

Scavenging of ^{137}Cs , ^{109}Cd , ^{65}Zn , and ^{153}Gd by Plankton of the Microbial Food Web in Pelagic Lake Erie Surface Waters

Michael R. Twiss^{1,2} and Peter G.C. Campbell

INRS-Eau, Université du Québec
C.P. 7500
Ste-Foy, Quebec G1V 4C7

ABSTRACT. Inorganic dissolved ^{137}Cs , ^{109}Cd , ^{65}Zn and ^{153}Gd were added, at concentrations well below their respective solubility limits, to screened water ($< 210\ \mu\text{m}$) sampled from the pelagic epilimnion of Lake Erie during the summers of 1994 and 1995. The hypotheses tested were that scavenging occurs in all of the ecologically significant size fractions that comprise the microbial food web (picoplankton, 0.2 to $2\ \mu\text{m}$; nanoplankton, 2 to $20\ \mu\text{m}$; microplankton, 20 to $210\ \mu\text{m}$), and that scavenging by plankton is directly related to the respective particle-reactivity of the elements ($\text{Gd} > \text{Zn} > \text{Cd} \gg \text{Cs}$). Size-selective filtration at intervals over periods of 22 to 30 h established that picoplankton and nanoplankton were the dominant scavenging phases in this environment. Scavenging of ^{153}Gd , ^{65}Zn , and ^{109}Cd by plankton was more similar than predicted on the basis of their anticipated particle-reactivity and ^{137}Cs was weakly scavenged. Except for the picoplankton, ^{65}Zn was the element most readily scavenged by the plankton size fractions. High accumulation of ^{109}Cd in the picoplankton may reflect the sorption of this element by calcite associated with autotrophic picoplankton. These experiments quantify the partitioning of trace metals within the plankton of the microbial food web (0.2 to $210\ \mu\text{m}$), a dynamic community of particles that dominates the seston in the pelagic surface waters of Lake Erie during thermal stratification, and suggest that plankton dynamics should be considered in predictions of the geochemical fate of trace metals in this environment.

INDEX WORDS: Trace metals, sorption, particles, fate, picoplankton, nanoplankton, microplankton.

INTRODUCTION

Scavenging, the sorption of particle-reactive trace metals to sedimenting particles, is generally accepted as the key factor controlling the concentration of dissolved trace metals in the surface waters of large lakes (Sigg 1994). Solid surfaces can scavenge particle-reactive metals by various sorptive mechanisms such as electrostatic adsorption, complexation, precipitation, and internalization by organisms (Stumm *et al.* 1994). The gravitational loss of particles to the sediment controls the flux of trace metals in large lake systems, where the residence time of particles is much less than the hydraulic residence time.

The elemental composition of particles in the surface waters of the Laurentian Great Lakes shows strong seasonality. Analyses of the rare earth element content of particles retained in sediment traps during isothermal conditions reveal that the majority of seston during this period is detrital material, whereas with the onset of thermal stratification epilimnetic particle composition shifts to autochthonous particles such as plankton and calcite (Robbins and Eadie 1991). Although calcite precipitation in the lower Great Lakes and Lake Michigan contributes a significant amount of particulate matter to the epilimnion during this time (Vanderploeg *et al.* 1987), the ability of calcite to scavenge most trace metals is considered to be inferior to that of biological surfaces (Sigg 1994), and even during whiting events particulate organic matter is generally considered to be the dominant phase responsible for the removal of particle-reactive trace metals from surface waters in large lakes (Robbins and

¹Present address: Department of Applied Chemical and Biological Sciences, Ryerson Polytechnic University, 350 Victoria Street, Toronto, Ontario M5B 2K3, Canada

²Corresponding author. Email: mtwiss@acs.ryerson.ca

Eadie 1991, Shafer and Armstrong 1991, Sigg 1994).

Particles in pelagic systems are dynamic. Earlier work on the scavenging of Cd and Zn by plankton considered that particles < 28 μm in offshore surface waters of Lake Michigan were "mainly non-living detrital material and mineral particles," especially during summer months (Parker *et al.* 1982). In their modeling of trace metal fluxes in Lake Michigan, Shafer and Armstrong (1991) considered biotic matter as sedimentable plankton, chiefly diatoms. The settling of this biological component of the seston undoubtedly contributes to loss of trace metals from surface waters, but metal cycling events can occur prior to this event. In light of the recent progress in understanding microbial food web dynamics in the Great Lakes (Fahnenstiel *et al.* 1986; Carrick and Fahnenstiel 1989; Fahnenstiel *et al.* 1991a, 1991b) and their influence on trace metal cycling (Twiss and Campbell 1995, Twiss *et al.* 1996), a re-examination of biotic influences on the geochemical fates of trace metals is warranted.

The microbial food web, wherein rapidly growing bacteria, cyanobacteria, and algae in the picoplankton size class (0.2 to 2 μm) are heavily grazed by mixotrophic and heterotrophic consumer organisms in the nanoplankton (2 to 20 μm) and microplankton (20 to 200 μm) size classes (Stockner and Porter 1988), is very active in surface waters of the Great Lakes (Weisse and Munawar 1989, Fahnenstiel *et al.* 1991a, 1991b). These consumer organisms collectively referred to as microzooplankton, are known to regenerate C, N, and P due to the incomplete assimilation of these nutrients from their prey (Caron and Goldman 1990); given this ability, it is conceivable that these microzooplankton, will have comparable effects on trace metal cycling. Recent studies conducted in marine systems support the hypothesis of trace metal regeneration by mesozooplankton and microzooplankton (Hutchins *et al.* 1995, and references cited therein). Rapid regeneration of ^{109}Cd and ^{65}Zn into the dissolved phase (< 0.2 μm) was observed when radiolabeled picoplankton prey were grazed by the natural microzooplankton community (3 to 210 μm) present in the pelagic surface water of Lake Erie (Twiss *et al.* 1996). In this latter study, marked differences in the trophic transfer and recycling of ^{109}Cd and ^{65}Zn from the radiolabeled prey into the nanoplankton (3 to 20 μm) and microplankton (20 to 210 μm) were observed—the study demon-

strated that the microbial food web has a significant influence on the partitioning of metals in surface waters, and suggested that the evolution of trace metal concentrations in surface waters during thermal stratification is linked to the intense growth and grazing activity within the microbial plankton community.

The objective of the present study was to examine the partitioning of trace metals from the dissolved phase into the plankton size fractions which comprise the microbial food web. Better appreciation of trace metal movement among various ecologically significant plankton size fractions should provide a basis for estimating how changes to the structure of the pelagic microbial food web, brought about by seasonal hydrography, reduced nutrient loading, or introduced species, will alter the geochemical fate of some trace metals. To this end, trace metal scavenging experiments were conducted in Lake Erie surface waters to evaluate the removal of cesium, cadmium, zinc, and the rare earth element gadolinium, chosen to represent a range in surface reactivity ($\text{Gd} > \text{Zn} > \text{Cd} \gg \text{Cs}$). This study used an ecologically-based plankton size fractionation scheme (Sieburth *et al.* 1978) for classifying the seston into the picoplankton (0.2 to 2 μm), nanoplankton (2 to 20 μm) and microplankton (20 to 210 μm). Two hypotheses concerning the partitioning of these elements were tested: i) measurable amounts of trace metal are accumulated within each of the ecologically significant size fractions, and ii) differences in relative affinities among the trace metals for a given plankton size fraction are attributable to differences in the particle-reactivity of the metals.

METHODS

Glassware/Plasticware Preparation

All plasticware and silanized glassware used in the experiments were rigorously cleaned prior to use. The cleaning protocol involved a warm soap wash (1% Liqui-Nox; Alconox, Inc.), methanol soak (HPLC grade; Baxter Healthcare Corp.), HNO_3 soak (1.6 M; Environmental Grade, Anachemia), and a soak in HCl (0.8 M; Suprapur, Merck), with a 7-fold rinse after each cleaning step using deionized water (≥ 17.5 Mohms/cm).

Trace Metal Sorption Experiments

The sorption of the gamma-emitting radionuclides ^{137}Cs , ^{109}Cd , ^{65}Zn , and ^{153}Gd by surface

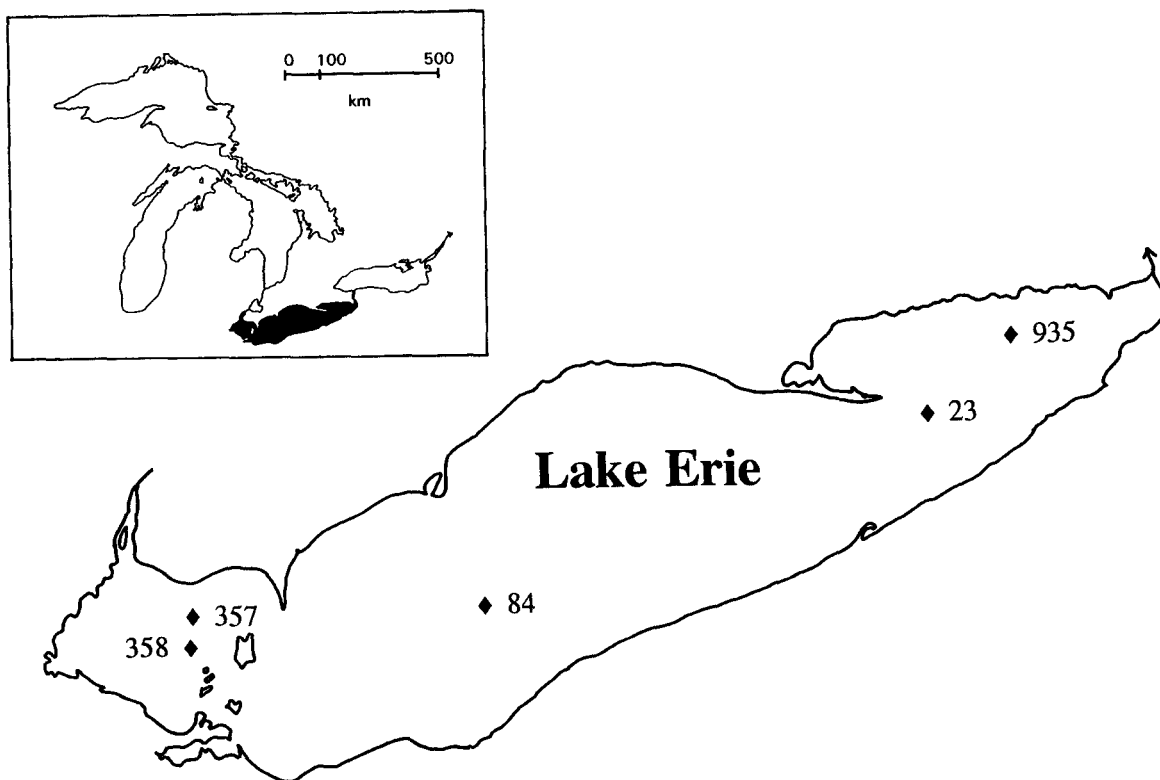


FIG. 1. Study site locations in the pelagic zone of Lake Erie. Lake Erie metrics: volume = 499 km³, surface area = 25,700 km², hydraulic residence time = 2.7 years (Quinn 1992).

water plankton was studied at several pelagic stations in Lake Erie (Fig. 1) during the period of thermal stratification in the summers of 1994 and 1995. A profile of temperature and light transmissivity was obtained at each sampling station using a conductivity/temperature/depth (CTD) probe (Sea-Bird Electronics; Bellevue, WA). Light transmission over a pathlength of 25 cm was measured at a wavelength of 670 nm. Temperature and transmissivity profiles at these stations revealed thermal stratification in the central and eastern basins and a well-mixed epilimnion at each of these stations, in contrast to the absence of stratification at the stations in the western basin (Fig. 2).

At each station, 16 L of lake water were collected from a depth of 5 m from the C.C.G.S. *Limnos* using an acid-cleaned, Teflon-coated 8-L Go-Flo bottle (General Oceanics) suspended on a non-metallic line. The sampling bottle was immediately transferred to a Class-100 portable cleanroom fixed to the deck of the ship where all subsequent manipulations were conducted. Lake water was filtered through a 210- μ m pore size polypropylene mesh

(Spectrum) and pooled, then 2-L portions were distributed to each of three 2-L polycarbonate bottles (Nalgene).

The scavenging experiments conducted during each of the three research cruises were relatively similar; the techniques employed in each cruise are described below. During the July 1994 cruise, a radioactive cocktail (75 μ L) of ¹³⁷Cs, ¹⁰⁹Cd, ⁶⁵Zn, and ¹⁵³Gd in 0.1 M HCl was added to each bottle immediately after the addition of an equivalent amount of NaOH (Gold Label, Johnson Matthey/Alfa-Aesar) to neutralize the acidity of the cocktail. Nominal added metal concentrations (and total radioactivities) were: Cs, 0.5 nM (133 kBq); Cd, 131 pM (111 kBq); Zn, 58 pM (122 kBq); Gd, 300 pM (56 kBq). Bottles were mixed gently by inversion, sampled for total radioactivity, and placed in an incubator designed to simulate *in situ* conditions at 5 m (21°C and a light intensity of \approx 120 μ mol photons/m²/s). During the September 1994 cruise, the nominal added trace metal concentrations (and total radioactivities) were: Cs, 1 nM (266 kBq); Cd, 179 pM (139 kBq); Zn, 58 pM (122 kBq); Gd, 317 pM (42

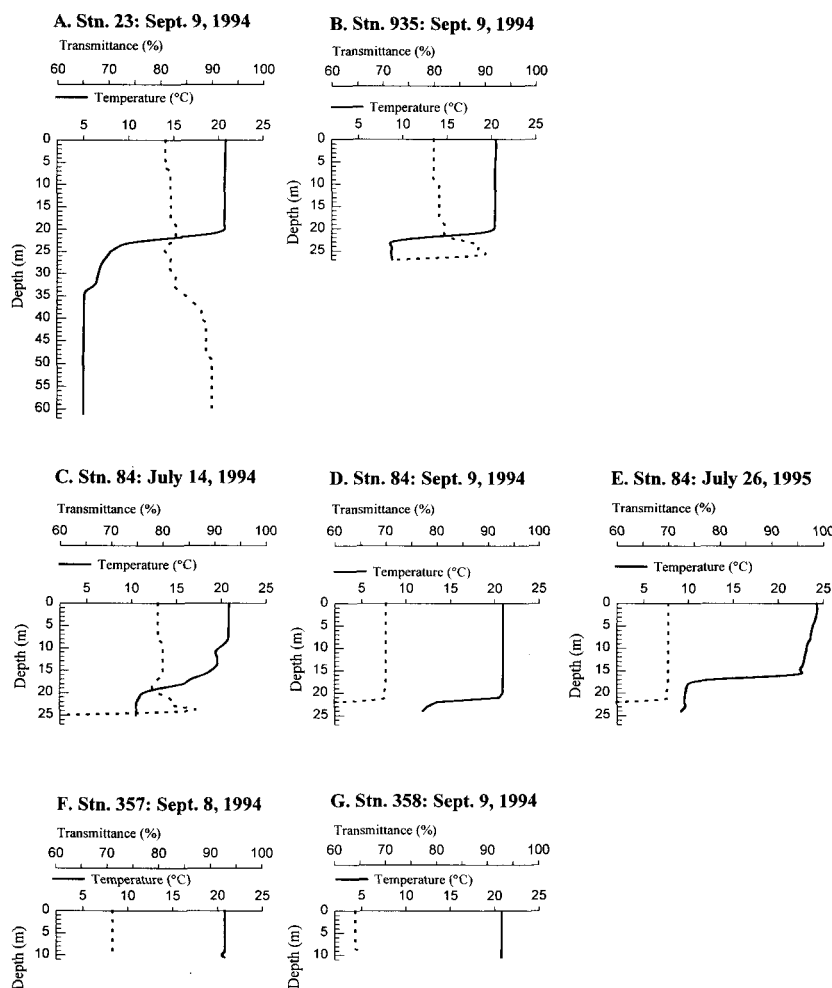


FIG. 2. Water column temperature and light transmissivity profiles from stations in Lake Erie sampled for the study of trace metal scavenging by particles $< 210 \mu\text{m}$. Station locations: Stns. 23 and 935, eastern basin; Stn. 84, central basin; Stns. 357 and 358, western basin.

kBq). All bottles were incubated on a shipdeck incubator, with temperature maintained at ambient surface water temperature (20°C) and natural light attenuated to 25% incident irradiance (e.g., 5 m depth) using two layers of neutral density screen. During the July 1995 cruise, the nominal added trace metal concentrations (and total radioactivities) were: Cd, 9.5 fM (33 kBq) and Zn, 44 pM (94 kBq); treatments during this cruise were incubated under simulated *in situ* conditions (20°C , and $150 \mu\text{mol photons/m}^2/\text{s}$).

At timed intervals over a period of 22 to 30 h, the fate of the trace metal radionuclides was determined by serial size differential filtration. Partition-

ing of the radionuclides among the plankton size classes was determined by size fractionating 100-mL aliquots from the treatment bottles using a $20\text{-}\mu\text{m}$ screen (Nitex, 47 mm dia.), followed by a $2\text{-}\mu\text{m}$ polycarbonate filter (Nuclepore, 47 mm dia.), and finally, a $0.2\text{-}\mu\text{m}$ polycarbonate filter (Nuclepore, 47 mm dia.). Volumes filtered at each fractionation were 100, 70, and 20 mL for the 20-, 2-, and $0.2\text{-}\mu\text{m}$ filters, respectively. Applied vacuums were less than 13 kPa; in previous laboratory studies a similar filtration technique was shown to induce minimal cell breakage of protozoa (Twiss and Campbell 1995). The total volume of water removed from the sample bottles was less than 20%, except for the

1995 experiment (*see below*). At each step in the filtration series, filtrate was collected and removed, the filter was rinsed with 10 mL of filter-sterilized lake water ($< 0.2 \mu\text{m}$), aspirated briefly to dryness, and removed. Two additional 2-mL samples from each bottle were removed at each sampling period to determine the total aqueous radioactivity.

During the July 1995 cruise size fractionation was conducted by parallel rather than serial filtration. Laboratory assays had established that there was no difference between results obtained for radionuclide partitioning if serial or parallel filtration was used to separate the delicate protozoan grazer, *Ochromonas danica*, from the picocyanobacterium *Synechococcus leopoliensis* (Twiss 1996, Appendix B). Parallel filtration was conducted for this single scavenging experiment since it allowed for numerous samples to be filtered in a short time period following the addition of the radioactive spike. In this method, separate aliquots of the sampled water were filtered directly onto a 20- μm filter, a 2- μm filter, or a 0.2- μm filter, and the filters were rinsed, as indicated above. Radionuclide accumulation by each plankton size fraction was determined by difference.

Water used in these scavenging experiments contained no mesozooplankton ($> 210 \mu\text{m}$), which might have naturally influenced particle concentrations through grazing and defecation. In order to reduce the effect of this factor, the scavenging experiments were not run for more than ≈ 30 h. Based on the study of Parker *et al.* (1982), which showed that mesozooplankton ($> 253 \mu\text{m}$) contribute only slightly to the total scavenging of radionuclides ($\leq 3.5\%$ ^{65}Zn , $\leq 7\%$ ^{109}Cd), one would not expect the absence of particles $> 210 \mu\text{m}$ to alter greatly the partitioning of radionuclides in the present experiments.

Analytical Techniques

Radioactivity was determined with a gamma-spectrometer (LKB Wallac Compugamma 1282; NaI crystal) equipped with a multi-isotope assay option (UltraTerm software). The radioactivity of each radionuclide was measured in the following energy ranges: ^{109}Cd , 20 to 38 keV; ^{153}Gd , 125 to 189 keV; ^{137}Cs , 628 to 756 keV; and ^{65}Zn , 990 to 1,268 keV. Background radioactivity (lake water or filter blanks) was subtracted from the sample counts. Controls for measuring the amount of radionuclides adsorbed to filters were prepared by re-filtering radiolabeled sterile lake water ($< 0.2 \mu\text{m}$)

through the appropriate filter and rinsing as usual. Propagated errors determined from the error of the sample and background counts were generally less than 10% ($P < 0.05$).

At each station, one liter of the filtered ($< 210 \mu\text{m}$) lake water was retained for measuring the initial pH and size-fractionated (0.2 to 2 μm , 2 to 20 μm , 20 to 210 μm) chlorophyll-*a* (chl-*a*) concentrations. Lake water pH was determined using the laboratory pH meter onboard the C.C.G.S. *Limnos*. Phaeophytin-corrected chl-*a* was determined onboard by fluorometric analysis after a 90% acetone extraction in the dark for 12 h at 4°C (Parsons *et al.* 1984).

Grazing and Growth Assays

The dilution assay technique of Landry and Hassett (1982) was used to assess the grazing and growth rates of phytoplankton in the picoplankton, nanoplankton and microplankton in water sampled from a depth of 5 m at Station 84 (July 1994) and Station 23 (September 1994). Details of the dilution assay procedure are provided in Twiss *et al.* (1996).

Trace Metal Inorganic Speciation

Calculations of inorganic Cs(I), Cd(II), Zn(II) and Gd(III) trace metal speciation in Lake Erie surface water were performed using a computerized chemical equilibrium model (MINEQL⁺, version 2.23; Schecher and McAvoy 1991). Stability constants for Gd, Zn, Cd, and Cs complexation were obtained from Turner *et al.* (1981). For the calculation of inorganic trace metal speciation, the ionic composition of Lake Erie water was based on a 1985 survey (Rockwell *et al.* 1989) of the central basin surface water during summer months (concentrations are mol/L): Na^+ , 3.8×10^{-4} ; K^+ , 3.4×10^{-5} ; Ca^{2+} , 8.7×10^{-4} ; Mg^{2+} , 3.4×10^{-4} ; Cl^- , 4.1×10^{-4} ; $\text{Si}(\text{OH})_4$, 5×10^{-6} ; PO_4^{3-} , 3.6×10^{-8} ; NO_3^- , 1.4×10^{-5} ; NH_3 , 1×10^{-6} ; SO_4^{2-} , 2.4×10^{-4} . Fluoride was considered to be 5.8×10^{-6} mol/L (Weiler and Chawla 1969). Chemical speciation for a system open to the atmosphere ($P\text{CO}_2 = 10^{-3.5}$ atm) was calculated for the pH range 6 to 9, at 22°C.

RESULTS AND DISCUSSION

Grazing and Growth Rates of Phytoplankton

Surface water sampled for scavenging experiments conducted at Stn. 84 (13 July 1994) and Stn. 23 (6 Sept. 1994) was also assayed for chl-*a*-based

specific rates of grazing and growth using dilution assays. Growth and grazing of autotrophic plankton occurred in all the surface water assayed (Fig. 3). In combination with dilution assays conducted at these stations on other dates and measurements of size-fractionated phytoplankton biomass (Table 1), these assays reveal a consistent trend of phytoplankton dynamics in the microbial food web of Lake Erie surface waters during summer (Table 2). The observed specific growth rates are within ranges published for Great Lakes photosynthetic picoplankton (0.05 to 1.5/d; Fahnenstiel *et al.* 1986, 1991a, 1991b) and total phytoplankton growth (0.05 to 0.6/d; Fahnenstiel and Scavia 1987, Scavia and Fahnenstiel 1987).

Trace Metal Sorption Experiments

Nominal added concentrations of Zn (44 to 58 pM) were an order of magnitude less than average concentrations reported for pelagic Lake Erie surface waters: 633 pM (Coale and Flegal 1989) and 1,330 pM (Nriagu *et al.* 1996). Added Cd (0.095 to 179 pM) was within, or below, the range of average reported Cd concentrations for this environment: 77 pM (Coale and Flegal 1989) and 249 pM (Nriagu *et al.* 1996). Added Cs (0.5 to 1 nM) exceeded values for dissolved stable Cs in the eastern basin (Sta. 23, 33 pM; Sta. 935, 27 pM) and central basin (Sta. 84, 16 pM; Sta. 953, 16 pM; Sta. 339, 17 pM) measured by inductively-coupled plasma mass spectroscopy (Finnigan Matt Element ICP-MS) on surface water samples (collected at 5 m depth on 29 to 31 July 1997 and filtered < 0.2 μ m). No reported measurements for dissolved gadolinium in Lake Erie could be found. For each of the added radionuclides, the majority of the metal did not sorb to plankton particles but remained in the dissolved phase. After 24 h, the average adsorptive losses to containers during assays were low: ^{153}Gd , $8.1 \pm 5.0\%$; ^{65}Zn , $7.8 \pm 3.9\%$; ^{109}Cd , $4.9 \pm 3.7\%$; and ^{137}Cs , $2.5 \pm 4.2\%$ (measured as a decrease in total aqueous radioactivity).

The reactivity of metals added in the trace metal radionuclide spike to the lake water might exceed that of the ambient forms of dissolved metal in the sample. The radionuclides were added at concentrations well below their respective solubility limits; under such conditions they should equilibrate rapidly with inorganic dissolved ligands. However, isotopic equilibration with non-radioactive metal complexed by dissolved, or especially colloidal, organic matter is expected to be slower (Piro *et al.*

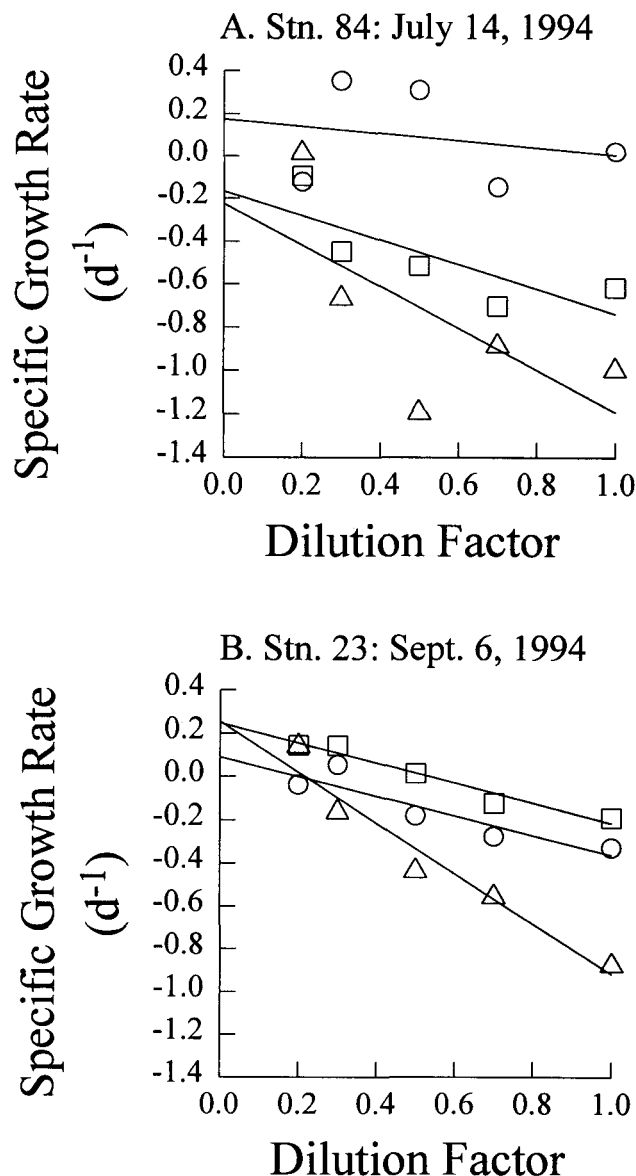


FIG. 3. Results from dilution assays used to estimate the chlorophyll-a based rates of grazing and growth among the picoplankton (Δ), nanoplankton (\square), and microplankton (\circ) size classes from the central basin (Fig. 3A) and eastern basin (Fig. 3B) of Lake Erie. Dilution factor is the ratio of whole lake water to sterile lake water in the treatment. The slope of the linear least squares regression of specific growth rate versus dilution represents the specific grazing rate whereas the intercept is the estimated intrinsic specific growth rate.

TABLE 1. Chlorophyll-*a* content of plankton size classes and characterization of water sampled from a depth of 5 m at various pelagic study sites in Lake Erie. Total chl-*a* does not include phytoplankton retained by the pre-filter (210 μm cut-off); water sampled from stations in the western basin had some algal/cyanobacterial filaments > 210 μm . Micro = microplankton, 20 to 210 μm ; Nano = nanoplankton, 2 to 20 μm ; Pico = picoplankton, 0.2 to 2 μm . %T = % light transmittance at 750 nm.

Station	Date	Total chl- <i>a</i> ($\mu\text{g/L}$)	Chlorophyll- <i>a</i> (%)			$^{\circ}\text{C}$	%T	pH
			Micro	Nano	Pico			
935 ^a	6 Sept. 94	2.26	26	34	41	20.4	80	8.2
23 ^b	7 July 94	1.48	20	46	35	21.0	—	8.1
23 ^{a,b}	6 Sept. 94	1.91	19	32	49	20.8	81	—
23	24 July 95	1.88	31	38	31	22.0	—	8.5
84 ^b	12 July 94	1.65	8	56	36	21.0	—	8.5
84 ^a	13 July 94	1.81	9	57	34	20.8	79	8.5
84 ^b	14 July 94	1.97	10	57	32	—	—	—
84 ^a	7 Sept. 94	4.57	13	43	44	21.0	70	—
84 ^a	26 July 95	5.53	58	29	13	23.8	75	8.9
357 ^a	8 Sept. 94	2.58	47	29	24	20.8	71	—
358 ^a	8 Sept. 94	3.71	33	41	26	20.8	64	—

Notes: ^a Stations at which a trace metal scavenging experiment was conducted. ^b Stations at which grazing and growth rate assays of photosynthetic plankton were conducted.

TABLE 2. Chlorophyll-*a* based specific growth (μ) and grazing (g) rates ($d^{-1} \pm SE$) in each plankton size fraction as determined using dilution assays. Calculated mean ($\pm SD$) is for the average of all four assays, with the exception of the negative growth rates determined for picoplankton and nanoplankton at Stn. 84 on 14 July 1994 (see Fig. 3 for details).

Growth:			
Stn. and Date	Picoplankton	Nanoplankton	Microplankton
Stn. 84, 14 July 14 1994	(-0.22 ± 0.40)	(0.17 ± 0.17)	0.17 ± 0.27
Stn. 84, 12 July 1994 ^a	0.50 ± 0.20	0.31 ± 0.08	0.68 ± 0.09
Stn. 23, 6 Sept. 1994	0.26 ± 0.10	0.25 ± 0.04	0.09 ± 0.07
Stn. 23, 11 July 1994 ^a	1.07 ± 0.10	0.74 ± 0.12	0.33 ± 0.08
Mean \pm SD	0.61 ± 0.42	0.43 ± 0.26	0.32 ± 0.26
Grazing:			
Stn. and Date	Picoplankton	Nanoplankton	Microplankton
Stn. 84, 14 July 1994	0.97 ± 0.63	0.57 ± 0.26	0.17 ± 0.41
Stn. 84, 12 July 1994	1.60 ± 0.32	0.67 ± 0.12	0.18 ± 0.13
Stn. 23, 6 Sept. 1994	1.17 ± 0.16	0.46 ± 0.06	0.45 ± 0.11
Stn. 23, 11 July 1994	1.93 ± 0.16	0.88 ± 0.19	0.28 ± 0.12
Mean \pm SD	1.42 ± 0.43	0.65 ± 0.18	0.27 ± 0.13

1972). Hence, the greater the proportion of non-labile metal present under ambient conditions, the less representative would be the radionuclide addition since the rate of scavenging obtained using the present experimental design would overestimate the true scavenging rate. Notwithstanding this question of isotopic equilibration, the addition of a largely labile pool of trace metal into the water samples, as conducted here, is similar to the atmospheric input

of trace metals into these lakes (Lum *et al.* 1987); inputs of Zn and Cd are largely in soluble form, however, no data are available for Cs or Gd solubility in wet or dry deposition. Inputs of these elements into Lake Erie from watershed erosion and industrial effluents are notable (Nriagu 1986), yet apt to be in chemical forms less available for scavenging reactions.

Accumulation of trace metal radionuclides into

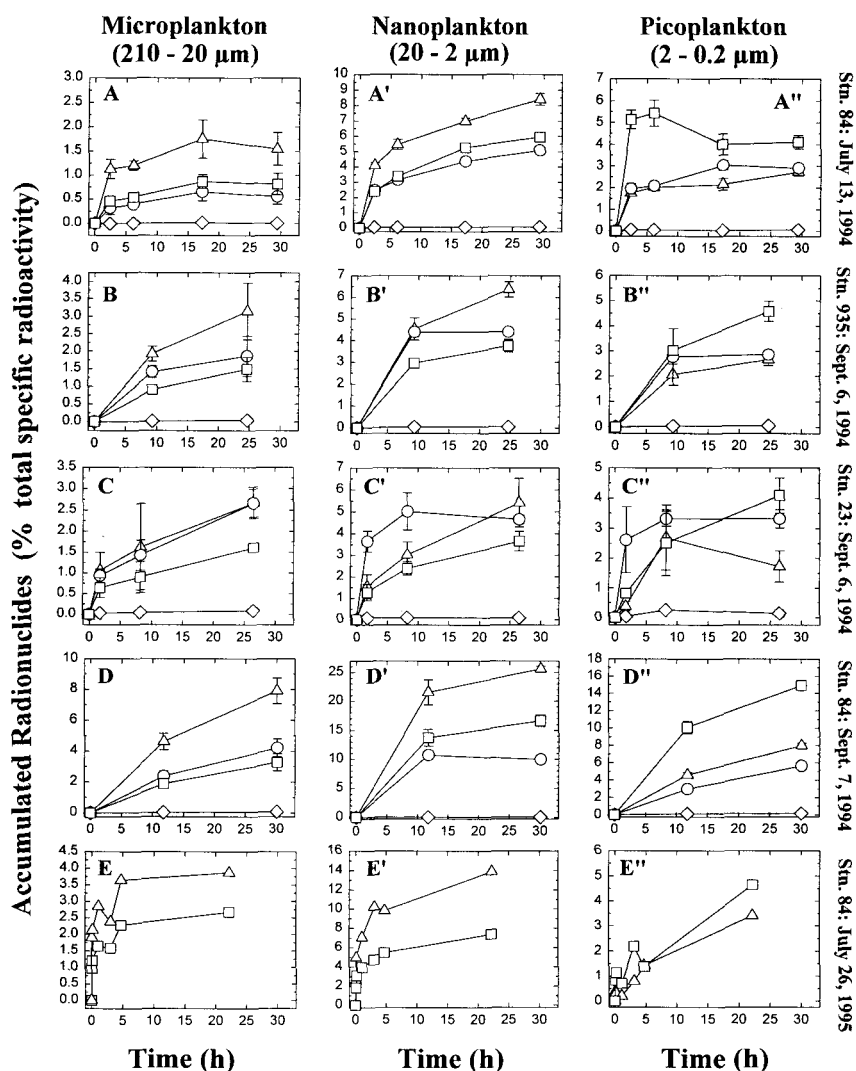


FIG. 4. Sorption of trace metal radionuclides by various plankton size classes in surface water samples collected at various stations in pelagic regions of the central and eastern basins of Lake Erie. Study sites are arranged in an order of increasing total chlorophyll-a content ($A < E$; see Table 1). Values represent mean \pm SD ($n = 3$), except E-E'' where $n = 1$. Trace metals were added in an inorganic dissolved form to each treatment at the beginning of the exposure period. Total added metal concentrations were: Gd, 300–317 pM; Zn, 44–58 pM; Cd, 0.01–179 pM; Cs, 0.5–1 nM (see Section 4.3.2 for details): \circ - ^{153}Gd ; \triangle - ^{65}Zn ; \square - ^{109}Cd ; \diamond - ^{137}Cs .

all the plankton size fractions occurred rapidly after the addition of the radioactive cocktail (Fig. 4). At many stations partitioning among the aqueous and particulate phases was approaching an apparent sorption equilibrium within 20 h. Similar asymp-

totic sorption equilibria occurred within ≈ 24 h when carrier-free ^{109}Cd and ^{65}Zn were added to non-filtered water (containing mesozooplankton) sampled from the epilimnion of Lake Michigan (Parker *et al.* 1982).

The nanoplankton consistently accumulated the most radionuclides (e.g., Fig. 4), except in the case of ^{109}Cd : this element was accumulated more in the picoplankton fraction than in the nanoplankton, with the notable exception of Stn. 84 (July 13, 1994; Fig. 4 A'-A''). Although the picoplankton also appeared to accumulate more ^{137}Cs than did the other size fractions after 20 h of exposure, this consistent trend was not statistically significant ($P > 0.05$).

Sorption of trace metal radionuclides to particle surfaces is generally considered to be highly dependent upon the metal's reactivity (Fisher 1986), which is directly related to its first hydrolysis constant, or respective charge density (charge to ionic radius ratio; z^2/r): Gd^{3+} (9.6) $>$ Zn^{2+} (5.4) $>$ Cd^{2+} (4.1) $>$ Cs^+ (0.6). This range in reactivities was not however directly reflected by the accumulation of these radionuclides into the various plankton size fractions in the Lake Erie surface waters examined here. Cesium behaved as expected; the least surface reactive of the elements studied, it never accumulated into the sum of the plankton size classes to levels greater than 1.2% of the total ^{137}Cs added (with the exception of accumulation by seston from stations in the western basin; see below). However, the accumulations of Gd, Zn, and Cd by the plankton size fractions were more similar than expected.

Gadolinium

Despite the fact that ^{153}Gd is the most strongly hydrolysed element among the added radionuclides and was thus expected to be the most readily scavenged element, total ^{153}Gd accumulations by plankton were equal to, or less than, those of ^{65}Zn or ^{109}Cd (Fig. 4). Similar to these observations made in Lake Erie, the observed volume concentration factor of ^{153}Gd ($[\text{Gd}]_{\text{algae}}/[\text{Gd}]_{\text{water}}$) for the diatom *Skeletonema costatum* cultured in sea water (pH 8.2) was $10^{5.4}$, compared with a measured concentration factor of $10^{4.9-5.5}$ for ^{65}Zn under the same conditions (Bingler *et al.* 1989). The present results from Lake Erie, and these observed levels of ^{153}Gd sorption by a marine diatom, contrast with the relative accumulations of radionuclides by the picoplanktonic cyanobacterium *Synechococcus leopoliensis* in an inorganic growth medium (pH 7.5), similar in chemical composition to Lake Erie but containing no dissolved organic matter (Twiss and Campbell 1995). In the laboratory assays, *S. leopoliensis* bioconcentrated ^{153}Gd

to values $10^{6.4}$ -times the aqueous concentration present in radiolabeled inorganic growth medium; this bioconcentration factor was approximately 10-fold greater than that for ^{65}Zn and ^{109}Cd . In preliminary studies of the present experimental design on surface waters of Lac Bedard, a circumneutral lake (pH 6.4, total chl-*a* = 6 $\mu\text{g/L}$) in the Laurentian Mountains north of Quebec City, total sorption of ^{153}Gd (9.3%) by particles after 25 h was far greater than that observed for ^{109}Cd (1.9%), ^{65}Zn (1.1%), and ^{137}Cs (0.3%). These differences in the accumulation of Gd may reflect differences between natural plankton and the cultured phytoplankton, those between natural waters and defined culture medium, or possibly the presence of a particulate mineral phase in Lac Bedard capable of preferentially binding Gd. However, variations in the ambient pH are likely the major factor affecting the sorption of Gd.

In support of the suggestion that Gd sorption is highly pH-dependent, inorganic speciation calculations indicate that Gd availability at the elevated pH of Lake Erie surface water in the summer was likely limited by its complexation with carbonate at elevated pH (Fig. 5). For example, at a total dissolved concentration of 300 pM Gd, the Gd^{3+} concentration would be only 0.06 pM at pH 9, but near 160 pM at pH 6.5. The presence of natural dissolved organic matter in surface waters may also have affected the speciation of Gd and its availability for sorption reactions, since Gd, like all rare earth elements, has a strong affinity for organic ligands (Sholkovitz 1995).

Cesium

Cesium speciation was dominated by the univalent Cs^+ cation (Fig. 5). Since over 99% of ^{137}Cs was in the dissolved phase in all sorption experiments (with the exception of the water sampled from the western basin; see below), the very low values for Cs sorption suggest that resuspended sediments ($> 0.2 \mu\text{m}$) were not abundant in the pelagic surface waters. Cesium has a high affinity for sediments (Hesslein *et al.* 1980), especially inorganic detrital material such as clay (Francis and Brinkley 1976). The observed high level of total ^{137}Cs sorption to particles from the western basin (3.6% at Stn. 357, 4.8% at Stn. 358), where the surface water was contiguous with the sediment (Fig. 2), is consistent with a higher affinity of Cs^+ for inorganic detrital materials than biological surfaces (Garnham *et al.* 1993).

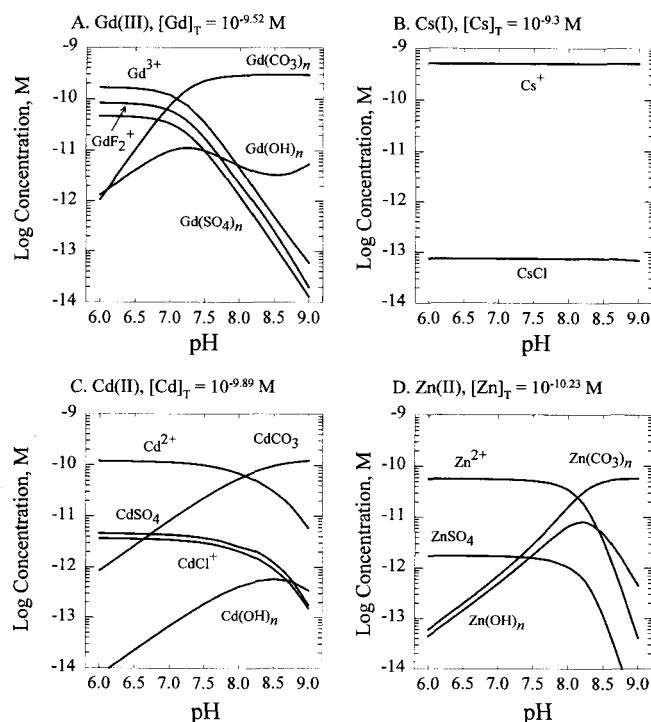


FIG. 5. Inorganic speciation of trace metals studied in scavenging experiments in simulated Lake Erie surface water (summer, central basin) over the pH range 6–9 (see text for a detailed description of water composition). The estimated speciation assumes the absence of natural organic metal-complexing ligands. Note: n denotes the sum of trace metal bound to a zspecific ligand, e.g., $\text{Gd}(\text{OH})_n = \text{GdOH}^{2+} + \text{Gd}(\text{OH})_2^+ + \text{Gd}(\text{OH})_3 + \text{Gd}(\text{OH})_4^-$.

Cadmium and Zinc

Differences in the relative amount of ^{109}Cd and ^{65}Zn accumulation by the nanoplankton and microp plankton were consistently observed: significantly more ^{65}Zn than ^{109}Cd was accumulated into these two plankton fractions. The opposite was observed for accumulation in the picoplankton. It appears that Cd was favorably sorbed by the picoplankton, or conversely, that Zn sorption by this size class was inhibited. Given the abundant dissolved pool for both these elements in the sorption experiments (> 85% of total), this difference in behavior cannot be attributed to a lack of available metal for sorption by particles. Although the calculated proportion of the free metal ion at pH 8.5 was greater for Cd (23%) than for Zn (6%), chemical

speciation cannot explain the consistent preferential sorption of Cd by the picoplankton—if so one would expect to find preferential Cd sorption on all particles, regardless of particle size.

Data from total dissolved trace metal concentrations in Lake Erie surface waters provide evidence of Cd depletion in surface waters when Zn becomes limiting (Nriagu *et al.* 1996). It is possible that Zn limitation could cause a shift toward Cd accumulation, since Cd can substitute effectively in metabolic processes for Zn in marine phytoplankton under Zn-limiting conditions (Morel *et al.* 1994). However, one would expect smaller organisms (bacteria, cyanobacteria, and algae) of the picoplankton size class to be at an advantage in accumulating low levels of Zn and thus to be less limited by Zn than the plankton of larger size classes. Therefore, with the information available, the suggestion that Zn-limiting conditions cause preferential Cd scavenging in only the picoplankton is incompatible with the scavenging patterns observed in the larger sized plankton classes ($\text{Zn} > \text{Cd}$).

One possible explanation for the differing behavior of Cd and Zn lies in their different reactions with the surface of calcite. Laboratory studies have established that Cd is more readily sorbed onto the surface of calcite, and less easily desorbed, than is Zn (Zachara *et al.* 1991). The warm temperature (20+°C) and high pH (≥ 8.1) during the study period favored the precipitation of biogenic calcite. It is conceivable that calcite formed on the surface of autotrophic picoplankton, as has been demonstrated for both carbonaceous mineral formation on the surface of *Synechococcus* (Schultze-Lam and Beveridge 1994) and plankton in the surface waters of Lake Ontario at comparable water temperatures (Hodell *et al.* 1998), is the solid phase that is responsible for the preferred sorption of Cd by the picoplankton.

Trace Metal Scavenging Potential of Various Plankton Size Fractions

Radionuclide accumulation into the various plankton size fractions was positively correlated with the chl-*a* content of a given size fraction (Fig. 6). Affinities of radionuclides for the various size fractions were derived from linear least squares regressions (Table 3). The affinity of ^{109}Cd and ^{65}Zn exceeded that of ^{153}Gd in all size fractions, and with the exception of the picoplankton, ^{65}Zn had a greater particle affinity than ^{109}Cd (Table 3). Note

that estimated particle affinity (slope) is a composite value and presumably reflects favorable binding sites on the particle surfaces and nutritive requirements (hence a high degree of internalization by microbiota in the case of Zn), as well as trophic transfer of radionuclides for size fractions containing consumer organisms (Twiss *et al.* 1996).

Peak sorption of ^{109}Cd and ^{65}Zn by total seston in offshore waters of Lake Michigan ($> 0.45\ \mu\text{m}$) coin-

cided with the period of maximum phytoplankton biomass in July (Parker *et al.* 1982); however, on an inter-seasonal basis (May to December), only the sorption of ^{65}Zn correlated significantly with primary productivity measured as $^{14}\text{CO}_2$ uptake. Since zinc is a required trace element, such a correlation between sorption and productivity is understandable. Based on the data from the present study, the hypothesized affinity of ^{109}Cd for biogenic calcite in the picoplankton size fraction (*see above*) may help to explain the significant correlation ($P < 0.01$) between chl-*a* and the sorption of this element during the time period in which these scavenging experiments were conducted. Calcite precipitation is linked to primary productivity during periods of intense photosynthetic activity and warm water temperatures, normally from June to early September in Lake Erie. Thus, the link between Cd scavenging and primary production would only be evident when primary production induces calcite precipitation; this may explain the lack of a significant correlation between chl-*a* and Cd sorption in Lake Michigan over the period from May to December reported by Parker *et al.* (1982).

In the plots of radionuclide accumulation *versus* chl-*a* concentration, the estimated intercepts (Table 3) represent the average non-chl-*a*-specific sorption of a given radionuclide for a given size fraction. Only ^{153}Gd possessed significant non-chlorophyll-specific sorption in the nanoplankton and picoplankton fractions, whereas the regressions of

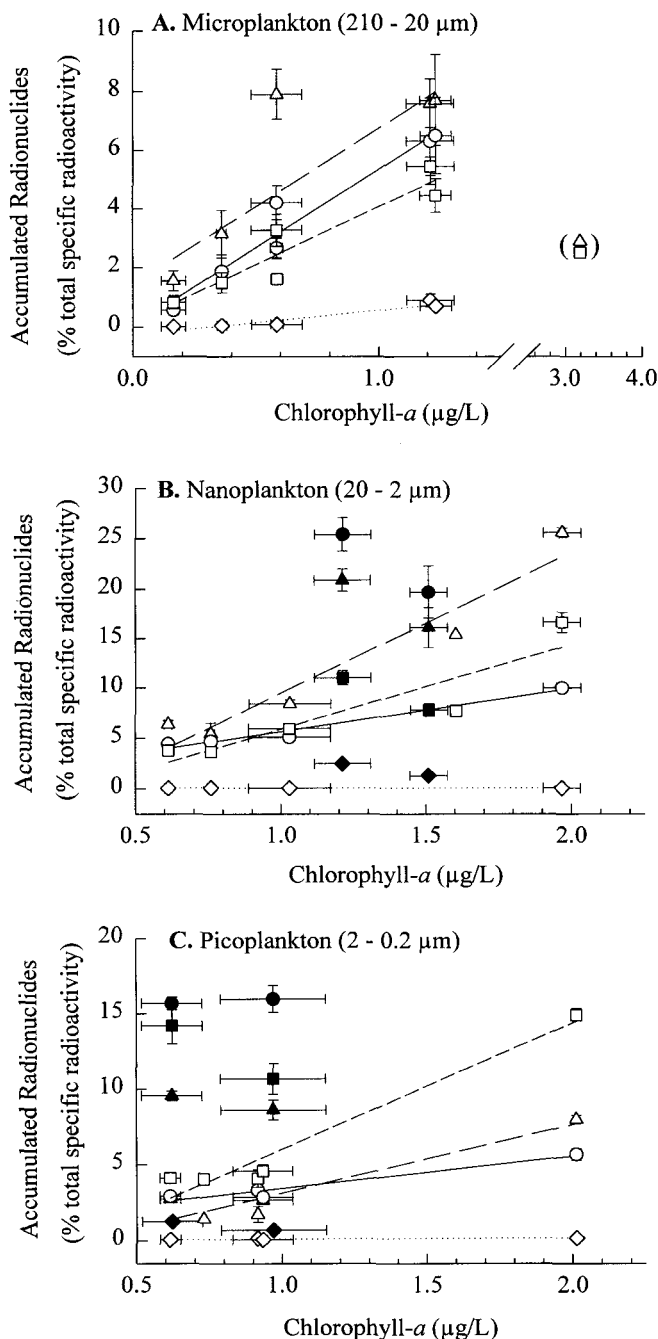


FIG. 6. Chlorophyll-specific sorption of trace metal radionuclides by various plankton size classes in pelagic surface waters of Lake Erie. Plotted values represent the accumulated radionuclides (mean \pm SD, $n = 3$) at the end of each assay (22-30 h) at the observed size-specific initial concentration of chlorophyll-*a* (mean \pm SD, $n = 2-3$). Data for ^{109}Cd and ^{65}Zn sorption by microplankton at Stn. 84 (24-07-95) were not considered in the regression analyses; microplankton was dominated by a bloom of colonial *Microcystis* at this sampling time. Solid symbols representing data collected from the western basin were not included in the regression analyses but are included for comparative purposes (see text for explanation). Trace metal radionuclides: \circ - ^{153}Gd ; \triangle - ^{65}Zn ; \square - ^{109}Cd ; \diamond - ^{137}Cs .

TABLE 3. Linear least squares regression analyses of sorbed trace metal radionuclides over 22 to 30 h as a function of chlorophyll-*a* content in various plankton size classes. Regressions are plotted in Figure 6; linear formula is $y = mx + b$, where y = accumulated metal (% total specific radioactivity added), m = slope, x = concentration of chl-*a*, b = y -intercept. Values of m and b are expressed \pm 95% confidence intervals. Regression correlation coefficients (r) are coded for significance levels: $< 1\%$ = ****; $< 2\%$ = ***; $< 5\%$ = **; $< 10\%$ = *; no significance levels are reported for d.f. < 3 .

Plankton Size	Metal	m	b	r	d.f.
Microplankton (20–210 μm)	^{153}Gd	5.33 ± 0.63	0.003 ± 0.62	0.973****	4
	^{65}Zn	5.32 ± 2.00	1.42 ± 1.97	0.800*	4
	^{109}Cd	3.94 ± 0.71	0.13 ± 0.70	0.940****	4
	^{137}Cs	0.83 ± 0.15	-0.27 ± 0.14	0.943****	4
Nanoplankton (2–20 μm)	^{153}Gd	4.29 ± 0.56	1.35 ± 0.59	0.984	2
	^{65}Zn	14.13 ± 2.31	-4.65 ± 2.65	0.962****	3
	^{109}Cd	8.54 ± 2.18	-2.66 ± 2.51	0.914**	3
	^{137}Cs	-0.001 ± 0.02	0.07 ± 0.02	0.041	2
Picoplankton (0.2–2 μm)	^{153}Gd	2.10 ± 0.36	1.33 ± 0.38	0.972	2
	^{65}Zn	4.50 ± 0.92	-1.38 ± 1.03	0.943***	3
	^{109}Cd	8.36 ± 1.06	-2.35 ± 1.19	0.977****	3
	^{137}Cs	0.08 ± 0.04	0.02 ± 0.05	0.781	2

^{65}Zn and ^{109}Cd sorption by the nanoplankton and picoplankton had negative intercepts. Further study in more oligotrophic environments would be required to explain these metal sorption/chl-*a* relationships fully. Stations sampled in the western basin of Lake Erie were eliminated from the regressions for nanoplankton (Fig. 6B) and picoplankton (Fig. 6C) since resuspended sediment was probably affecting the composition of the seston. The epilimnion at these stations during the sampling period was contiguous with sediment whereas strong thermal stratification prevailed at all other stations, as indicated by CTD profiles (Fig. 2). Wave action and shipping activity are suspected to have resuspended sediment at these sites in the western basin. The influence of non-chlorophyllous particles on radionuclide sorption by the nanoplankton and picoplankton at these stations is evident in Figure 6. Since the resuspended sediment did not have a noticeable influence on radionuclide sorption in the microplankton size fraction (i.e., resuspended particles were presumably $< 20 \mu\text{m}$), the values for accumulation by the microplankton at these stations were retained for the regression analyses.

Biogeochemical Implications of Trace Metal Scavenging by Microbial Food Web Organisms

The relationship of trace metal sorbed per unit chl-*a* (Fig. 6) illustrates well the importance of the

various ecologically significant size fractions to trace metal scavenging. However, such a relationship is mechanistically limited: it does not address the numerous means by which a metal can enter a given size fraction, namely, surface sorption, internalization (transmembrane uptake), trophic transfer, and the generation of particulate fecal matter resulting from consumption.

One possible method to control for the relative contribution of surface sorption would be to use a biological inhibitor. In this manner, metal accumulated by particles would be dominated by the surface sorption of metals. Such a technique was employed in preliminary experiments with surface water from Lac Bedard (Twiss 1996, Appendix C) in which sodium azide (154 mM), formaldehyde (170 mM), or near freezing temperature ($\approx 0^\circ\text{C}$) were used to inhibit biological activity. Radionuclide sorption into plankton fractions was compared with a treatment that received no inhibitor. In the presence of inhibitors, less ^{137}Cs , ^{109}Cd , ^{65}Zn , and ^{153}Gd accumulated into the plankton in comparison with the living treatment (data not shown). However, when metabolic inhibitors are used, interpretation of the observed scavenging behavior is difficult since the value for partitioning in the controls (inhibitors present) refers to trace metal adsorbed to particles that existed when the inhibitor was added. Particle dynamics in a living sample (e.g., growth, consumption, fecal matter production) are such that

the relative importance of different particle populations may well vary over time, generating subtle differences between living and inhibited treatments. Examples of microbial planktonic community dynamics are evident in the observed rates of phytoplankton growth and grazing in the plankton fractions < 210 μm (Table 2). Thus, metabolic inhibitors have limited applicability in following the path of trace metals in a rapidly changing planktonic world.

In their study of Zn and Cd fate in Lake Michigan surface waters, Parker *et al.* (1982) observed that the majority of ^{65}Zn ($\geq 63\%$) and ^{109}Cd ($\geq 76\%$) scavenged by the seston > 0.45 μm was scavenged by the fraction 0.45 to 28 μm . A similar result was observed in the present study where the majority of scavenged trace metal (0.2 to 210 μm) after 20 h was scavenged by particles in the size fraction 0.2 to 20 μm (^{153}Gd , $83\% \pm 7\%$; ^{65}Zn , $80\% \pm 6\%$; ^{109}Cd , $85\% \pm 5\%$; ^{137}Cs , $76\% \pm 6\%$; mean \pm SD). However, as documented in the present study, the subdivision of this wide particle size spectrum into ecologically meaningful size classes yields a better appreciation of the important geochemical roles that microbial food web organisms play.

The approach used here to assess the partitioning of trace metals within the plankton of the microbial food web has provided new information on trace metal fates in the surface water of Lake Erie during thermal stratification. The data support the hypothesis that appreciable amounts of trace metals are scavenged by ecologically important size fractions, primarily the picoplankton (0.2 to 2 μm) and nanoplankton (2 to 20 μm). The hypothesis that trace metal scavenging by plankton is proportional to the metal's particle-reactivity is partially supported by the data. For example Cs, the most weakly particle-reactive metal studied here, was also the most weakly scavenged. However, the chemical speciation of trace metals under the conditions present in Lake Erie surface waters appears to play an important role in limiting the availability of hydrolysable elements (e.g., Gd) for scavenging reactions. Based on recent studies in oceanic surface waters (Bruland *et al.* 1991) and in Swiss lakes (Xue *et al.* 1995), where high affinity metal-complexing ligands have been shown to control the chemical speciation of several trace metals, it is conceivable that Cd and Zn speciation in Lake Erie surface waters is also dominated by similar ligands (cf. Twiss *et al.* 1996), but these ligands were not measured in this study. Existence of these com-

plexes would have substantial impact on trace metal speciation in Lake Erie.

In addition, measureable differences in the metal binding characteristics of particles among size fractions are considered to be the reason for the greater scavenging of Cd over Zn in the picoplankton size fraction. Cell washing solution containing metal complexing ligands could be used to remove surface-bound metal (e.g., Twiss *et al.* 1996) and differentiate among different scavenging mechanisms, e.g. internalization versus surface sorption.

Autochthonous particles such as plankton and biogenic calcite dominate the suspended particulate matter in pelagic surface waters during thermal stratification (Robbins and Eadie 1991), and the measurements of growth and grazing rates of pelagic Lake Erie phytoplankton < 210 μm (Table 2) demonstrate that the autotrophic members of this autochthonous particle population are continuously changing. This observation suggests that plankton dynamics should be considered in predictions of the geochemical fate of trace metals in this environment. In an accompanying paper (Twiss and Campbell 1998), the trace metal and plankton dynamics reported here are incorporated into a dynamic model that is used to evaluate the impact of the microbial food web on trace metal cycling in pelagic Lake Erie surface waters during the period of thermal stratification.

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