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Speciation and potential long-term behaviour of chromium in urban sediment particulates

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	suggest most Cr within the urban sediment cascade may be resistant to environmental processes that could mobilise other toxic metals.
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TRANSFER OF SEDIMENTS AND CONTAMINANTS IN CATCHMENTS AND RIVERS

Speciation and potential long-term behaviour of chromium in urban sediment particulates

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Abstract

Purpose: Chromium, a potentially harmful element, occurs commonly within the urban sediment cascade as a result of abundant industrial and transport-related sources. The risks that Cr-bearing particles pose to ecosystems and humans depend on the solid phase chemical speciation of Cr and its environmental mobility. In this study, we adopt an integrated geochemical approach to investigate and determine the long-term fate of Cr in the urban sediment cascade.

Materials and methods: We use bulk chemical digests, sequential chemical extraction analysis, electron microscopy, electron microprobe and microfocus XANES analysis to describe the solid-phase speciation, geochemical characteristics and potential long-term behaviour of Cr in urban particulate matter from both aquatic sediment and road dust sediment (RDS) in Manchester, UK.

Results and discussion: Cr-bearing grains within RDS and aquatic sediment are predominantly iron oxides and alumino-silicate glass grains. Electron microprobe analysis indicates Cr concentrations up to 3,300 µg g^{-1} and 133,400 µg g^{-1} in the RDS and aquatic grains, respectively. XANES analysis indicates that Cr(III) is the dominant oxidation state, with only trace amounts of Cr(VI). Importantly, Cr speciation does not appear to have changed between sedimentary environments and the dominance of Cr(III) suggests limited bioavailability or toxicity under predominant environmental (anoxic and neutral pH) conditions in the aquatic sediment sink. Furthermore, geochemical analyses suggest the environmental mobility of Cr in the aquatic sediment sink is low (compared to other toxic metals) due to its association mainly with alumino-silicate glass grains and its inclusion as an integral part of the glass structure.

Conclusions: Industrial glass grains are a major component of urban sediment worldwide. The speciation and geochemical investigations performed in this study suggest most Cr within the urban sediment cascade may be resistant to environmental processes that could mobilise other toxic metals.

Keywords Chromium • Cr(III) • Cr(VI) • Glass grain • Urban sediment • XANES

1. Introduction

Chromium (Cr) has long been known to be a potentially harmful element within the environment (Nriagu and Nieboer 1988). Humans and ecosystems can be exposed to Cr through natural and anthropogenic pathways in water and particulate (soil, sediment and aerosol) matter (Werner et al. 2007). However, the risks that Cr-bearing particles pose to ecosystems and humans depend on the solid phase chemical speciation and environmental mobility of Cr in the particles (Kotas and Stasicka 2000). In the environment, Cr exists primarily in two oxidation states – trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)]. Under anoxic conditions, cationic Cr(III) is typically the dominant form and is relatively stable and non-toxic at circum-neutral pH (6.5 – 8.5) due to the formation of insoluble hydroxide and oxide compounds and strong complexation with minerals and organic matter (Martello et al. 2007). Chromium(III) is an essential element for organisms and in small quantities is required for sugar and lipid metabolism (Anderson 1989; Broadway et al. 2010). Under oxic conditions, anionic Cr(VI) tends to dominate; it is soluble and can be mobile across the full pH range. There is clear evidence of the toxicological risk and carcinogenic properties of Cr(VI) in humans and aquatic ecosystems (Broadway et al. 2010; Ohgami et al. 2015; Stern 2010). As such, Cr is widely recognized as a potentially harmful element and listed as a contaminant of serious concern in environmental legislation worldwide.

Chromium occurs within urban environments around the globe as a result of abundant industrial and transport-related sources (Owens et al. 1999). Important sources are vehicle tyres and brake linings, steel production, combined sewer overflows (CSOs), municipal discharges, and industrial effluents including chromite ore processing residue (COPR) and tannery effluent. Chromium contamination of urban freshwater sediments, road dust sediment and air-borne particulate matter has been widely reported (Valerio et al. 1988; Yu et al. 2008) and speciation studies have generally observed Cr(III) to dominate (Broadway et al. 2010; Landrot et al. 2012; Martello et al. 2007; Swietlik et al. 2011; Werner et al. 2007). This information has proved useful for assessing the potential toxicity of Cr in urban particulate matter assuming stable environmental conditions. However, environmental change driven by the dynamic urban environment and / or climatic forces has the potential to affect the long-term environmental mobility and toxicity of Cr in these sediments (Butler 2009; Calmano et al. 1993; Knott et al. 2009). In order to understand the potential long-term behaviour of Cr in complex substances such as urban particulate matter, a synergistic and grain-specific approach is required that incorporates bulk and grain-specific chemical analysis and spectroscopic techniques such as scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and synchrotron-based X-ray absorption spectroscopy (XAS) techniques such as X-ray absorption near edge structure (XANES) (Barrett et al. 2010; Barrett et al. 2011; Berry and O'Neill 2004; Chen et al. 2010; Manceau et al. 2002; Wei et al. 2007; Xia et al. 1997). The major advantage of grain-specific analyses over bulk sediment analyses is that the major host species for contaminants can be identified and subjected to geochemical analyses to determine environmental mobility. A case in point are the metal-rich glass grains that are major constituents of both terrestrial (Lottermoser 2002) and freshwater (Taylor and Boult 2007) urban particulates as a consequence of furnace-derived slag from steel production. These are known to contain high concentrations of trace elements (Pb, Cu, Cr, Zn, Ni) and have been identified in urban particulate matter worldwide (Kida and Sakai 2001; Lind et al. 2001; Reich 2003; Saffarzadeh et al. 2009; Taylor and Robertson 2009). Following deposition in urban water bodies, the ultimate sink for contaminated urban particulates, these glass grains have been observed to undergo dissolution and early diagenetic reactions potentially releasing Cr to interstitial and overlying waters (Taylor and Boult 2007).

In this paper, we adopt an integrated speciation and geochemical approach to describe the solid-phase speciation and environmental mobility of Cr in urban particulate matter from the Greater Manchester urban conurbation, UK. To the authors knowledge, this is the first time such an integrated approach has been adopted to study toxic element cycling through urban sediment systems. The specific objectives of this study were to: (1) investigate the association of Cr with terrestrial and aquatic urban particulates; (2) confirm the speciation of Cr in these particulates; (3) investigate the potential long-term geochemical mobility of Cr associated with urban particulates. This innovative approach could provide a strong evidence base for assessing the long-term risk of Cr to human health and ecosystems in urban environments.

2. Materials and methods

2.1 Study area and sampling procedures

The contaminated sediment described in this study are from the urban conurbation of Manchester, UK. The RDS samples were obtained from locations within Manchester city centre that comprised heavily urbanised environments with high traffic densities (Fig. 1a). Samples were collected by sweeping with a polyethylene dustpan and brush. High metal (Fe, Mn, Pb, Zn, Cu) concentrations have been reported in these sediments and sequential extraction analysis has shown some metals (Fe, Mn, Zn) are largely associated with the reducible fraction, suggesting changes in ambient pH and / or Eh could mobilise these metals (Robertson et al. 2003). Trace metals (Pb, Cu, Zn, Cr, Ni) in the RDS material are hosted mainly in iron oxides and iron-rich glass grains (Taylor and Robertson 2009). Speciation studies using X-ray absorption spectroscopy (XAS) have identified both Pb (Barrett et al. 2010) and Zn (Barrett et al. 2011) to exist in phases that are potentially harmful to human health. The aquatic sediment was sampled from the Salford Quays (Fig. 1b), a historically contaminated urban water body that received domestic and industrial sewage and road runoff prior to commencement of remediation activities in the late 1980s. Urban water bodies represent major sinks for contaminated sediment in urban centres worldwide (Taylor and Owens 2009). Sediment cores were retrieved from Basin 9 of the Salford Quays in 2000 and 2001 using a stainless steel corer and contain a mix of natural and anthropogenic detrital grains, the latter dominated by alumino-silicate glass grains (Taylor and Boult 2007). Petrographic analysis indicated these glass grains were undergoing chemical dissolution supplying Fe and Zn to porewaters while bacterial Fe(III) and Mn(IV) reduction was hypothesized to supply Fe^{2+} and Mn^{2+} to porewaters. Whilst these previous studies (and others) have greatly increased our understanding of trace metal geochemistry in urban environments, they have tended to focus on elements (e.g. Fe, Mn, Zn, Pb, Cu) that represent, by mass, the bulk of metal contaminants found in urban environments. Here, we focus specifically on the trace metal Cr, an element which may display different geochemical and mobility characteristics to those more typically studied metals.

2.2 Elemental analysis of RDS and aquatic sediment

Petrographic and quantitative chemical data were obtained through the use of scanning electron microscopy and electron microprobe analysis. Air-dried samples of RDS and aquatic sediment were impregnated with epoxy resin and polished surface blocks were produced. The petrography of the samples was analysed with JEOL 5600LV (for RDS) and JEOL JXA 8100 (for aquatic sediment) electron microprobes using backscattered electron imagery. Wavelength dispersive spectrometers (WDS) were used to obtain quantitative data on major and trace element composition of mineral grains. Analysis of SiO_2, Al_2O_3, TiO_2, CaO, Na_2O, K_2O, Fe_2O_3, MnO, MgO, P_2O_5, SO_3 (all in wt. %) and Cr (in ppm) were undertaken in WDS mode using an accelerating voltage of 15 kV, current of 2.5 nA, electron beam diameter of 1 µm, and counting time of 10 s. The analyses were calibrated against standards of natural silicates, oxides and Specpure® metals with the data corrected using a ZAF program.

2.3 Molecular-scale analysis of RDS and aquatic sediment

XANES is sensitive to the oxidation state, continuation and bonding environment around a central atom of transition elements such as Cr, both in single and mixed complexes, for example, amorphous material, silicate glasses and particulate matter (Farges 2009; Pantelouris et al. 2004). XANES data were collected at station I18 at the Diamond Light Source, UK, in September 2010. XAS spectra were collected at the Cr K-edge (5989 eV). Operating conditions for the storage ring were 3 GeV and 200 mA. On I18, which is an undulator beamline, the X-rays are focused by a pair of Kirkpatrick-Baez (KB) mirrors after being monochromated by a Si (111) double-crystal monochromator. Experiments were performed at ambient temperature. Standard spectra were collected for model compounds [$Cr(OH)_3$, Cr foil, Cr(III), Cr(VI)], and these were analysed in transmission mode. The urban particulate samples were presented to the beam in resin-impregnated polished blocks. In these, the distribution of Cr in individual grains was mapped using µXRF and Cr XAS data were collected in fluorescence mode for qualitatively high-Cr areas (µXRF did not quantify the Cr concentrations). Data processing was carried out using *ATHENA* (to convert from monochromator position in millidegrees to energy in eV, and to average multiple spectra from individual standards and samples; Ravel and Newville (2005)) and *PySpline* (to carry out background subtraction and normalisation; Tenderholt et al. (2007)). The fluorescence signal is calculated as the total windowed fluorescence counts divided by I_o. The normalisation was done by fitting a 1st order polynomial to the pre-edge region and extrapolating this to the end of the spectrum, then subtracting. A 2nd order polynomial was fitted to the post-edge region and subtracted. The edge step was normalised to 1. No linear combination modelling was undertaken due to the uncertainties around the appropriate model compounds.

2.4 Geochemical analysis of alumino-silicate glass grains

Alumino-silicate glass grains were identified as a major constituent of terrestrial and aquatic sediments and were therefore subjected to further geochemical analysis to determine the environmental mobility of associated Cr. Glass grains were hand-picked from the aquatic sediment under a binocular microscope. Samples of sediment were washed in distilled water and the <63 µm fraction was sieved away leaving behind silt- and sand-sized fractions. The glass grains were generally coarse sand in size and were also dark and shiny, allowing easy separation. Pseudo-total Cr concentrations of the glass grains were determined by aqua-regia digestion in closed vessels using a microwave apparatus (MARS Xpress, CEM). A three-step sequential extraction procedure (SEP) recommended by the Standards, Measurements and Testing programme (SM&T) of the European Union (Rauret *et al*., 1999) was utilised to extract bioavailable Cr from the glass grains. The chemical procedure extracts metals bound to three specific geochemical phases: (1) acid-soluble, easily exchangeable and bound to carbonates; (2) reducible, bound to iron and manganese oxides; (3) oxidisable, bound to organic and sulphide compounds. The SM&T procedure is the only SEP with a certified reference material (CRM 701) (Quevauviller et al. 1997) for all three phases of extraction allowing validation of the procedure and comparison of results between studies. The SEP included two sample duplicates, one blank and the certified reference material. The Cr content in the residual fraction of the glass grains was estimated as the difference between pseudo-total content (microwave extraction) and the sum of the contents of the other fractions obtained by SEP. The supernatants produced after both extraction procedures were acidified to pH 2 and stored at 4ºC prior to analysis. All solutions were analysed within a month using Inductively Coupled Plasma (ICP) Optical Emission Spectroscopy (OES) (Perkin-Elmer Optima 2100DV). Detection limits of the ICP-OES were 0.05 ppm Cr. High precision (±10%) of the control standards is reported and calibration curves had a coefficient value better than 0.99. The relative standard deviation was less than 2% above 0.05 ppm Cr. Recovery rates for Cr in the CRM 701 were 95% for step 1, 91% for step 2, and 101% for step 3.

3. Results

3.1 Elemental analysis of RDS and aquatic sediment

Cr-bearing grains within RDS and aquatic sediments are characterized primarily by iron oxides and alumino-silicate glass grains derived from industrial waste. Aquatic sediment is dominated by glass grains comprising Fe-rich and Fe-poor varieties with inclusions of metal-rich blebs and dark crystalline areas. Electron microprobe analysis indicates the Fe-rich glasses have high concentrations of Cr (mean 347 µg g^{-1}), Fe (mean 38.5% FeO) and Al (mean 7.93% Al_2O_3) (Table 1). The Fe-poor glasses contain lower concentrations of Fe (mean 9.15% FeO), Cr (mean 226 µg g^{-1}) and other metals (Table 1). Dark glass inclusions in the Fe-rich glasses contain Cr-rich areas up to 133,360 µg g^{-1} (mean 69,800 µg g^{-1}). Cr-bearing grains within the RDS are predominantly iron oxide grains but Cr-bearing silicate glass grains are also present. Electron microprobe analysis indicates concentrations of Cr up to 3,300 µg g^{-1} (mean 425 µg g^{-1}) in these grains (Table 1). Examples of Cr-bearing grains in the RDS samples are shown in Fig. 2. WDS analysis of these grains shows them to be Fe oxides ((a), (b), (e) and (f)), a mixed Fe-Al-silicate and Fe-Mg-silicate (c) and an Fe-silicate (d) (Table 1). All grains except (d) are texturally and chemically heterogeneous.

3.2 Molecular scale analysis of RDS and aquatic sediments

The influence of oxidation state on the XANES spectra is revealed in differences in the shape and the position of the edge, as well as the presences of pre-edge and multi-scattering resonances (MSR). As illustrated by the four model compounds in Fig. 3, a shift in the edge position of the Cr *K*-edge XANES to higher energies is generally discerned with increasing oxidation state. Such a shift may be used as a qualitative indicator of the presence of Cr(III), Cr(VI) or mixtures of different Cr oxidation states. Table 3 summarizes the energy values of pre-edge resonances, shoulder, absorption edge, edge crest and multi-resonance structures in XANES spectra at Cr *K*-edge for model compounds and environmental samples.

Consideration of the environmental samples finds that the aquatic grain XANES spectra display similar profiles. The lack of an intense peak in the pre-edge region coupled with two small pre-edge resonances indicates that Cr in such samples is present mainly in the octahedrally coordinated trivalent form, and that the contribution of tetrahedrally coordinated Cr(VI) is estimated to be ≤5% (Huggins et al. 1999). Comparison of the pre-edge and edge position energies of the two aquatic samples spectra show comparability to the XANES spectra of the Cr(III) model compounds. In particular, the equivalence noted between the energies of the pre-edge resonance, edge crest and second MSR reported for Aquatic 1- 51028 and those of $Cr(OH)_3$ suggests that $Cr(OH)_3$ is likely to be a main contributor to the Cr speciation of this sample. Differences in the energies of the pre-edge resonance and the second MSR reported for Aquatic 2- 51029 may imply that Cr_2O_3 may also influence the Cr speciation of the Aquatic 2- 51029.

Qualitative analysis of the XANES spectra of the RDS grains identifies a greater degree of variance between the individual spectra of the RDS. The edge position energies for the RDS grains, with the exception of RDS3-51050, appear to conform with values reported for the Cr(III) model compounds (6001.74 eV; 6002.43eV) suggesting that Cr speciation is dominated by trivalent Cr species in the RDS samples. As with the aquatic samples, the presence of two low intensity pre-edge resonances identified in all the RDS samples, except RDS3-51050 and the absence of any sharp high intensity peak in the pre-edge region implies that Cr(VI) species play a secondary role to Cr(III) in the Cr speciation of RDS. Visual comparison of the five RDS spectra (Fig. 3) identifies strong similarities between RDS2-51044 and RDS5-51082 and to an extent RDS1-51407. Consideration of the pre-edge resonance, edge and MSR energies determined for RDS2-51044 and RDS5-51082 finds agreement with those reported for $Cr(OH)_3$ (Table 3). Although, RDS1-51407 spectra shows some comparability with that of $Cr(OH)_3$, similarities to the edge position and MSR energies reported for Cr_2O_3 suggest that a combination of the two model compounds may be influential in this sample. The occurrence of shoulder structures in the XANES spectra of samples RDS3-51050 and RDS4-51059 infer that mixed oxidation states may exist in such samples (Berry and O'Neill 2004). The XANES spectrum of RDS3-51050 with the presence of a shoulder structure around 5990 eV and edge crest and MSR energies of 6007 and 6022 eV respectively, displays characteristics of Cr in metallic and trivalent forms. By contrast, XANES spectrum of RDS3-51059, is characterized by the prominence of an absorption edge shoulder, which is likely to result from a 1*s*→4*s* transition indicative of Cr(III) being present and a MSR at approximately 6021 eV.

3.3 Geochemical analysis of alumino-silicate glass grains

Pseudo-total metal concentration results for glass grains in the aquatic sediment are summarized in Table 2. All of the metals investigated have very high concentrations and can be classified as grossly contaminated when compared to Environment Agency (of England) guidelines for bulk sediments. Iron exhibits the highest mean metal concentration of 119,700 µg g^{-1}. Chromium shows the lowest mean metal concentration of 260 µg g^{-1} which is similar to values reported for electron microprobe analysis. Sequential extraction analysis results for the glass grains are summarized in Table 2 and are represented as percentages associated with each geochemical phase in Fig. 4. Metals are primarily associated with the residual phase, although there is considerable variation between metals in the percentage found in chemically-defined form. Over 60% of Zn is found in bioavailable forms, whereas less than 20% of Cr is found in these fractions. In terms of bioavailable fractions, all of the metals are primarily associated with the reducible fraction. The next most common association for metals is the oxidisable fraction. Lead and Cr show only weak associations with the exchangeable phase. Zinc exhibits the greatest percentage in the exchangeable phase and is the most widely distributed metal between phases – exchangeable (12%), reducible (29%), oxidisable (24%), and residual (35%). In comparison, Cr shows the least distribution between phases – exchangeable (1%), reducible (7%), oxidisable (7%), and residual (85%).

4. Discussion

4.1 Speciation of chromium

Chromium is present in high concentrations in urban particulate matter in Manchester and generally well above what is considered safe by soil and sediment quality guidelines. XANES analysis of Cr speciation suggests the dominance of relatively stable and non-toxic Cr(III) in both of the major grain types under study, with some trace amounts of Cr(VI) also detected. One of the key sources of Cr-rich grains in the Salford Quays sediment is historically deposited slag. The findings of the present study that Cr exists in such material in the Cr(III) form, concurs with research carried out (Chaurand et al. 2007; Chaurand et al. 2006) on the Cr speciation of Basic Oxygen Furnace steel slag, using XANES spectroscopy; Cr in BOF material was found to be present mainly in the octahedrally coordinated trivalent form. The dominance of Cr(III) species in RDS samples, may reflect the usage of by-products from industrial processes, in which Cr predominantly as exists in the trivalent form, in road construction (Chaurand et al. 2006). Experimental XANES spectra for the present study show strong similarities with those reported by Huggins et al. (2000) and Werner et al. (2007) for chromite and Cr-Fe spinel, respectively, in ambient air particulate matter (AAPM). Potential sources of Cr-Fe spinel to RDS include combustion by-products of Cr-Fe containing fuel, road aggregate as well as a soil component (Werner et al. 2007). Given the significant contribution Cr^0, Cr_2O_3 and $Cr(OH)_3$ to the Cr speciation in urban $PM_{2.5}$ (Huggins et al. 2000; Werner et al. 2007), this suggests that RDS may be a potential and key source of Cr in AAPM. The dominance of Cr(III) in both the Manchester RDS and aquatic sediment suggests there might be limited biogeochemical weathering and opportunity for speciation change as the grains are transferred through the urban sediment cascade. However, it is impossible to confirm this hypothesis without undertaking similar analyses on sediment collected from pathways linking RDS and aquatic sinks.

Electron microbeam analysis of the particulate matter has found Cr to exist predominantly in Fe-rich and Fe-poor glass grains in aquatic sediment and in both Fe oxides and Fe-rich glass grains in RDS. This supports earlier work on

Manchester sediment (Taylor and Boult 2007; Taylor and Robertson 2009) and urban sediment worldwide (Kida and Sakai 2001; Lind et al. 2001; Reich 2003; Saffarzadeh et al. 2009) that suggests Fe-oxides, derived from vehicular wear and tear, and Fe-rich glass grains, derived from metal smelting and concrete, are major hosts for contaminant metals in urban particulates. Iron oxides and Fe(III) oxyhydroxides are known to be important Cr scavengers and Cr(III) can readily substitute for Fe(III) in metal oxides (Frommer et al. 2009). Cr(III) can also co-precipitate with goethite (FeOOH) to form an (Fe,Cr)OOH phase, due to structural similarities between the host Fe(III) mineral and the pure Cr surface precipitate phase (CrOOH) (Charlet and Manceau 1992; Hansel et al. 2003). Cr(III) has also been found to dominate in hematite (Fe_2O_3)-bearing red mud from the Ajka (Hungary) tailings dam spill (Burke et al. 2012).

4.2 Control of Eh and pH on the long-term environmental mobility of chromium

Oxyanion-forming elements such as Cr have strong pH- and redox-dependent sorption behaviour. In anoxic conditions (e.g. in Salford Quays sediment), Cr(III) may be relatively stable as $Cr(OH)_3$ or adsorbed to Fe oxides and glass grains. Phosphorus has been reported to scavenge trace metals (Zn, Cu, Pb) in the Salford Quays by incorporating them into the mineral precipitate vivianite ($Fe^{3+}(PO_4)_2 \cdot 8H_20$) (Taylor and Boult 2007), although Cr was not considered in this previous study. Minor sulphate reduction has also been found in the Salford Quays which has been shown to be immobilizing Cu as an insoluble sulphide (Taylor and Boult 2007). However, Cr is not a divalent metal and will therefore not form an insoluble metal sulphide under reducing conditions. Chromium(III) solubility in anoxic sediments is further limited by complexation with solid-phase organic ligands which also facilitate the rapid reduction of Cr(VI) to Cr(III) (James 2002). The Salford Quays sediment is known to be rich in organic matter (up to 10% TOC in the upper, metal-rich layers) (Taylor and Boult 2007).

Several studies have noted the oxidation of Cr(III) to Cr(VI) by Mn oxides in anoxic conditions (Apte et al. 2006; Fendorf and Zasoski 1992; Kazakis et al. 2015; Tang et al. 2014). This natural oxidation is primarily related to the presence of Mn(III,IV) hydroxides which are considered as direct oxidising agents. Extensive experiments on the oxidation capacity of Cr(III) have shown that the Mn(IV) phase oxidizes the highest amount of Cr(III) (Landrot et al. 2012). Manceau and Charlet (1992) and Landrot et al. (2012), observed that Cr(III) was tightly sorbed as an inner-sphere complex to Mn(IV) in Cr(III)-reacted MnO_2 analysed by EXAFS. Manganese hydroxides were not found to be a major constituent of the urban particulate matter in the Salford Quays sediment (mean 0.75% MnO in Fe-rich glasses; mean 0.37% MnO in RDS). However, these relatively low quantities of Mn can still make a significant difference to sorption behaviour (Jenne 1968) and the oxidation of Cr(III) to Cr(VI) by Mn oxides cannot be ruled out in urban aquatic sediment sinks.

Oxic conditions are not usual in sedimentary basins such as the Salford Quays due to limited water column mixing and high organic matter loading that maintains a high sediment oxygen demand. However, oxidation of canal, reservoir and harbour sediments can occur in response to dredging, flooding and bioturbation, leading to the phase transfer of some metals to more bioavailable species (Calmano et al. 1993; Zoumis et al. 2001). In the Salford Quays, Helixor pumps have been employed to oxygenate water in an effort to improve water quality and promote immobilization of cationic metals as hydroxides. Chromium(III) is still thermodynamically favourable even under mildly oxidising conditions (Martello et al. 2007), but it is possible that the introduction of oxygen into the water column may promote oxidation of surface sediments leading to the oxidation of Cr(III) to Cr(VI). This could only occur, however, at Eh greater than 0.7 volts (Takeno 2005). Enhanced Cr(VI) production has been reported previously in surface sediments of seasonally anoxic lakes (Achterberg and van den Berg 1997). However, in field experiments, Bloomfield and Pruden (1980) found both oxic and anoxic soil conditions increased the reduction of Cr(VI). Importantly, these experiments considered a typical soil pH of between 4 and 7, with Cr(VI) reduction being most efficient at pH <5. While Eh is an important control on Cr speciation and mobility in sediment systems, Cr(VI) can only exist in both an oxic and high pH environment.

The most favourable environment for the formation of Cr(VI) species is Eh >0.5 volts and pH >8 (Takeno 2005). The typical pH range for Salford Quays sediment is 6.6 – 7.6, and although Eh has not been measured, predominant anoxic conditions are inferred from the pore water chemistry (Taylor and Boult 2007). Therefore, future large-scale oxidation of Cr(III) to Cr(VI) is unlikely to occur in the Salford Quays sediment. However, this may not be the case in other Cr-contaminated urban water bodies and careful investigation of the environmental processes that might drive Cr transformation is needed in order to comprehensively evaluate environmental risk. The formation of soluble Cr(III) species due to the dissolution of Cr(III) minerals and adsorbed species is the most likely mechanism by which Cr may mobilise from the sediments. The solubility of chromium hydroxide [$Cr(OH)_3$] is low between pH 6 and 12 and under reducing and mildly oxic conditions (Takeno 2005). As long as anoxic conditions remain, Cr-bearing Fe oxides may also exist as insoluble sulphide minerals or, more likely, incorporated into the phosphate mineral vivianite. However, most Cr in the aquatic sediment was found to be associated with glass grains. Furnace-derived glasses in contaminated soils and sediments are known to be prone to chemical dissolution at sub-neutral pH due to organic acid generation as part of early sediment diagenesis (Lottermoser 2002; Parsons et al. 2001). Taylor and Boult (2007) found evidence from petrographic observations of chemical dissolution occurring in Fe-rich glass grains and associated contaminant metal (Zn) release. However, Cr concentrations in pore waters were not measured so it remains unknown as to whether chemical dissolution may affect the cycling of Cr in urban aquatic sediment sinks. Evidence from the chemical extractions performed in the present study suggests Cr(III) has limited mobility and is not easily leached compared to other trace and toxic metals. However, the timeframe of exposure to low pH may be an important factor. Aqueous Cr species (e.g. Cr^{2+}, Cr^{3+}) can generally only exist at pH below 4 and while such low pH levels can occur in acidic soils, they are rarely encountered in sediments. Therefore, the release of organic acids during early diagenetic organic matter oxidation may not impact upon glass solubility and Cr mobility. However, it must be acknowledged that the presence of glass slag phases as major hosts of Cr is not reflected in grain-specific sequential chemical extraction methodologies (including BCR).

5. Conclusions

This study has provided important speciation and geochemical information that may have consequences for the long-term cycling of Cr in urban environments.

Chromium has been found to exist primarily in two major grain types in urban particulate matter from the major urban conurbation of Manchester, UK. Chromium is mainly associated with Fe oxides and industrial glass grains in urban aquatic sediment. XANES analysis suggests this Cr exists primarily as the relatively non-toxic Cr(III) species. The predominant anoxic and neutral pH of the Salford Quays sediments suggests that this Cr(III) may be stable as long as these environmental conditions are maintained. While oxidation of the sediments may occur under a variety of scenarios, it is unlikely that sediment pH can be maintained at a high enough level, in conjunction with oxic conditions, to mobilise Cr(III) as more soluble and toxic Cr(VI). Of course, this may not be the case in other urban aquatic sediment sinks that exhibit different environmental conditions to the Salford Quays. Aside from the issue of speciation, geochemical analyses have shown that most Cr is incorporated within the crystalline structure of industrial glass grains in the aquatic sediment and therefore exhibits limited environmental mobility in comparison to other trace metals. These glass grains may be prone to chemical dissolution at low pH; however, it is unlikely that sediment pH can reach a low enough level to mobilise aqueous Cr species. Industrial glass grains are a major component of urban sediment worldwide suggesting most Cr within the urban sediment cascade may be resistant to environmental processes that could mobilise more bioavailable forms. Future research should, through experiments and geochemical modelling, address this potential mobility under a variety of environmental scenarios. These data would facilitate the development of environmental risk models for Cr mobility and cycling in urban environments.

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References

Achterberg EP, van den Berg CMG (1997) Chemical speciation of chromium and nickel in the western Mediterranean Deep-Sea Res Pt Ii 44:693-720. doi: 10.1016/S0967-0645(96)00086-0

Anderson RA (1989) Essentiality of Chromium in Humans. Sci Total Environ 86:75-81. Doi 10.1016/0048-9697(89)90196-4

Apte AD, Tare V, Bose P (2006) Extent of oxidation of Cr(III) to Cr(VI) under various conditions pertaining to natural environment. J Hazard Mater 128:164-174 doi:10.1016/j.jhazmat.2005.07.057

Barrett JES, Taylor KG, Hudson-Edwards KA, Charnock JM (2010) Solid-Phase Speciation of Pb in Urban Road Dust Sediment: A XANES and EXAFS Study. Environ Sci Technol 44:2940-2946 doi:10.1021/es903737k

Barrett JES, Taylor KG, Hudson-Edwards KA, Charnock JM (2011) Solid-phase speciation of Zn in road dust sediment. Mineral Mag 75:2611-2629 doi:10.1180/minmag.2011.075.5.2611

Berry AJ, O'Neill HSC (2004) A XANES determination of the oxidation state of chromium in silicate glasses. Am Mineral 89:790-798

Bloomfield C, Pruden G (1980) The behaviour of Cr(VI) in soil under aerobic and anaerobic conditions. Environ Pollut Series A, Ecological and Biological 23:103-114

Broadway A et al (2010) Determination of the bioaccessibility of chromium in Glasgow soil and the implications for human health risk assessment. Sci Total Environ 409:267-277

Burke IT, Mayes WM, Peacock CL, Brown AP, Jarvis AP, Gruiz K (2012) Speciation of Arsenic, Chromium, and Vanadium in Red Mud Samples from the Ajka Spill Site, Hungary. Environ Sci Technol 46:3085-3092 doi:10.1021/es3003475

Butler BA (2009) Effect of pH, ionic strength, dissolved organic carbon, time, and particle size on metals release from mine drainage impacted streambed sediments. Water Res 43:1392-1402

Calmano W, Hong J, Forstner U (1993) Binding and mobilisation of heavy metals in contaminated sediments affected by pH and redox potential. Water Sci Technol 28:223-235

Charlet L, Manceau A (1992) Insitu Characterization of Heavy-Metal Surface-Reactions - the Chromium Case. Int J Environ an Ch 46:97-108 Doi 10.1080/03067319208027001

Chaurand P et al (2007) Environmental impacts of steel slag reused in road construction: A crystallographic and molecular (XANES) approach. J Hazard Mater 139:537-542 doi:10.1016/j.jhazmat.2006.02.060

Chaurand P, Rose J, Domas J, Bottero JY (2006) Speciation of Cr and V within BOF steel slag reused in road constructions. J Geochem Explor 88:10-14 doi:10.1016/j.gexplo.2005.08.006

Chen LX, Zhang XY, Lockard JV, Stickrath AB, Attenkofer K, Jennings G, Liu DJ (2010) Excited-state molecular structures captured by X-ray transient absorption spectroscopy: a decade and beyond. Acta Crystallogr A 66:240-251 doi:10.1107/S0108767309051496

Farges F (2009) Chromium speciation in oxide-type compounds: application to minerals, gems, aqueous solutions and silicate glasses. Phys Chem Miner 36:463-481 doi:10.1007/s00269-009-0293-3

Fendorf SE, Zasoski RJ (1992) Chromium(Iii) Oxidation by Delta-Mno2 .1. Characterization. Environ Sci Technol 26:79-85. doi 10.1021/es00025a006

Frommer J, Nachtegaal M, Czekaj I, Weng TC, Kretzschmar R (2009) X-ray Absorption and Emission Spectroscopy of Cr-III (Hydr)Oxides: Analysis of the K-Pre-Edge Region. J Phys Chem A 113:12171-12178. doi:10.1021/jp902604p

Hansel CM, Wielinga BW, Fendorf SR (2003) Structural and compositional evolution of Cr/Fe solids after indirect chromate reduction by dissimilatory iron-reducing bacteria. Geochimica Et Cosmochimica Acta 67:401-412. doi:Pii S0016-7037(00)01081-5. Doi 10.1016/S0016-7037(02)01081-5

Huggins FE, Najih M, Huffman GP (1999) Direct speciation of chromium in coal combustion by-products by X-ray absorption fine-structure spectroscopy. Fuel 78:233-242. Doi 10.1016/S0016-2361(98)00142-2

Huggins FE, Shah N, Huffman GP, Kolker A, Crowley S, Palmer CA, Finkelman RB (2000) Mode of occurrence of chromium in four US coals. Fuel Process Technol 63:79-92. Doi 10.1016/S0378-3820(99)00090-9

James BR (2002) Chemical transformation of chromium in soils relevance to mobility, bio-availability and remediation The Chromium File 8

Jenne EA (1968) Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. In: Baker RA (ed) Trace Inorganics in Water. Advances in Chemistry Series. American Chemical Society, Washington, pp 337-387

Kazakis N, Kantiranis N, Voudouris KS, Mitrakas M, Kaprara E, Pavlou A (2015) Geogenic Cr oxidation on the surface of mafic minerals and the hydrogeological conditions influencing hexavalent chromium concentrations in groundwater. Sci Total Environ 514:224-238. doi:10.1016/j.scitotenv.2015.01.080

Kida A, Sakai S (2001) Metallic-phase lead in slag of municipal solid waste incineration ash and leaching characteristics. Waste Manage 3:66-72

Knott NA, Aulbury JP, Brown TH, Johnston EL (2009) Contemporary ecological threats from historical pollution sources: impacts of large-scale resuspension of contaminated sediments on sessile invertebrate recruitment. J Appl Ecol 46:770-781

Kotas J, Stasicka Z (2000) Chromium occurrence in the environment and methods of its speciation. Environ Pollut 107:263-283 doi:Doi 10.1016/S0269-7491(99)00168-2

Landrot G, Tappero R, Webb SM, Sparks DL (2012) Arsenic and chromium speciation in an urban contaminated soil. Chemosphere 88:1196-1201 doi:10.1016/j.chemosphere.2012.03.069

Lind BB, Fallman AM, Larsson LB (2001) Environmental impact of ferrochrome slag in road construction. Waste Manage 21:255-264 doi:Doi 10.1016/S0956-053x(00)00098-2

Lottermoser B (2002) Exposure assessment of naturally metal enriched topsoils, Port Macquarie, Australia. Environ Geochem Health 24:183-190 doi:Doi 10.1023/A:1016056615002

Manceau A, Charlet L (1992) X-Ray Absorption Spectroscopic Study of the Sorption of Cr(Iii) at the Oxide Water Interface .1. Molecular Mechanism of Cr(Iii) Oxidation on Mn Oxides. J Colloid Interf Sci 148:425-442 doi:Doi 10.1016/0021-9797(92)90181-K

Manceau A, Marcus MA, Tamura N (2002) Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques. Rev Mineral Geochem 49:341-428 doi:DOI 10.2138/gsrmg.49.1.341

Martello L, Fuchsman P, Sorensen M, Magar V, Wenning RJ (2007) Chromium geochemistry and bioaccumulation in sediments from the Lower Hackensack River, New Jersey. Arc Environ Contam Toxicol 53:337-350 doi:10.1007/s00244-006-0164-6

Nriagu JO, Nieboer E (eds) (1988) Chromium in the natural and human environments. John Wiley, New York

Ohgami N, Yamanoshita O, Dinh Thang N, Nakano C, Wenting W, Ohnuma S, Kato M (2015) Carcinogenic risk of chromium, copper and arsenic in CCA-treated wood. Environ Pollut 206:456-460 doi:10.1016/j.envpol.2015.07.041

Owens PN, Walling DE, Leeks GJL (1999) Use of floodplain sediment cores to investigate recent historical changes in overbank sedimentation rates and sediment sources in the catchment of the River Ouse, Yorkshire, UK. Catena 36:21-47

Pantelouris A, Modrow H, Pantelouris M, Hormes J, Reinen D (2004) The influence of coordination geometry and valency on the K-edge absorption near edge spectra of selected chromium compounds. Chem Phys 300:13-22 doi:10.1016/j.jchemphys.2003.12.017

Parsons MB, Bird DK, Einaudi MT, Alpers CN (2001) Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California. Appl Geochem 16:1567-1593

Quevauviller P, Rauret G, LopezSanchez JF, Rubio R, Ure A, Muntau H (1997) Certification of trace metal extractable contents in a sediment reference material (CRM 601) following a three-step sequential extraction procedure. Sci Total Environ 205:223-234 doi:Doi 10.1016/S0048-9697(97)00205-2

Ravel B, Newville M (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. Journal of Synchrotron Radiation 12:537-541 doi:10.1107/S0909049505012719

Reich J (2003) Slag from hazardous waste incineration: Reduction of heavy metal leaching. Waste Manage Res 21:110-118

Robertson DJ, Taylor KG, Hoon SR (2003) Geochemical and mineral magnetic characterisation of urban sediment particulates, Manchester, UK. Appl Geochem 18:269-282 Doi 10.1016/S0883-2927(02)00125-7

Saffarzadeh A, Shimaoka T, Motomura Y, Watanabe K (2009) Characterization study of heavy metal-bearing phases in MSW slag. J Hazard Mater 164:829-834 doi:10.1016/j.jhazmat.2008.08.093

Stern AH (2010) A quantitative assessment of the carcinogenicity of hexavalent chromium by the oral route and its relevance to human exposure. Environ Res 110:798-807 doi:10.1016/j.envres.2010.08.002

Swietlik R, Molik A, Molenda M, Trojanowska M, Siwiec J (2011) Chromium(III/VI) speciation in urban aerosol. Atmos Environ 45:1364-1368 doi:10.1016/j.atmosenv.2010.12.001

Takeno N (2005) Atlas of Eh-pH diagrams. Intercomparison of thermodynamic databases. National Institute of Advanced Industrial Science and Technology

Tang YZ, Webb SM, Estes ER, Hansel CM (2014) Chromium(III) oxidation by biogenic manganese oxides with varying structural ripening. Environ Sci-Proc Imp 16:2127-2136 doi:10.1039/c4em00077c

Taylor KG, Boult S (2007) The role of grain dissolution and diagenetic mineral precipitation in the cycling of metals and phosphorus: A study of a contaminated urban freshwater sediment. Appl Geochem 22:1344-1358 doi:10.1016/j.apgeochem.2007.01.008

Taylor KG, Owens PN (2009) Sediments in urban river basins: a review of sediment-contaminant dynamics in an environmental system conditioned by human activities. J Soils Sediments 9:281-303 doi:10.1007/s11368-009-0103-z

Taylor KG, Robertson DJ (2009) Electron microbeam analysis of urban road-deposited sediment, Manchester, UK: Improved source discrimination and metal speciation assessment. Appl Geochem 24:1261-1269 doi:10.1016/j.apgeochem.2009.03.011

Tenderholt A, Hedman B, Hodgson KO (2007) PySpline: A modern, cross-platform program for the processing of raw averaged XAS edge and EXAFS data X-Ray Absorption Fine Structure-XAFS13 882:105-107

Valerio F, Brescianini C, Mazzucotelli A, Frache R (1988) Seasonal-Variation of Thallium, Lead, and Chromium Concentrations in Airborne Particulate Matter Collected in an Urban Area. Sci Total Environ 71:501-509 doi: 10.1016/0048-9697(88)90224-0

Wei M et al. (2007) Interaction between uranium and humic acid (I): Adsorption behaviors of U(VI) in soil humic acids. Nucl Sci Tech 18:287-293 doi: 10.1016/S1001-8042(07)60063-3

Werner ML, Nico PS, Marcus MA, Anastasio C (2007) Use of micro-XANES to speciate chromium in airborne fine particles in the Sacramento Valley. Environ Sci Technol 41:4919-4924 doi:10.1021/es070430q

Xia K, Mehadi A, Taylor RW, Bleam WF (1997) X-ray absorption and electron paramagnetic resonance studies of Cu(II) sorbed to silica: Surface-induced precipitation at low surface coverages. J Colloid Interf Sci 185:252-257 doi:DOI 10.1006/jcis.1996.4590

Yu XZ, Gu JD, Xing LQ (2008) Differences in uptake and translocation of hexavalent and trivalent chromium by two species of willows. Ecotoxicology 17:747-755 doi:10.1007/s10646-008-0224-y

Zoumis T, Schmidt A, Grigorova L, Calmano W (2001) Contaminants in sediments: remobilisation and demobilisation. Sci Total Environ 226:195-202

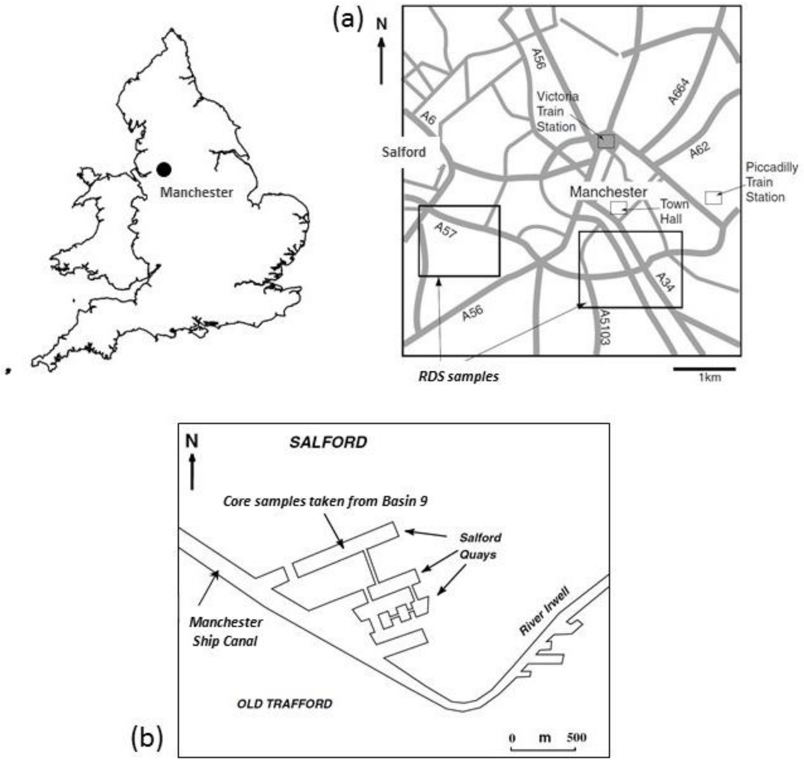

Figure 1. Location of Manchester showing (a) RDS sampling sites in Manchester city centre and (b) aquatic sediment sampling site in the Salford Quays.

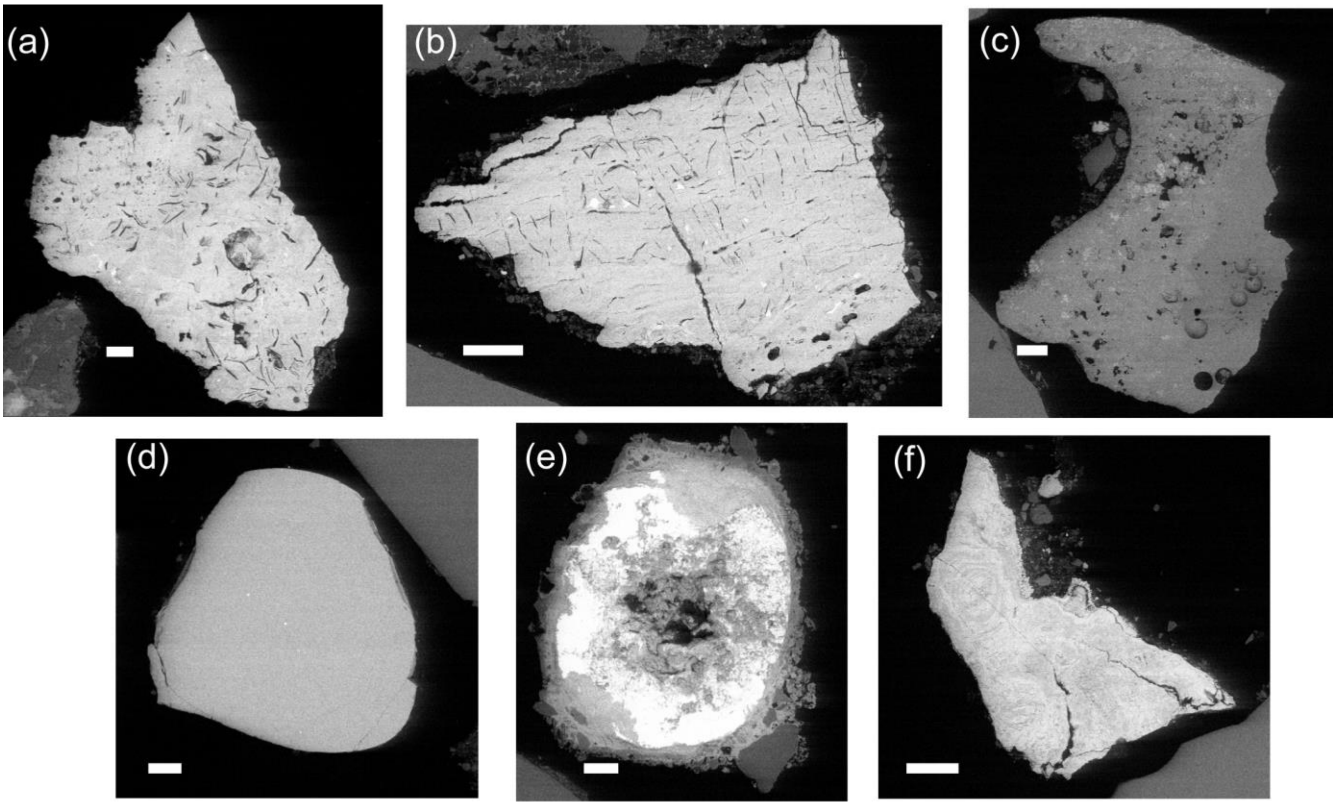

Figure 2. Scanning electron microscope photomicrographs of Cr-bearing grains from RDS sample. Scale bar in each photomicrograph is 100 μm. Grains (a), (b), (e) and (f) are Cr-bearing Fe oxides, grain (c) is a mixed Cr-bearing Fe-Al silicate and Cr-bearing Fe-Mg-silicate, and grain (d) is a Cr-bearing Fe silicate.

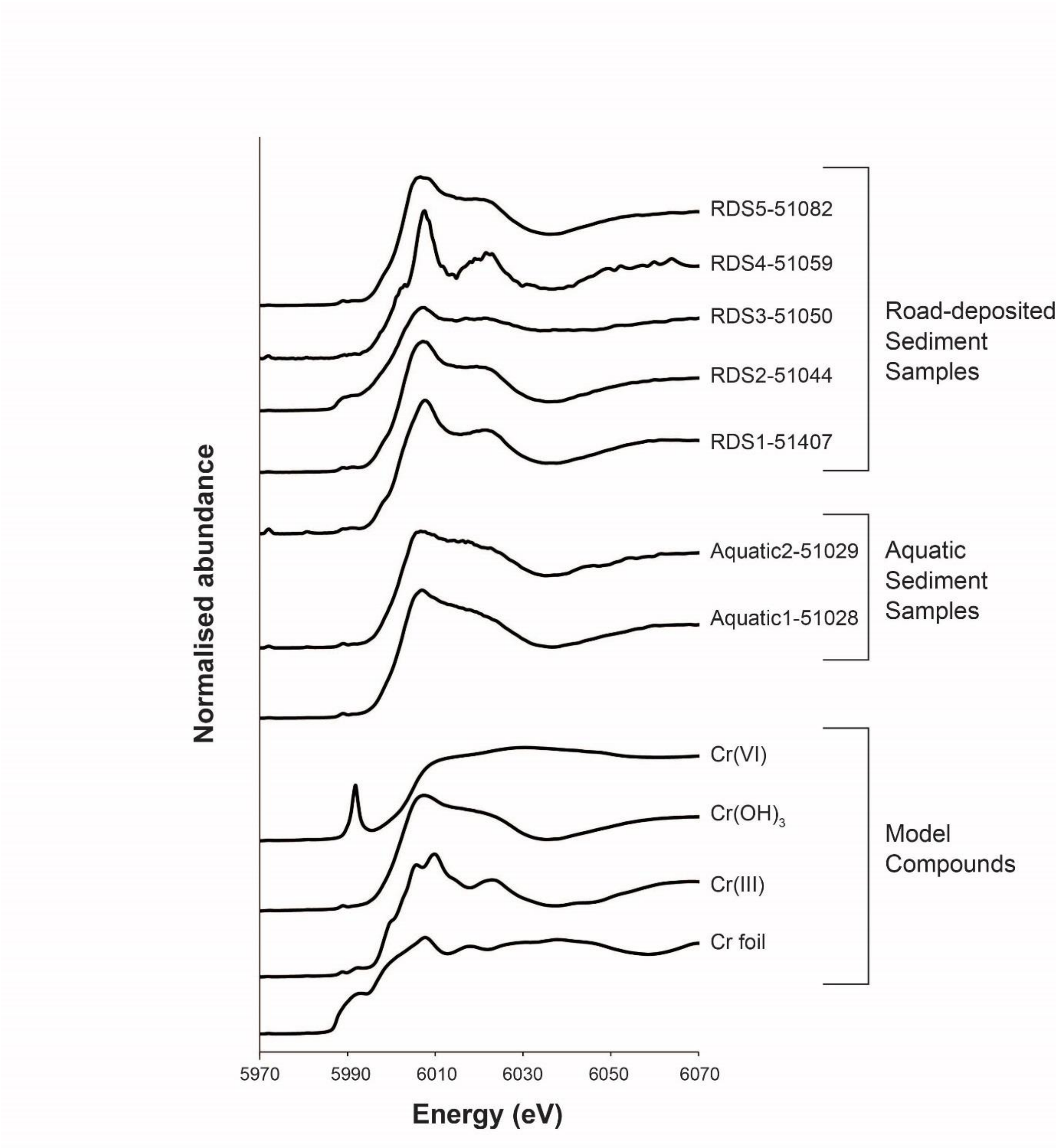

Figure 3. Representative Cr K-edge XANES spectra for sediment particulates and Cr K-edge XANES spectra for model compounds. Note the dominance of Cr(III) and only small amounts of Cr(VI) in aquatic sediment particulates.

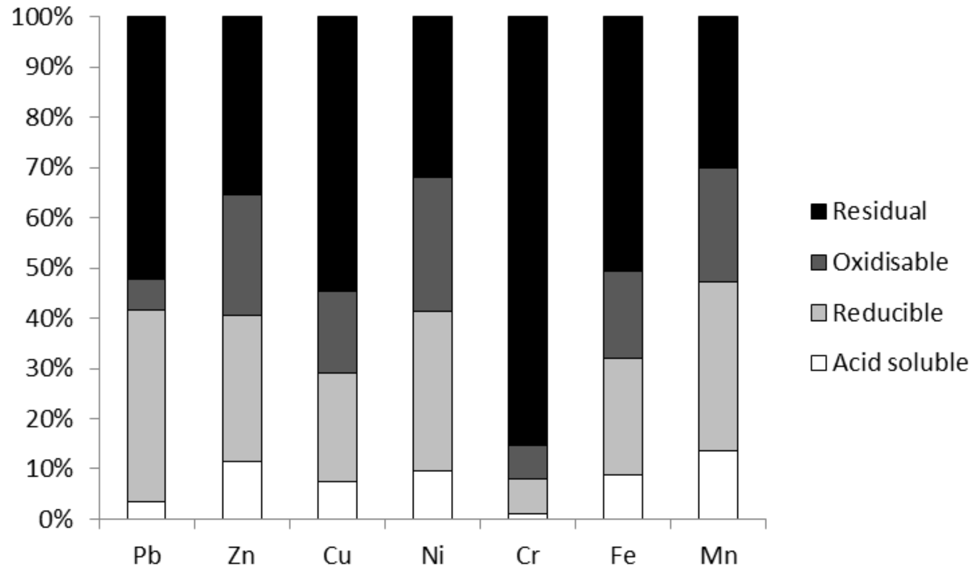

Figure 4. Mean sequential extraction and residual Pb, Zn, Cu, Ni, Cr, Fe and Mn concentrations (n = 3) from glass grains. Results are shown as percentages associated with each phase.

Table 1. Mean elemental composition of glass grains in aquatic sediment and RDS determined by electron microprobe analysis.

	SiO_2 (wt. %)	TiO_2 (wt. %)	Al_2O_3 (wt. %)	MgO (wt. %)	CaO (wt. %)	MnO (wt. %)	FeO^ or Fe_2O_3* (wt. %)	Na_2O (wt. %)	K_2O (wt. %)	Cr (ppm)
Salford Quays aquatic sediment										
Fe-rich glasses (n=15)	27.2 ± 2.8	0.32 ± 0.07	7.93 ± 0.90	5.09 ± 0.43	6.20 ± 1.9	0.75 ± 0.15	38.5^ ± 5.4	0.71 ± 0.17	0.37 ± 0.03	347 ± 340
Dark inclusions in Fe-rich glasses (n=6)	2.00 ± 2.3	0.18 ± 0.07	39.6 ± 5.2	5.37 ± 1.5	0.37 ±0.45	0.29 ± 0.08	23.1^ ± 2.5	0.54 ± 0.14	0.02 ± 0.02	69,800 ± 38,000
Fe-poor glasses (n=10)	46.0 ± 2.2	1.04 ± 0.14	26.7 ± 2.5	2.20 ± 0.38	7.37 ± 3.2	0.13 ± 0.03	9.15^ ± 2.6	0.98 ± 0.33	3.29 ±0.42	226 ± 100
Manchester road-deposited sediment										
Grain 1 (n=5)	3.18 ± 1.7	0.00 ± 0.0	0.05 ± 0.04	0.02 ± 0.01	0.54 ± 0.29	0.39 ± 0.14	92.9* ± 1.9	0.58 ± 0.10	0.04 ± 0.03	119 ± 61
Grain 2 (n=5)	4.01 ± 4.8	0.00 ± 0.0	0.03 ± 0.03	0.11 ± 0.19	0.61 ± 0.55	0.75 ± 0.33	90.3* ± 7.2	1.00 ± 0.68	0.15 ± 0.20	1420 ± 1500
Grain 3 (n=5)	34.1 ± 1.1	0.24 ± 0.01	3.33 ± 0.02	0.76 ± 0.03	2.24 ± 0.02	0.04 ± 0.02	58.4* ± 0.61	0.87 ± 0.05	0.81 ± 0.03	312 ± 64
Grain 4 (n=5)	0.13 ± 0.08	0.00 ± 0.01	0.01 ± 0.02	0.01 ± 0.01	0.00 ± 0.00	0.10 ± 0.15	149” ± 2.8	0.06 ± 0.06	0.00 ± 0.00	500 ± 730

Grain 5 (n=5)	0.09 ± 0.10	0.01 ± 0.02	0.05 ± 0.03	0.01 ± 0.01	0.13 ± 0.04	0.15 ± 0.09	98.1* ± 0.79	0.09 ± 0.03	0.01 ± 0.01	54 ± 52
Grain 6 (n=5)	35.0 ± 20	0.36 ± 0.34	28.0 ± 14	5.71 ± 6.6	8.16 ± 5.5	0.78 ± 0.62	15.2* ± 8.0	0.29 ± 0.19	3.90 ± 2.3	146 ± 170

‘’ The total of 149 wt. % is too high for Fe_2O_3, so we assume that this is iron metal (Fe).

Table 2. Mean concentrations (µg g^{-1}) of metals in industrial glass particles from Salford Quays sediment (n = 3). Results are shown for pseudo-total metals and each geochemical phase of the sequential extraction.

	Pb	Zn	Cu	Ni	Cr	Fe	Mn
Acid-soluble	71 ±18	1570 ±60	512 ±21	86 ±5	2.68 ±0.08	10500 ±340	275 ±14
Reducible	807 ±109	4000 ±80	1500 ±59	284 ±9	18.1 ±0.51	27700 ±260	675 ±13
Oxidisable	130 ±41	3290 ±116	1130 ±43	241 ±8	17.57 ±1.72	20800 ±530	459 ±17
Residual	1100 ±77	4870 ±103	3800 ±112	285 ±51	221 ±15	60800 ±1200	609 ±67
Pseudo-total	2110 ±183	13700 ±214	6950 ±109	897 ±64	259 ±13	120000 ±1300	2020 ±99
EA TEL guidelines*	35	123	36.5	18	137.3	-	-

* Environment Agency of England and Wales draft Threshold Effect Level (TEL) guidelines (µg g^{-1}) for total metals in freshwater sediments (Environment Agency, 2008).

Table 3: Energy values of pre-edge resonances, shoulder, absorption edge, edge crest and multi-resonance structures in XANES spectra at chromium *K*-edge for model compounds and environmental samples (values reported on eV).

Sample	Speciation		Pre-edge resonances(s)		Shoulder	Edge position	Edge crest		Multi-scattering resonance (MSR)				
	Z	Symmetry											
Cr Foil	0	Cubic				5989.24	5992.71		6007.64	6018.06	6030.56	6037.85	6070.14
Cr (III) ($Cr_2O_{3\ \mathrm{syn}}$)	III	Oh (distorted)	5988.54	5992.36		6002.43	6005.56	6009.72	6022.92	6042.71	6068.06		
$Cr(OH)_3$	III	Oh (~regular)	5988.89			6001.74	6007.29		6021.88	6072.22			
Cr(VI) ($K_2Cr_2O_{7\ \mathrm{syn}}$)	VI	Td	5991.67			6005.56	6011.81		6029.51				
Aquatics 1-51028			5988.89	5990.97		6001.74	6006.94		6019.44	6072.22			
Aquatics 2-51029			5988.54	5991.32		6001.39	6006.50		6018.06	6070.86			
RDS 1 - 51407			5988.54	5991.32	5998.61	6002.08	6007.64		6021.53	6060.70			
RDS 2 - 51044			5988.89	5991.32		6001.04	6006.94		6020.49	6071.18			
RDS 3 - 51050					5990.28	6000.34	6007.29		6021.85	6076.39			
RDS 4 - 51059			5989.24	5991.67	6003.13		6007.64		6021.53	6063.88			
RDS 5 - 51082			5988.89	5991.67		6001.74	6006.60		6021.18	6072.22			