Source identification of chromium in the sediments of the Xiaoqing River and Laizhou Bay: A chromium stable isotope perspective

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ABSTRACT

Hexavalent chromium, Cr(VI), is a heavy metal contaminant and the reduction of Cr(VI) is accompanied by large isotopic fractionation. In this study, the sources of Cr were explored using the Cr isotopic composition of sediments from the Xiaoqing River, a heavily polluted river located in the Shandong Province of China, which flows into Laizhou Bay. The results show that $\delta^{53}\text{Cr}$ values of the sediments are the highest upstream near the pollution source, and gradually decrease along the river toward the range for igneous reservoirs observed near the estuary. Based on the calculation of authigenic Cr isotopic composition ($\delta^{53}\text{Cr}_{\text{auth}}$) using the detrital index and leaching experiments, we suggest that the authigenic Cr in the sample near the pollution source with the highest $\delta^{53}\text{Cr}_{\text{auth}}$ value mainly comes from the reduction of Cr(VI) discharged by anthropogenic activity, and authigenic Cr in other samples in the midstream with $\delta^{53}\text{Cr}_{\text{auth}}$ values slightly higher than the range of igneous reservoirs may come from natural oxidative Cr weathering products. By introducing a Rayleigh model, we calculate that at least 31%–55% of Cr(VI) in the river water had been reduced to Cr(III) near the pollution source. Due to the self-purification ability of the river, Cr(VI) was reduced; thus, there is no record of high $\delta^{53}\text{Cr}_{\text{auth}}$ values in the downstream of the Xiaoqing River and Laizhou Bay, indicating no obvious Cr pollution in these locations. The limited variation of $\delta^{53}\text{Cr}$ values for samples from a sediment core in Laizhou Bay is also indicative of no obvious Cr pollution in the history. The Cr isotopic compositions of the river sediments are useful for the identification of Cr sources and can be used to advise environmental remediation on Cr pollution.

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1. Introduction

Hexavalent chromium, is a common metal contaminant in natural water systems and mainly comes from mining, leather manufacturing, electroplating, and so on (e.g. Fendorf, 1995; Testa et al., 2004). In surface environments, Cr exists as either Cr(III) or

Cr(VI). Oxidized Cr(VI) always forms ionic groups such as HCrO_4^- , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$, which are soluble in aqueous fluids and highly toxic. In contrast, the reduced form [Cr(III)], as the main valence state in igneous rocks, is less soluble and toxic (Ellis et al., 2002; Johnson and Bullen, 2004; Miretzky and Cirelli, 2010; Wanner et al., 2012). Therefore, the effective way to remediate Cr pollution is to reduce Cr(VI) into Cr(III). The common approach to monitor Cr(VI) remediation is to determine the Cr(VI) concentrations in different sites along the transportation path over a long time period. However, this approach cannot resolve whether any observed decrease of Cr(VI) results from reduction or from dilution, convection, or adsorption (Berna et al., 2010).

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Stable Cr isotope system is a potential tool for the quantitative determination of Cr(VI) reduction. Chromium has four stable isotopes: ^{50}Cr (4.31 wt%), ^{52}Cr (83.76 wt%), ^{53}Cr (9.55 wt%), and ^{54}Cr (2.38 wt%). Cr(VI) reduction by aqueous Fe(II), Fe(II)-bearing minerals, organic molecules, or microorganism in sediments and water column is accompanied by Cr isotopic fractionation, and the reduction degree is quantitatively related to the Cr isotopic composition of the remaining Cr(VI) (e.g. Ellis et al., 2002; Kitchen et al., 2012; Sikora et al., 2008). The isotopic fractionation is related to the break of the Cr–O bond during Cr(VI) reduction. Chemical bonds formed by light isotopes have a higher vibration frequency and lower bond energy than those formed by heavier isotopes, so these bonds break more easily, resulting in the enrichment of light isotopes in the products (Schauble et al., 2004). As Cr(III) is usually insoluble, the remaining Cr(VI) in the aqueous system will become increasingly heavier. Therefore, Cr isotopic composition can be used to assess the degree of Cr(VI) reduction in contaminated groundwater systems (e.g. Berna et al., 2010; Izbicki et al., 2008; Novak et al., 2017). Many previous studies on tracing Cr pollution with isotope tracers have been conducted for groundwater systems (Berna et al., 2010; Economou-Eliopoulos et al., 2014; Heikoop et al., 2014; Izbicki et al., 2008; Izbicki et al., 2012; Novak et al., 2014; Novak et al., 2017; Raddatz et al., 2010). For instance, Raddatz et al. (2010) used the Cr isotopic compositions of groundwater to determine if the decrease in Cr(VI) concentrations resulted from removal via reduction, and Heikoop et al. (2014) found that reduction of Cr(VI) happened in vadose zone basalts based on Cr isotopes. However, there are few studies about Cr isotopic composition in polluted rivers. Surface water is also vulnerable to Cr pollution. Besides, the Cr in rivers is more easily subjected to the influence of oxidative chemical weathering than groundwater. Several studies showed that $\delta^{53}\text{Cr}$ values of river water without obvious anthropogenic Cr pollution range from -0.2‰ to 4.0‰ (D'Arcy et al., 2016; Farkaš et al., 2013; Frei et al., 2014; Goring-Harford et al., 2020; Novak et al., 2014; Paulukat et al., 2015; Wu et al., 2017). Frei et al. (2014) found that there is almost no Cr isotopic variability during the long riverine transport in a subtropical region of South America. The climate is also not a determinant of Cr isotopic composition during weathering and riverine transport (Wu et al., 2017), instead, the catchment conditions play a major role, e.g. the high $\delta^{53}\text{Cr}$ values are found from stream water flowing through serpentinized ultramafic rocks areas in Czech Republic (Farkaš et al., 2013).

The Xiaoqing River located in Shandong province, eastern China, is one of the most polluted rivers flowing into Laizhou Bay due to industrial development (Heydebreck et al., 2015; Jiang et al., 2017; Zhen et al., 2018). There are some factories (electroplate factory, thermal power plant, steel work and pharmaceutical factory) upstream, which can potentially discharge Cr(VI) to the river. Therefore, in this work we aimed at identifying the sources of Cr in the Xiaoqing River based on Cr isotopes and evaluating the impact of Cr pollution to Laizhou Bay. Considering the high flow of the river water and irregular discharge, the Cr pollution in river water may change dramatically over time. Therefore we measured the Cr isotopic compositions of the river sediments from the upstream to estuary along the Xiaoqing River, which can record the average Cr pollution signal over a long time period. Besides, the Cr isotopic compositions of samples from a sediment core in Laizhou Bay were measured to estimate the effect of pollution in history.

2. Sampling and methods

2.1. Sampling

The Xiaoqing River is one of the major rivers in the central area

of Shandong Province, originating from the springs in the city of Jinan. It flows through Licheng, Zhangqiu, Zouping, Gaoqing, Huantai, Boxing, Guangrao, Shouguang and other counties, and finally flows into Laizhou Bay, Bohai Sea. The total length is 237 km and the drainage area is 10,340 km² (Zhen et al., 2018). The Xiaoqing River is used to control flooding, irrigation and shipping, but due to the discharge of industrial and sewage waste water, it has become one of the heaviest polluted rivers flowing into Laizhou Bay (Heydebreck et al., 2015; Jiang et al., 2017; Zhen et al., 2018). Twelve surface sediment samples (0–5 cm) were collected with a stainless steel grab bucket from the upstream region down to the estuary of the river in April 2014 (Fig. 1). Among these samples, sample XQH10 is from a tributary, sample LZW30 is from the estuary, and sample LZW25 is from Laizhou Bay (Fig. 1). There are some factories, especially a electroplate factory near the sample site of XQH1, which can potentially release Cr contaminant to the river. All the samples were sealed in polyethylene (PE) bags and preserved in a freezer ($-20\text{ }^{\circ}\text{C}$) after sampling. In order to understand the pollution history, a sediment core from Laizhou Bay (the circle outlined in Fig. 1) was collected with a vibratory core sampler in October 2012. The longitude and latitude is $37^{\circ} 29' 04.440'' \text{ N}$ and $119^{\circ} 17' 25.979'' \text{ E}$, respectively, and the length of the sediment core is 3.3 m. All the samples were dried under natural conditions and were milled to 200 mesh using an agate grinding mortar.

2.2. Methods

2.2.1. Leaching experiments

Sequential extraction procedures are effective methods to measure trace metal concentrations in different components. Here we followed a modified three-step sequential extraction procedure proposed by the Commission of the European Communities Bureau of Reference (BCR), which had been successfully applied in sediments, soils and sewage sludges (e.g. Ure et al., 1993; Rauret et al., 2000; Žemberyová et al., 2006). The BCR three-step sequential extraction divides the Cr in sediments into four different forms: exchangeable (extraction Step 1), reducible-iron/manganese oxides (extraction Step 2), oxidizable-organic matter and sulfides (extraction Step 3), and residual Cr (Žemberyová et al., 2006). The standardized procedure of BCR sequential extraction was described in detail in Rauret et al. (2000). Briefly, in the first step, 32 mL of 0.11 M acetic acid was added to 0.8 g sediment in a 50 mL centrifuge tube, and the mixture was shaken in a mechanical shaker for 16 h at $22 \pm 5\text{ }^{\circ}\text{C}$ (overnight). Then the reaction product was centrifuged and the supernatant was pipetted into a polyethylene container. The residue was washed by 4 mL distilled water (twice) and shaken for 15 min. In the second step, 32 mL of freshly prepared 0.5 M hydroxylammonium chloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) (adjusted to pH 2–3 with nitric acid) was added to the residue and shaken in a mechanical shaker for 16 h. The separation method was the same as that described for the first step. The third step was to add 8 mL high-purity hydrogen peroxide (H_2O_2) to the residue slowly. The tub was capped loosely and was set at room temperature for 1 h with occasional manual shaking. Then the tub was capped and heated at $85 \pm 5\text{ }^{\circ}\text{C}$ for 1 h, with occasional shaking for the first 30 min. The mixture was then dried to less than 3 mL. The mixture was added with another aliquot of 8 mL H_2O_2 and heated at $85 \pm 5\text{ }^{\circ}\text{C}$ until the volume of liquid was reduced to $\sim 1\text{ mL}$. 40 mL of 1.0 M ammonium acetate (NH_4Ac) (adjusted to pH 2 with nitric acid) was added to the cool moist residue and shaken for 16 h at $22 \pm 5\text{ }^{\circ}\text{C}$. The solution-residue separation step was the same as described above. At the last step, the residue was dried and weighted. About 0.05 g residue was digested by 1 mL concentrated HF and 3 mL concentrated HNO_3 in a Microwave Digestion System (WX-8000). The sample-acid mixtures were heated at $220\text{ }^{\circ}\text{C}$ until

Fig. 1. Overview of the sampling sites for the Xiaoqing River (modified after Heydebreck et al., 2015). The sediment samples from the Xiaoqing River are shown by black triangles, and the sediment core from Laizhou Bay is shown by a circle.

the sample was dissolved completely.

2.2.2. Major and trace elements analysis

About 0.05 g whole-rock sample was digested by 1 mL concentrated HF and 3 mL concentrated HNO₃ in a Microwave Digestion System at 220 °C. The major and trace elemental compositions of the whole rocks and leachates were analyzed using iCAP 7200 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and PerkinElmer Elan DRCII Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at USTC, respectively.

2.2.3. Cr-isotope analysis

The detailed Cr purification procedure was given in Qin et al. (2010) and Shen et al. (2015, 2018). In brief, sample solutions which contained about 1 µg Cr were first mixed with ⁵⁰Cr–⁵⁴Cr double spike solution and dried on a hot plate before column chemistry. Then the sample was dissolved in 0.2 mL of 6 M HCl and heated at 120–130 °C for 3 h. The purification of Cr was accomplished through a two-step cation exchange chromatography procedure with Bio-Rad AG 50-X8 resin (200–400 mesh). The full procedural blank was typically <10 ng and the yield was 70–90%.

The Cr isotopic compositions of the whole rocks were measured on a Neptune plus Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS; Thermo Fisher Scientific, Germany) at USTC. The samples were diluted to 200 ppb in 2% HNO₃ for analysis and were nebulized with an Aridus II desolvator system at an uptake rate of 50 µL min⁻¹. All four Cr isotopes (⁵⁰Cr⁺, ⁵²Cr⁺, ⁵³Cr⁺, and ⁵⁴Cr⁺), as well as ⁴⁹Ti⁺, ⁵¹V⁺, and ⁵⁶Fe⁺ (to correct for the interferences from ⁵⁰Ti⁺ and ⁵⁰V⁺ on ⁵⁰Cr⁺ and from ⁵⁴Fe⁺ on ⁵⁴Cr⁺), were measured on Faraday cups L2, C, H1, H2, L4, L1, and H4, respectively. Each cup was connected to a 10¹¹ Ω resistor. Medium to high mass resolution modes (5500 < M/ΔM < 11,000) were used to avoid the interferences from polyatomic species such as ⁴⁰Ar¹³N⁺, ⁴⁰Ar¹⁴N⁺, and ⁴⁰Ar¹⁶O⁺ on ⁵³Cr⁺, ⁵⁴Cr⁺ and ⁵⁶Fe⁺, respectively (Bonnand et al., 2016). A total of 4 blocks with 30 cycles per block were obtained for each analysis. The Cr isotopic ratios are expressed as the permil variation relative to National Institute of

Standards and Technology (NIST) Standard Reference Material (SRM) 979:

$$\delta^{53}\text{Cr} = \left[\frac{\left(\frac{^{53}\text{Cr}}{^{52}\text{Cr}} \right)_{\text{sample}}}{\left(\frac{^{53}\text{Cr}}{^{52}\text{Cr}} \right)_{\text{SRM 979}}} - 1 \right] \times 1000\text{‰}. \quad (1)$$

Each sequence began with the measurements of the spiked internal Cr isotope standard SCP (Science, ON, Canada) and NIST SRM 3112a, and the internal standard SCP was analyzed at intervals of four or five samples. Samples were measured once and uncertainties reported here were the largest one among 2 standard error (2SE) of single sample measurement, 2 standard deviations (2SD) of repeated SCP measurements in the same analytical session, and the long-term reproducibility for the standard solution (SCP and NIST SRM 3112a; 0.05‰). More details of the methods were described in Shen et al. (2018) and Chen et al. (2019a).

The Cr isotopic compositions of the leachates were analyzed using a Triton plus multi-collector thermal-ionization mass spectrometer (TIMS) at USTC. For these analyses, about 0.1–1 µg Cr was loaded in 3 M HNO₃ on outgassed Re filaments with silica gel, saturated boric acid, and aluminum oxide. The rest of the procedure is the same with Shen et al. (2018) and only briefly described here. The standards and samples were measured at ionization temperatures between 1270 °C and 1390 °C to avoid possible isobaric interferences at lower or higher ionization temperatures. The Cr isotope signals (⁵⁰Cr⁺, ⁵²Cr⁺, ⁵³Cr⁺, and ⁵⁴Cr⁺) were collected on the Faraday detectors L3, L1, axial, and H1. The typical beam intensity of ⁵²Cr is 3–7 V measured on 10¹¹ Ω amplifiers. To monitor interferences of ⁵⁰Ti⁺ and ⁵⁰V⁺ on ⁵⁰Cr⁺ and ⁵⁴Fe⁺ on ⁵⁴Cr⁺, the ionic intensities of ⁴⁹Ti⁺, ⁵¹V⁺, and ⁵⁶Fe⁺ were measured simultaneously at the Faraday cups L4, L2, and H2, respectively. Each analysis consisted of 200 cycles of isotopic ratios with each cycle integrating the beam intensity for 8.389 seconds. Double spike calculations were performed off-line to correct any mass fractionation during purification and instrumental analysis. Samples were measured twice and uncertainties reported here were the largest one among

2SE of single sample measurement, 2SD of repeated sample measurements, and the long-term reproducibility for the standard solution (SCP and NIST SRM 3112a; 0.03‰).

3. Results

3.1. Whole-rock analyses

Major and trace element concentrations and Cr isotopic compositions for the surface sediments from Xiaoqing River and Laizhou Bay and the sedimentary core samples from Laizhou Bay are presented in Table S1 and Table 1. The Cr concentrations in these sediments range from 54 ppm to 485 ppm and the $\delta^{53}\text{Cr}$ values range from $-0.19 \pm 0.05\text{‰}$ to $0.28 \pm 0.05\text{‰}$. The sample XQH1 from upstream near the electroplate factory has the second-highest Cr concentration (345 ppm) and the most positive $\delta^{53}\text{Cr}$ value ($0.28 \pm 0.05\text{‰}$), while the Cr concentration (78 ppm) in sample XQH2 which is just 1.2 km downstream from the sampling location of XQH1 is considerably lower and the $\delta^{53}\text{Cr}$ value is $0.00 \pm 0.05\text{‰}$ (Figs. 2 and 3). The Cr concentration in sample XQH3 is the highest (485 ppm) but its $\delta^{53}\text{Cr}$ value is only $0.03 \pm 0.05\text{‰}$. The $\delta^{53}\text{Cr}$ values of the sediments in the estuary and Laizhou Bay are the lowest, around the average value of igneous reservoirs ($-0.12 \pm 0.10\text{‰}$, 2SD) (Fig. 2) (Schoenberg et al., 2008; Xia et al., 2017), and the sediments from the midstream have intermediate $\delta^{53}\text{Cr}$ values. The trend of Cr concentrations from midstream to estuary is similar to that of $\delta^{53}\text{Cr}$ values except for sample XQH10. The sample XQH10 comes from a tributary of the Xiaoqing River, and its $\delta^{53}\text{Cr}$ value is higher than those of the samples from the midstream. The $\delta^{53}\text{Cr}$ values of sediment core samples from Laizhou Bay show little variation with depth, all falling within the range of igneous reservoirs.

3.2. Leaching experiment results

Chromium in Step 1 and Step 2 contributes a very small proportion to the total Cr in the samples, which is 0.3–1.1% and 0.4–2.8%, respectively (Table 2). Most Cr resides in Step 3 and the residue, which accounts for 5.0–70.7% and 25.3–111.7%, respectively. The total yield is 97.0–117.4%. The Cr isotopic compositions of Step 2 of all 8 samples are more positive than the whole rocks, ranging from $0.28 \pm 0.05\text{‰}$ to $1.02 \pm 0.03\text{‰}$, and there is a decreasing trend from upstream to estuary (Fig. 4). The $\delta^{53}\text{Cr}_{\text{Step 3}}$ values of sample XQH1, XQH2, and XQH10 ($0.418 \pm 0.03\text{‰}$, $0.293 \pm 0.03\text{‰}$, and $0.278 \pm 0.03\text{‰}$, respectively) are obviously

more positive than the respective $\delta^{53}\text{Cr}_{\text{bulk}}$ values (Fig. 4). The $\delta^{53}\text{Cr}_{\text{residue}}$ values of all 5 selected samples are more negative than the whole rocks, which lie in the range of igneous reservoirs (Fig. 4).

4. Discussion

4.1. The variations of authigenic Cr isotopic composition

In order to understand the influence of riverine transport on Cr isotopic variations, $\delta^{53}\text{Cr}$ values were plotted as a function of distance from the first sample location near the pollution source area along the main channel (Fig. 3A). The $\delta^{53}\text{Cr}$ value of sample XQH1 is much more positive than other samples, and $\delta^{53}\text{Cr}$ values decrease with the distance (Fig. 3A). The geological maps (Digital library of National Geological Archives of China; <http://ngac.org.cn/Document/Map.aspx?MapId=EC7E1A7A7A061954E0430100007F182E>) show that most of the overlying rocks in the catchment of the Xiaoqing River are Quaternary clay and sandstone, ruling out the possibility of the influence from serpentinized ultramafic rocks, which are significantly isotopically heavier than major igneous reservoirs (Farkaš et al., 2013; Wang et al., 2016). In addition, the Cr concentration and $\delta^{53}\text{Cr}$ value of sample XQH2 which is just 1.2 km away from sample XQH1 are both low, further excluding the influence from catchment conditions.

Chromium in the river sediments has various sources, including anthropogenic discharge, oxidative chemical weathering and detritus. The detritus portion, which is depleted in ^{53}Cr relative to authigenic Cr (including the anthropogenic discharge and oxidative chemical weathering here), will suppress the signal from authigenic Cr. Thus, it is necessary to correct the Cr isotopic compositions of the contribution from the detritus. To date, there are two independent approaches to make such corrections. One method is using a detritus correction index (e.g. Reinhard et al., 2014; Wang et al., 2016). The other method uses the reagents to step-wise leach out the Cr associated with particular phases. The BCR three-step sequential extraction procedure is widely used on soils and sediments to assess the bioavailable metal fraction and the mobility of trace metals. In this study, both methods were used and the results using the two different methods are compared below.

4.1.1. The authigenic Cr isotopic compositions ($\delta^{53}\text{Cr}_{\text{auth-I}}$) calculated using the detrital index

Titanium is relatively resistant to chemical weathering so that Ti in sediments is mostly from the detritus (Konhauser et al., 2011).

Table 1
Cr isotopic compositions for surface sediments and the sedimentary core samples from the Xiaoqing River and Laizhou Bay.

Sample	Distance (km)	Cr (ppm)	Ti ($\times 10^3$ ppm)	Cr/Ti	$\delta^{53}\text{Cr}$ (‰)	N	$\delta^{53}\text{Cr}_{\text{auth-I}}$ (‰)
XQH1	0	345	2.2	0.16	0.28 ± 0.05	1	0.35 ± 0.06
XQH2	1	78	1.4	0.06	0.00 ± 0.05	1	0.09 ± 0.12
XQH3	20	485	3.5	0.14	0.03 ± 0.05	1	0.06 ± 0.06
XQH5	54	198	2.4	0.08	-0.04 ± 0.05	1	0.00 ± 0.08
XQH6	75	171	2.3	0.07	-0.02 ± 0.05	1	0.02 ± 0.09
XQH7	95	135	2.2	0.06	-0.05 ± 0.05	1	0.00 ± 0.11
XQH15	157	137	2.3	0.06	-0.13 ± 0.05	1	-0.13 ± 0.11
XQH17	173	79	2.2	0.04	-0.09 ± 0.05	1	-0.02 ± 0.27
XQH18	184	107	2.4	0.04	-0.10 ± 0.05	1	-0.07 ± 0.17
LZW30	200	54	2.1	0.03	-0.10 ± 0.05	1	0.16 ± 1.50
XQH10	tributary	68	1.1	0.06	0.10 ± 0.05	1	0.23 ± 0.11
LZW25	Laizhou Bay	56	2.1	0.03	-0.07 ± 0.05	1	0.45 ± 1.28
LZWcore-9		73	3.2	0.02	-0.14 ± 0.05	1	
LZWcore-17		67	2.8	0.02	-0.19 ± 0.05	1	
LZWcore-25		58	2.4	0.02	-0.11 ± 0.05	1	
LZWcore-33		72	3.2	0.02	-0.13 ± 0.05	1	
LZWcore-126		58	2.8	0.02	-0.18 ± 0.05	1	

Fig. 2. $\delta^{53}\text{Cr}$ values of surface sediment samples from the Xiaoqing River and Laizhou Bay (orange diamonds) and sediment core samples from Laizhou Bay (blue diamonds). Sample XQH10 is from a tributary of the Xiaoqing River and sample LZW30 is from the estuary. The grey band represents the value range of igneous reservoirs (Schoenberg et al., 2008; Xia et al., 2017) and the dashed line represents the median of the range. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 3. $\delta^{53}\text{Cr}$ (A) and $\delta^{53}\text{Cr}_{\text{auth-I}}$ (B) values for surface sediments from the Xiaoqing River as a function of distance from the first sample location near the pollution source area along the main channel. The grey band represents the value range of igneous reservoirs (Schoenberg et al., 2008; Xia et al., 2017) and the dashed line represents the median of the range.

Therefore, Ti concentration in the sediments can serve as an index of the detrital contribution in order to estimate the concentration of detrital Cr, which is then used to calculate the authigenic Cr isotopic

composition ($\delta^{53}\text{Cr}_{\text{auth-I}}$). Titanium has a close correlation with Al and Th, which are also identified as indexes of the detrital contribution (Fig. S1). The correction for detrital Cr is made using the

Table 2
Cr isotopic compositions of four Cr forms for the selected samples from the Xiaoqing River and Laizhou Bay.

Sample	Step 1 (%)	Step 2 (%)	$\delta^{53}\text{Cr}_{\text{Step 2}} (\text{‰})$	N	Step 3 (%)	$\delta^{53}\text{Cr}_{\text{Step 3}} (\text{‰})$	N	Residue (%)	$\delta^{53}\text{Cr}_{\text{Residue}} (\text{‰})$	N	Yield (%)	$\delta^{53}\text{Cr}_{\text{auth-II}} (\text{‰})$
XQH1	0.5	0.6	1.02 ± 0.03	2	70.6	0.42 ± 0.03	2	25.3	-0.04 ± 0.03	2	97.0	0.42 ± 0.03
XQH2	0.8	1.1	0.78 ± 0.03	2	37.6	0.29 ± 0.03	2	75.7	-0.17 ± 0.03	2	115.2	0.31 ± 0.03
XQH3	0.5	1.0	0.78 ± 0.03	2	70.7	0.07 ± 0.03	2	35.0	-0.12 ± 0.03	2	107.3	0.08 ± 0.03
XQH6	1.0	2.8	0.48 ± 0.03	2	64.4	-0.01 ± 0.03	2	47.4			115.6	0.01 ± 0.03
XQH10	0.5	0.7	0.51 ± 0.03	2	53.5	0.28 ± 0.03	2	53.6	-0.06 ± 0.03	2	108.4	0.28 ± 0.03
XQH15	0.7	1.6	0.51 ± 0.03	2	45.9	-0.22 ± 0.03	2	50.3			98.5	-0.19 ± 0.03
LZW30	1.1	2.5	0.28 ± 0.05	3	23.7	-0.12 ± 0.03	2	94.8	-0.12 ± 0.03	2	122.0	-0.09 ± 0.03
LZWcore-33	0.3	0.4	0.38 ± 0.03	2	5.0	-0.21 ± 0.03	2	111.7			117.4	-0.16 ± 0.03

Fig. 4. The Cr isotopic compositions of different Cr forms in the sediments. The grey band represents the value range of igneous reservoirs (Schoenberg et al., 2008; Xia et al., 2017).

following formula described by Reinhard et al. (2014):

$$[\text{Cr}]_{\text{auth-I}} = [\text{Cr}]_{\text{total}} - ([\text{Ti}]_{\text{total}} \times [\text{Cr}/\text{Ti}]_{\text{UCC}}), \quad (2)$$

$$\delta^{53}\text{Cr}_{\text{auth-I}} = \left(\delta^{53}\text{Cr}_{\text{bulk}} - \left[(1 - f_{\text{auth-I}}) \times \delta^{53}\text{Cr}_{\text{det}} \right] \right) \times f_{\text{auth-I}} \quad (3)$$

where $[\text{Cr}]_{\text{auth-I}}$ is the authigenic Cr concentrations, $[\text{Cr}]_{\text{total}}$ and $[\text{Ti}]_{\text{total}}$ are the measured whole-rock Cr and Ti concentrations, respectively, and $[\text{Cr}/\text{Ti}]_{\text{UCC}}$ is the Cr/Ti ratio of the upper continental crust (0.024; Rudnick and Gao, 2003). $\delta^{53}\text{Cr}_{\text{bulk}}$ is the bulk Cr isotopic composition that we measured, $\delta^{53}\text{Cr}_{\text{det}}$ represents the mean Cr isotopic composition of the detrital component which is -0.12‰ (Schoenberg et al., 2008), and $f_{\text{auth-I}}$ denotes the authigenic fraction of Cr ($f_{\text{auth-I}} = [\text{Cr}]_{\text{auth-I}}/[\text{Cr}]_{\text{total}}$). The uncertainties ($2\text{SD}_{\text{auth-I}}$) of $\delta^{53}\text{Cr}_{\text{auth-I}}$ is propagated error according to Eqs. (2) and (3). The detrital contributions to the Cr in the four samples (XQH15, XQH17, XQH18, and LZW30) from the downstream and estuary are

too high, leading to significant corrections and large uncertainties in $\delta^{53}\text{Cr}_{\text{auth-I}}$ for these samples relative to other samples (Fig. 3B). The corrected isotopic compositions showed that $\delta^{53}\text{Cr}_{\text{auth-I}}$ of the sample (XQH1) near the pollution source is the most positive, and $\delta^{53}\text{Cr}_{\text{auth-I}}$ values decrease in the midstream portion of the river to values between $0.00 \pm 0.08\text{‰}$ to $0.02 \pm 0.09\text{‰}$ (Fig. 3B).

4.1.2. The authigenic Cr isotopic compositions ($\delta^{53}\text{Cr}_{\text{auth-II}}$) calculated using the BCR leaching procedure

The modified BCR extraction procedure is operationally defined and the reagent used at each step is intended to release metals associated with particular phases. The nominal target phases are soil solutions, carbonates, and exchangeable metals in Step 1, Fe/Mn oxides/oxyhydroxides in Step 2, organic matter and sulfides in Step 3, and the residual (Žemberyová et al., 2006). Chromium in Step 1, 2, and 3 are considered as the authigenic Cr. The fraction of the Step 1 is very small and it is difficult to perform Cr isotope analysis. Excluding this fraction does not affect the results. Thus, the $\delta^{53}\text{Cr}_{\text{auth-II}}$ value is the weighted average of $\delta^{53}\text{Cr}_{\text{Step 2}}$ and $\delta^{53}\text{Cr}_{\text{Step 3}}$

3. Since the fraction of Step 2 is relatively small, the $\delta^{53}\text{Cr}_{\text{auth-II}}$ value is close to the $\delta^{53}\text{Cr}_{\text{Step 3}}$ values (Fig. 4). There is a similar tendency for the authigenic Cr isotopic compositions obtained using the two different approaches (Figs. 3 and 4).

4.2. The different sources of Cr identified from Cr isotopic signature

The authigenic Cr in the sediments comes not only from the anthropogenic discharge but also from oxidative chemical weathering processes. Previous studies of weathering profiles showed that the heavy Cr isotopes are depleted in the weathering residues (Berger and Frei, 2014; Frei et al., 2014). Frei et al. (2014) found that there is limited Cr isotopic variation in the water samples from the Paraná River at NW Argentina. Compared to that site, the drainage basin of the Xiaoqing River is much smaller, and the overlying rocks in the catchment should be simpler. Thus, the Cr in the river water from oxidative chemical weathering processes in the area should have homogeneous isotopic composition. Although the variation of dissolved $\delta^{53}\text{Cr}$ from the Connecticut River estuary was larger than 1‰, possibly as a result of Cr release from particles to solution during the transition from brackish to salt water, the particulate $\delta^{53}\text{Cr}$ remained stable at about 0.1‰ (Sun et al., 2019). The suspended $\delta^{53}\text{Cr}$ of the whole Connecticut River also varied little (Wu et al., 2017), indicating that the $\delta^{53}\text{Cr}$ values of sediments which have more detritus portion than particulate should also be homogeneous when there is no anthropogenic discharge. The authigenic Cr in the sediments mainly comes from the reduction of Cr(VI) in river water, and the organic matters are common electron donors and can reduce Cr(VI) effectively (e.g. Kitchen et al., 2012; Šillero et al., 2014). The plots of $\delta^{53}\text{Cr}_{\text{auth-I}}$ versus TOC (Fig. 5B) show that Cr isotopic compositions do not vary with TOC except for samples XQH1 and XQH10, which may be influenced by anthropogenic discharge. The $\delta^{53}\text{Cr}_{\text{auth-II}}$ values of sample XQH1 and XQH10 are $0.42 \pm 0.03\text{‰}$ and $0.31 \pm 0.03\text{‰}$, which are similar to the $\delta^{53}\text{Cr}_{\text{auth-I}}$ values ($0.35 \pm 0.06\text{‰}$ and $0.23 \pm 0.11\text{‰}$, respectively). However, for XQH2, the $\delta^{53}\text{Cr}_{\text{auth-II}}$ value ($0.31 \pm 0.03\text{‰}$) is more positive than the $\delta^{53}\text{Cr}_{\text{auth-I}}$ value ($0.09 \pm 0.12\text{‰}$) (Fig. 5C). The lower concentration of Cr_{auth-I} leads to the imprecise determination of authigenic Cr isotopic composition using Cr/Ti index. Thus, our Cr isotopic result showed that the sampling site of XQH2 still suffers from anthropogenic discharge, but the Cr concentration from pollution is low.

The Cr concentration for sample XQH3 is even higher than sample XQH1 while the Ti concentration for XQH3 is also higher than other samples, leading to slightly lower Cr/Ti than that of XQH1 (Fig. 5A). Both samples have high Cr/Ti, however, the $\delta^{53}\text{Cr}$ values are quite different, indicating the addition of reduction product of Cr(VI) from anthropogenic discharge to XQH1, resulting in the positive $\delta^{53}\text{Cr}$ value in XQH1. The high Cr/Ti and low $\delta^{53}\text{Cr}$ value in XQH3 may result from oxidative chemical weathering products which have relatively low $\delta^{53}\text{Cr}$ values. Similarly, we suggest that the Cr isotopic compositions of midstream and downstream samples are resulted from mixing between oxidative chemical weathering and detritus. For sample XQH10 from the tributary, the $\delta^{53}\text{Cr}_{\text{auth}}$ value is more positive than other samples from the midstream sites, indicative of the influence of anthropogenic discharge. This conclusion is supported by the existence of an industrial district in the vicinity of the sampling location of XQH10.

For the Fe–Mn-oxide-bound Cr, the Cr isotopic compositions are more positive than other leaching parts and there is a more obvious decreasing tendency from upstream to downstream (Fig. 4). Previous studies showed that the Cr isotopic compositions of marine ferromanganese oxides are negative than the seawater, probably because the Mn-oxides preferentially adsorb the lighter Cr isotopes (Wei et al., 2018), and there is no obvious Cr isotopic fractionation during Cr(VI) sorption on goethite at equilibrium (Ellis et al., 2004).

Fig. 5. TOC versus Cr/Ti (A), $\delta^{53}\text{Cr}_{\text{auth-I}}$ (B), and $\delta^{53}\text{Cr}_{\text{auth-II}}$ (C) for surface sediment samples from the Xiaoqing River. The TOC data are from He et al. (2018). The green circles refer the $\delta^{53}\text{Cr}_{\text{auth}}$ values for upstream and midstream samples and the orange diamonds refer the bulk $\delta^{53}\text{Cr}$ values for downstream samples which cannot be calculated due to the significant detrital contributions. The $2\text{SD}_{\text{auth-I}}$ (B) of downstream samples is large, thus we use $\delta^{53}\text{Cr}_{\text{bulk}}$ (orange diamonds) instead. The grey band represents the value range of igneous reservoirs (Schoenberg et al., 2008; Xia et al., 2017) and the dashed line represents the median of the range. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The Mn concentration in the extracting solution is much lower than the Fe concentration (Table S2), thus the Fe–Mn-oxide-bound Cr obtained in Step 2 is mainly from the Fe oxides. Therefore, $\delta^{53}\text{Cr}$ values of this fraction might more or less record the $\delta^{53}\text{Cr}$ values of the river water. The decreasing tendency suggests that this part of Cr should not solely come from the oxidative chemical weathering, because the $\delta^{53}\text{Cr}$ values of the river water without pollution have an increasing tendency from the upstream to the estuary (D'Arcy et al., 2016). More likely, it suggests a mixing between

anthropogenic discharge and natural weathering.

For the sedimentary core samples from Laizhou Bay, the $\delta^{53}\text{Cr}_{\text{bulk}}$ values are similar to the average value of igneous reservoirs indicating that Cr mainly comes from detritus. The residual Cr isotopic compositions of all 5 selected samples lie in the range of igneous reservoirs, further indicative of a detrital component. This also shows the effectiveness of the BCR leaching experiment. The Cr concentrations (58–73 ppm) for the samples from Laizhou Bay are lower than the primary sediment criteria (80 ppm) of Marine Sediment Quality (GB 18668–2002) issued by the China State Bureau of Quality and Technical Supervision (CSBTS, 2002). The low Cr concentrations and negative $\delta^{53}\text{Cr}$ values show that there is no obvious Cr pollution in Laizhou Bay, and the limited variation in the sediment core with depth is also indicative of no obvious Cr pollution in Laizhou Bay in the history. Overall, similar conclusions on the source of Cr can be drawn based on the authigenic Cr isotopic compositions calculated with the detrital index and using the BCR leaching protocol.

4.3. The quantification of in situ Cr(VI) reduction

Chromium isotopes can be used to evaluate the extent of Cr(VI) reduction in groundwater (e.g. Berna et al., 2010; Izbicki et al., 2008). Here, we use Cr isotopes to estimate the degree of Cr(VI) reduction on the basis of the Rayleigh fractionation model. It is generally believed that the Cr isotopic fractionation will follow the Rayleigh fractionation model if the Cr(VI) reduction takes place in a closed system, the Cr(VI) concentration is homogeneous in the solution, the reduction product Cr(III) is removed from the system immediately, and the kinetic fractionation factor remains constant. In a river system, we focus on the water mass with contamination. It is assumed that once the water mass flows away from the factories, no further Cr contamination is added to it. The reduction product Cr(III) will precipitate into the sediment or get adsorbed by particles immediately because of its low solubility. In addition, the kinetic fractionation factor is almost invariant due to the similar water environment along the Xiaoqing River. The Rayleigh fractionation model is expressed as

$$\delta^{53}\text{Cr} = \left[\left(\delta^{53}\text{Cr}_{\text{ini}} + 10^3 \right) f^{(\alpha-1)} \right] - 10^3, \quad (4)$$

where $\delta^{53}\text{Cr}_{\text{ini}}$ is the $\delta^{53}\text{Cr}$ value of the initial anthropogenic source, f is the fraction of remaining Cr(VI), and α is the fractionation factor ($\alpha = R_{\text{reactant}}/R_{\text{product}}$), which can be expressed in terms of the isotopic enrichment factor ε as:

$$\varepsilon = (\alpha - 1) \times 1000, \quad (5)$$

where ε is approximately the difference in $\delta^{53}\text{Cr}$ values between the reactant and the product.

$$\varepsilon \approx \delta^{53}\text{Cr}_{\text{rea}} - \delta^{53}\text{Cr}_{\text{pro}}. \quad (6)$$

According to previous work, the value of ε obtained in laboratory conditions ranges from 0.2‰ to 5‰, and most of the results are in the range of 2‰–4‰ (e.g. Chen et al., 2019b; Ellis et al., 2002; Berna et al., 2010; Jamieson-Hanes et al., 2012a; Jamieson-Hanes et al., 2012b; Qin and Wang, 2017; Zink et al., 2010). However, because of the reservoir effects in a natural system, a smaller “effective” enrichment factor, ε_{eff} should be applied (Berna et al., 2010; Clark and Johnson, 2008). The studies of river sediments are lacking but the Cr(VI) reduction experiments with the natural groundwater sediments had been conducted (Berna et al., 2010). As these two kinds of sediments have similar components, here we use the ε_{eff} value of 1.37‰ estimated from groundwater sediments

in Berna et al. (2010).

The calculated $\delta^{53}\text{Cr}_{\text{auth-I}}$ value for sample XQH1 is 0.35‰ and the $\delta^{53}\text{Cr}_{\text{auth-II}}$ value is 0.42‰. However, the Fe–Mn-oxide-bound Cr probably contains the absorbed Cr(VI), not only the reduced product, and the leaching experiment can give a more accurate value, thus the $\delta^{53}\text{Cr}_{\text{Step 3}}$ value (0.42‰) is used here to represent the instantaneous reduction product of the remaining Cr(VI) from the anthropogenic discharge at this site. We note that this value also includes the contribution from oxidative weathering. The mean value of $\delta^{53}\text{Cr}_{\text{auth-I}}$ for the three midstream samples (sample XQH5, XQH6, and XQH7) which represent the contribution from oxidative weathering is 0.01‰, very close to zero. The $\delta^{53}\text{Cr}_{\text{auth-II}}$ value for sample XQH6 is 0.01‰, consistent with the $\delta^{53}\text{Cr}_{\text{auth-I}}$ value. Because oxidative weathering is prevailing everywhere and we are interested in mainly the reduction of anthropogenic Cr, we neglect the contribution from oxidative weathering and estimate the lower limit on the reduction extent. According to Eq. (6), the lower limit of $\delta^{53}\text{Cr}$ value for the remaining Cr(VI) from the anthropogenic discharge in the river water at the sampling site of XQH1 is 1.79‰. The $\delta^{53}\text{Cr}$ values for the solution in the plating bath is between 0.20‰ and 0.83‰ (Berna et al., 2010; Ellis et al., 2002; Novak et al., 2017), and the chromating bath is also lying in this range (Novak et al., 2017). Thus, this range is used as the $\delta^{53}\text{Cr}$ values for the pollution source. Based on the Rayleigh fractionation model, we calculate that f is 31%–50%. Namely, during the transportation of Cr(VI) from the source to the site of XQH1, at least 31%–50% of Cr(VI) had been reduced to Cr(III). Using the same calculation method, at least 34%–55% of Cr(VI) at the site of XQH2 had been reduced to Cr(III). Similarly, the $\delta^{53}\text{Cr}_{\text{Step 3}}$ value of the tributary sample XQH10 is 0.28‰, and a reduction of 35%–55% of the Cr(VI) can be calculated at that sampling location.

5. Conclusions

The Cr isotopic compositions in the sediments facilitate the identification of different Cr sources in the Xiaoqing River. Based on the calculation of authigenic Cr isotopic compositions using the detrital index and leaching experiments, we found that the most positive $\delta^{53}\text{Cr}$ value near the pollution source of the Xiaoqing River was influenced by anthropogenic discharge of Cr(VI). Due to the self-purification of river water, this signal was not recorded in sediments from downstream sampling sites. Using a Rayleigh model for isotopic fractionation, we estimated that at least 31%–55% of Cr(VI) in the river water near the pollution source was reduced to Cr(III). Combining with Cr/Ti and TOC, we suggest that the slightly positive $\delta^{53}\text{Cr}$ values in the midstream mostly represent the signal from oxidative weathering, and the $\delta^{53}\text{Cr}$ values in the range of igneous reservoirs for the sediments near the estuary and in Laizhou Bay indicate that the Cr mainly comes from detritus. Similarly, the limited variation of $\delta^{53}\text{Cr}$ values for the sedimentary core samples in Laizhou Bay reveals no Cr pollution in history.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Xiaoqing He: Investigation, Methodology, Writing - original draft. **Guojun Chen:** Resources. **Ziyao Fang:** Formal analysis, Writing - review & editing. **Wenjian Liang:** Investigation. **Boda Li:** Investigation. **Jianhui Tang:** Resources, Writing - review & editing. **Yongge Sun:** Writing - review & editing. **Liping Qin:**

Conceptualization, Supervision, Writing - review & editing.

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Appendix A. Supplementary data

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