8	27.02
4D	04 May 06	20:09	40.268	73.958	3	12.9	27.14
4E	04 May 06	21:45	40.246	73.963	3	15.6	25.38
4F	04 May 06	22:29	40.202	73.962	3	14.1	26.69
5C	05 May 06	14:48	40.000	73.918	2	12.6	29.08
5D	05 May 06	17:02	39.860	73.854	2	13.8	29.46
5E	05 May 06	18:42	40.005	73.858	2	13.0	29.02
5F	05 May 06	20:31	40.067	73.782	2	14.6	28.58
5G	06 May 06	00:02	40.048	73.770	2	14.3	27.70
6A	06 May 06	12:33	39.982	73.754	2	14.5	27.70
6B	06 May 06	18:43	39.982	73.755	2	15.5	27.95
7A	07 May 06	12:28	39.978	73.612	5	10.2	32.09
7B	07 May 06	15:21	40.021	73.570	5	10.2	32.17
7C	07 May 06	17:04	40.024	73.644	5	10.4	32.04
7D	07 May 06	18:47	40.020	73.761	5	11.2	31.51
7F	07 May 06	20:48	40.020	73.870	5	13.3	30.05
7G	07 May 06	22:36	40.021	73.911	5	13.1	29.86
7H	07 May 06	23:47	40.018	73.939	5	12.7	29.98
7I	07 May 06	00:55	40.018	73.969	5	12.6	30.42

Five metals (Ag, Cd, Cu, Hg, and Zn) have the potential to cause sublethal toxic effects in marine copepods (Hook and Fisher 2001, 2002; Bielmyer et al. 2006), and Ag is a tracer of wastewater effluent (Sañudo-Wilhelmy and Flegal 1992). This work was conducted as part of the Lagrangian Transport and Transformation Experiment (LaTTE), which was designed both to track the buoyant plume of the Hudson River as it enters the New York Bight and to assess the transport, transformation, and fate of nutrients and contaminants in relation to plume dynamics (Chant et al. 2008; Moline et al. 2008). Here, we specifically examine the accumulation of contaminant trace metals in plume copepods with respect to the physical structure of the plume and the composition of its planktonic assemblages, compare model predicted metal accumulation with observations, and assess the potential toxicity of accumulated metals.

## Methods

**Field sampling**—Discharge from the Hudson River was tracked in April 2005 and May 2006 with the use of a broad suite of shipboard, moored, remotely operated, and land- and satellite-based instruments (Chant et al. 2008). The April 2005 field experiments were conducted after a major river discharge event that resulted in the formation of a large rotating eddy in the New York Bight. In contrast, the

May 2006 experiment was conducted during moderate discharge that resulted in a broad, southward-flowing coastal current, which formed an offshore jet south of the New York Bight.

**Sample collection**—Zooplankton samples were collected from the Hudson River plume and waters on the inner shelf from the R/V *Oceanus*. Mesozooplankton were collected with a 1-m diameter ring net (202- $\mu$ m mesh fitted with a nonfiltering cod end) that was towed vertically (~25 m min<sup>-1</sup>) through the upper mixed layer (< 10 m) at each sampling station (Table 1). Zooplankton adhering to the net on retrieval were washed gently into the cod end before processing on deck. The contents of the cod end were transferred to a small plastic tub, and the > 202- $\mu$ m fraction of the sample was further concentrated by gently passing the entire sample through a 202- $\mu$ m plastic sieve. Concentrated zooplankton samples were size fractionated with nylon sieves (4000, 2000, 1000, 500, and 200  $\mu$ m). Material retained on the 1000-, 500-, and 200- $\mu$ m sieves was transferred with a clean plastic spatula to acid-cleaned cryovials and stored frozen.

Surface water was collected from the Hudson River plume with the aid of an underway sampling system on a second ship, the R/V *Cape Hatteras*. The underway sampling system consisted of a capped and perforated Teflon pipe attached to a 1.25-cm outer diameter Teflon

tube attached to the seaward side of an aluminum bracket at the end of a vertically mounted stainless steel pole. The Teflon pipe extended 30 cm forward of the aluminum bracket and approximately 1.5 m outboard of the ship's hull. Samples were pumped onboard with a Teflon and polypropylene bellows pump at a rate of at 3–4 L min<sup>-1</sup>. Before use, all wetted parts of the uptake system were leached in 10% HCl for a minimum of 72 h and rinsed copiously with ultra-high-purity water. In addition, the uptake system was flushed extensively with surface water from the Middle Atlantic Bight beyond the influence of the Hudson River plume before sampling.

Surface water samples were handled using trace metal clean techniques during all phases of collection and manipulation to minimize contamination. Seawater was pumped directly into a clean bench enclosed on three sides with plastic sheeting and supplied with positive air pressure from a class 100 high-efficiency particulate air (HEPA) filter. Whole-water samples were transferred to an adjacent clean bench for filtering. Samples for dissolved metals were filtered in-line with a high-capacity 0.2- $\mu$ m polypropylene cartridge filter and collected in acid-cleaned polyethylene bottles. Samples for particulate metals were collected in either 4- or 8-L acid-cleaned polycarbonate carboys, homogenized, and vacuum filtered at < 130 mm Hg to minimize cell lysis. In April 2005, particulate metal samples were filtered in parallel to obtain separate size fractions of > 0.2  $\mu$ m, > 2  $\mu$ m, and > 20  $\mu$ m. In May 2006, only particles in the > 20- $\mu$ m size fraction were analyzed for trace metals. The > 2- $\mu$ m and > 20- $\mu$ m fractions were filtered onto acid-cleaned, 47-mm polycarbonate filters, and the > 0.2- $\mu$ m size fractions were filtered onto polyethersulfone (Supor<sup>®</sup>) filters. All filters were held in acid-cleaned Teflon filter supports. Filters were frozen immediately and stored at -20°C until masses were determined and metals analyzed. Difficulties in metal extraction and salt mass correction associated with the 0.2- $\mu$ m Supor filters resulted in uncertainties in quantification of metal concentrations in the 0.2–2.0- $\mu$ m size fraction (Wright 2008), which are not discussed here.

*Trace metal analyses*—Before analysis, thawed zooplankton samples were rinsed with ultra-pure water on a 160- $\mu$ m Nitex mesh to remove extraneous material (e.g., phytoplankton and salt). The resulting samples were transferred to acid-cleaned, preweighed polypropylene microcentrifuge tubes in preparation for digestion. Samples for determination of trace element composition (except those for Hg analysis; see below) were dried at 40°C to constant mass. Microcentrifuge tubes with dried zooplankton were weighed to  $\pm$  0.1 mg, and zooplankton dry weights were determined by difference. Samples were digested for  $\sim$  12 h in hot (60°C), 4-mol L<sup>-1</sup> nitric acid. Following digestion, samples were transferred to acid-cleaned, 15-mL centrifuge tubes and diluted to 5% acidity. Samples were then analyzed by radial inductively coupled plasma-optical emission spectrometry (ICP-OES; Varian, Vista-Pro). The accuracy of radial ICP-OES when quantifying low concentrations (nmol L<sup>-1</sup>) of some metals (Ag, Cd, and Pb) in diluted samples was enhanced approxi-

mately 5- to 10-fold by employing a high-sensitivity desolvating spray chamber (APEX E, Elemental Scientific). Yttrium was added to all samples, standards, and blanks as an internal standard to correct for variations in sensitivity (all corrections were < 10%). Whenever possible, multiple spectral lines were used to determine the concentration of each element and minimize the influence of spectral interferences. Appropriate analytical wavelengths selected for each element according to sensitivity and likelihood of spectral interferences were: 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, and Zn 334.502 nm. Where multiple wavelengths could be used for calibration of a given metal, good agreement (within 10%) generally was obtained. Digestion blanks were diluted in the same manner as the sample and analyzed with each sample run. More than 80% of blanks did not contain detectable concentrations of targeted metals. Repeat analysis of a quality assurance (QA) standard during each analytical batch yielded analytical precisions of 2–3%, measured as relative standard deviations (RSD, 1 $\sigma$ ) for the metals reported. The QA standard was prepared with the metals of interest at the following concentrations ( $\mu$ g L<sup>-1</sup>): Ag 14.4, Cd 6.0, Cu 30, Pb 2.5, Zn 30.

Zooplankton samples for Hg analysis were freeze dried and shipped to Quicksilver Scientific (Lafayette, Colorado) for analysis. Zooplankton were leached with acidic thiourea and subsequently analyzed for MeHg and 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 in zooplankton (Hg<sub>T</sub>) was calculated as the sum of MeHg and Hg(II). For MeHg in zooplankton, analytical precision ranged from 0.3% to 1.6% RSD, and for Hg(II), ranged from 1.3% to 4.2% RSD.

Particulate metals were digested in aqua regia and analyzed by high-resolution ICP mass spectrometry (HR-ICP-MS) using In as an internal standard to monitor drift in instrument sensitivity (Wright 2008). To minimize interference, all elements were determined in medium resolution (mass:  $\Delta$ mass = 4000) except Ag and Pb, which were determined in low resolution. To minimize matrix effects, calibration curves were constructed by spiking samples with various concentrations of a multielement standard solution. Ongoing precision and recovery were monitored by reanalyzing standards after every 10th sample. Coefficients of determination ( $R^2$ ) of calibration curves were typically > 0.998, and repeated analysis of standards throughout an analytical batch yielded precisions of 3–10% RSD (1 $\sigma$ ) for the reported elements. Dry weights of particulate matter were determined by weighing in triplicate to  $\pm$  0.1 mg before digestion, and these measurements were corrected for salt content using the results of sodium determination by ICP-OES.

Particulate Hg(II) was determined as the difference between particulate total Hg and particulate MeHg. Particulate total Hg was determined as the difference between total (unfiltered) and dissolved (<0.2  $\mu$ m filtered)

Table 2. Dissolved ( $> 0.2 \mu\text{m}$ ) trace metal concentrations in the Hudson River plume, April 2005 and May 2006. Values are means of 2–28 replicate samples for each location. The Cd value for April 2005 is based on direct-injection ICP-MS analyses of plume eddy samples ( $n = 8$ ). April 2005 samples were grouped as those from the plume's recirculating eddy, partially diluted plume water (transition), or inner shelf surface water (see Fig. 1). May 2006 samples were grouped as those from the plume's broad coastal current, the plume's offshore jet, a nearshore intrusion of shelf water, or inner shelf surface water. nd, not determined.

Event	Location	Concentration (nmol L <sup>-1</sup> )					
		Ag	Cd	Cu	Hg(II)	Pb	Zn
April 2005	Plume eddy	0.05	0.4	10	0.0024	0.11	10.9
	Transition	0.04	nd	5	0.0019	0.08	7.5
	Inner shelf	0.02	nd	2	0.0013	0.07	6.4
May 2006	Coastal current	0.05	nd	10	0.0030	0.17	9.0
	Offshore jet	0.04	nd	5	0.0030	0.16	9.2
	Intrusion	0.04	nd	5	0.0030	0.13	7.0
	Inner shelf	0.02	nd	2	0.0030	0.03	1.5

Hg. Samples for total and dissolved Hg analysis were preserved with 0.3% (v/v) BrCl immediately after collection and analyzed by SnCl<sub>2</sub> reduction, gold amalgamation, and cold vapor atomic fluorescence spectroscopy (Bloom and Creclius 1983). The precision for total unfiltered and dissolved Hg analyses ranged from 0.3% to 19% RSD and 2% to 8% RSD, respectively. Samples for particulate MeHg (10–40 L) were collected on 120-mm GF/F filters that had previously been baked in a muffle furnace at 500°C for 12 h before use and were held in a Teflon support. Loaded filters were transferred to acid-cleaned polystyrene filter holders and immediately frozen until analysis. Analysis of particulate MeHg was performed by Quicksilver Scientific.

The percent mass contributions of crustal rock to suspended particle samples were calculated as the ratios of the mass concentrations of Al in plume suspended particles and that in Hudson River suspended particles. An Al concentration of 4% was used for Hudson River suspended particles on the basis of values for Appalachian (3%) and New England (5%) rivers reported in Windom (1990).

Concentrations of dissolved trace metals were determined by dilution and direct-injection HR-ICP-MS (Ag and Cd, based on Field et al. 1999) or chelating column preconcentration and matrix separation HR-ICP-MS (Cu, Pb, and Zn, as in Wright 2008, based on Beck et al. 2002). In these analyses, blanks were generally 2–5% of Coastal Atlantic Surface Seawater (CASS-4) certified reference material and 3–10% of North Atlantic Surface Seawater (NASS-5) certified reference material (National Research Council, Canada) for elements other than Cd, in which the blank was generally  $< 1\%$  of reference material. Replicate analyses of CASS-4 and NASS-5 on three separate occasions were within 2–15% of certified values, with the exception of Cu, which was consistently below the certified value of CASS-4, and low, but generally within the certified range, for NASS-5. Replicate analyses yielded analytical precisions of 2–17% RSD ( $1\sigma$ ), which were typically lower than those associated with CASS-4 and NASS-5 certified values (CASS-4: Cd  $0.026 \pm 0.003$ , Cu  $0.592 \pm 0.055$ , Pb  $0.0098 \pm 0.0036$ , Zn  $0.381 \pm 0.057$ ; NASS-5: Cd  $0.023 \pm$

$0.003$ , Cu  $0.297 \pm 0.046$ , Pb  $0.008 \pm 0.005$ , Zn  $0.102 \pm 0.039$ ). Note that Ag values were compared with an in-house standard because neither reference material has a certified value for Ag.

*Bioaccumulation modeling*—Total and trophic accumulation of metals in plume copepods were estimated by a kinetic bioaccumulation model (Reinfelder et al. 1998; Wang and Fisher 1998). In this model, the total steady-state concentration of a metal in copepods ( $C_{ss}$ ), accumulated from both food and by direct uptake from the dissolved phase, is given by

$$C_{ss} = (AE \times IR \times C_p) / (k_{ef} + G) + (k_u \times C_w) / (k_{ew} + G) \quad (1)$$

where AE is the assimilation efficiency (%) of ingested metal; IR is the ingestion rate ( $\text{d}^{-1}$ );  $C_p$  is the concentration of metal in the copepod's food ( $\text{nmol g}^{-1}$ );  $k_{ef}$  and  $k_{ew}$  are the efflux rate constants ( $\text{d}^{-1}$ ) for metal accumulated from food and the dissolved phase, respectively;  $G$  is the zooplankton growth rate ( $\text{d}^{-1}$ );  $k_u$  is the rate constant for uptake of metal from the dissolved phase ( $\text{L g}^{-1} \text{d}^{-1}$ ); and  $C_w$  is the dissolved metal concentration ( $\text{nmol L}^{-1}$ ). Dissolved metal concentrations measured in the Hudson River plume in the same water masses as the zooplankton and suspended particle samples were used for  $C_w$  (Table 2). For dissolved MeHg, the average value for Raritan Bay measured by Balcom et al. (2008) was used for  $C_w$ . Metal concentrations measured in plume suspended particulate matter (Table 3) were used as those in food for copepods ( $C_p$ ). Other model parameters were drawn from the literature (Table 4). The model parameters AE and  $k_{ef}$  are relatively insensitive to the size of ingested phytoplankton (Wang et al. 1996b), but AE is sensitive to metal concentration in food (Xu et al. 2001) and food abundance (Xu and Wang 2001). Although studied in bivalves (Wang et al. 1996a) and some crustaceans (Rainbow and Black 2002), how metal accumulation and loss parameters vary with salinity in copepods is unknown. Copepod IR varies with food concentration and temperature (Durbin and Durbin 1992) and is perhaps the most variable parameter in the model. Ingestion rates were calculated from those measured by Lonsdale et al. (1996) in the lower Hudson

Table 3. Trace metal concentrations and percent crustal rock contribution in Hudson River plume suspended particles. Values are medians (nmol g<sup>-1</sup>, except MeHg and Hg(II), pmol g<sup>-1</sup>; Zn,  $\mu$ mol g<sup>-1</sup>) for size fractions of 2–20  $\mu$ m and > 20  $\mu$ m in April 2005 and for suspended particles > 20  $\mu$ m in May 2006. For both years, MeHg concentrations are for > 0.7- $\mu$ m particles and Hg(II) for > 0.2- $\mu$ m particles. Sample locations as in Fig. 1 and Table 3. curr., current; nd, not determined; ns, not sampled.

Event	Location	Median concentration							Crustal (%)
		Ag	Cd	Cu	Pb	Zn	MeHg	Hg(II)	
April 2005 (2–20 $\mu$ m)	Plume eddy	4.2	19	247	142	2.5	ns	ns	25
	Transition	3.5	105	174	103	1.6	ns	ns	22
	Inner shelf	0.7	448	49	52	nd	ns	ns	9
April 2005 (>20 $\mu$ m)	Plume eddy	3.0	20	192	75	nd	4.5	565	13
	Transition	1.6	21	120	39	nd	ns	350	6
	Inner shelf	0.6	8	37	20	nd	3.6	106	3
May 2006 (>20 $\mu$ m)	Coastal curr.	3.9	nd	213	138	2.4	23	4000	13
	Offshore jet	1.8	nd	102	48	1.8	17	1700	4
	Intrusion	1.6	nd	92	24	0.9	ns	1500	3
	Inner shelf	0.4	nd	4	22	0.5	13	250	0.2

Table 4. Parameters for model of metal bioaccumulation in copepods (*see text for model and parameter descriptions*). Ingestion rates (IR) were calculated from those measured by Lonsdale et al. (1996) in the lower Hudson River estuary in June, corrected for phytoplankton abundance (Gismervik and Andersen 1997) and temperature (Durbin and Durbin 1992). Curr., current.

Metal	Model parameters*				April 2005	IR (d <sup>-1</sup> )	May 2006	IR (d <sup>-1</sup> )
	AE (%)	$k_{ef}$ (d <sup>-1</sup> )	$k_u$ (L g <sup>-1</sup> d <sup>-1</sup> )	$k_{ew}$ (d <sup>-1</sup> )				
Ag	18 <sup>1</sup>	0.3 <sup>2</sup>	10 <sup>2</sup>	0.2 <sup>2</sup>	Eddy	0.39	Coastal curr.	0.56
					Trans	0.34	Offshore jet	0.52
					Shelf	0.24	Intrusion	0.48
Cd	30 <sup>1</sup>	0.3 <sup>2</sup>	0.7 <sup>2</sup>	0.1 <sup>2</sup>	Eddy	0.39	Coastal curr.	0.56
					Trans	0.34	Offshore jet	0.52
					Shelf	0.24	Intrusion	0.48
Cu	40 <sup>3</sup>	0.08 <sup>4</sup>	1 <sup>4</sup>	0.08 <sup>4</sup>	Eddy	0.39	Coastal curr.	0.56
					Trans	0.34	Offshore jet	0.52
					Shelf	0.24	Intrusion	0.48
Hg(II)	15 <sup>5</sup>	0.02 <sup>6</sup>	10 <sup>†</sup>	0.02 <sup>6</sup>	Eddy	0.39	Coastal curr.	0.56
					Trans	0.34	Offshore jet	0.52
					Shelf	0.24	Intrusion	0.48
MeHg	62 <sup>5</sup>	0.001 <sup>6</sup>	1 <sup>‡</sup>	0.001 <sup>6</sup>	Eddy	0.39	Coastal curr.	0.56
					Trans	0.34	Offshore jet	0.52
					Shelf	0.24	Intrusion	0.48
Pb	5 <sup>§</sup>	0.35 <sup>10</sup>	10 <sup>†</sup>	0.1 <sup>10</sup>	Eddy	0.39	Coastal curr.	0.56
					Trans	0.34	Offshore jet	0.52
					Shelf	0.24	Intrusion	0.48
Zn	60 <sup>2</sup>	0.08 <sup>2</sup>	2.7 <sup>2</sup>	0.11 <sup>2</sup>	Eddy	0.39	Coastal curr.	0.56
					Trans	0.34	Offshore jet	0.52
					Shelf	0.24	Intrusion	0.48
							Shelf	0.35

\* References: <sup>1</sup> Reinfelder and Fisher 1991, <sup>2</sup> Wang and Fisher 1998, <sup>3</sup> Chang and Reinfelder 2000, <sup>4</sup> Chang and Reinfelder 2002, <sup>5</sup> Mason et al. 1996, <sup>6</sup> Fowler et al. 1978, <sup>7</sup> Ritterhoff and Zauke 1997.

† The uptake rate constant of dissolved Ag was used for Hg(II) and Pb.

‡ Based on  $k_u$  values for Cu and Cd.

§ Pb AE based on values for other particle-reactive, nonessential metals (Wang et al. 1996b).

Table 5. Trace metal concentrations in Hudson River plume zooplankton, April 2005 and May 2006. Samples were size fractionated into size classes of 202–500, 500–1000, and > 1000  $\mu\text{m}$ . Samples from the > 1000  $\mu\text{m}$  size class were not collected at sites where there was insufficient biomass. bd, below detection; c, suspected contamination; nd, not determined.

Station	Size ( $\mu\text{m}$ )	Ag (nmol g <sup>-1</sup> )	Cd (nmol g <sup>-1</sup> )	Cu (nmol g <sup>-1</sup> )	Pb (nmol g <sup>-1</sup> )	Zn ( $\mu\text{mol g}^{-1}$ )	MeHg (pmol g <sup>-1</sup> )	Hg(II) (pmol g <sup>-1</sup> )	Hg <sub>T</sub> (pmol g <sup>-1</sup> )
April 2005									
10B1	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
11C2	202	bd	bd	883	c	10.4	nd	nd	nd
	500	bd	12.4	419	c	5.5	171	149	320
12B2	202	bd	15.3	486	42.4	31.7	nd	nd	988
	500	bd	8.1	553	bd	6.1	nd	nd	287
13A1	202	15.5	22.9	420	28.0	6.5	162	188	350
	500	9.5	15.8	504	bd	3.3	nd	nd	313
14G1	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	bd	2.4	192	17.0	2.5	nd	nd	664
14K1	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
17J1	202	16.9	20.9	549	c	5.4	39	59	98
	500	bd	15.2	570	c	4.7	nd	nd	218
18H1	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
19A1	202	4.3	3.5	128	bd	0.8	223	215	438
	500	15.1	14.1	481	3.6	4.8	nd	nd	287
May 2006									
3F	202	35	10.3	386	11.9	4.2	241	240	481
	500	42	7.8	527	11.1	5.4	159	320	479
4A	202	28	14.4	578	30.3	16.8	nd	nd	nd
	500	42	13.6	707	24.5	7.2	nd	nd	nd
4C	202	24	11.2	328	16.4	4.2	nd	nd	nd
	500	29	12.7	505	14.6	5.1	nd	nd	nd
4D	202	26	15.9	699	87.2	17.6	260	343	603
	500	31	7.8	496	20.1	5.7	276	311	586
4E	202	28	8.4	463	62.8	4.7	285	294	579
	500	38	7.2	470	11.4	4.9	150	313	463
4F	202	32	9.2	338	34.1	5.1	224	340	563
	500	31	9.8	341	15.6	5	236	344	580
5C	202	29	34	317	9.3	5.3	nd	nd	nd
	500	51	10.5	1236	8.8	7.4	nd	nd	nd
5D	202	43	31.4	307	19.9	10.1	159	439	598
	500	65	12.1	326	12.9	6.6	121	482	602
5E	202	47	10.5	399	9.2	5.9	nd	nd	nd
	500	40	8.2	740	19	6.8	nd	nd	nd
5F	202	32	18.4	333	24.1	5.3	181	370	551
	500	37	34.4	297	23.3	6.9	153	440	593
5G	202	33	16	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
6A	202	34	11.6	175	10.4	12.4	294	365	659
	500	43	10.1	395	18.8	17.9	124	304	428
6B	202	35	20.3	391	8.1	4.9	nd	nd	nd
	500	38	16.4	388	13.2	5.7	nd	nd	nd
7A	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
7B	202	30	60.1	285	10.6	4.9	96	214	310
	500	14	26.5	213	3.4	2.7	233	224	456
7C	1000	8	9.6	173	22	3.1	99	182	281
	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

Table 5. Continued.

Station	Size ( $\mu\text{m}$ )	Ag ( $\text{nmol g}^{-1}$ )	Cd ( $\text{nmol g}^{-1}$ )	Cu ( $\text{nmol g}^{-1}$ )	Pb ( $\text{nmol g}^{-1}$ )	Zn ( $\mu\text{mol g}^{-1}$ )	MeHg ( $\text{pmol g}^{-1}$ )	Hg(II) ( $\text{pmol g}^{-1}$ )	Hg <sub>T</sub> ( $\text{pmol g}^{-1}$ )
7D	202	20	10.3	209	7	4.2	nd	nd	nd
	500	67	11.9	521	7	3.9	nd	nd	nd
	1000	22	5.6	210	7.6	3.7	nd	nd	nd
7F	202	57	12.2	304	19.6	4.7	107	350	457
	500	68	7.8	333	11	3.8	122	321	443
	1000	53	5.6	252	10.4	4.5	110	334	444
7G	202	70	11.4	268	11.4	6.3	155	355	510
	500	74	35.6	324	10.3	7.4	119	449	568
7H	202	74	15.4	291	14.1	4.6	93	321	415
	500	73	12.6	332	19.4	5.1	122	488	610
7I	202	77	11.2	288	10.1	4.8	128	290	419
	500	77	11.7	348	11.3	4.3	96	388	484

River estuary in June, corrected for plume phytoplankton abundance (Gismervik and Andersen 1997) and temperature (Durbin and Durbin 1992). The proportion of metals in copepods accumulated from food was calculated as

$$C_{\text{zpf}}/C_{\text{ss}} \quad (2)$$

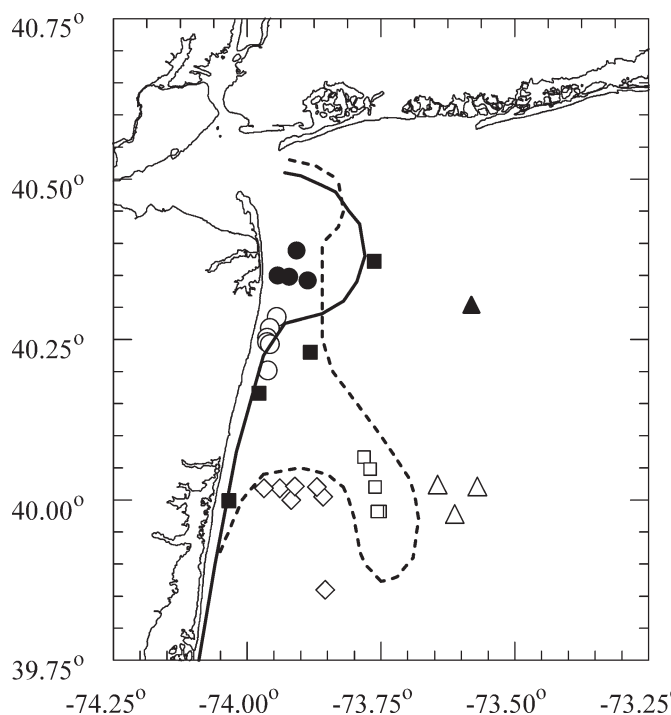


Fig. 1. Locations where copepods were sampled within the Hudson River plume, April 2005 (solid symbols) and May 2006 (open symbols). Approximate plume boundaries for April 2005 (solid line) and May 2006 (dashed line) as defined by isohalines of 24 and 27, respectively, also are shown. For April 2005, spatial groups of samples represent a recirculating eddy (solid circles), partially diluted plume water (solid squares), and inner shelf surface water (solid triangle). For May 2006, spatial groups represent the broad coastal current (open circles), a nearshore intrusion of shelf water (open diamonds), an offshore jet (open squares), and shelf surface water (open triangles).

where

$$C_{\text{zpf}} = (\text{AE} \times \text{IR} \times C_{\text{p}}) / (k_{\text{ef}} + G) \quad (3)$$

*Potential metal toxicity*—The potential toxicities of Ag, Cd, Cu, Hg(II), and Zn in plume copepods were evaluated by comparing measured body burdens to those determined in lethal and sublethal laboratory toxicity tests conducted by Hook and Fisher (2001, 2002) and Bielmyer et al. (2006).

*Statistical analyses*—Most of the distributions of metal concentrations in zooplankton collected from the buoyant plume during April 2005 and May 2006 departed significantly ( $p > 0.05$ ) from normal or log-normal distributions according to the Kolmogorov–Smirnov test of normality. Distributions of metal concentrations were therefore compared with each other among size classes, spatial groups, and sampling years, as well as to previously reported values for oceanic copepods by the two-sample Kolmogorov–Smirnov test (95% confidence).

## Results

*Composition of plume mesozooplankton*—During both sampling events (i.e., April 2005 and May 2006), mesozooplankton assemblages in the Hudson River plume and surface waters of the adjacent inner continental shelf were dominated numerically (> 90%) by juvenile and adult calanoid copepods (primarily *Acartia hudsonica*; Moline et al. 2008). Therefore, trace metal concentrations measured in mesozooplankton samples collected in this study (Table 5) are considered to be representative of calanoid copepods. All copepods collected in this study, including those from inner shelf waters (see Fig. 1), were from surface waters that are influenced by the Hudson River discharge (Chant et al. 2008); therefore, they are collectively referred to as “plume copepods.”

*Copepod sizes and metal accumulation*—No significant differences in metal burdens were observed in plume copepods collected in 200- and 500- $\mu\text{m}$  size fractions during either sampling event, although ratios of median

Table 6. Median metal concentrations in samples of Hudson River plume copepods, collected in April 2005 and May 2006, and in oceanic copepods. For plume–ocean comparisons, significant differences (Diff.) are indicated with + for enrichment ( $p < 0.05$ ) in Hudson River plume copepods relative to oceanic copepods and with – when plume copepods have a significantly lower concentration than oceanic copepods. For comparisons of Hudson River plume copepods from April 2005 and May 2006, + indicates that concentrations in May 2006 were significantly higher ( $p < 0.05$ ) than concentrations in April 2005. ns, metal concentrations were not significantly different.

	Plume vs. oceanic copepods					
	Oceanic median*	April 2005 plume		May 2006 plume		Difference, 2005 vs. 2006
		Median	Diff.	Median	Diff.	
Ag (nmol g <sup>-1</sup> )	1.4	11	+	35	+	+
Cd (nmol g <sup>-1</sup> )	20	15	–	12	–	ns
Cu (nmol g <sup>-1</sup> )	100	490	+	330	+	–
Hg(II) (pmol g <sup>-1</sup> )	250	150	–	330	+	+
MeHg (pmol g <sup>-1</sup> )	70	140	+	150	+	ns
Hg <sub>T</sub> (pmol g <sup>-1</sup> )	280	310	ns	500	+	+
Pb (nmol g <sup>-1</sup> )	3.1	11	+	12	+	ns
Zn (μmol g <sup>-1</sup> )	2.1	4.8	+	4.9	+	ns

\* Metal concentrations for oceanic copepods are from Fisher et al. (2000; Ag, Cd, Zn), Zauke and Schmalenbach (2006; Cd, Cu, Pb, Zn), and Stern and MacDonald (2005; Hg(II), MeHg).

values (200 : 500 μm) varied from 0.8 to 3.4. In May 2006, concentrations of all metals were 30–60% lower in the 1000-μm size fraction than in either the 200- or 500-μm size fractions. However, because 1000-μm samples accounted for only 6 of 48 samples collected in May 2006, metal concentrations in plume copepod size fractions were pooled for further analyses.

*Comparison of metals in plume and oceanic copepods*—Plume copepods were enriched in most trace metals relative to reported values for oceanic copepods (Table 6). Oceanic copepods were collected in the Beaufort, Greenland, Mediterranean, and North Seas; the Fram Strait; and the German Bight (Fisher et al. 2000; Stern and MacDonald 2005; Zauke and Schmalenbach 2006). They include calanoid copepod species from the genera *Acartia*, *Calanus*, *Centropages*, *Euchaeta*, *Metridia*, and *Temora*. In April 2005, plume copepods had significantly higher ( $p < 0.05$ ) concentrations of Ag (8-fold), Cu (5-fold), MeHg (2-fold), Pb (3.5-fold), and Zn (2.3-fold), but 40% lower concentrations of Hg(II), than oceanic copepods. Concentrations of Hg<sub>T</sub> in plume copepods from April 2005 were not significantly different from those in oceanic copepods. In May 2006, plume copepods had significantly higher concentrations of Ag (25-fold), Cu (3-fold), Hg(II) (1.3-fold), MeHg (2-fold), Hg<sub>T</sub> (1.8-fold), Pb (4-fold), and Zn (2.3-fold) than oceanic copepods ( $p < 0.05$ ). During both sampling events, plume copepods had 25% and 40% lower Cd concentrations, respectively, relative to oceanic copepods ( $p < 0.05$ ).

*Metals in plume copepods from two sampling events*—Significant differences in the concentrations of Ag, Cu, and Hg were observed between copepods collected during the 2005 and 2006 sampling events (Table 6). Concentrations of Ag, Hg(II), and total Hg were 3-, 2.2-, and 1.6-fold

higher, and Cu was 33% lower ( $p < 0.05$ ), in copepods collected in May 2006 than in April 2005. The concentrations of Cd, MeHg, Pb, and Zn in plume copepods were not significantly different between the two years.

*Spatial trends of metal concentrations in plume copepods*—Spatial variation of trace metal concentrations in plume copepods collected within the dominant physical features of the plume–inner shelf system was examined. In April 2005, after a period of high river discharge, low-salinity plume waters formed a recirculating eddy within the New York bight. A broad plume–shelf water transition zone was observed at the eddy’s seaward edge that was bounded by higher salinity inner shelf surface water (Fig. 1; Chant et al. 2008). During this sampling event, Cu and Zn concentrations in copepods collected from the recirculating eddy were 1.2- and 1.6-fold higher than in copepods collected from the plume–shelf transition area and 2-fold higher than in those from inner shelf surface waters (Fig. 2). Concentrations of all other metals showed no significant spatial variation within the plume–inner shelf system in April 2005.

In May 2006, under moderate river discharge, the Hudson River plume formed a broad coastal current in the New York bight (Chant et al. 2008). South of the bight, the plume formed a southeast-flowing jet of low-salinity plume water and a narrow coastal current, which were separated by an intrusion of higher salinity shelf water (Fig. 1). As was observed in April 2005, Cu and Zn concentrations were 2.2 and 1.4 times higher in copepods collected from the low-salinity coastal current than in copepods collected from the inner shelf (Fig. 2). However, median Zn concentrations were similar in copepods collected from the coastal current and shelf water intrusion. In May 2006, Ag, MeHg, and Pb were also significantly elevated (by factors of 1.7–2) in copepods from the coastal

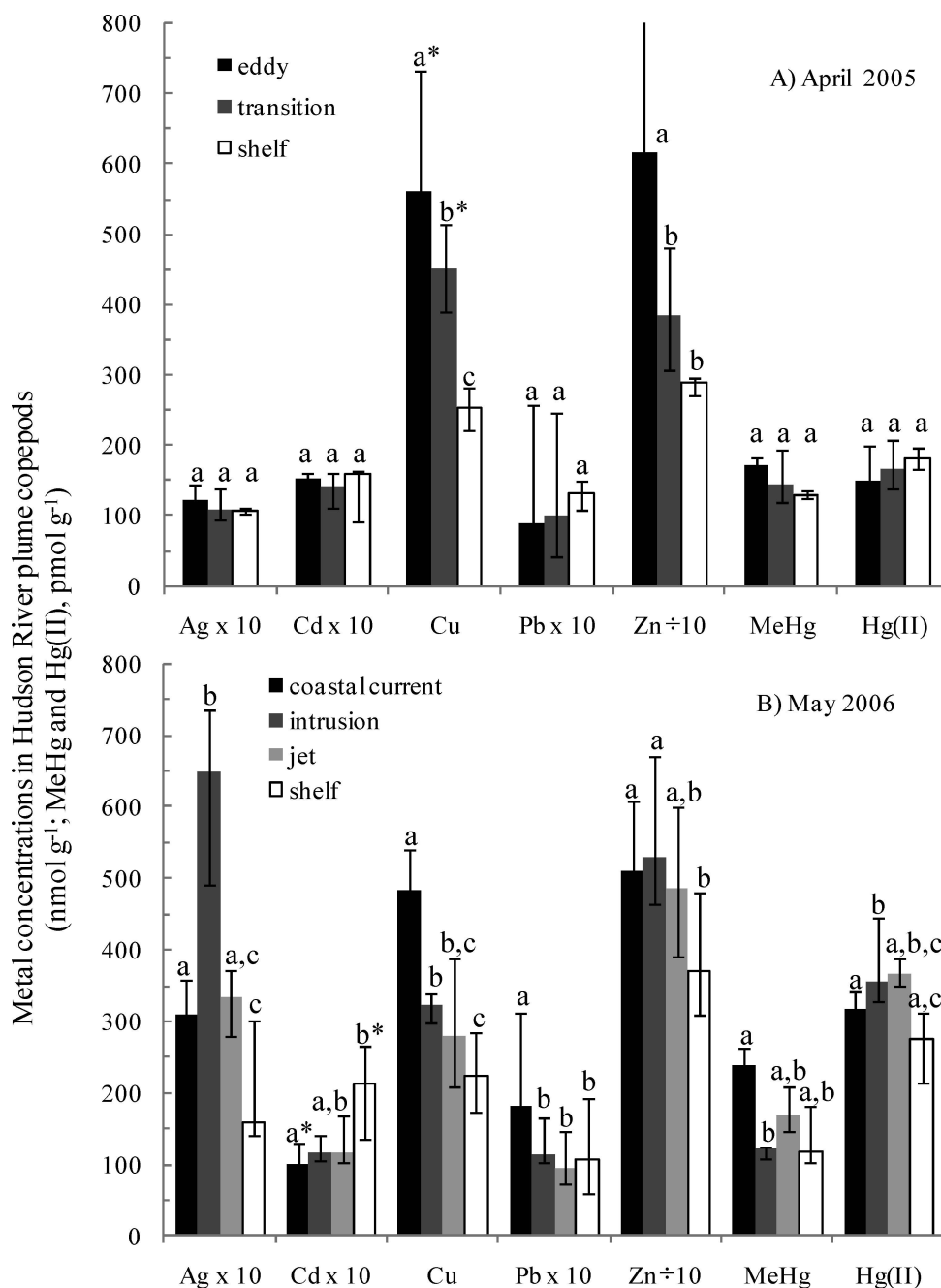


Fig. 2. Median trace metal concentrations ( $\pm$  first and third quartiles) in copepods from spatial regions (see Fig. 1) of the Hudson River plume and adjacent shelf waters during April 2005 and May 2006. (A) April 2005 samples were grouped as those within the plume's recirculating eddy, partially diluted plume water (transition), or inner shelf surface water. (B) May 2006 samples were grouped as those in the plume's broad coastal current, a nearshore intrusion of shelf water (intrusion), the plume's offshore jet (jet), or the inner shelf surface water (shelf). Within each sampling season, letters indicate values from significantly different distributions (Kolmogorov–Smirnov test,  $p < 0.05$ , except for those labeled with asterisks, where  $p < 0.1$ ).

current relative to those from the shelf. Interestingly, Cd in copepods showed the opposite trend, with a median Cd concentration in the coastal current equal to half that in copepods from the inner shelf (Fig. 2). The concentrations

of Ag, Cd, Zn, and MeHg in copepods collected from within the plume's offshore jet were similar to those from the lower salinity coastal current closer to the mouth of the Hudson River (Fig. 2). However, copepods from the

offshore jet had significantly lower Cu and Pb, but higher Hg(II) concentrations ( $p < 0.05$ ) than copepods collected farther upstream in the plume.

As the May 2006 plume's coastal current moved offshore, a mixture of high-salinity shelf water and aged plume water rotated clockwise around the southern end of the plume's offshore jet and formed a high-salinity intrusion (Fig. 1). This intrusion was relatively stable, and it was not affected by upwelling during the sampling period (R. J. Chant pers. comm.). Copepods associated with the shelf water intrusion had significantly higher Ag and Hg(II) concentrations, but lower Cu, Pb, and MeHg concentrations ( $p < 0.05$ ), than those collected from the plume's coastal current (Fig. 2).

*Dissolved metals in the Hudson River plume*—Dissolved metal concentrations in the Hudson River plume measured during the two LaTTE experiments were generally lower than those in the Hudson River estuary (Sanudo-Wilhelmy and Gill 1999) and decreased from the heart of the plume to inner shelf waters of the New Jersey coast (Table 2). Hudson River plume (surface) water had concentrations of dissolved Cu, Pb, and Zn similar to New Jersey coastal water samples collected 2 m off the bottom in 1995 (Field et al. 1999). Dissolved concentrations of Cd, Cu, Hg, Pb, and Zn in the Hudson River plume were generally within a factor of two of those reported for the marine plumes of San Francisco Bay (Hurst and Bruland 2008), the Danube River (Guieu et al. 1998), and the Scheldt River (Baeyens et al. 1998). Dissolved Ag concentrations in the Hudson River plume (20–50 pmol L<sup>-1</sup>) were somewhat higher than those measured in the San Diego Bay plume (20 pmol L<sup>-1</sup>; Sanudo-Wilhelmy and Flegal 1992) and the San Francisco Bay outlet (28–36 pmol L<sup>-1</sup>; Smith and Flegal 1993).

*Particulate metals, biomagnification factors, and trophic accumulation of metals in plume copepods*—Suspended particles were dominated by phytoplankton but also included 3–25% crustal material in April 2005 and 0.2–13% crustal material in May 2006 (Table 3). Crustal silt can be ingested by copepods (Turner and Tester 1989), but the bioavailability of metals from such material in copepods is unknown. Concentrations of metals in Hudson River plume suspended particles decreased with salinity in both April 2005 and May 2006. However, in April 2005, Cd concentrations in the 2–20- $\mu$ m size fraction increased with salinity from the plume eddy to the plume transition and inner shelf. Particulate concentrations of Cd, Cu, and Pb in the low-salinity areas of the Hudson River plume in April 2005 and May 2006 were nearly identical to those in the San Francisco Bay plume (Hurst and Bruland 2008) but were factors of 2, 10, and 30, respectively, lower than those in the Scheldt River plume (Baeyens et al. 1998). Particulate Hg in the Hudson River plume was about 10-fold lower than that in the Scheldt River plume (Baeyens et al. 1998) and nearly 100 times lower than that in the Hg mining-affected Isonzo River plume (Covelli et al. 2007). Particulate Ag in the Hudson River plume was 3–8 times higher than that in the San Francisco Bay outlet (Smith and Flegal 1993), although this could be because particulate Ag in San

Table 7. Model predicted and measured metal concentrations and percent accumulation from food in Hudson River plume copepods collected within the recirculating eddy during the April 2005 sampling event and within the coastal current during the May 2006 event. Values include modeled metal concentrations in copepods from trophic accumulation ( $C_{zp-food}$ ) and direct uptake of dissolved metal ( $C_{zp-water}$ ). Modeled values were calculated using median metal concentrations, measured in suspended particles in size fractions of 2–20  $\mu$ m for April 2005 and > 20  $\mu$ m for May 2006, and bioaccumulation parameters for each metal (Table 5) according to Eqs. 1–3.

	April 2005				May 2006			
	$C_{zp-food}$ (nmol g <sup>-1</sup> )	$C_{zp-water}$ (nmol g <sup>-1</sup> )	% food	Measured (nmol g <sup>-1</sup> )	$C_{zp-food}$ (nmol g <sup>-1</sup> )	$C_{zp-water}$ (nmol g <sup>-1</sup> )	% food	Measured (nmol g <sup>-1</sup> )
Ag	0.91	2.7	25	12	1.2	2.7	31	31
Cd	7	2.1	77	15	13	2.1	86	10
Cu	381	100	79	562	479	100	83	483
Hg(II)	0.82	0.60	58	0.15	8.4	0.75	92	0.32
MeHg	0.051	0.0027	95	0.17	0.38	0.003	99	0.24
Pb	7.4	8.2	47	8.9	10	12	45	18
Zn	5910	224	96	6200	8250	185	98	5100

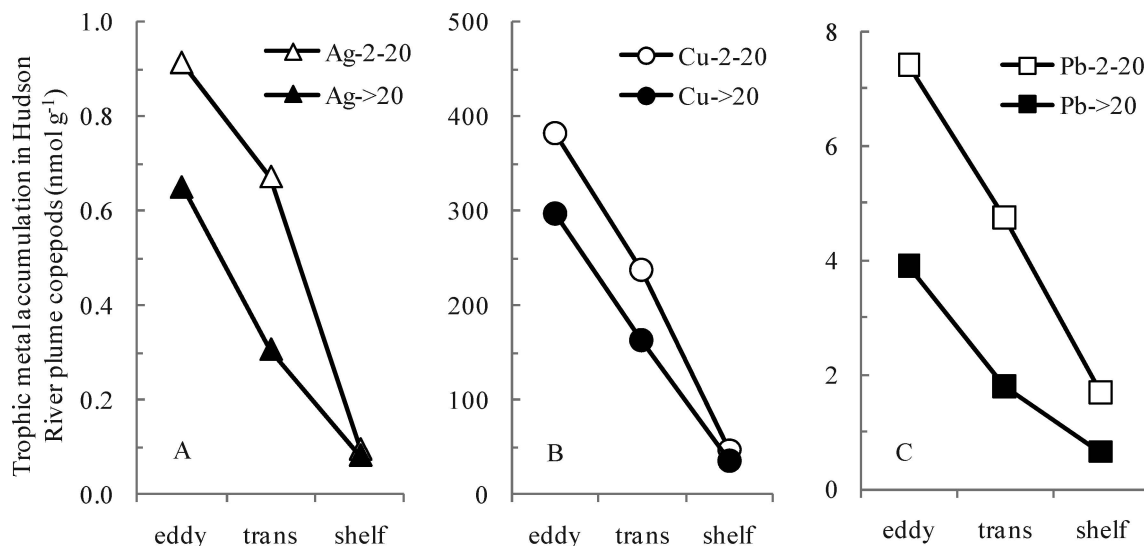


Fig. 3. Model-predicted trophic accumulation of (A) Ag, (B) Cu, and (C) Pb in Hudson River plume copepods during the April 2005 sampling event. Steady-state metal concentrations were calculated using median metal concentrations measured in suspended particles in the 2–20- $\mu\text{m}$  (open) and > 20- $\mu\text{m}$  (filled) size fractions and bioaccumulation parameters for each metal (Table 4) according to Eq. 3.

Francisco Bay was determined by difference in unfiltered and dissolved samples. Mass specific concentrations of Ag, Cu, and Pb in the 2–20- $\mu\text{m}$  size fraction were elevated (1.3–1.9-fold) compared with the > 20- $\mu\text{m}$  size fraction (Table 3).

Trace metal biomagnification factors for the lowest salinity regions of the Hudson River plume (recirculating eddy in April 2005 and coastal current in May 2006) were estimated as the ratios of median metal concentrations in copepods and simultaneously collected > 20  $\mu\text{m}$  suspended particles. Biomagnification factors for plume copepods in April 2005 decreased in the order MeHg (38), Ag (4), Cu (3), Hg(II) (0.3), and Pb (0.1). In May 2006, the order of biomagnification factors was MeHg (10), Ag (8), Cu and Zn (2), and Hg(II) and Pb (0.1). On the basis of limited measurements of Cd in plume suspended particles, its biomagnification factor for plume copepods is estimated to be close to unity.

Estimated biomagnification factors in plume copepods indicate that food could be important to the accumulation of Ag, Cu, MeHg, and Zn, but less so for Hg(II) and Pb. This is supported by model results showing that trophic transfer accounted for 80% to > 95% of total Cu, MeHg, and Zn, but < 50% of total Pb accumulated in plume copepods collected during both sampling events (Table 7). However, model results indicate that 60–90% of total Hg(II) and < 30% of total Ag were accumulated from food. Of the three metals predicted to be accumulated in copepods primarily from food—Cu, MeHg, and Zn—only Cu and MeHg showed strong correlations between concentrations in copepods and suspended particles ( $r^2 \geq 0.92$ ).

*Modeling metal accumulation and potential toxicity in plume copepods*—The bioaccumulation model did a good job of predicting the total concentrations of Cd, Cu, Pb,

and Zn in copepods from the areas of the Hudson River plume closest to the mouth of the estuary to within less than a factor of two (Table 7). However, the model overpredicted concentrations of Hg(II) in plume copepods by factors of 9 and 28 for April 2005 and May 2006, respectively. Concentrations of Ag in plume copepods were underpredicted by the bioaccumulation model by factors of three to eight. MeHg levels in plume copepods were reasonably well predicted by the model for May 2006 but were underpredicted by a factor of three for April 2005.

Copepods in the Hudson River plume were presented with small- and large-sized phytoplankton, although feeding on > 20- $\mu\text{m}$  phytoplankton was limited in April 2005, in large part because of a preponderance of large, chain-forming diatoms that resulted in a mismatch between food size and copepod feeding capabilities (Moline et al. 2008). Thus, the potential effect on metal accumulation of copepod feeding on different phytoplankton size classes was evaluated for Ag, Cu, and Pb, metals with complete sets of values for suspended particles from both size classes, and the three spatial areas sampled in April 2005. Predicted trophic accumulation of all three metals was higher in copepods feeding on small (2–20  $\mu\text{m}$ ) rather than large (> 20  $\mu\text{m}$ ) phytoplankton in the plume's recirculating eddy and transition zone, but less so in shelf surface waters (Fig. 3).

In April 2005, median copepod concentrations of Ag and Zn exceeded sublethal toxicity thresholds reported by Hook and Fisher (2001, 2002) and Bielmyer et al. (2006) by factors of nearly two, whereas Cd, Cu, and Hg(II) were generally below their respective sublethal toxicity thresholds. In May 2006, median Ag and Zn concentrations again exceeded their sublethal toxicity thresholds by factors of eight and two, respectively, whereas Cd, Cu, and Hg(II) were generally below their sublethal toxicity thresholds. Bioaccumulation modeling results show that for Ag,

< 30% of total accumulation in plume copepods was from food, whereas for Zn, food might have contributed > 95% of total Zn in plume copepods. In April 2005, the median body burden of Ag in plume copepods was 11 nmol g<sup>-1</sup>. Thus, the amount of Ag accumulated by plume copepods from food was similar to the threshold level found to cause decreased egg viability (3 nmol g<sup>-1</sup>; Hook and Fisher 2002). In May 2006, however, plume copepods had a median Ag concentration of 35 nmol g<sup>-1</sup> and might have accumulated > 10 nmol g<sup>-1</sup> of Ag from their diets, which exceeds the sublethal toxicity threshold observed by Hook and Fisher (2002).

## Discussion

*Metal accumulation in river plume copepods*—Estuaries and their coastal plumes are physically dynamic and biologically productive ecosystems that are very often subject to contaminant trace metal loads from adjacent urban areas (Sañudo-Wilhelmy and Gill 1999; Moline et al. 2008). Contaminant metals accumulate in estuarine sediments after their adsorption to suspended particles but are returned to the water column and redistributed laterally through sediment resuspension (Feng et al. 2002; Balcom et al. 2008). As a result, a portion of the metal load to estuaries is transported to the sea with coastal river plumes (Windom 1990). The transport of trace metals in estuarine plumes to the coastal ocean is evident in this study by the relatively high dissolved and suspended particle trace metal concentrations measured closest to the Hudson River estuary and the decrease in metal concentrations as plume water mixed with shelf water to the south and east of the New York bight. This transport is also reflected in the significantly elevated levels of all metals except Cd, and perhaps inorganic Hg, in Hudson River plume copepods compared with oceanic copepods.

Expected spatial trends in copepod metal concentrations—highest close to the mouth of the Hudson River and lower offshore—were only clearly observed during both sampling events for Cu and Zn. In May 2006, Ag and Pb were significantly lower in shelf compared with plume coastal current copepods, but these metals showed no trend in April 2005, and the other metals showed little or no consistent pattern of decrease with increasing salinity during either sampling event.

Salinity affects metal bioaccumulation in euryhaline invertebrates (Wang et al. 1996a; Lee et al. 1998; Blackmore and Wang 2003), but its effects have rarely been examined in copepods. No significant difference in Cu accumulation was observed in the copepod *Acartia tonsa* exposed to Cu in both water and diet at salinities of 15 and 30, and in water-only exposures, Cu accumulation was only 23% higher at a salinity of 15 compared with 30 (Pinho et al. 2007). Clearly salinity cannot explain the more than twofold range in Cu concentrations in plume copepods collected over the range of salinities in this study (23.5–31.5 in April 2005 and 26.1–32.2 in May 2006). In marine bivalves, Zn accumulation from the dissolved phase generally increases at lower salinity (Wang et al. 1996a), but in some bivalves, salinity had no effect on uptake of

dissolved Zn (Lee et al. 1998), and in certain crustaceans, Zn accumulation decreased at lower salinities (Rainbow and Black 2002). Given the dominant complexation of Cu and Zn by organic ligands in estuaries (Kozelka and Bruland 1998), salinity-driven changes in Cu and Zn speciation are unlikely to have a major effect on the bioaccumulation of these metals in river plume copepods. However, salinity-driven physiological changes in copepods could potentially affect metal accumulation in river plumes.

With > 80% of total Cu and Zn accumulation in copepods derived from food, the concentrations of these metals in river plume copepods are directly linked to declining concentrations in suspended particles. However, the decrease in concentrations of Cu and Zn in copepods by smaller factors (~ 2.5) than dissolved and particulate concentrations ( $\geq 5$ ) indicates that the bioavailabilities (assimilation efficiencies, etc.) of these two metals in plume copepods decline as plume water ages. In contrast, our results suggest that the bioavailabilities of other metals increase as river plumes mix with shelf water because the concentrations of these metals in plume copepods remained relatively constant, whereas they decreased in suspended particles and the dissolved phase.

The spatial trend of Cd concentrations in plume copepods in May 2006 was opposite those of Cu and Zn. This finding and the observation of lower Cd levels in plume copepods relative to oceanic copepods during both sampling events indicate that well-known biologically controlled trace metal uptake antagonisms among Cd, Cu, and Zn in marine phytoplankton (Sunda and Huntsman 1996) also affect Cd accumulation in coastal zooplankton. Concentration trends of dissolved and particulate Cu and Zn apparently result in lower Cd accumulation in copepods during the early stages of a river plume, but higher Cd accumulation as Cu and Zn decrease offshore.

Spatial distributions of Ag and Hg(II) in plume copepods in May 2006 were strikingly different from those in suspended particles and the dissolved phase. Higher concentrations of Ag and Hg(II) in copepods from the shelf water intrusion than closer to the estuary in the plume's coastal current could have resulted from (1) higher inputs of Ag and Hg(II) from the Hudson River estuary before copepod sampling in May 2006, leading to higher concentrations in older plume water associated with the intrusion, (2) additional inputs of Ag and Hg(II) from sewage outfalls along the New Jersey coast (Hires et al. 1990) or (3) and higher bioavailability of dissolved or particulate Ag and Hg(II) in the shelf water intrusion than elsewhere in the plume. Because Ag and Hg(II) concentrations in suspended particles were lower in the intrusion than elsewhere in the May 2006 plume, it is unlikely that the fluxes of Ag and Hg(II) from the Hudson River estuary were significantly higher just before the May 2006 sampling event or that the older plume water associated with the intrusion had higher dissolved and particulate metal concentrations. It is also unlikely that inputs of Ag and Hg from offshore sewage outfalls along the New Jersey coast affected copepods in the shelf water intrusion because outfall discharges tend to travel along the bottom in a

north to south line, parallel to the shore (Obropta and Hires 2007). In addition, most sewage outfalls are too far inshore ( $> 10$  km from the center of the intrusion) to influence metal accumulation in copepods from this area.

Elevated concentrations of particulate Ag or Hg(II) were not evident in the offshore jet or shelf water intrusion of the May 2006 plume, which would be expected if the bioavailability of dissolved Ag or Hg(II) increased because of a decrease in their complexation by organic ligands (Ratte 1999; Gorski et al. 2008). There is negligible variation in the inorganic speciation of Ag and Hg(II) over the salinity range of the plume. Moreover, dissolved organic carbon showed a fairly linear mixing line with respect to salinity in May 2006, indicating little biological consumption or production within the plume (R. Chen pers. comm.). Thus, a change in the bioavailability of dissolved Ag and Hg(II) seems unlikely to have caused the increase in these metals in copepods collected from the shelf water intrusion.

Changes in plankton community structure resulting in increased bioavailability of particulate Ag and Hg(II) to mesozooplankton could have contributed to the observed increase in copepod Ag and Hg(II) in the shelf water intrusion. In the absence of abundant phytoplankton, copepods are likely to consume a greater proportion of microzooplankton (Fessenden and Cowles 1994). Because copepods assimilate Ag and Hg(II) significantly more efficiently from certain microzooplankton than from phytoplankton (Twining and Fisher 2004), a greater abundance of microzooplankton in the postbloom shelf water intrusion than in the plume's coastal current could have resulted in an increase in the bioavailabilities of ingested Ag and Hg(II) in the intrusion. This indicates that the accumulation of certain nonessential metals in river plume copepods is modulated by the types of available planktonic food and that body burdens of metals in copepods can increase without a proportional increase in the concentrations of metals in their food.

The influence of physical and biological factors on the bioavailability of metals to copepods in coastal river plumes can also be evaluated by comparing metal accumulation for the two sampling events that followed periods of very different levels of discharge from the Hudson River. In April 2005, the Hudson River basin experienced a 10-year flood with a peak discharge of nearly  $8000 \text{ m}^3 \text{ s}^{-1}$  on April 5 (Chant et al. 2008). In contrast, peak discharge of the Hudson River before the May 2006 sampling season was only  $1500 \text{ m}^3 \text{ s}^{-1}$ . Differences in river discharge, associated nutrient inputs, and physical processes operating in the nearshore coastal system resulted in a biologically more productive plume in April 2005 than May 2006 (O. Schofield pers. comm.).

On the basis of a comparison of metal concentrations measured in copepods during the two sampling events, river discharge appears to have had the greatest effect on the accumulation of Ag, Cu, and Hg(II). Lower concentrations of Ag and Hg(II) in copepods collected after the high discharge event in April 2005 than after moderate river discharge in May 2006 indicate that high river discharge lowers the bioavailability of these highly particle

reactive, nonessential metals. This could have occurred as a result of the dilution of these metals during the rapid growth of phytoplankton or copepods in April 2005; however, growth dilution was found to have no effect on the bioaccumulation of inorganic Hg(II) in freshwater zooplankton (Pickhardt et al. 2002, 2005). For Hg(II), lower accumulation in plume copepods collected in April 2005 than in May 2006 could have resulted from differences in the chemical speciation (organic complexation) of dissolved Hg(II) between the two sampling events. Lower bioavailability of dissolved Hg(II) in April 2005 is consistent with the observation of sevenfold lower weight-specific Hg(II) concentrations in plume suspended particles in April 2005 than in May 2006, despite only 20–30% lower dissolved Hg(II) concentrations.

Variation in the bioavailability of dissolved Ag was unlikely to have caused the observed differences in Ag levels in plume copepods events because concentrations of Ag in suspended particulate matter ( $> 20 \mu\text{m}$ ) were very similar during the two sampling periods. Other factors, such as feeding behavior, food selection, or both, are more likely to have caused the apparent difference in bioavailability of Ag and perhaps Hg(II) between the two years. Size-selective feeding by coastal copepods is not universally observed (Turner and Tester, 1989), but it is most likely to occur at high concentrations of food (Cowles 1979), such as those present during the April 2005 event. In large part because of a size mismatch between small copepods and large, chain-forming diatoms, plume copepods fed primarily on cryptophyte phytoplankton in April 2005 (Moline et al. 2008) which might have presented a less bioavailable form of Ag and Hg(II) than the diatoms or microzooplankton present in May 2006.

In contrast to Ag and Hg(II), the bioavailability of Cu in plume copepods was higher after the high discharge event in April 2005 than in May 2006. As with Ag, the concentrations of Cu in plume suspended particles were similar during both sampling events, indicating that bioavailability (speciation) of dissolved Cu was also similar in April 2005 and May 2006 and not responsible for observed differences in Cu bioaccumulation in plume copepods. Differences in phytoplankton growth rates, species composition, or both between high and low river discharge events apparently have opposite effects on the bioavailabilities of Ag and Hg(II) compared with Cu in ingested food and, therefore, the bioaccumulation of these metals in plume copepods.

A further evaluation of the effects of river discharge on metal accumulation in plume copepods is provided by the comparison of model predicted and measured metal concentrations for copepods collected from plume water closest to the mouth of the estuary. For the high river discharge April 2005 sampling event, the bioaccumulation model underpredicted the concentrations of Cd and MeHg but overpredicted Pb in plume copepods, whereas the concentrations of these metals in copepods were fairly accurately predicted by the model for May 2006. These results indicate that the uptake of Pb will diminish but the bioavailabilities of MeHg and Cd will increase in copepods from coastal plumes associated with high river discharge

events, with greater volumes of water and higher concentrations of phytoplankton and suspended particles than low or moderate discharge plumes.

With a model assimilation efficiency of 30%, higher than predicted accumulation of Cd in plume copepods from April 2005 is likely due to greater bioavailability of Cd in copepod food. For MeHg, however, with a model assimilation efficiency of > 60%, higher than predicted accumulation in plume copepods from April 2005 must be partly the result of increased bioavailability of dissolved MeHg. With > 50% of total Pb accumulation from the dissolved phase and a 1.5-fold decrease in dissolved Pb in April 2005 compared with May 2006, much of the observed difference between modeled and measured Pb concentrations in plume copepods was likely due to decreased dissolved uptake.

Model predicted concentrations of Ag and Hg(II) in plume copepods were very different from measured values for both sampling events, whereas Cu and Zn concentrations were well predicted by the model for both April 2005 and May 2006. Because the model overpredicted Hg(II) accumulation and predicted that 60–90% of total Hg(II) was accumulated from food, Hg(II) associated with ingested particles in the river plumes could be even less bioavailable to copepods than observed in laboratory experiments. In contrast, dissolved or particulate forms of Ag in the river plume are apparently more bioavailable to copepods than expected on the basis of laboratory metal accumulation studies. If the observed differences in Ag accumulation between April 2005 and May 2006 are representative of Ag bioaccumulation in high and moderate river discharge plumes, then our results indicate that toxic levels of Ag in plume copepods are more likely to occur after periods of moderate river discharge.

Model predicted metal bioaccumulation in copepods could be improved with the incorporation of metal assimilation efficiencies for various types of prey and parameters for uptake from the dissolved phase that varied with metal speciation.

The potential for river plume copepods to transfer metals to pelagic consumers in the coastal ocean depends in part on the levels of accumulation in copepods relative to their food. Biomagnification is well known for MeHg in aquatic food webs but is rarely encountered for Ag, Cu, and Zn (Cheung and Wang 2008). Modeling results suggest that the apparent biomagnification of Ag was due to relatively high accumulation of dissolved compared with ingested metal, whereas that of Cu, MeHg, and Zn was primarily due to accumulation of metals from food. Zinc accumulates to high levels in marine invertebrates (Small and Fowler 1973; Reinfelder et al. 1997) and has the potential to biomagnify in some bivalves (Reinfelder et al. 1998) and fish (Zhang and Wang 2007), but biomagnification is not commonly observed for Zn in the marine environment (Barwick and Maher 2003) outside of hydrothermal ecosystems (Colaco et al. 2006).

The results of this study show that metal accumulation by plume copepods is modulated by plume size and physical structure, which depend on river discharge and wind speed and direction (Chant et al. 2008), and by phytoplankton

productivity and community composition, which depend on nutrient inputs and plume water residence times (Moline et al. 2008). Thus, physical and biological river plume dynamics need to be considered to understand and accurately predict the accumulation and toxic effects of metals in zooplankton from urban-influenced river plumes and their potential transfer to and effects in coastal pelagic food webs.

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