

## Chromium Geochemistry and Bioaccumulation in Sediments from the Lower Hackensack River, New Jersey

L. Martello · P. Fuchsman · M. Sorensen ·  
V. Magar · R. J. Wenning

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**Abstract** Total and hexavalent chromium [Cr(VI)] were measured in sediment and sediment porewater in the lower Hackensack River (NJ) to assess the relationship between sediment geochemistry and chromium speciation, which in turn controls the mobility, bioavailability, and toxicity of chromium. Between 2003 and 2005, >100 surface (0 to 15 cm) sediment samples were tested for total chromium and Cr(VI), acid-volatile sulfides (AVS), ferrous iron (Fe(II)), divalent manganese (Mn(II)), ammonia, and organic carbon. Sediment porewater samples were collected by centrifugation or using *in situ* samplers colocated with the collection of sediments. In whole sediments, total chromium and Cr(VI) concentrations ranged from 5 to 9190 mg/kg dry weight (dw) and from <0.47 to 31 mg/kg dw, respectively. Sediment porewater concentrations ranged from <10 to 83 µg/l for total chromium; Cr(VI) was not detected in sediment porewater ( $n = 78$ ). Concentrations of AVS (ranging between <10.6 to 4178 mg/kg) and other geochemistry measurements indicated anoxic, reducing conditions in the majority of sediment samples. In polychaetes (*Nereis virens*) and clams (*Macoma*

*nasuta*) exposed in the laboratory for 28 days to sediments contained between 135 and 1780 mg/kg dw total chromium, concentrations in whole tissues after 24-hour depuration ranged between 1.2 and 14.8 mg/kg wet weight (ww; median 1.6 mg/kg ww) total chromium. In whole tissues of indigenous polychaetes collected from the sediment, tissue concentrations of total chromium ranged between 1.0 and 37.5 mg/kg ww (median = 2.1 mg/kg ww). Chromium concentrations in whole tissues of animals exposed in the field or in the laboratory showed no relationship with total chromium or Cr(VI) concentrations in the sediment. There were no statistical differences among animals exposed to sediments from site and reference locations. The results of this study are consistent with sediment studies conducted elsewhere indicating low chromium bioavailability in sediment under reducing conditions. This study also highlights the importance of sediment geochemistry and *in situ* porewater measurements to understand the ecological significance of chromium in sediment and the potential for human health and ecological exposures.

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L. Martello (✉) · R. J. Wenning  
ENVIRON International Corporation, 6001 Shellmound Street,  
Suite 700, Emeryville, CA 94608, USA  
e-mail: lmartello@environcorp.com

M. Sorensen  
ENVIRON International Corporation, 1600 Parkwood Circle,  
Suite 310, Atlanta, GA 30039, USA

P. Fuchsman  
ENVIRON International Corporation, 13801 West Center Street,  
Suite 1, Burton, OH 44021, USA

V. Magar  
ENVIRON International Corporation, 123 North Wacker Drive,  
Suite 250, Chicago, IL 60606, USA

Chromium concentrations in excess of naturally occurring background levels are widespread in sediments in urbanized and industrialized estuaries because of runoff from road surfaces, combined sewer overflows, and municipal and industrial discharges (Paul et al. 2002; United States Environmental Protection Agency [USEPA] 2004). Although early efforts to evaluate sediment quality and the significance of chromium in sediment focused on analyses of total chromium (Long et al. 1995), recent studies suggest that chromium speciation in sediment must be understood to support more accurate evaluations of potential ecological impacts (Berry et al. 2004; Besser et al. 2004; USEPA 2005).

Historically, predicting the biological effects of chromium in sediments has been difficult because chromium

exists in multiple oxidation states, primarily trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)], which exhibit widely differing geochemical and ecotoxicologic properties. Cr(VI) exhibits much greater solubility, mobility, bioavailability, and toxicity than Cr(III) in sediments and surface waters (Richard & Bourg 1991; James 2002; USEPA 1984, 2005). Cr(III) is relatively insoluble at environmentally relevant pH because of the formation of insoluble hydroxide and oxide compounds. In sediment, Cr(III) solubility is further limited by strong complexation with sediment minerals and solid-phase organic ligands (Sass & Rai 1987; Fendorf & Zasoski 1992; James 2002). For example, binding of Cr(III) by iron oxides can decrease solubility (James 2002). The inherent insolubility of Cr(III) limits its bioavailability and mobility. Indeed, because of a lack of Cr(III) toxicity in saltwater exposures, the USEPA has adopted saltwater criteria only for Cr(VI) to protect aquatic life (USEPA 1984).

Although the hexavalent state is thermodynamically favored under aerobic conditions, Cr(VI) is rarely found in the aquatic environment (Barnhart 1997). Reduction of Cr(VI) is rapid under reducing or even mildly oxidizing conditions, occurring within minutes to days depending on the reducing agent(s) (Schroeder & Lee 1975; Stollenwerk & Grove 1985; Richard & Bourg 1991; Masscheleyn et al. 1992; Lin 2002; Berry et al. 2004). Several organic and inorganic constituents in anaerobic sediments—including sulfides, ferrous iron, and organic matter (Hansel et al. 2003)—facilitate rapid reduction of Cr(VI) to Cr(III); bacterially mediated reduction of Cr(VI) has also been reported (Schmieman et al. 1998). A summary of geochemical parameters recognized in the scientific literature as influential to chromium geochemistry and bioavailability in sediment is listed in Table 1.

Once reduced, Cr(III) is stable in aquatic environments and unlikely to oxidize to Cr(VI), even in the presence of dissolved oxygen (Schroeder & Lee 1975; Saleh et al. 1989; Eary & Rai 1987). The extent to which Cr(III) oxidizes to Cr(VI) depends on the presence and mineralogy of Mn(III,IV) (hydr)oxides, pH, and the form and solubility of Cr(III) (James & Bartlett 1983; Fendorf & Zasoski 1992; Milačić & Štupar 1995; Weaver & Hochella 2003). Oxidation of Cr(III) is less likely to occur in aquatic environments than under laboratory conditions because aged waste materials containing Cr(III) are typically less soluble and more inert to oxidation, and Cr(OH)<sub>3</sub> precipitates may form on Mn(III,IV) (hydr)oxide surfaces (James & Bartlett 1983; Fendorf & Zasoski 1992; Fendorf 1995). Furthermore, potential Cr(III) oxidants are fewer and less abundant than potential Cr(VI) reductants in natural sediments, and Cr(III) oxidation is slower than Cr(VI) reduction, such that reduction is kinetically favored over oxidation (Stanin 2005; Eary & Rai 1987; Masscheleyn et al. 1992).

Because reducing conditions are incompatible with the presence of Cr(VI), the USEPA (2005) has concluded that the presence of detectable acid-volatile sulfide (AVS), which is an indicator of sediment reducing conditions, is a strong indicator of the likelihood of chromium reduction to Cr(III) in sediment. As originally conceived by Di Toro et al. (1990), extracting AVS from sediment provides a measure of the reactive pool of reduced sulfur in sediments, which has the potential to combine with divalent metals to form insoluble metal sulfides (MeS). When molar concentrations of this pool of sulfur exceed the concentrations of divalent simultaneously extracted metals, sufficient sulfides are available to precipitate divalent metals as insoluble MeS, rendering them relatively nontoxic to the benthic invertebrates and aquatic biota that interact with the sediment. Chromium is not a divalent metal and does not form a MeS; however, where AVS is present, chromium in whole sediment has been shown to occur as Cr(III), and the sediments are generally not toxic because of chromium (Berry et al. 2004; Besser et al. 2004; Becker et al. 2006). Therefore, in the case of chromium, AVS can indeed serve as an indicator of the reduction potential of the sediment. Work by Besser et al. (2004) and Peterson et al. (1996) suggest, however, that vertical or seasonal changes in redox potential and AVS gradients in natural sediments should be considered when addressing metal bioavailability. Chromium reduction from Cr(VI) to Cr(III) occurs by way of an electron transfer reaction between a reductant and Cr(VI). Sulfides and reduced iron are the most common reductants, but other organic and inorganic reductants also contribute to this thermodynamically favored reaction.

The Hackensack River (NJ) is one of two large tributaries that flow into the northern portion of Newark Bay, a part of the larger New York–New Jersey Harbor Estuary. Newark Bay, including the lower reaches of both tributaries, has been challenged by significant waterfront development, loss of aquatic habitat, contaminated sediments, and poor environmental quality for the past two centuries (Crawford et al. 1995; Iannuzzi et al. 1997; Iannuzzi & Ludwig 2004). Sediments along the eastern shore of Drovers Point Reach, near the confluence with Newark Bay, are known to contain chromium, which is attributable in part to surface runoff and groundwater from a 0.14-km<sup>2</sup> former waterfront commercial property that was used for disposal of approximately 800,000 m<sup>3</sup> chromite ore processing residue (COPR) from 1905 to 1954. COPR is produced during chromite and bichromate chemical manufacturing and contains between approximately 2% and 7% chromium (primarily as Cr(VI); Burke et al. 1991). Other sources of chromium in the sediment are believed to be from both bay and upriver sources associated with historical releases from combined sewer outfalls, paint and pigment manufacturers, tanneries, smelters, and metal-plating facilities operating

**Table 1** Geochemical parameters in sediments affecting chromium speciation, bioavailability, and toxicity

Parameter	Description	Reference
AVS	Cr(VI) is rapidly reduced to Cr(III) in the presence of AVS.	Di Toro et al. 1990
Fe(II)	Similar to AVS, Fe(II) is an important reducing agent mediating the transformation of Cr(VI) to Cr(III).	Hansel et al. 2003
Mn(III,IV) (hydr)oxides	Mn-oxides are widely known as strong metal sorbents, scavengers, and oxidizers. Mn-oxides have been shown to oxidize Cr(III) to Cr(VI) under laboratory conditions.	Eary and Rai 1987; Masscheleyn et al. 1992; Weaver and Hochella 2003
DO	Reducing agents for chromium (AVS and Fe(II)) are typically abundant in anaerobic sediments ( <i>i.e.</i> , in the absence of DO). DO can vary with temperature and season.	Stanin 2005; Eary and Rai 1987
Salinity and Conductivity	The toxicity of Cr(III) in freshwater decreases with increasing hardness, and essentially no toxicity occurs in saltwater. Salinity may also affect Cr(III) solubility. Naturally occurring ligands and sequestering agents in seawater may decrease the toxicity of Cr(VI) and other metals.	Eisler 1986; Gambrell et al. 1994
Eh	Eh affects the dissolution or precipitation of various metals, indicating the thermodynamically favored form of the metal and its solubility; however, kinetic constraints must also be considered, Cr(III) is stable, even under oxidizing conditions. whereas Cr(VI) is unstable under reducing or even mildly oxidizing conditions.	USEPA 2005
TOC	Metals can form complexes with organic material; therefore, metals will be less bioavailable at higher concentrations of TOC. Organic ligands also can serve as reducing agents for chromium transformation, although the reduction kinetics are slower than for AVS or Fe(II).	Eisler 1986; Sprague 1985
DOC	Chromium has been shown to form complexes with dissolved organic carbon, which may increase the apparent solubility of Cr(III) but likewise decreases its bioavailability and oxidation potential.	Icopini and Long 2002
pH	Cr(III) solubility increases at low pH; such low pH levels occur in acidic soils but are rarely encountered in sediments. Chromium speciation is affected by both Eh and pH, such that Cr(VI) is stable under moderately oxidizing conditions at high pH.	James 2002; Rai et al. 1987; Saleh et al. 1989
Grain size	Grain size can affect metal bioavailability both directly and as it is correlated with TOC. Generally, increased fines content is associated with decreased bioavailability.	Forstner and Whittman 1981

Eh = reduction–oxidation potential; DO = dissolved oxygen; DOC = dissolved organic carbon; TOC = total organic carbon

until the mid-1900s (Iannuzzi & Ludwig 2004). The waterfront property is located on Route 440 in Jersey City, NJ, and has been designated as Study Area 7 by the New Jersey Department of Environmental Protection (NJDEP) Hudson County Chromate Project.

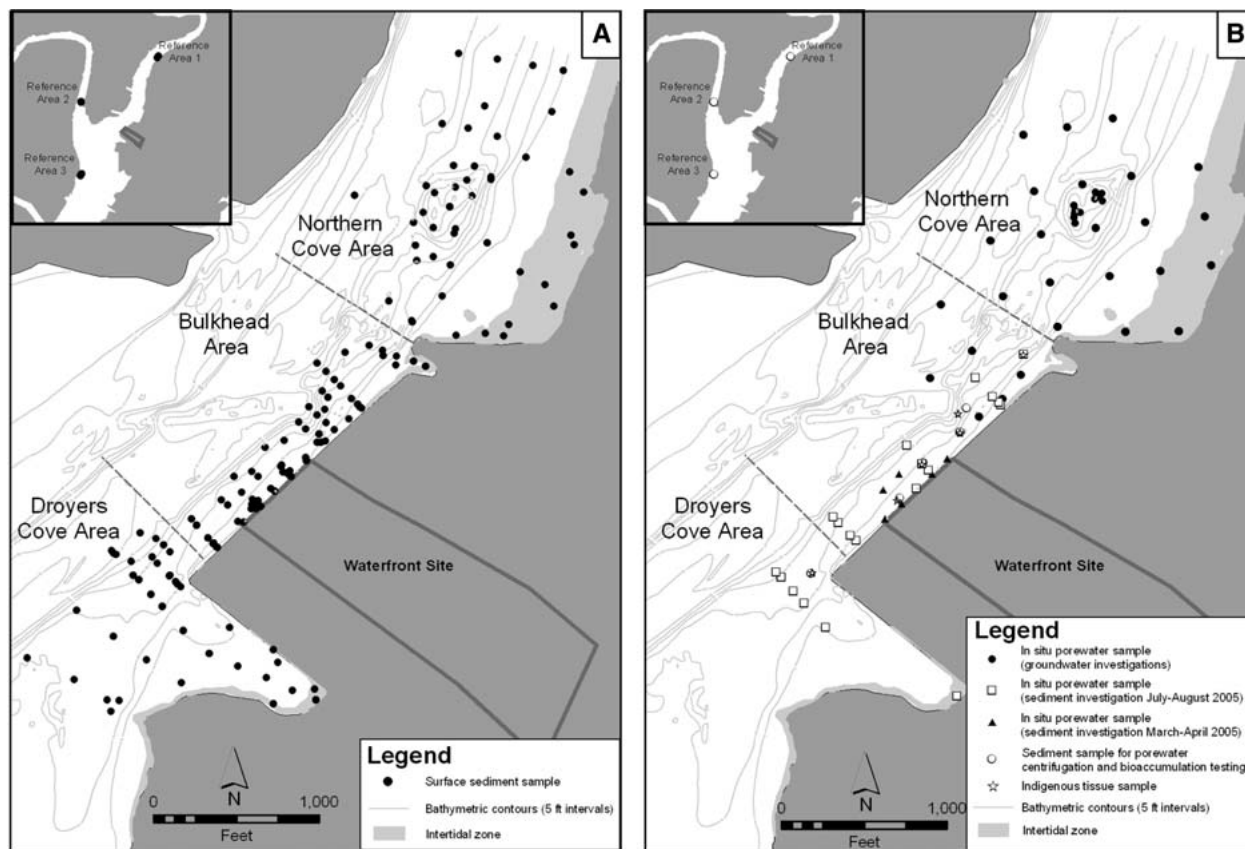
This article presents the results of an investigation of chromium speciation and bioavailability in sediments collected offshore in the vicinity of Study Area 7 (Fig. 1). The purpose of this study was to determine geochemistry conditions and the ecological significance of chromium in the biologically active zone in the sediments, including consideration of ecotoxicity and bioaccumulation in benthic organisms. The concentrations of total chromium, Cr(VI), and several geochemical parameters were measured in both surface sediments and sediment porewater. Bioaccumulation potential was determined in two species of benthic organisms, the polychaete *Nereis virens* and the clam *Macoma nasuta*, which were exposed in laboratory experiments and by collection and testing of whole tissues of indigenous organisms. Results were compared with those reported in sediment studies of chromium geochemistry conducted elsewhere. The information gleaned from this

study represents an important line of evidence contributing to the evaluation of remediation strategies for addressing chromium in sediments in the vicinity of Study Area 7.

## Methods

### Site Description

The lower Hackensack River flows through an intensely urban landscape that has been highly modified from its preindustrial salt marsh structure (Crawford et al. 1994). Water depths in the vicinity of Study Area 7 generally range from <1 to 3 m at low tide, with some shoreline sediments in the intertidal zone exposed in Droyers Cove to the south and in a cove to the north of the site. The navigation channel, which has not been dredged since 1983, is approximately 300 ft from shore. Tidal flows predominate over freshwater input, with a monthly average tidal range of 1.6 m and salinity >20 ppt during low river flow conditions. Although surface waters are generally well mixed and oxygenated, before the 1970s when most of the chro-



**Fig. 1** Site map showing surface (0–15 cm) (a) whole-sediment sample locations and (b) porewater and tissue sample locations

mium entered the river, anaerobic conditions often prevailed because of direct discharges of sewage and industrial wastes above and below the site (Crawford et al. 1994).

#### Collection of Sediment

Sediment samples were collected during four sampling events conducted from October through December 2003, November 2004, March through April 2005, and July through August 2005 at the locations indicated in Fig. 1. A total of 193 surface sediment samples were collected from 148 sampling locations as were 14 samples from 3 reference locations located in comparable sediment environments not influenced by activities at Study Area 7. The selection of locations for reference stations was based on similarity to Study Area 7, both in terms of benthic physical habitat and immediate nearby land uses, with the ultimate goal of characterizing baseline conditions of the local estuary. Reference stations in this study were not intended to represent pristine or ideal benthic habitats. Because sediments offshore from Study Area 7 lie in a tidally influenced reach of the river, reference stations were

selected that had comparable salinity ranges (11 to 16 g/L) both upstream and downstream of the site. Reference stations were located approximately 2 km south in Newark Bay, 1.5 km northwest in the Passaic River, and 2.5 km north in the Hackensack River (Fig. 1).

Sediment for chemical and physical testing was collected from the top 15 cm of sediment using either piston or vibracoring methods or a Ponar grab sampler. Sample handling did not include homogenization of sediments in the field. Sediment for laboratory bioaccumulation experiments and porewater extraction by centrifugation was collected in November 2003 using a 0.1 m<sup>2</sup> Van Veen grab sampler. Subsamples from cores or grab samplers were preserved in commercial laboratory-supplied glass sample containers and shipped at 4°C for chemical and physical analyses. Remaining sediment from the Van Veen grab sampler was placed in food-grade polypropylene bags, shipped at 4°C to a commercial laboratory, stored for 4 to 5 weeks, and sieved (2000 μm) to remove large debris before use in bioaccumulation experiments. Sampling activities were performed in accordance with New Jersey and USEPA technical guidance (USEPA and United States Army Corps of Engineers [USACE] 1998; NJDEP 1998; USEPA 2005a).

### Collection of Sediment Porewater

Sediment porewater was collected using either centrifugation or *in situ* sampling methods (Hesslein 1976; Bufflap & Allen 1995). In November 2003, porewater was collected from surface (0 to 15 cm) sediment samples from six site locations and three reference locations. The sediments were collected as described previously and centrifuged at 1000 × gravity for 15 minutes. The collected unfiltered water was transferred to commercial laboratory-supplied glass sample containers and shipped at 4°C for chemical analyses. Each container was filled to overflow to avoid, to the extent practical, the opportunity for aeration of the sample during storage and shipping.

Centrifugation methods to measure metals in porewater have been shown to cause a high bias in porewater concentrations for some metals (USEPA 2005b). It is generally accepted that when feasible, *in situ* sampling is preferable rather than centrifugation sampling (USEPA 2005). *In situ* samplers require less sample manipulation, best represent *in situ* equilibrium conditions, and minimize the potential for sample oxidation and other chemical changes compared with *ex situ* methods, such as centrifugation (Carr & Nipper 2001). *In situ* samplers were used to collect porewater from March to April 2005 at nine locations in the vicinity of Study Area 7 and 38 locations in an area of suspected groundwater upwelling through sediment and from July to August 2005 at 19 locations in the vicinity of Study Area 7. Samplers were deployed in triplicate within an approximately 0.2-m<sup>2</sup> area at certain locations to characterize small-scale spatial variability. Similar to the devices described by Serbst et al. (2003), *in situ* samplers consisted of one 125-ml and one 250-ml polyethylene wide-mouth 4-cm diameter container, each with a 125- $\mu$ m nylon screen covering the open end of the container. The nylon screen was held in place using an open-faced cap. The pore size chosen for the screen was large enough to admit fine sand, which promoted more rapid equilibration with interstitial water compared with the longer equilibrium time required using a true diffusion sampling device. Samplers were filled with deionized water purged with nitrogen to achieve a dissolved oxygen concentration <0.5 mg/L, placed beneath the sediment surface by divers (Fathom Research, LLC, Bedford, MA) with the screened opening in a horizontal orientation, and tied to a small floating buoy. Divers were instructed to gently work the samplers into the sediment surface until completely buried beneath approximately 2 to 4 cm of sediment. In March through April 2005, *in situ* samplers remained in place for 2 weeks and were retrieved from the surface by hand. The screened end of each container was sealed and shipped at 4°C for chemical analyses. From July through August 2005, *in situ* samplers remained in place for 35 days and were retrieved by divers to further

minimize the potential for oxygenation of the contents after removal from the sediment. On retrieval, samplers were placed in a portable argon gas bag, and the contents were transferred to laboratory-supplied glass sample containers and shipped at 4°C for chemical analyses. Each container was filled to overflow to avoid, to the extent practical, the opportunity for aeration of the sample during storage and shipping.

### Sediment Profile Imaging

Sediments throughout the study area were characterized *in situ* in October 2006 using a sediment profile imaging device developed by Germano & Associates (Bellevue, WA). An Ocean Imaging Systems Model 3731 sediment profile camera was used to acquire cross-sectional images of the upper 20 cm of the river bottom according to methods described by Rhoads and Germano (1982) and Valente et al. (1992). The camera used a prism with a Plexiglas faceplate and an angled mirror to provide images analogous to the view through the side of an aquarium half-filled with sediment. The images provided visual evidence of vertical redox profiles and the depth of sediment bioturbation. A total of 495 sediment images were collected at 162 study area stations and 3 reference locations.

### Bioaccumulation Testing

Bioaccumulation in polychaetes was determined in laboratory bioaccumulation experiments and by collection and analysis of whole tissues of indigenous organisms. Laboratory bioaccumulation experiments were conducted from November through December 2003 by MEC Analytical Laboratory Systems (Carlsbad, CA) using the polychaete worm *N. virens* and the bivalve *M. nasuta* exposed to sediments for 28 days in accordance with USEPA (1993) and USEPA/USACE (1991) methods. Control sediment was collected from Discovery Bay, WA (*N. virens* experiment) and Booth Bay Harbor, MA (*M. nasuta* experiment) by Aquatic Research Organisms (Hampton, NH). Organisms were exposed to sediments in 20-L fiberglass tanks with a continuous flow (21 mL/min) of clean, filtered (5  $\mu$ m), ultraviolet light-sterilized seawater (28 to 32 ppt salinity) at 15°C  $\pm$  2°C. Exposures were conducted with a 16-h photoperiod. Three replicates of 10 organisms (*N. virens*) or 5 replicates of 25 organisms (*M. nasuta*) were placed in 5 L test sediments. Animals were not fed during the test. Ancillary overlying water quality (salinity, pH, dissolved oxygen, and temperature) was monitored daily in all replicates at the initiation of exposure (day 0) and daily in 1 replicate/treatment for the remainder of the experiments. Porewater ammonia was measured on days 0 and

28, and overlying ammonia was measured on day 0 and every 7 days thereafter. At test conclusion, surviving animals were placed in sediment-free, flow-through aquaria under test conditions for 24 hours to purge gut contents. After gut purging, animals were placed in clean glass jars with Teflon-lined lids, frozen, homogenized, and shipped at 4°C for total chromium analysis.

Indigenous polychaetes were collected in sediments from four locations in the vicinity of Study Area 7 and two reference locations in July, 2005. Sediment was collected using a Ponar grab sampler and sieved through a 0.1-mm mesh screen rinsed with river water at each sampling location. Animals were held for 24 hours in aerated river water to purge gut contents. After gut purging, animals were placed in clean glass jars with Teflon-lined lids, frozen, homogenized, and shipped at 4°C for total chromium analysis. One composite sample was prepared for each sampling location; one field duplicate also was prepared.

### Chemical and Physical Analyses

Sediments and whole tissues of benthic organisms were analyzed for chemical and physical parameters by certified commercial analytical laboratories according to standard protocols (USEPA 2003a). Chemical testing for total chromium, Cr(VI), and other sediment parameters was performed by Columbia Analytical Services (Rochester, NY) and Severn Trent Laboratories (Edison, NJ). Tissue analyses were performed by Severn Trent Laboratories (Colchester, VT).

Total chromium in surface sediment and whole polychaete tissue was determined by inductively coupled plasma–atomic emission spectrometry using USEPA Method 6010B after extraction by acid digestion (USEPA Method 3050B). All sediment data are reported on a dry weight (dw) basis. Tissue data are presented on a wet-weight (ww) basis.

Sediments were analyzed colorimetrically for Cr(VI) by ion chromatography using USEPA Method 7199 after extraction by alkaline digestion with magnesium suppression (USEPA Method 3060A). The magnesium-suppression procedure involves the addition of  $Mg^{2+}$  in a phosphate buffer to the alkaline solution, which is intended to suppress method-induced oxidation of chromium. Distillation extraction and spectrophotometric analysis of AVS in sediment was conducted according to the method described by Allen et al. (1993). For Fe(II) and Mn(II) analyses, aqueous samples were extracted from sediment by adding 100 ml 2% HCl solution to 1.0 g sediment and shaking vigorously for 5 minutes. The extracts were analyzed spectrophotometrically for Fe(II) using Standard Method 3500-Fe D, which uses phenanthroline to chelate

the ferrous iron in solution, and for Mn(II) by ion chromatography using modified USEPA Method 7199. For ammonia and pH analyses, deionized water was added to aliquots of sediment samples, and the suspensions were stirred or shaken for 5 minutes; the aqueous phases were subsequently analyzed for ammonia by flow injection using USEPA Method 350.1 and for pH by electrometrics using USEPA Method 9045D, modified from 9040C for soils and waste samples. Sediment samples were analyzed for total organic carbon (TOC) by gas chromatography after combustion using the Kahn (1988) method.

Porewater samples were analyzed for dissolved total chromium, dissolved Cr(VI), Fe(II), Mn(II), ammonia, pH, and dissolved organic carbon (DOC) using the same analytical methods described for sediment with the exception that extraction procedures were not required. Analyses of Cr(VI) in porewater were completed within 24 hours of sample collection. Cr(VI) was not measured in centrifuged samples. Acid-soluble sulfides were determined by distillation (USEPA Method 9030B) and iodometric titration (USEPA Method 9034). All porewater samples were filtered (0.45  $\mu$ m) before analysis. Because precautions were not sufficient to maintain redox conditions and minimize exposure to oxygen, porewater results for rapidly oxidizable constituents [sulfide, Fe(II), and Mn(II)] were not reported in samples collected from March through April 2005. During July through August 2005, the use of divers to retrieve *in situ* samplers and portable anaerobic argon gas bags during sample handling improved confidence in the measurement of sulfide, Fe(II), and Mn(II); these results are reported in this article. Porewater samples designated for sulfide analysis were preserved at the time of collection with zinc acetate and sodium hydroxide. Chloride was analyzed colorimetrically using USEPA Method 325.2. Chloride was measured in porewater and overlying river water to confirm equilibration of the *in situ* sampler with the interstitial water. DOC was determined in laboratory-filtered samples using USEPA Method 9060.

## Results

### Sediment Geochemistry

Sediment cores collected in the vicinity of Study Area 7 were generally characterized by three distinct strata; a red-brown, glaciolacustrine sediment stratum beneath a gray silty-fine sandy alluvial deposit with an average thickness of 1 m and a surficial deposit of mayonnaise-like dark colored organic-rich silty clay sediment ranging in thickness from <0.3 to 7.5 m. The average fines (silt plus clay) content of the surficial stratum typically exceeded 65%, with an average TOC content of 4%. This organic-rich

stratum constituted approximately 86% of the river bottom within the study area.

Analytical results for total chromium and Cr(VI) in surficial sediments in the vicinity of Study Area 7 and three reference locations are listed in Table 2. Total chromium concentrations in surface sediments ranged between 5 and 9190 mg/kg; the arithmetic mean and median concentrations were 499 and 188 mg/kg, respectively. Total chromium concentrations in the vicinity of Study Area 7 were above ambient (background) levels representative of upper Newark Bay and the lower Hackensack River. The arithmetic mean and median concentrations of total chromium in surface sediments from the three reference areas were 166 and 140 mg/kg, respectively. According to the National Oceanic and Atmospheric Administration (2003), the median background concentration of total chromium in sediments in this area is 138 mg/kg ( $n = 7$ ). Rice (1999) reported that typical median total chromium concentrations in United States streambeds least affected by anthropogenic discharges range between 46 and 110 mg/kg.

The highest concentration of total chromium (9190 mg/kg) was found within 25 ft of shore immediately adjacent to the site. Total chromium concentrations in surface sediment appeared to vary in three different portions of the study area. In Droyers Cove, situated in the southern portion of the study area (see Fig. 1), total chromium concentrations ranged between 10 and 1320 mg/kg ( $n = 50$ ), and the median concentration was 157 mg/kg. Adjacent to the waterfront bulkhead at Study

Area 7, concentrations ranged between 7 and 9190 mg/kg ( $n = 94$ ), and the median concentration was 275 mg/kg. In the northern cove area, situated to the north of Study Area 7, total chromium concentrations ranged between 5 and 2460 mg/kg ( $n = 49$ ), and the median concentration was 182 mg/kg.

In the same sediment samples, Cr(VI) concentrations varied widely from nondetectable to as high as 31 mg/kg. Independent review of the analytical results suggested that 5 mg/kg was the approximate limit of analytic sensitivity for reliably detecting Cr(VI) in the sediment; concentrations  $<5$  mg/kg were likely artifacts of the analytical test method, which is consistent with observations reported in other studies (see Discussion). Cr(VI) was measured above 5 mg/kg in surface sediments at some locations despite evidence of strong reducing conditions in the sediment (Table 2).

AVS and SEM concentrations in surface sediments ranged between 0.33 and 130  $\mu\text{mol/g}$  and 0.07 to 29  $\mu\text{mol/g}$ , respectively. Arithmetic mean AVS (20  $\mu\text{mol/g}$ ) was significantly higher than mean SEM (3.8  $\mu\text{mol/g}$ ). The range and mean concentrations of AVS and SEM at the three reference sites were comparable with those measured in sediment in the vicinity of Study Area 7.

As listed in Table 3, there were no significant differences in AVS, TOC, and Fe(II) levels or pH in sediments containing Cr(VI) concentrations either  $>5$  mg/kg or  $<5$  mg/kg. Cr(VI) concentrations in whole sediment showed no correlation with AVS concentrations (Fig. 2). The highest AVS concentrations ( $>50$  mg/kg) were consistently

**Table 2** Summary of surficial (0 to 15 cm) sediment results

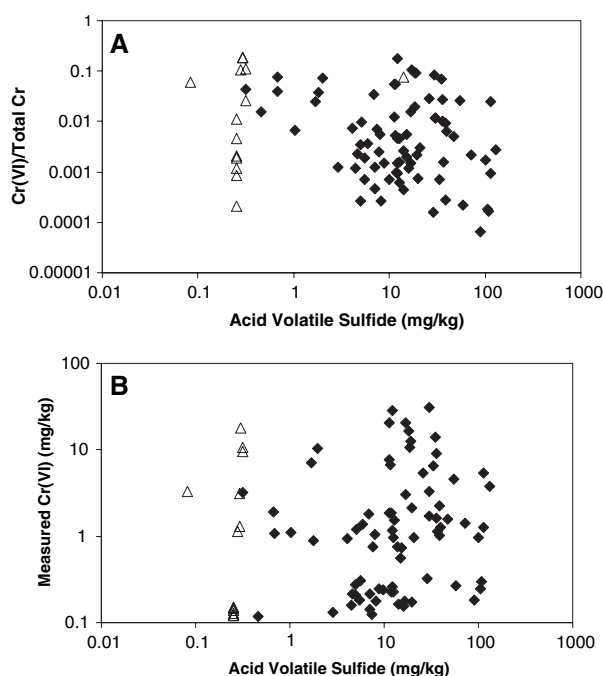
Constituent	Units	Detection Frequency <sup>(a)</sup>	Range	Median <sup>(b)</sup>	Arithmetic mean <sup>(b)</sup>
Lower Hackensack River, NJ Study Area					
Total chromium	mg/kg	193/193	5 to 9,190	188	499
Cr(VI)	mg/kg	84/118	$<0.47$ to 30.7	1.3	3.5
AVS	mg/kg	115/152	$<10.6$ to 4,177.8	242	599.2
Mn (II)	mg/kg	18/19	12.1 to 304	60	119
Fe (II)	mg/kg	74/77	$<11.7$ to 9,260	1,430	1,962
pH	Unitless	160/160	6.5 to 9.1	8.0	8.0
Ammonia	mg/kg	71/96	$<6.0$ to 267	24.1	40.8
TOC	%	127/128	0.08 to 12	2.3	2.5
Reference Locations					
Total chromium	mg/kg	14/14	85.9 to 306	140	166.4
Cr(VI)	mg/kg	7/9	$<0.9$ to 5.9	1.4	1.93
AVS	mg/kg	12/14	54.5 to 2,228.2	393	665.7
Ammonia	mg/kg	8/9	$<8$ to 142	48	62.3
pH	Unitless	12/12	7.0 to 8.2	7.8	7.7
TOC	%	8/8	1.8 to 11.2	3.5	4.4

<sup>(a)</sup> Differences in number of samples among constituents reflect changes in target analyses between sample rounds as well as exclusion of any data not meeting quality-assurance requirements based on independent data review

<sup>(b)</sup> Values are derived using one-half the detection limit for nondetected concentrations

**Table 3** Comparison of sediment characteristics associated with two ranges of Cr(VI) concentrations

Total chromium (mg/kg)	Cr (VI) (mg/kg)	AVS (mg/kg)	Fe(II) (mg/kg)	TOC (%)	Ammonia (mg/kg)	pH (unitless)
<i>Cr(VI) &lt; 5 mg/kg</i>						
Median	191	1.07	337	1,995	2.3	28.4
Range	7–4,240	0.23–4.78	5.5–4,178	5.9–9,260	0.08–7.7	3.02–201
N	94	94	72	42	73	61
<i>Cr(VI) &gt; 5 mg/kg</i>						
Median	209	10.1	545	1,310	2.4	39.5
Range	60–9,190	5.3–30.7	19.2–3655	61.7–5,190	0.18–7.5	6.3–267
N	24	24	19	12	11	11
<i>Wilcoxon rank sum test</i>						
<i>p</i>	0.479	<0.0001	0.367	0.572	0.613	0.925



**Fig. 2** Relationship between whole-sediment acid volatile sulfide (AVS) concentrations and (a) the proportion of total chromium reported as Cr(VI) in whole-sediment analyses, and (b) reported whole-sediment Cr(VI) concentrations. No correlations are evident. Symbols indicate: ♦ samples containing detectable AVS, and △ samples containing no detectable AVS. The reported occurrence of Cr(VI) reducing sediments appears to be due in part to method-induced oxidation

associated with low Cr(VI) concentrations ( $\leq 5$  mg/kg), however. Median total chromium and Cr(VI) concentrations (63 mg/kg and 0.72 mg/kg, respectively) were also relatively low in sediments containing nondetectable AVS. The highest Cr(VI) concentrations in sediments with nondetectable AVS were 10.6 and 17.7 mg/kg. Sediments with nondetectable AVS were generally situated furthest from shore (that is, nearest to the river's navigation channel), where conditions are likely more erosional compared with

nearshore areas. TOC content was typically low ( $<1\%$ ) in the sediments at these locations. However, Fe(II), Mn(II), and/or ammonia were detected in all sediment samples where AVS was not detected, although at relatively low levels, suggesting that conditions may have been weakly reducing rather than oxygenated.

Sediment profile imaging provided two indicators of sediment conditions, specifically, the depths of the apparent redox potential discontinuity (RPD) and bioturbation. The apparent RPD depth measured in sediment throughout the study area ranged from 0 to 6.2 cm, with an arithmetic mean of 1.7 cm. The depth of the apparent RPD is indicative of the boundary between the generally oxic ferric hydroxide condition at the sediment–surface water interface and the underlying anoxic gray to black sediment. Measured bioturbation depths in the study area ranged from 0 to approximately 15.5 cm, with an average of 7.8 cm. Thus, the whole-sediment samples collected for this study (0 to 15 cm depth) represent the outer limit of the biologically active zone, and *in situ* porewater samplers were placed within the biologically active zone represented by the average depth of bioturbation in the study area.

#### Porewater Chemistry

Sediment porewater results are listed in Table 4. Among porewater samples collected using centrifugation, four of nine filtered samples contained detectable concentrations of total chromium, including two reference samples and two site samples where concentrations ranged from 10.7 to 17.1  $\mu\text{g/L}$ . Total chromium concentrations in whole-sediment samples at the four locations ranged from 137 to 1780 mg/kg, and AVS concentrations ranged from 632 to 3460 mg/kg. Total chromium concentrations were lower than both the saltwater Cr(VI) criterion of 50  $\mu\text{g/L}$  and the freshwater Cr(III) criterion of 230  $\mu\text{g/L}$  (assuming 400 mg/L hardness; site hardness is much

**Table 4** Summary of centrifuged and *in situ* porewater sampling results

Constituent	Units	Detection Frequency <sup>(a)</sup>	Range	Median <sup>(b)</sup>	Arithmetic Mean <sup>(b)</sup>
Centrifuged porewater (study area & reference locations)					
Dissolved chromium study area	mg/L	2/6	<0.01–0.017	0.01	0.008
Dissolved chromium reference locations	mg/L	2/3	<0.01–0.011	0.011	0.009
In situ-collected porewater (study area)					
Dissolved Chromium <sup>(c)</sup>	mg/L	2/23	<0.01–0.0825	<0.01	0.009
Dissolved Cr(VI)	mg/L	0/78	–	<0.005	C
Acid Soluble Sulfides	mg/L	4/23	<1.0–3.9	<1.0	0.83
Fe[II]	mg/L	17/20	<0.1–1.0	0.45	0.46
Divalent Manganese (Mn[II])	mg/L	20/20	0.1–3.9	0.25	0.88
pH (unitless)	mg/L	35/35	6.91–7.74	7.22	7.23
Ammonia	mg/L	36/36	0.216–30.4	5.41	7.09
DOC	mg/L	35/35	1.5–21.4	3.42	3.97
Chloride	mg/L	23/23	8,190–17,500	11,300	11,253

<sup>(a)</sup> Porewater samples from the northern cove area were analyzed only for Cr(VI). Triplicate samples are included as independent analyses

<sup>(b)</sup> Values are derived using one-half the detection limit [0.005 mg/L for Cr(VI) and 0.01 mg/L for total chromium] for nondetected concentrations

<sup>(c)</sup> Aqueous Cr(VI) and total chromium analyses met quality-control requirements of precision, accuracy, and completeness, with the exception of dissolved total chromium in March through April 2005 porewater samples; those data have been excluded

higher, which would further mitigate ecotoxicity). The USEPA (1984) has not adopted saltwater criteria for Cr(III) because of a lack of data demonstrating toxicity in saltwater exposures.

Among porewater samples collected using *in situ* samplers, Cr(VI) was not detected in any sample ( $n = 78$ ). Total chromium was detected in 2 of 23 *in situ* samples (18.5 and 82.5  $\mu\text{g/L}$ ) at concentrations well below the freshwater Cr(III) criterion (Table 4). At paired surface sediment and porewater sampling locations, sediments contained total chromium ranging from 10.6 to 6220 mg/kg and AVS ranging from <32 to 910 mg/kg. Seven of the porewater samples were collected at locations where AVS was not detected in the sediment, and 8 porewater samples were collected in intertidal areas, maximizing the potential to measure aqueous Cr(VI) if present in porewater. Triplicate sample results indicated that small-scale variability (within 0.2  $\text{m}^2$ ) was similar to larger-scale variability within the site; therefore, triplicate sample results for porewater are listed as independent data in Table 4.

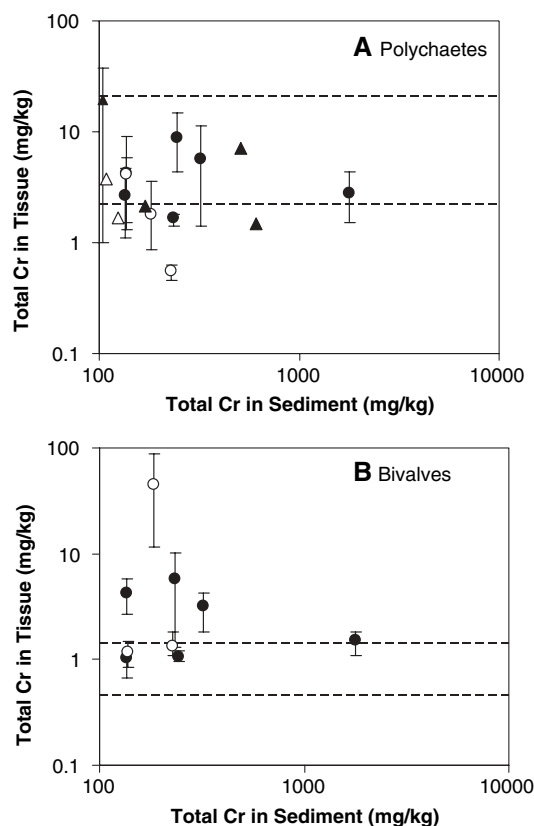
*In situ* porewater samples collected from July through August 2005 contained ammonia, sulfide, Fe(II), and/or Mn(II), providing positive indications of reducing conditions. Soluble sulfides were detected in only 4 of 23 porewater samples, possibly because of relatively high detection limits associated with the titration method; an alternative test method, such as methylene blue colorimetric analysis, might have been more sensitive to the presence of sulfide. Sulfide oxidation or hydrogen sulfide volatilization also could have occurred despite measures taken to minimize sampling artifacts. Chloride concentra-

tions in the *in situ* samplers approximated ebb-tide surface-water salinity levels, indicating that the *in situ* samplers had reached equilibrium with the sediment at some point during the 35-day deployment period.

Total chromium was detected in two filtered porewater samples collected from locations where samplers were deployed in sandy sediment with little TOC and no detectable AVS. Results appeared to be unrelated to total chromium concentrations in the sediment (10.6 and 62.1 mg/kg). Ammonia, Fe(II), and Mn(II), which are formed only under reducing conditions, were detected in the porewater. The pH and DOC results for both samples were similar to mean levels reported in porewater samples containing no detectable total chromium.

#### Bioaccumulation Results

In the laboratory bioaccumulation tests, total chromium concentrations in whole tissues of *N. virens* and *M. nasuta* (Fig. 3) ranged from 1.2 to 14.8 mg/kg (median 1.6 mg/kg) and showed no correlation with total chromium or Cr(VI) concentrations in sediment or total chromium in porewater (Spearman rank order correlations,  $p > 0.1$ ). Total chromium concentrations in the sediment ranged between 135 and 1780 mg/kg, and AVS concentrations ranged between 632 and 3460 mg/kg. For *N. virens*, the highest chromium concentrations were found in the control organisms, whereas for *M. nasuta*, the highest chromium concentrations were found in organisms exposed to reference sediment. For *M. nasuta*, differences in chromium bioaccumulation were observed among sediments, but these



**Fig. 3** Relationship between total chromium in sediment and tissue for (a) polychaetes and (b) bivalves. Symbols indicate: ● Laboratory-exposed organisms, study area; ○ laboratory-exposed organisms, reference locations; ▲ indigenous organisms, study area; △ indigenous organisms, reference locations. Error bars represent minimum and maximum replicate concentrations. Dashed lines show tissue concentrations in laboratory control organisms

differences were correlated to test-organism health (survival) rather than chromium exposures. If external chromium exposures did not affect chromium bioaccumulation, some internal mechanism would seem to be implicated; we speculate that toxicity related to other chemicals (especially polycyclic aromatic hydrocarbons; Sorensen et al. 2007) might have disrupted the organisms' internal regulation of chromium.

Control survival in the laboratory bioaccumulation tests was acceptable (100% for *N. virens* and 92% for *M. nasuta*). Water-quality parameters were generally within recommended limits, with the exception of slight salinity variations caused by natural fluctuations of salinity in the source water; these deviations were not considered significant. Mean survival of *N. virens* exceeded 95% in all test exposures. However, significant mortality of *M. nasuta* was observed in one reference sample (37% survival) and one site sample (68% survival). Total chromium concentrations were 202 mg/kg in the reference sample and 1780 mg/kg in the site sample. The whole sediment Cr(VI) concentrations

were <1 mg/kg at both locations, and AVS concentrations were 1190 mg/kg in the reference sample and 3460 mg/kg in the site sample. In other treatments, *M. nasuta* survival was  $\geq 85\%$ . A detailed assessment of the relationship between sediment chemistry and toxicity in these samples is provided by Sorensen et al. (2007).

Total chromium concentrations in indigenous polychaetes collected from the study area ranged from 1.5 to 37.5 mg/kg (median = 2.1 mg/kg). Total chromium concentrations in sediments from which polychaetes were obtained ranged from 104 to 610 mg/kg, and sulfide concentrations ranged from <32 to 910 mg/kg. As shown in Fig. 3, total chromium concentrations in indigenous polychaete tissues were consistent with concentrations measured in laboratory experiments using *N. virens*. Results were not correlated with exposures to total chromium in the sediment (Spearman Rank correlation,  $p > 0.1$ ).

## Discussion

In this study, chromium speciation and bioavailability were investigated by measuring the concentrations of total chromium, Cr(VI) and several geochemical parameters in both surface sediments and sediment porewater. The potential for chromium bioaccumulation was also assessed through laboratory experiments and by analysis of whole tissues of indigenous organisms. Although whole-sediment Cr(VI) concentrations were far lower than total chromium concentrations, the co-occurrence of Cr(VI) with indicators of reducing conditions was unexpected. However, Cr(VI) was never detected in sediment porewater ( $n = 78$ ). Chromium concentrations in whole tissues of animals exposed in the field or in the laboratory showed no relationship with total chromium or Cr(VI) concentrations in the sediment or porewater. There were no statistical differences among animals exposed to sediments from site and reference locations.

Estuarine sediments, particularly in heavily industrialized urban environments, tend to be anoxic within a few centimeters of the sediment–water interface (Lin et al. 2003). Bioturbation and physical mixing processes can play important roles in sediment geochemistry and the depth of the RPD and result in deeper penetration of oxic conditions (Fenchel 1996; Thamdrup et al. 1994), but the slow rate of diffusion from the overlying water column and typically high sediment oxygen demand result in limited oxygen supply in the sedimentary environment (Luther et al. 1998). Estuarine sediments particularly tend toward anaerobic conditions during summer months because of decreased freshwater inputs, high water temperatures, and increased biological activity (Rozañ et al. 2002). Therefore, it is important to consider seasonality when assessing

indicators of reducing conditions. Because most of the sediment sampling for this study was conducted in late fall and early spring, it is unlikely that the reducing capacity of the sediments was overestimated.

Seemingly anomalous observations of colocated AVS and Cr(VI) have been encountered by other researchers. Working with Shipyard Creek sediments, for example, Berry et al. (2004) attributed the detection of trace (*i.e.*, <5 mg/kg) concentrations of Cr(VI) to method-induced oxidation. Besser et al. (2004) reached the same conclusion in a separate study of chromium in soil, sediment, and wetland samples. Becker et al. (2006) also suspected that analytical artifacts were responsible for some results.

Zatka (1985) reported an extensive investigation of both the mechanism behind method-induced oxidation and the amount of Cr(VI) that can present itself as false positive based on method-induced oxidation. According to Zatka, the order of reagent addition is important; that is, the addition of the alkaline digestion solution before the Mg salt creates a higher bias toward method-induced oxidation than when the Mg salt is added first. Although the whole-sediment Cr(VI) analyses performed for this study followed procedures written and approved by NJDEP, the standard operating procedure specifies adding the Mg salt after the alkaline digestion solution (*i.e.*, the Mg salt was added in the less-than-optimal sequence). Therefore, it is safe to assume that method-induced oxidation resulted in a finite contribution (0.2 to 4 mg/kg according to Zatka) to the measurement of Cr(VI) in whole-sediment samples. In addition to method-induced oxidation, false-positive results for Cr(VI) have been documented due to interference by soluble organo-Cr(III) (Walsh & O'Halloran 1996). However, such an interference appears unlikely in this study because Cr(VI) also would have been reported in porewater, which was not the case.

Although method-induced oxidation may explain the presence of low levels of detectable Cr(VI), some of the detected Cr(VI) may not be artifacts and may indicate the presence of low Cr(VI) levels in whole-sediment samples. This seems difficult to reconcile with the understanding that Cr(VI) is not stable in anaerobic environments; that chromate-containing phases within COPR particles are not stable below approximately pH 11; and that Cr(VI) was not detected in porewater. However, small-scale physical separation between Cr(VI) and potential reductants, either vertically along redox gradients or on a microscale within sediment particles, would explain the apparent anomaly. Intraparticulate sequestration of Cr(VI) has been shown (Anderson et al. 1994), whereas occurrence of Cr(VI) in oxygenated surface sediment is considered unlikely, as further discussed later in this article.

According to Anderson et al. (1994), the rate of Cr(VI) reduction depends on reactions between soluble Cr(VI) and

surface-bound Fe(II) (not soluble Fe(II)), and the initial reduction reaction is instantaneous for surface-available Fe(II). A subsequent and much slower reaction is limited by the rate of Cr(VI) diffusion through intragranular porosity to reduction sites within the particle. Their work suggests a gradient across the boundary between internal oxidized and external reduced regions of the particle, in which the concentration of Cr(VI) in the latter is zero. Perhaps Cr(VI) particles in the localized oxidation zone (inside a particle) make up a fraction of the Cr(VI) measured in the alkaline digestion process. This Cr(VI) may be detectable by the chromium digestion process but would not be present in sediment porewater and would not be bioavailable. The reducing zones surrounding the Cr(VI) particles and slow (rate-limiting) diffusion of Cr(VI) would make the Cr(VI) tightly bound and unavailable to porewater and *in situ* organisms. Consistent with the USEPA (2005), interstitial sediment porewater should form the basis of sediment risk assessments for metals because total (dw) metal concentrations in anaerobic sediments are not predictive of bioavailability. Organisms are not exposed to nonbioavailable Cr(VI) sequestered within sediment particles.

Although oxygenated conditions are evident in a thin layer at the sediment surface, the occurrence of potentially bioavailable Cr(VI) in this oxygenated layer is not a likely explanation for the observation of detectable Cr(VI) in whole sediment. Because of its solubility, nonsequestered Cr(VI) does not persist in sediment or porewater unless a persistent source is present. Candidate sources include upwelling groundwater, surface water, and oxidation of *in situ* Cr(III). If upwelling groundwater were acting as a Cr(VI) source to the surface, then oxidized conditions would prevail throughout the groundwater flow path rather than in a thin surface layer; otherwise, the Cr(VI) would be reduced as the groundwater passed through the anaerobic sediment column. If a surface water Cr(VI) source existed, it would be revealed in surface water analyses, but this was not the case in the study area (data not shown). Finally, oxidation of *in situ* Cr(III) would require a suite of conditions that are highly improbable in this setting: Cr(III) must be soluble and not complexed with organic ligands; manganese must be present in oxidized form at high concentrations and in a fresh and amorphous state; and organic carbon concentrations must be low (Fendorf 1995; Kozuh et al. 2000; Masscheleyn et al. 1992; Tzou et al. 2002; Wu et al. 2005). To further confirm the low likelihood of Cr(III) oxidation to Cr(VI), a site-specific sediment resuspension and oxidation test was conducted according to standard USACE dredging elutriate test methods (DiGiano et al. 1995) (ENVIRON 2006, unpublished data). Vigorous aeration and prolonged mixing of sediment suspensions resulted in no detectable formation of Cr(VI).

The absence of Cr(VI) in porewater samples, even in areas with low sulfides, strongly suggests that Cr(VI) concentrations reported in whole-sediment samples were either artifacts or representative of biologically unavailable Cr(VI). Either way, porewater Cr(VI) results are assumed to be more indicative of bioavailability and risk than are the whole-sediment measurements. Extensive research has shown that chemical concentrations in porewater are much more closely linked than whole-sediment concentrations to toxicity and bioaccumulation end points and that water-only toxicity thresholds typically provide a good approximation of porewater toxicity thresholds (Di Toro et al. 1991; USEPA 2003b, 2005). Therefore, comparison of Cr(VI) concentrations in porewater with appropriate saltwater criteria is much more informative than, for instance, comparison of total chromium concentrations in whole-sediment with generic sediment-screening values, such as effects range-low or -median values.

This study's tissue data also provide supporting evidence indicating that chromium in study area sediments is minimally or not bioavailable. Because Cr(VI) is rapidly converted to Cr(III) in biologic tissues (Integrated Risk Information System 2003; Peternac & Legovic 1986), and Cr(III) is biologically regulated as an essential nutrient (Eisler 1986), total chromium concentrations in biological tissue are not a definitive indicator of chromium bioavailability and exposure. However, Norwood *et al.* (2006) found that for the majority of species tested, bioaccumulation did increase with increased exposure to Cr(VI). The lack of correlation between total chromium concentrations in sediment or porewater and biologic tissue in this study, as well as the similarity in bioaccumulation between site and reference locations, is consistent with geochemical evidence that chromium is present in sediment as Cr(III); is not bioavailable; and therefore is not a toxic agent in study area sediments.

Total chromium concentrations measured in benthic invertebrates in this study were comparable with or lower than those observed in two studies conducted on the Hackensack River. Kraus (1989) evaluated chromium bioaccumulation above the estuarine range of the river in freshwater, where the average concentrations of total chromium in sediments and midges were 2100 and 42 mg/kg, respectively; the investigators did not report whether tissue concentrations represented the ww or dw basis. Hall and Pulliam (1995) evaluated chromium bioaccumulation in blue crab from a tidal wetland, in which the average sediment concentration of total chromium was 720 mg/kg. Adjusting the results from dw to ww assuming 80% moisture content, chromium concentrations in blue crab averaged 2.3 mg/kg and were similar to concentrations reported from a nearby reference area; concentrations in

blue crab hepatopancreas averaged 26 mg/kg and were greater than samples from the reference area.

Despite the occurrence of increased concentrations of total chromium in sediments of the lower Hackensack River, the results of this study indicate that little, if any, of the chromium is present as Cr(VI), and therefore risks associated with chromium exposure are low. Although the occurrence of localized, trace concentrations of Cr(VI) cannot be completely ruled out, Cr(VI) was never detected in porewater. These results are consistent with multiple geochemical indicators showing reducing conditions in porewater and sediment. The low bioaccumulation of chromium demonstrated in both laboratory bioaccumulation testing and *in situ* benthic invertebrates also was consistent with these conclusions.

Analysis of several geochemical parameters proved useful to understanding chromium speciation and the limited toxicity and bioaccumulation observed in two species of benthic organisms. The use of *in situ* porewater collection methods and careful sampling handling precautions, such as the use of divers to retrieve samplers and an argon blanket to preserve the contents of samplers, greatly helped minimize the potential oxidation of geochemical indicator parameters [namely, sulfide, Fe(II), and Mn(II)] before chemical testing. Our data suggest that whole-sediment measures of Cr(VI) are unreliable and, at best, are of limited utility. Challenges in chromium analytic methods remain a factor for assessing speciation and risk in chromium-contaminated sediments. Geochemical measures, including Fe(II) and sulfide, and *in situ* porewater sampling of chromium provided the most consistent evidence of chromium speciation and bioavailability.

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