

Removal of hexavalent chromium by hyporheic zone sediments in an urbanized estuary

Hun Bok Jung, Jake Severini and Emaje Hall

ABSTRACT

More than 2 million tons of chromium ore processing residue (COPR) waste was disposed of in Hudson County of New Jersey, which was known as the center of the production of chromate in the 20th century. The Cr(VI) removal experiments were conducted with the hyporheic zone (HZ) sediments collected along the shore of an urbanized estuary located in and near Hudson County to investigate the natural remediation of Cr(VI). Fine-grained and organic-rich Passaic River sediments showed the highest removal capacity for Cr(VI), whereas the lowest removal of Cr(VI) occurred in coarse-grained and organic-poor sediments from Newark Bay. In general, Cr(VI) removal increased with higher amounts of sediment organic matter, sulfur, and silt and clay fractions, as well as lower pH conditions. The removal of hexavalent chromium in organic-rich sediments is attributed mainly to the reduction of Cr(VI) to Cr(III), resulting in less reversible immobilization of Cr(VI), while reversible adsorption could also remove Cr(VI). The results suggest that the organic-rich, fine-grained HZ sediments can act as a natural reactive barrier for the remediation of Cr(VI) transport from subsurface to surface water in the estuary. Further research is needed to understand the long-term mobility of Cr along the urban estuary.

Key words | chromium ore processing residue, chromium reduction, hexavalent chromium, Hudson County, hyporheic zone

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HIGHLIGHTS

- The HZ sediments of an urban estuary in Hudson County, NJ, are enriched with Cr.
- Fine-grained and organic-rich sediment showed a high removal capacity for Cr(VI).
- Removal of Cr(VI) in organic-rich sediment is attributed to the reduction to Cr(III).
- The HZ sediments can act as a natural reactive barrier for remediating Cr(VI) in the estuary.

INTRODUCTION

Chromium (Cr) is a historical contaminant commonly found in the urban environment because it has been used in many industrial processes such as plating, alloying, tanning, and metallurgy (Palumbo-Roe *et al.* 2017). Under oxic conditions, Cr(VI) is the dominant form, existing as either hydrogen chromate (HCrO_4^-) or chromate (CrO_4^{2-}) depending on pH, while dichromate ($\text{Cr}_2\text{O}_7^{2-}$) forms at low pH (Rifkin *et al.* 2004). Under anoxic conditions, Cr(VI) is readily reduced to Cr(III) by chemical and microbial processes, and forms $\text{Cr}(\text{OH})_3$ at mid-range pH values (Chen

et al. 2015). Cr(VI) is considered highly toxic and carcinogenic for the human body, leading to lung cancer, skin allergy, asthma and renal diseases, whereas Cr(III) is a required nutrient for human health (Bobrowski *et al.* 2009). Cr(VI) in the environment is also toxic to both plants and animals, even at low concentrations (Rifkin *et al.* 2004).

Millions of tons of chromite ore processing residue (COPR) have been deposited in urban environments including Glasgow, United Kingdom, and Hudson County, New

Jersey, USA (Burke *et al.* 1991; James 1996; Farmer *et al.* 1999). COPR contains approximately 2 to 7% chromium as both Cr(III) and Cr(VI) because of incomplete oxidation of the ore, incomplete leaching of chromate, and generation of Cr-bearing minerals such as brownmillerite during processing (Burke *et al.* 1991). For seven decades, chromate production was an active industry in Jersey City and neighboring Kearny in Hudson County, New Jersey (Stern *et al.* 2013). Approximately 2–3 million tons of chromium ore processing residue (COPR) had been generated until the mid-1970s by three plants located in Hudson County that employed the high-lime roasting process (Burke *et al.* 1991; Chrysochoou *et al.* 2009). COPR was distributed in many residential, commercial or industrial locations throughout Hudson County and surrounding areas, where it was used for fill and dikes due to its sand-like properties. According to the New Jersey Department of Environmental Protection, over 160 sites contaminated with COPR have been identified in Hudson and Essex Counties, including urban residential areas (Burke *et al.* 1991). Because COPR is unstable and will undergo weathering reactions that release Cr(VI), the COPR deposits are an important source of Cr contamination of nearby soils, sediments, and water (Elzinga & Cirno 2010).

Newark Bay and two large tributaries, the Passaic and Hackensack Rivers located in Hudson and neighboring counties of New Jersey have experienced significant industrialization and urbanization for the past two centuries, which resulted in contamination of water and sediment as well as the loss of coastal habitats. Sediments along the estuary are reported to contain high levels of chromium, partially due to surface runoff and groundwater from a former waterfront commercial property that was used for disposal of COPR (Martello *et al.* 2007; Magar *et al.* 2008). Because of the risk of Cr(VI) transport from COPR landfill sites to groundwater and surface water as well as consequent impacts on coastal ecosystems and human health, it is important to understand geochemical behavior and mobility of Cr(VI) in the hyporheic zone (HZ) along an urbanized estuary surrounded by dense human population. The hyporheic zone, which is a transitional region where groundwater and surface water exchange and mix, may offer natural attenuation potential for contaminants (Palumbo-Roe *et al.* 2017). The sediments in the hyporheic zone may contain various reductants such as Fe(II), sulfide, and organic matters as well as reactive minerals that can immobilize toxic heavy metals including Cr(VI), and thus the HZ may act as a natural reactive barrier for groundwater Cr (Xu *et al.* 2017).

The objectives of this study are to understand the geochemical mobility of Cr(VI) in the sediments of the hyporheic zone along an urbanized estuary in Hudson County and neighboring areas that have been historically affected by COPR waste and to evaluate the natural remediation capability of the hyporheic zone sediments for hexavalent chromium. This study will provide valuable insights into the mechanisms to control the geochemical behavior of Cr(VI) in the HZ sediments and will contribute to improving the environmental management of urbanized and industrialized estuaries.

METHODS

Surficial sediment ($n = 15$) and coastal aquifer sediment ($n = 7$) samples were collected along the shore of Newark Bay as well as the lower Passaic and Hackensack Rivers (Figure 1). Surficial sediments in shallow water were collected using a shovel, while coastal aquifer sediments were collected from the water table at the depth of 70–130 cm using a soil auger with extensions (AMS) (Jung 2017, 2020).

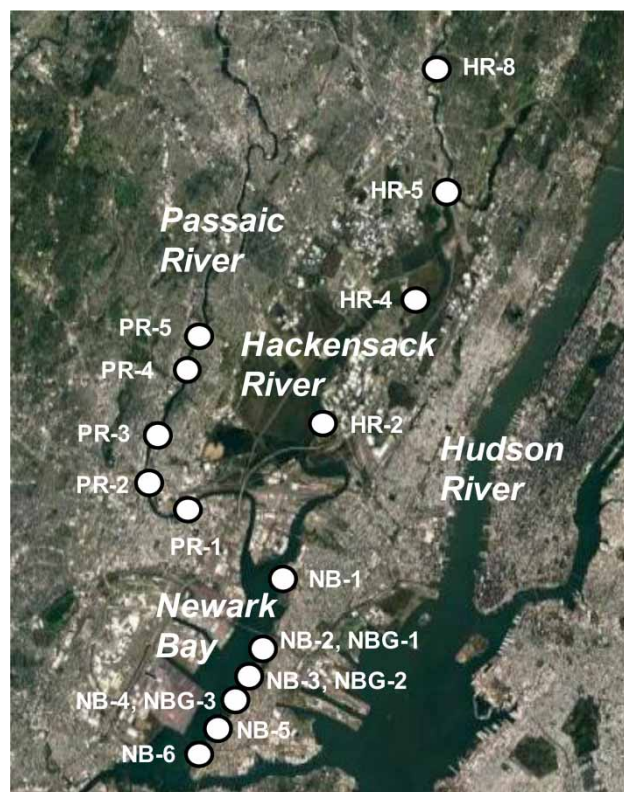


Figure 1 | Locations of sediment sampling along the Passaic River (PR), the Hackensack River (HR), and Newark Bay (NB and NBG) in and near Hudson County, New Jersey.

Sediment analysis

After sediment samples were air-dried and homogenized in the laboratory, sediment grain size analysis was performed using stainless steel sieves (WS Tyler). Chemical composition of bulk sediment samples (<2 mm grain size) was determined using a portable X-ray fluorescence (Niton™ XL3t XRF Analyzer; Thermo Scientific) (Jung 2017). The calibration of XRF was performed using NIST (National Institute of Standards and Technology) standard reference materials 1646a (Estuarine Sediment) and 2709a (San Joaquin Soil). Five replicate XRF analyses were conducted for each sediment sample, which showed typically less than $\pm 20\%$ variation. Sediment organic matter content was determined for bulk sediment (<2 mm grain size) by the loss on ignition (LOI) method (Heiri *et al.* 2001). Approximately 10 g of air-dried sediment samples in crucibles were placed in an oven (Thermo Scientific) and heated at 105 °C overnight, which was followed by heating at 550 °C in a muffle furnace (Thermo Scientific) for 4 hours. The sediment organic matter content was determined based on the weight loss between the heating at 105 °C and 550 °C.

Hexavalent chromium removal experiments

The solutions of 0.1 and 0.5 mg/L Cr(VI) were prepared by diluting the Hach hexavalent chromium standard solution (50 mg/L) with deionized water. The Cr(VI) removal experiments were conducted by reacting a 25 mL of Cr(VI) solution with 3 g or 5 g of sediment in a 50-mL plastic centrifuge tube for 2 days on a rugged rotator. After the reaction, the samples were centrifuged at a speed of 3,000 RPM (revolution per minute) for 7 minutes to separate the solid and the liquid. Then the solution was filtered through a 0.45 μm syringe filter (Whatman). The concentrations of Cr(VI) in solutions were measured by a Hach DR 900 colorimeter using the 1,5-diphenylcarbohydrazide method. The estimated detection limit of Cr(VI) by this method is 0.01 mg/L. Accuracy of measurements was validated using a standard Cr(VI) solution from Hach Company, which showed measurement error below $\pm 10\%$. The pH of each sample was measured by a pH meter (HQ40d, Hach Company) before and after each experiment. The pH of Cr(VI) solution was approximately 9.1 prior to the reaction. After the Cr(VI) removal experiment with 3 g of sediment and 25 mL of 0.5 mg/L Cr(VI) solution, the sediment was subsequently reacted with 25 mL of deionized

water for 5 days to investigate the remobilization of Cr(VI) removed by the sediment.

RESULTS AND DISCUSSION

Chemical and physical characteristics of sediments

The concentrations of total Cr in the surficial sediments from the estuary ranged from 58 mg/kg to 347 mg/kg (Table 1). The average concentrations of total Cr in the Passaic River (PR; $n = 5$), the Hackensack River (HR; $n = 4$), and Newark Bay (NB; $n = 6$) were 162, 124, and 143 mg/kg, respectively. However, the subsurface sediments collected from coastal aquifers (NBG; $n = 7$) along Newark Bay showed significantly elevated concentrations of total Cr ranging up to 5,775 mg/kg. The average Cr concentration for NBG-1 site ($n = 3$) was 4,519 mg/kg, while it was 304 mg/kg for NBG-2 and NBG-3 sites ($n = 4$) (Table 1). Those Cr-enriched aquifer sediments and groundwater with alkaline pH of ~ 8 at NBG-1 site (Jung 2020) suggest that COPR wastes were probably buried there because COPR is known to contain a large quantity of residual Cr ranging from 2,000 to 40,000 mg/kg and is highly alkaline with paste pH of 8.1–12.3 (Weng *et al.* 1994; Higgins *et al.* 1998; Tinjum *et al.* 2008). It is reported that the COPR used as fill in Hudson County, New Jersey has a pH of 11–12 and typically contains 3–7% chromium present as both Cr(III) and Cr(VI) (NJDEP 2005).

While the sediments from the estuary consisted mainly of sand, the amount of fine-grained sediment fractions including silt and clay (<63 μm) was significantly higher in the PR sediments than in the HR or NB sediments (Jung 2017). Silt and clay fractions were on average 21 and 6% for the PR sediments and the HR sediments, respectively, while they were almost non-existent for NB or NBG sediments (Table 2). Organic matter content was highest in the PR sediments (8.6 wt%), followed by the HR sediments (5.4 wt%), the NB sediments (2.1 wt%), and the NBG sediments (0.5–2.0 wt%) (Table 2).

The concentrations of chromium were significantly higher in the HZ sediments of the study area than in sediments from the eastern U.S. seashore, which showed Cr concentrations of 3.8–130.9 mg/kg in 1994 and 0.8–98.1 mg/kg in 1995 (Hyland *et al.* 1998). Elevated levels of sediment Cr in the estuary are attributable to historical disposal of chromite ore processing residue in Hudson County. The geochemical speciation of Cr in the HZ sediments was not determined in this study, but previous

Table 1 | XRF data showing the concentrations (mg/kg) of elements in the hyporheic zone sediments from the Passaic River (PR), the Hackensack River (HR), and Newark Bay (NB: surficial sediments, NBG: coastal aquifer sediments)

| Sample ID | Latitude | Longitude | Cr | Cu | Fe | Mn | Pb | S | Zn |
|-----------|----------|-----------|-------|-----|--------|------|-----|-------|-----|
| PR-1 | 40.7342 | 74.1453 | 180 | 183 | 39416 | 492 | 215 | 7338 | 492 |
| PR-2 | 40.7462 | 74.1652 | 165 | 197 | 36259 | 636 | 196 | 4266 | 582 |
| PR-3 | 40.7640 | 74.1588 | 144 | 135 | 36889 | 542 | 211 | 3528 | 377 |
| PR-4 | 40.7839 | 74.1478 | 175 | 182 | 40474 | 874 | 216 | 3378 | 476 |
| PR-5 | 40.7935 | 74.1412 | 148 | 121 | 29020 | 772 | 141 | 1929 | 414 |
| AVG | | | 162 | 164 | 36412 | 663 | 196 | 4088 | 468 |
| HR-2 | 40.7625 | 74.0878 | 78 | 160 | 71360 | 1474 | 52 | 1291 | 153 |
| HR-4 | 40.8064 | 74.0436 | 116 | 48 | 21120 | 1185 | 40 | 1987 | 148 |
| HR-5 | 40.8466 | 74.0318 | 92 | 31 | 12380 | 772 | 50 | 1220 | 75 |
| HR-8 | 40.8854 | 74.0349 | 210 | 133 | 34960 | 433 | 104 | 7619 | 306 |
| AVG | | | 124 | 93 | 34955 | 966 | 62 | 3029 | 171 |
| NB-1 | 40.7123 | 74.1036 | 142 | 74 | 16240 | 171 | 102 | 3835 | 237 |
| NB-2 | 40.6889 | 74.1124 | 58 | 10 | 4448 | 242 | nd | 1323 | 21 |
| NB-3 | 40.6786 | 74.1170 | 347 | 21 | 11,240 | 152 | 29 | 1,872 | 63 |
| NB-4 | 40.6702 | 74.1269 | 85 | 55 | 34,540 | 804 | 78 | 2,032 | 150 |
| NB-5 | 40.6621 | 74.1323 | 66 | 30 | 19,240 | 286 | 64 | 3,029 | 69 |
| NB-6 | 40.6557 | 74.1387 | 158 | 65 | 16,000 | 172 | 50 | 3,244 | 127 |
| AVG | | | 143 | 43 | 16,951 | 305 | 64 | 2,556 | 111 |
| NBG 1-1 | 40.6888 | 74.1121 | 3,771 | 19 | 18,320 | 413 | 4 | 1,749 | 47 |
| NBG 1-2 | 40.6888 | 74.1121 | 5,775 | 25 | 20,240 | 275 | 13 | 696 | 69 |
| NBG 1-3 | 40.6888 | 74.1121 | 4,011 | 25 | 22,920 | 445 | 39 | 1,655 | 66 |
| AVG | | | 4,519 | 23 | 20,493 | 378 | 19 | 1,367 | 61 |
| NBG 2-1 | 40.6785 | 74.1169 | 419 | 25 | 12,760 | 190 | 38 | 2,826 | 72 |
| NBG 2-2 | 40.6785 | 74.1169 | 640 | 43 | 17,980 | 234 | 44 | 1,690 | 107 |
| NBG 3-2 | 40.6719 | 74.1241 | 47 | 52 | 15,460 | 177 | 51 | 1,387 | 121 |
| NBG 3-3 | 40.6719 | 74.1241 | 112 | 52 | 21,920 | 297 | 85 | 1,206 | 136 |
| AVG | | | 304 | 43 | 17,030 | 225 | 55 | 1,778 | 109 |

studies suggest that Cr in sediments is most likely in the form of Cr(III) (Elzinga & Cirimo 2010). Martello *et al.* (2007) reported that total chromium in whole sediments from the lower Hackensack River ranged from 5 to 9,190 mg/kg, while Cr(VI) concentrations ranged from <0.47 to 31 mg/kg (Martello *et al.* 2007). Becker *et al.* (2006) also reported a wide range of total Cr concentrations (199–3,970 mg/kg) in sediments collected from the Hackensack River and nearly all Cr was present as Cr(III) in most sediments containing measurable concentrations of acid-volatile sulfide (AVS) (Becker *et al.* 2006). Weng *et al.* (1994) confirmed that the bulk of chromium in the New Jersey COPR-enriched soil was mostly in the form of Cr(III) (Weng *et al.* 1994).

Cr(VI) removal by the HZ sediments

The kinetics of Cr(VI) removal was studied with four sediment samples from the estuary. The highest removal of Cr(VI) occurred in the PR-1 sediment sample, which showed almost 100% removal of 0.5 mg/L Cr(VI) in 2 days (Figure 2). NBG-1, HR-4, and NB-2 sediment samples removed 53, 26, and 6% of 0.5 mg/L Cr(VI), respectively in 2 days (Figure 2). In general, the Cr(VI) removal occurred in two steps: initially, rapid removal of Cr(VI) within 1 hour followed by the slow removal of Cr(VI) over 2 days. The removal of Cr(VI) was nearly complete in all four sediment samples within 24 hours.

Table 2 | Summary of Cr(VI) removal experiments with 5 g of HZ sediments and 25 mL solutions of 0.1 mg/L and 0.5 mg/L Cr(VI) including Cr(VI) removal % and equilibrium pH after 2-day reactions as well as silt and clay % and loss on ignition (LOI) % in sediments

| Sample ID | 0.1 mg/L Cr(VI) | | 0.5 mg/L Cr(VI) | | Silt + Clay% | LOI% |
|-----------|-----------------|-----------|-----------------|-----------|--------------|------|
| | pH | Removal % | pH | Removal % | | |
| PR-1 | 6.80 | 100 | 6.73 | 100 | 30.5 | 10.1 |
| PR-2 | 6.46 | 100 | 6.45 | 98 | 25.8 | 10.5 |
| PR-3 | 6.44 | 100 | 6.52 | 96 | 13.2 | 6.0 |
| PR-4 | 6.27 | 100 | 6.17 | 100 | 31.6 | 11.7 |
| PR-5 | 6.82 | 91 | 6.85 | 68 | 5.0 | 4.8 |
| AVG | 6.56 | 98 | 6.54 | 92 | 21.2 | 8.6 |
| HR-2 | 6.65 | 64 | 6.64 | 40 | 5.4 | 2.7 |
| HR-4 | 6.76 | 73 | 6.8 | 66 | 4.8 | 7.3 |
| HR-5 | 7.52 | 45 | 7.42 | 28 | 4.4 | 2.7 |
| HR-8 | 6.54 | 91 | 6.57 | 98 | 9.0 | 8.8 |
| AVG | 6.87 | 68 | 6.86 | 58 | 5.9 | 5.4 |
| NB-1 | 6.40 | 50 | 6.55 | 11 | 0.0 | 3.9 |
| NB-2 | 6.99 | 18 | 7.02 | 4 | 0.0 | 0.7 |
| NB-3 | 6.87 | 45 | 6.92 | 15 | 0.0 | 2.3 |
| NB-4 | 6.93 | 27 | 6.87 | 13 | 0.0 | 1.6 |
| NB-5 | 6.98 | 64 | 6.85 | 53 | 0.0 | 1.1 |
| NB-6 | 6.71 | 45 | 6.76 | 38 | 0.8 | 3.2 |
| AVG | 6.81 | 42 | 6.83 | 22 | 0.1 | 2.1 |
| NBG1-1 | 7.23 | 64 | 7.16 | 49 | 0.0 | 0.5 |
| NBG1-2 | 7.22 | 9 | 7.18 | 9 | 0.0 | 0.5 |
| NBG1-3 | 6.87 | 18 | 7.05 | 15 | 0.0 | 0.5 |
| AVG | 7.11 | 30 | 7.13 | 25 | 0.0 | 0.5 |
| NBG2-1 | 7.02 | 45 | 6.88 | 43 | 0.0 | 2.7 |
| NBG2-2 | 6.88 | 27 | 6.74 | 36 | 0.0 | 2.4 |
| NBG3-2 | 7.04 | 9 | 6.90 | 9 | 0.3 | 1.6 |
| NBG3-3 | 7.60 | 55 | 7.61 | 9 | 0.3 | 1.3 |
| AVG | 7.14 | 34 | 7.03 | 25 | 0.2 | 2.0 |

As 5 g of sediments from the estuary was reacted with 25 mL solution of 0.1 mg/L or 0.5 mg/L Cr(VI) over 2 days, the PR sediments removed Cr(VI) to the highest extent (Table 2). The PR sediment removed on average 98% of 0.1 mg/L Cr(VI) and 92% of 0.5 mg/L Cr(VI). The HR sediments removed on average 68% of 0.1 mg/L Cr(VI) and 58% of 0.5 mg/L Cr(VI). The average removal rates of 0.1 mg/L Cr(VI) and 0.5 mg/L Cr(VI) by the NB sediments were 42 and 22%, respectively, while they were 32 and 25% for the NBG sediments (Table 2). While the initial pH of 0.1 mg/L and 0.5 mg/L Cr(VI) solution was

9.14 and 9.18, respectively, the pH was equilibrated to circumneutral pH after 2-day reactions with sediments, which ranged from 6.54 to 7.14 on average (Table 2).

The concentrations of Cr(VI) in solution measured after the reaction of sediment samples with deionized water without adding Cr(VI) ranged from 0.01 to 0.04 mg/L, which indicated that the mobilization of pre-existing Cr(VI) from the HZ sediments of the estuary was insignificant at circumneutral pH (6.20–7.40) over 2 days. This is consistent with the previous studies that revealed limited mobility and bioavailability of chromium in the Hackensack River sediments (Becker et al. 2006; Martello et al. 2007; Magar et al. 2008).

Geochemical factors affecting Cr(VI) removal in sediments

For both Cr(VI) solutions of 0.1 mg/L and 0.5 mg/L, the Cr(VI) removal by sediments (3 and 5 g) was correlated with sediment properties including silt and clay fractions, organic matter content (LOI %) and sediment sulfur content, as well as solution pH (Figure 3). The Cr(VI) removal percentage generally increased with higher amounts of silt and clay (Figure 3). The Cr(VI) removal was nearly 100% in sediments with silt and clay fractions higher than 10%. The Cr(VI) removal was also higher in sediments with higher content of organic matter determined by the loss on ignition method. Therefore, the high extent of Cr(VI) removal by the PR sediments was attributed to fine sediment grains and high organic matter content. In addition, the extent of Cr(VI) removal decreased with increasing solution pH (Figure 3) although the correlation was less obvious compared to silt and clay fractions or organic matter content. Pearson correlation coefficients for the removal of 0.5 mg/L Cr(VI) by 5 g of sediment also demonstrate a strong or very strong correlations between the Cr(VI) removal and silt and clay fractions ($r = 0.807$), sediment organic matter content ($r = 0.869$), and solution pH ($r = -0.641$) (Table 3).

The correlations between the Cr(VI) removal and the concentrations of Fe, S and Mn in sediments were also examined (Figure 4). For both 0.1 mg/L and 0.5 mg/L Cr(VI), the Cr(VI) removal generally increased with higher concentrations of Fe and S in the sediment. The Pearson correlation coefficients (Table 3) indicated a strong correlation ($r = 0.711$) between Cr(VI) removal and sediment S content and a moderate correlation ($r = 0.510$) between Cr(VI) removal and sediment Fe content, whereas the Cr(VI) removal was poorly correlated with sediment Mn content ($r = 0.353$).

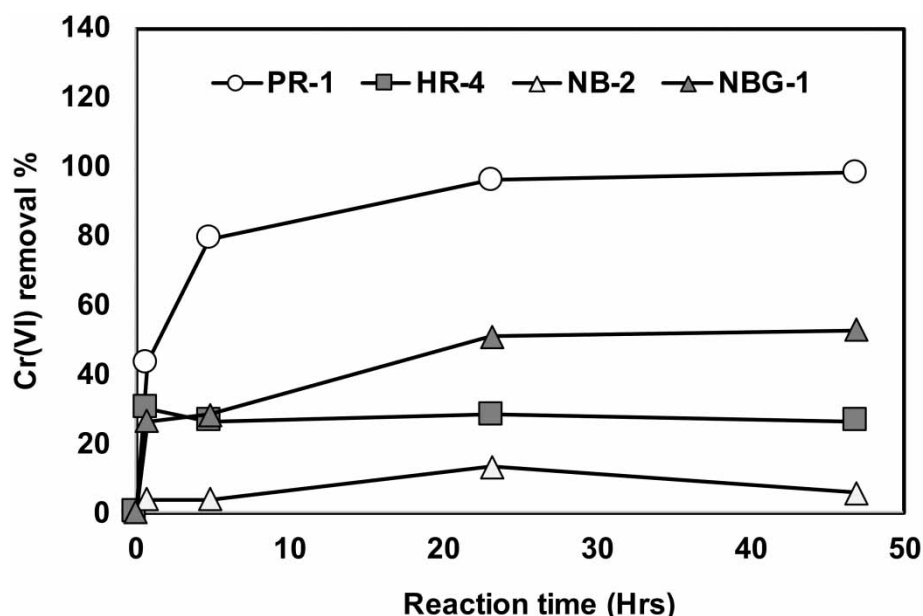


Figure 2 | Kinetics of Cr(VI) removal (0.5 mg/L) by the hyporheic zone sediments (3 g) from the estuary over 48 hours.

Physical and chemical properties of sediments were correlated with each other. Sediment organic matter content (LOI%) was very strongly correlated with the silt and clay fractions (Table 3; $r = 0.899$), which indicates that finer-grained sediments tend to be more organic rich (Figure 5). The PR sediments showed the highest amount of organic matter (average: 8.6%) as well as the highest percentage of silt and clay fractions (average: 21.2 wt%), whereas the NB or NBG sediments showed the lowest level of silt and clay fractions (average: 0.0–0.2 wt%) and organic matter content (average: 0.5–2.1%) (Table 2). Sediment organic matter content was also associated with sediment Fe and S content (Figure 5), showing a strong correlation between LOI % and sediment S ($r = 0.725$) and a moderate correlation between LOI % and sediment Fe ($r = 0.463$) (Table 3). The Pearson correlation coefficient also indicates a moderate to strong correlation between silt and clay fractions and sediment Fe or sediment S content (Table 3). Sediment organic matter content was also strongly correlated with pH ($r = -0.704$), which decreased with increasing LOI % (Table 3). The correlation between sediment organic matter content and sediment Mn content was weak. Sediment Fe was weakly correlated to sediment S, while sediment Fe was strongly correlated with sediment Mn (Figure 5). Overall, the correlations of sediment properties indicate that the finer-grained sediments with higher silt and clay fractions (e.g. the PR sediments) contained higher content of organic matter (LOI %) and sulfur, which may indicate that those sediments are more reducing.

In general, higher removal of Cr(VI) in the hyporheic zone sediments was associated with finer sediment grains, higher organic matter content, and higher Fe and S content as well as lower pH conditions. The removal of Cr(VI) by the sediments can result from adsorption and/or reduction, which are affected by the combined effects of organic matter, Fe(II), pH, and sediment particle size distribution (e.g. silt and clay fractions).

Remobilization of Cr(VI) from sediments

After the removal of 0.5 mg/L Cr(VI) by sediment samples from the estuary for 2 days, the sediments were subsequently exposed to 25 mL of deionized water for 5 days to examine the potential remobilization of Cr(VI) from sediments. After the 5-day exposure, the solution pH was circumneutral ranging from 6.50 to 7.59. The lowest rate of Cr(VI) remobilization was found from the PR sediments, which was on average 6% and ranged from 2 to 13%, while the remobilization of Cr(VI) from the NB sediments ranged approximately from 30 to 100%, with the average remobilization of 67%. The HR sediments showed an intermediate rate of Cr(VI) remobilization, which was on average 32% and ranged from 17 to 40% (Figure 6).

After the 5-day remobilization of Cr(VI), the amount of chromium that remained immobilized in the PR sediments was on average 3.8 mg/kg and ranged from 2.3 to 4.3 mg/kg (Figure 6). The average amount of immobile chromium in the HR sediments and the NB sediments was

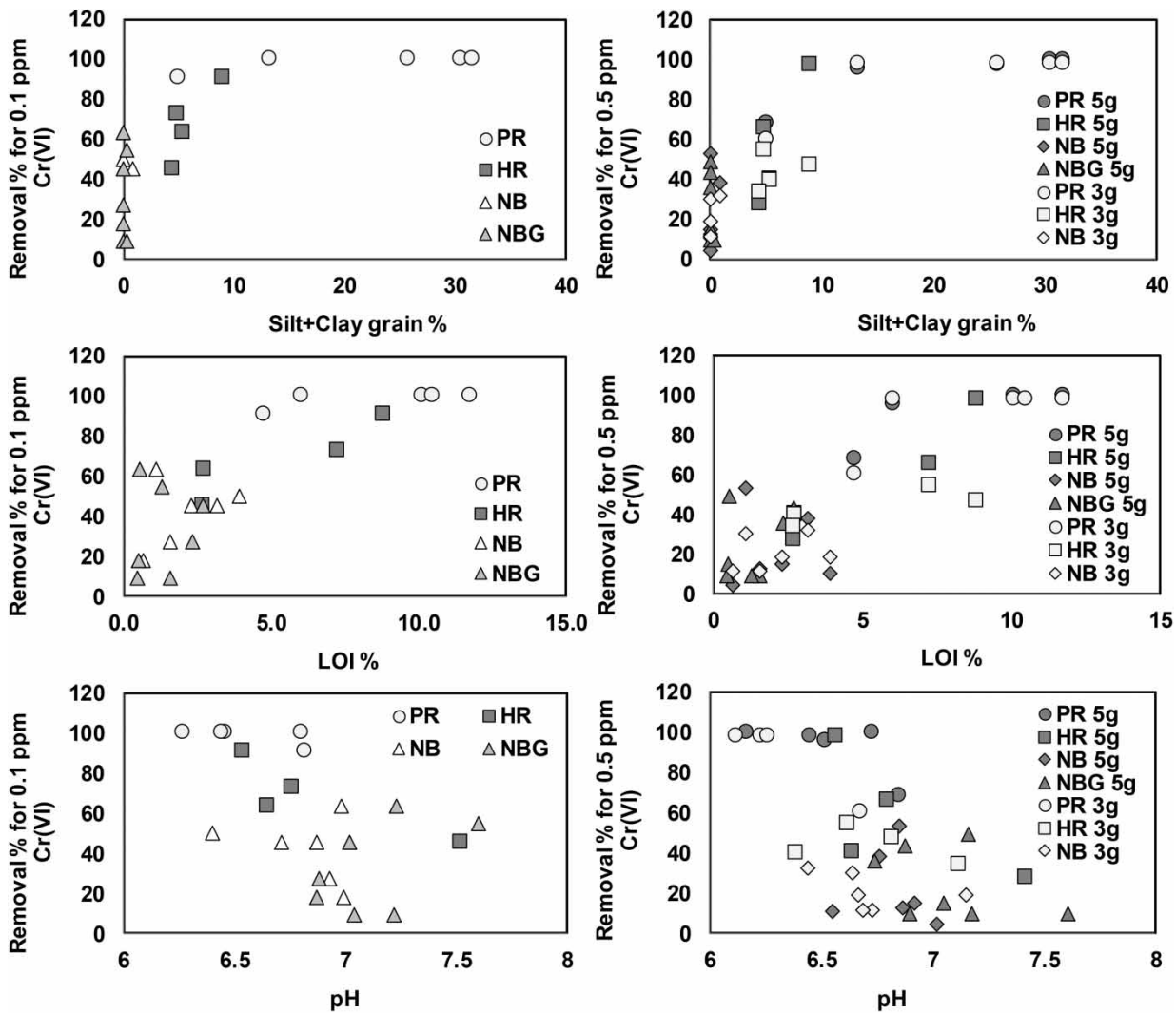


Figure 3 | Relationships between the removal percentage of Cr(VI) and sediment properties such as fine sediment grains % and organic matter content (LOI %) as well as solution pH after 2-day reactions. **Left:** 25 mL solution of 0.1 mg/L Cr(VI) + 5 g sediment; **Right:** 25 mL solution of 0.5 mg/L Cr(VI) + 3 g or 5 g sediment.

Table 3 | Pearson correlation coefficients for the removal of 0.5 mg/L Cr(VI) by 5 g of HZ sediments ($n = 22$)

| | Cr(VI) removal % | Silt + Clay % | LOI % | pH | Sediment Fe | Sediment S | Sediment Mn |
|------------------|------------------|---------------|---------------|--------|--------------|------------|-------------|
| Cr(VI) removal % | 1 | | | | | | |
| Silt + Clay % | 0.807 | 1 | | | | | |
| LOI % | 0.869 | 0.899 | 1 | | | | |
| pH | -0.641 | -0.594 | -0.704 | 1 | | | |
| Sediment Fe | 0.510 | 0.527 | 0.463 | -0.485 | 1 | | |
| Sediment S | 0.711 | 0.611 | 0.725 | -0.547 | 0.295 | 1 | |
| Sediment Mn | 0.353 | 0.336 | 0.356 | -0.244 | 0.725 | -0.071 | 1 |

The bold numbers indicate a strong to very strong correlation.

1.3 mg/kg and 0.4 mg/kg, respectively, which was significantly lower than the amount of chromium immobilized in the PR sediments (Figure 6). The results showed that the

PR sediments have a greater capacity for immobilizing Cr(VI) compared to the HR or NB sediments. Once Cr(VI) is removed by the fine-grained and organic-rich PR

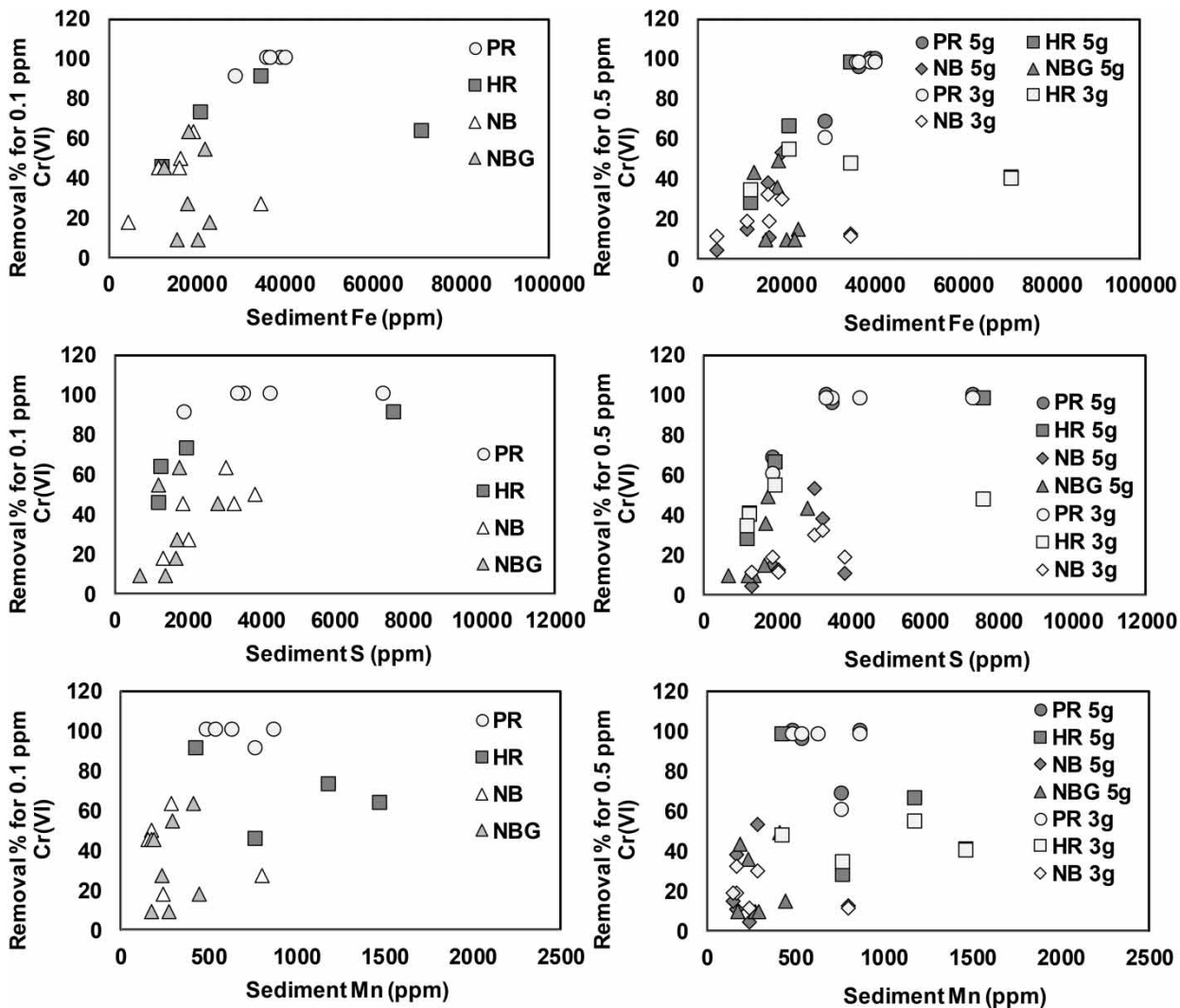


Figure 4 | Relationships between the removal percentage of Cr(VI) and sediment Fe, S, and Mn. **Left:** 25 mL solution of 0.1 mg/L Cr(VI) + 5 g sediment; **Right:** 25 mL solution of 0.5 mg/L Cr(VI) + 3 g or 5 g sediment.

sediments, Cr(VI) is less likely to be remobilized from the sediment, although the long-term behavior of immobilized Cr(VI) in sediments needs to be further investigated. In contrast, Cr(VI) removed by the coarse-grained and organic-poor NB sediments is predominantly reversible and is subject to remobilization.

Irreversible immobilization of Cr(VI) can perhaps result from a specific adsorption of hexavalent chromium or reduction of Cr(VI) to Cr(III), which leads to strong retention. Once reduced, Cr(III) is stable in aquatic environments because oxidation of Cr(III) by dissolved oxygen is generally insignificant and very slow at pH above 5 (Eary & Rai 1987; Rai *et al.* 1989). It is unlikely that manganese oxides (MnO_2) and favorable pH conditions will cause a significant oxidation of Cr(III) to Cr(VI) in soil

or sediment because mobile Cr(III) is unavailable (Bartlett 1991). Therefore, it appears that less reversible removal of Cr(VI) in the organic-rich PR sediments is attributable to the reduction of Cr(VI) to Cr(III) by organic matter, while more reversible removal of Cr(VI) in the organic-poor NB sediments may be associated with the adsorption of Cr(VI).

Mechanism of Cr(VI) removal by the hyporheic zone sediments

Two main mechanisms are thought to control the mobility of hexavalent chromium, which include Cr(VI) reduction into Cr(III) and adsorption (Rai *et al.* 1989). In Fe(II)- and organic matter-rich environments, reduction of Cr(VI) is more likely to occur, while Cr(VI) can be removed by

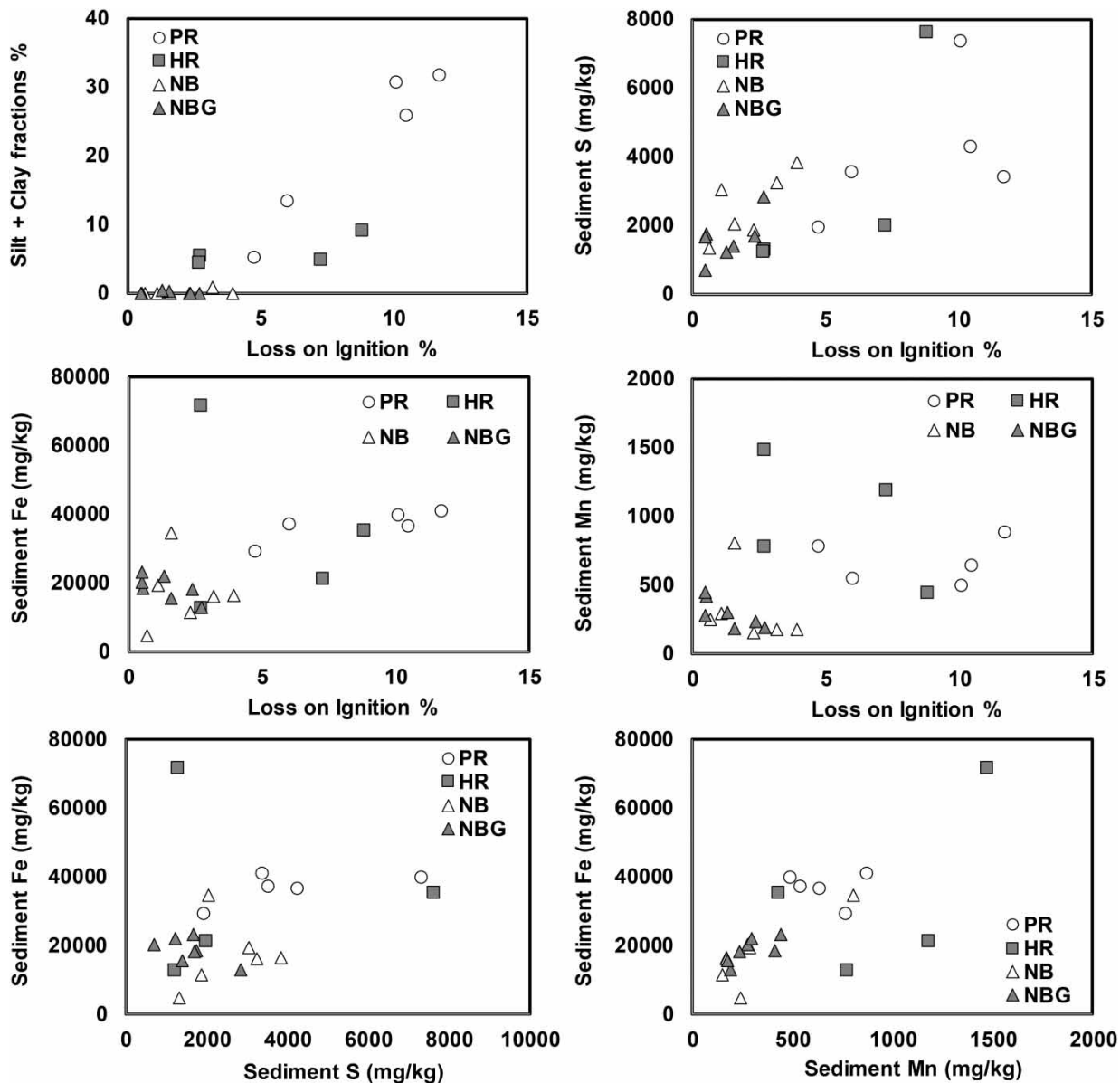


Figure 5 | Correlations of organic matter content (LOI %), silt and clay fractions, and the concentrations of Fe, Mn, and S in the hyporheic zone sediments of the Passaic River (PR), the Hackensack River (HR), and Newark Bay (NB and NBG).

adsorption processes in soils or sediments with high content of Fe and Mn oxides or clay minerals under acidic and oxidizing conditions (Eary & Rai 1987; Rai *et al.* 1989). Adsorption of Cr(VI) by natural sediments and soils is low to moderate in circumneutral pH ranges because adsorption of Cr(VI) decreases with increasing pH due to the decrease in positive surface charge of the sorbents. Although soil organic matter (SOM) provides important adsorption sites for most heavy metals, it mainly serves as a reductant to reduce Cr(VI) to Cr(III). Surficial soils and sediments commonly contain appreciable natural organic matter that can

potentially promote the reduction of Cr(VI) to Cr(III) species. Cr(VI) has shown to be readily reduced to Cr(III) and then precipitates as $\text{Cr}(\text{OH})_3$ or as the solid solution $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$ in soils or sediments at circumneutral pH by organic matter (Higgins *et al.* 1998), while Cr(VI) adsorption to many soils or sediments is not strong under alkaline to slightly acidic pH conditions (Weng *et al.* 1994). Although Cr(VI) can also be reduced by inorganic reductants such as Fe(II), Cr(VI) reduction by Fe(II) becomes less significant under neutral and alkaline pH conditions because of limited release of Fe(II) from Fe(II)-bearing minerals (Eary & Rai 1987).

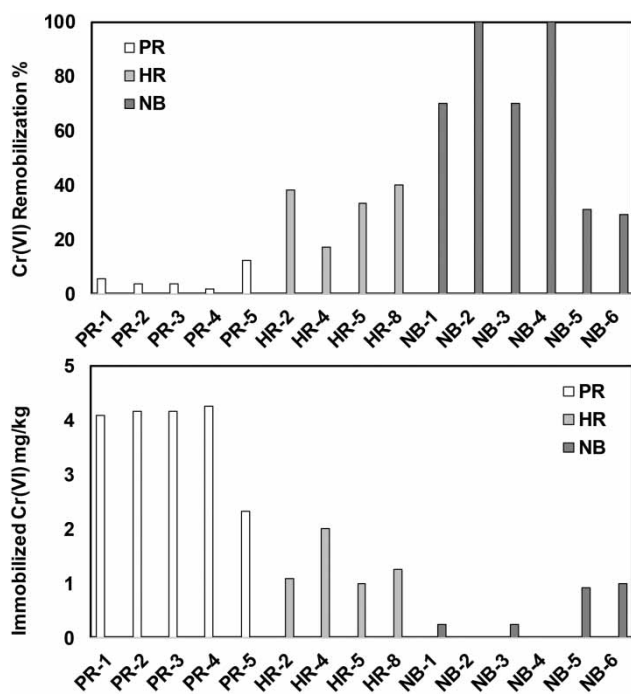


Figure 6 | The percentage of Cr(VI) remobilized from sediments over 5 days after 2-day Cr(VI) removal reactions (a) and the amount of Cr(VI) retained in sediments (b).

Because Cr(VI) was readily and irreversibly removed by the PR sediments with high organic matter content at circumneutral pH condition, the removal of Cr(VI) by the PR sediments is attributed to the reduction of Cr(VI) to Cr(III) by organic matter and subsequent precipitation of Cr(III)-containing solids. This removal mechanism of Cr(VI) in the organic-rich PR sediments is consistent with a number of previous studies that showed high accumulation of Cr as well as low toxicity and bioavailability of Cr in natural sediments of estuaries and rivers due to redox transformation of Cr(VI) to Cr(III) under reducing conditions (Becker *et al.* 2006; Martello *et al.* 2007; Magar *et al.* 2008; Wadhawan *et al.* 2013; Xu *et al.* 2017).

However, adsorption could also be an important mechanism to remove Cr(VI) in the NB and NBG sediments, which contained low amounts of organic matter. Both adsorption and reduction of Cr(VI) could be responsible for the removal of Cr(VI) in the HR sediments to a similar extent. As both reduction of Cr(VI) to Cr(III) and the adsorption of Cr(VI) can occur simultaneously in many soils and sediments, it is not always possible to attribute Cr(VI) removal precisely to reduction or adsorption (Bartlett 1991). Because the relationship between adsorption and reduction of chromium is a complex and interrelated process that is not fully understood, further studies are needed to better determine the mechanisms governing the

potential removal of Cr(VI) in the hyporheic zone along the urbanized estuary.

CONCLUSIONS

While remediation of numerous COPR legacy sites contaminating groundwater around the world is challenging because of the high cost and health risk of traditional remediation strategies such as excavation and disposal (Whittleston *et al.* 2011), natural sediment in the hyporheic zone may play a role as a natural permeable barrier for removing groundwater Cr during groundwater discharge into a river system (Xu *et al.* 2017). Our experimental study with the HZ sediments of an urbanized estuary showed that higher removal of Cr(VI) was associated with finer sediment grains, higher contents of organic matter, Fe and S as well as lower pH conditions. The removal of Cr(VI) in organic-rich sediment with limited remobilization was attributed to the reduction to Cr(III), while the removal of Cr(VI) in organic-poor sediments with moderate to significant remobilization could result from adsorption. Although our study suggests that fine-grained and organic-rich HZ sediment can effectively immobilize hexavalent chromium and attenuate environmental impacts on the estuary, it is difficult to predict whether this Cr(VI) immobilization will operate indefinitely in the hyporheic zone because of limited reduction capacity and adsorption sites in the sediment. The oxidation of Cr(III) to Cr(VI) may potentially occur while sediment is resuspended and reoxygenated as a result of dredging, bioturbation, and flooding (Wadhawan *et al.* 2013). Redox conditions in subsurface environments often fluctuate because of groundwater-surface water interactions. Therefore, it is important to understand and monitor the long-term stability of Cr in the hyporheic zone of the urbanized estuary where biogeochemical and hydrological conditions are affected by both natural and anthropogenic activities.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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