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

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Abstract:	<p>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.</p> <p>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.</p> <p>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 $\mu\text{g g}^{-1}$ and 133,400 $\mu\text{g g}^{-1}$ 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.</p> <p>Conclusions: Industrial glass grains are a major component of urban sediment worldwide. The speciation and geochemical investigations performed in this study</p>

	suggest most Cr within the urban sediment cascade may be resistant to environmental processes that could mobilise other toxic metals.
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Opposed Reviewers:	

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1 TRANSFER OF SEDIMENTS AND CONTAMINANTS IN CATCHMENTS AND
2 RIVERS

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5 4 **Speciation and potential long-term behaviour of chromium in urban sediment**
6 **particulates**

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24 **Abstract**

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20
21 35 sediment and road dust sediment (RDS) in Manchester, UK.

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52

53 53 **Keywords** Chromium • Cr(III) • Cr(VI) • Glass grain • Urban sediment • XANES

54 54

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

88 by the dynamic urban environment and / or climatic forces has the potential to affect
89 the long-term environmental mobility and toxicity of Cr in these sediments (Butler
90 2009; Calmano et al. 1993; Knott et al. 2009). In order to understand the potential
91 long-term behaviour of Cr in complex substances such as urban particulate matter, a
92 synergistic and grain-specific approach is required that incorporates bulk and grain-
93 specific chemical analysis and spectroscopic techniques such as scanning electron
94 microscopy (SEM), X-ray powder diffraction (XRD) and synchrotron-based X-ray
95 absorption spectroscopy (XAS) techniques such as X-ray absorption near edge
96 structure (XANES) (Barrett et al. 2010; Barrett et al. 2011; Berry and O'Neill 2004;
97 Chen et al. 2010; Manceau et al. 2002; Wei et al. 2007; Xia et al. 1997). The major
98 advantage of grain-specific analyses over bulk sediment analyses is that the major
99 host species for contaminants can be identified and subjected to geochemical
100 analyses to determine environmental mobility. A case in point are the metal-rich
101 glass grains that are major constituents of both terrestrial (Lottermoser 2002) and
102 freshwater (Taylor and Boulton 2007) urban particulates as a consequence of furnace-
103 derived slag from steel production. These are known to contain high concentrations
104 of trace elements (Pb, Cu, Cr, Zn, Ni) and have been identified in urban particulate
105 matter worldwide (Kida and Sakai 2001; Lind et al. 2001; Reich 2003; Saffarzadeh et
106 al. 2009; Taylor and Robertson 2009). Following deposition in urban water bodies,
107 the ultimate sink for contaminated urban particulates, these glass grains have been
108 observed to undergo dissolution and early diagenetic reactions potentially releasing
109 Cr to interstitial and overlying waters (Taylor and Boulton 2007).

110
111 In this paper, we adopt an integrated speciation and geochemical approach to
112 describe the solid-phase speciation and environmental mobility of Cr in urban
113 particulate matter from the Greater Manchester urban conurbation, UK. To the
114 authors knowledge, this is the first time such an integrated approach has been
115 adopted to study toxic element cycling through urban sediment systems. The specific
116 objectives of this study were to: (1) investigate the association of Cr with terrestrial
117 and aquatic urban particulates; (2) confirm the speciation of Cr in these particulates;
118 (3) investigate the potential long-term geochemical mobility of Cr associated with
119 urban particulates. This innovative approach could provide a strong evidence base
120 for assessing the long-term risk of Cr to human health and ecosystems in urban
121 environments.

122

123 **2. Materials and methods**

124 **2.1 Study area and sampling procedures**

125 The contaminated sediment described in this study are from the urban conurbation
126 of Manchester, UK. The RDS samples were obtained from locations within
127 Manchester city centre that comprised heavily urbanised environments with high
128 traffic densities (Fig. 1a). Samples were collected by sweeping with a polyethylene
129 dustpan and brush. High metal (Fe, Mn, Pb, Zn, Cu) concentrations have been
130 reported in these sediments and sequential extraction analysis has shown some
131 metals (Fe, Mn, Zn) are largely associated with the reducible fraction, suggesting
132 changes in ambient pH and / or Eh could mobilise these metals (Robertson et al.
133 2003). Trace metals (Pb, Cu, Zn, Cr, Ni) in the RDS material are hosted mainly in
134 iron oxides and iron-rich glass grains (Taylor and Robertson 2009). Speciation
135 studies using X-ray absorption spectroscopy (XAS) have identified both Pb (Barrett
136 et al. 2010) and Zn (Barrett et al. 2011) to exist in phases that are potentially harmful
137 to human health. The aquatic sediment was sampled from the Salford Quays (Fig.
138 1b), a historically contaminated urban water body that received domestic and
139 industrial sewage and road runoff prior to commencement of remediation activities in
140 the late 1980s. Urban water bodies represent major sinks for contaminated sediment
141 in urban centres worldwide (Taylor and Owens 2009). Sediment cores were retrieved
142 from Basin 9 of the Salford Quays in 2000 and 2001 using a stainless steel corer and
143 contain a mix of natural and anthropogenic detrital grains, the latter dominated by
144 alumino-silicate glass grains (Taylor and Boulton 2007). Petrographic analysis
145 indicated these glass grains were undergoing chemical dissolution supplying Fe and
146 Zn to porewaters while bacterial Fe(III) and Mn(IV) reduction was hypothesized to
147 supply Fe²⁺ and Mn²⁺ to porewaters. Whilst these previous studies (and others) have
148 greatly increased our understanding of trace metal geochemistry in urban
149 environments, they have tended to focus on elements (e.g. Fe, Mn, Zn, Pb, Cu) that
150 represent, by mass, the bulk of metal contaminants found in urban environments.
151 Here, we focus specifically on the trace metal Cr, an element which may display
152 different geochemical and mobility characteristics to those more typically studied
153 metals.

154

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 SiO₂, Al₂O₃, TiO₂, CaO, Na₂O, K₂O, Fe₂O₃, MnO, MgO, P₂O₅, SO₃ (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

186 convert from monochromator position in millidegrees to energy in eV, and to average
187 multiple spectra from individual standards and samples; Ravel and Newville (2005))
188 and *PySpline* (to carry out background subtraction and normalisation; Tenderholt et
189 al. (2007)). The fluorescence signal is calculated as the total windowed fluorescence
190 counts divided by I_0 . The normalisation was done by fitting a 1st order polynomial to
191 the pre-edge region and extrapolating this to the end of the spectrum, then
192 subtracting. A 2nd order polynomial was fitted to the post-edge region and
193 subtracted. The edge step was normalised to 1. No linear combination modelling
194 was undertaken due to the uncertainties around the appropriate model compounds.

196 **2.4 Geochemical analysis of alumino-silicate glass grains**

197 Alumino-silicate glass grains were identified as a major constituent of terrestrial and
198 aquatic sediments and were therefore subjected to further geochemical analysis to
199 determine the environmental mobility of associated Cr. Glass grains were hand-
200 picked from the aquatic sediment under a binocular microscope. Samples of
201 sediment were washed in distilled water and the <63 μm fraction was sieved away
202 leaving behind silt- and sand-sized fractions. The glass grains were generally coarse
203 sand in size and were also dark and shiny, allowing easy separation. Pseudo-total Cr
204 concentrations of the glass grains were determined by aqua-regia digestion in closed
205 vessels using a microwave apparatus (MARS Xpress, CEM). A three-step sequential
206 extraction procedure (SEP) recommended by the Standards, Measurements and
207 Testing programme (SM&T) of the European Union (Rauret *et al.*, 1999) was utilised
208 to extract bioavailable Cr from the glass grains. The chemical procedure extracts
209 metals bound to three specific geochemical phases: (1) acid-soluble, easily
210 exchangeable and bound to carbonates; (2) reducible, bound to iron and manganese
211 oxides; (3) oxidisable, bound to organic and sulphide compounds. The SM&T
212 procedure is the only SEP with a certified reference material (CRM 701)
213 (Quevauviller *et al.* 1997) for all three phases of extraction allowing validation of the
214 procedure and comparison of results between studies. The SEP included two
215 sample duplicates, one blank and the certified reference material. The Cr content in
216 the residual fraction of the glass grains was estimated as the difference between
217 pseudo-total content (microwave extraction) and the sum of the contents of the other
218 fractions obtained by SEP. The supernatants produced after both extraction

219 procedures were acidified to pH 2 and stored at 4°C prior to analysis. All solutions
220 were analysed within a month using Inductively Coupled Plasma (ICP) Optical
221 Emission Spectroscopy (OES) (Perkin-Elmer Optima 2100DV). Detection limits of
222 the ICP-OES were 0.05 ppm Cr. High precision ($\pm 10\%$) of the control standards is
223 reported and calibration curves had a coefficient value better than 0.99. The relative
224 standard deviation was less than 2% above 0.05 ppm Cr. Recovery rates for Cr in
225 the CRM 701 were 95% for step 1, 91% for step 2, and 101% for step 3.

227 3. Results

228 3.1 Elemental analysis of RDS and aquatic sediment

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

246 3.2 Molecular scale analysis of RDS and aquatic sediments

247 The influence of oxidation state on the XANES spectra is revealed in differences in
248 the shape and the position of the edge, as well as the presences of pre-edge and
249 multi-scattering resonances (MSR). As illustrated by the four model compounds in
250 Fig. 3, a shift in the edge position of the Cr *K*-edge XANES to higher energies is

251 generally discerned with increasing oxidation state. Such a shift may be used as a
252 qualitative indicator of the presence of Cr(III), Cr(VI) or mixtures of different Cr
253 oxidation states. Table 3 summarizes the energy values of pre-edge resonances,
254 shoulder, absorption edge, edge crest and multi-resonance structures in XANES
255 spectra at Cr *K*-edge for model compounds and environmental samples.

256
257 Consideration of the environmental samples finds that the aquatic grain XANES
258 spectra display similar profiles. The lack of an intense peak in the pre-edge region
259 coupled with two small pre-edge resonances indicates that Cr in such samples is
260 present mainly in the octahedrally coordinated trivalent form, and that the
261 contribution of tetrahedrally coordinated Cr(VI) is estimated to be $\leq 5\%$ (Huggins et
262 al. 1999). Comparison of the pre-edge and edge position energies of the two aquatic
263 samples spectra show comparability to the XANES spectra of the Cr(III) model
264 compounds. In particular, the equivalence noted between the energies of the pre-
265 edge resonance, edge crest and second MSR reported for Aquatic 1- 51028 and
266 those of Cr(OH)₃ suggests that Cr(OH)₃ is likely to be a main contributor to the Cr
267 speciation of this sample. Differences in the energies of the pre-edge resonance and
268 the second MSR reported for Aquatic 2- 51029 may imply that Cr₂O₃ may also
269 influence the Cr speciation of the Aquatic 2- 51029.

270
271 Qualitative analysis of the XANES spectra of the RDS grains identifies a greater
272 degree of variance between the individual spectra of the RDS. The edge position
273 energies for the RDS grains, with the exception of RDS3-51050, appear to conform
274 with values reported for the Cr(III) model compounds (6001.74 eV; 6002.43eV)
275 suggesting that Cr speciation is dominated by trivalent Cr species in the RDS
276 samples. As with the aquatic samples, the presence of two low intensity pre-edge
277 resonances identified in all the RDS samples, except RDS3-51050 and the absence
278 of any sharp high intensity peak in the pre-edge region implies that Cr(VI) species
279 play a secondary role to Cr(III) in the Cr speciation of RDS. Visual comparison of the
280 five RDS spectra (Fig. 3) identifies strong similarities between RDS2-51044 and
281 RDS5-51082 and to an extent RDS1-51407. Consideration of the pre-edge
282 resonance, edge and MSR energies determined for RDS2-51044 and RDS5-51082
283 finds agreement with those reported for Cr(OH)₃ (Table 3). Although, RDS1-51407
284 spectra shows some comparability with that of Cr(OH)₃, similarities to the edge

285 position and MSR energies reported for Cr₂O₃ suggest that a combination of the two
286 model compounds may be influential in this sample. The occurrence of shoulder
287 structures in the XANES spectra of samples RDS3-51050 and RDS4-51059 infer
288 that mixed oxidation states may exist in such samples (Berry and O'Neill 2004). The
289 XANES spectrum of RDS3-51050 with the presence of a shoulder structure around
290 5990 eV and edge crest and MSR energies of 6007 and 6022 eV respectively,
291 displays characteristics of Cr in metallic and trivalent forms. By contrast, XANES
292 spectrum of RDS3-51059, is characterized by the prominence of an absorption edge
293 shoulder, which is likely to result from a 1s→4s transition indicative of Cr(III) being
294 present and a MSR at approximately 6021 eV.

3.3 Geochemical analysis of aluminosilicate glass grains

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

317 4. Discussion

318 4.1 Speciation of chromium

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

345
346 Electron microbeam analysis of the particulate matter has found Cr to exist
347 predominantly in Fe-rich and Fe-poor glass grains in aquatic sediment and in both
348 Fe oxides and Fe-rich glass grains in RDS. This supports earlier work on

1 349 Manchester sediment (Taylor and Boulton 2007; Taylor and Robertson 2009) and
2 350 urban sediment worldwide (Kida and Sakai 2001; Lind et al. 2001; Reich 2003;
3 351 Saffarzadeh et al. 2009) that suggests Fe-oxides, derived from vehicular wear and
4 352 tear, and Fe-rich glass grains, derived from metal smelting and concrete, are major
5 353 hosts for contaminant metals in urban particulates. Iron oxides and Fe(III)
6 354 oxyhydroxides are known to be important Cr scavengers and Cr(III) can readily
7 355 substitute for Fe(III) in metal oxides (Frommer et al. 2009). Cr(III) can also co-
8 356 precipitate with goethite (FeOOH) to form an (Fe,Cr)OOH phase, due to structural
9 357 similarities between the host Fe(III) mineral and the pure Cr surface precipitate
10 358 phase (CrOOH) (Charlet and Manceau 1992; Hansel et al. 2003). Cr(III) has also
11 359 been found to dominate in hematite (Fe₂O₃)-bearing red mud from the Ajka
12 360 (Hungary) tailings dam spill (Burke et al. 2012).

23 361

24 362 **4.2 Control of Eh and pH on the long-term environmental mobility of chromium**

25 363 Oxyanion-forming elements such as Cr have strong pH- and redox-dependent
26 364 sorption behaviour. In anoxic conditions (e.g. in Salford Quays sediment), Cr(III) may
27 365 be relatively stable as Cr(OH)₃ or adsorbed to Fe oxides and glass grains.
28 366 Phosphorus has been reported to scavenge trace metals (Zn, Cu, Pb) in the Salford
29 367 Quays by incorporating them into the mineral precipitate vivianite (Fe³⁺(PO₄)₂ · 8H₂O)
30 368 (Taylor and Boulton 2007), although Cr was not considered in this previous study.
31 369 Minor sulphate reduction has also been found in the Salford Quays which has been
32 370 shown to be immobilizing Cu as an insoluble sulphide (Taylor and Boulton 2007).
33 371 However, Cr is not a divalent metal and will therefore not form an insoluble metal
34 372 sulphide under reducing conditions. Chromium(III) solubility in anoxic sediments is
35 373 further limited by complexation with solid-phase organic ligands which also facilitate
36 374 the rapid reduction of Cr(VI) to Cr(III) (James 2002). The Salford Quays sediment is
37 375 known to be rich in organic matter (up to 10% TOC in the upper, metal-rich layers)
38 376 (Taylor and Boulton 2007).

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40 378 Several studies have noted the oxidation of Cr(III) to Cr(VI) by Mn oxides in anoxic
41 379 conditions (Apte et al. 2006; Fendorf and Zasoski 1992; Kazakis et al. 2015; Tang et
42 380 al. 2014). This natural oxidation is primarily related to the presence of Mn(III,IV)

381 hydroxides which are considered as direct oxidising agents. Extensive experiments
1 382 on the oxidation capacity of Cr(III) have shown that the Mn(IV) phase oxidizes the
2 383 highest amount of Cr(III) (Landrot et al. 2012). Manceau and Charlet (1992) and
3 384 Landrot et al. (2012), observed that Cr(III) was tightly sorbed as an inner-sphere
4 385 complex to Mn(IV) in Cr(III)-reacted MnO₂ analysed by EXAFS. Manganese
5 386 hydroxides were not found to be a major constituent of the urban particulate matter
6 387 in the Salford Quays sediment (mean 0.75% MnO in Fe-rich glasses; mean 0.37%
7 388 MnO in RDS). However, these relatively low quantities of Mn can still make a
8 389 significant difference to sorption behaviour (Jenne 1968) and the oxidation of Cr(III)
9 390 to Cr(VI) by Mn oxides cannot be ruled out in urban aquatic sediment sinks.
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20 392 Oxidic conditions are not usual in sedimentary basins such as the Salford Quays due
21 393 to limited water column mixing and high organic matter loading that maintains a high
22 394 sediment oxygen demand. However, oxidation of canal, reservoir and harbour
23 395 sediments can occur in response to dredging, flooding and bioturbation, leading to
24 396 the phase transfer of some metals to more bioavailable species (Calmano et al.
25 397 1993; Zoumis et al. 2001). In the Salford Quays, Helixor pumps have been employed
26 398 to oxygenate water in an effort to improve water quality and promote immobilization
27 399 of cationic metals as hydroxides. Chromium(III) is still thermodynamically favourable
28 400 even under mildly oxidising conditions (Martello et al. 2007), but it is possible that the
29 401 introduction of oxygen into the water column may promote oxidation of surface
30 402 sediments leading to the oxidation of Cr(III) to Cr(VI). This could only occur,
31 403 however, at Eh greater than 0.7 volts (Takeno 2005). Enhanced Cr(VI) production
32 404 has been reported previously in surface sediments of seasonally anoxic lakes
33 405 (Achterberg and van den Berg 1997). However, in field experiments, Bloomfield and
34 406 Pruden (1980) found both oxic and anoxic soil conditions increased the reduction of
35 407 Cr(VI). Importantly, these experiments considered a typical soil pH of between 4 and
36 408 7, with Cr(VI) reduction being most efficient at pH <5. While Eh is an important
37 409 control on Cr speciation and mobility in sediment systems, Cr(VI) can only exist in
38 410 both an oxic and high pH environment.
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56 412 The most favourable environment for the formation of Cr(VI) species is Eh >0.5 volts
57 413 and pH >8 (Takeno 2005). The typical pH range for Salford Quays sediment is 6.6 –
58 414 7.6, and although Eh has not been measured, predominant anoxic conditions are
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415 inferred from the pore water chemistry (Taylor and Boulton 2007). Therefore, future
416 large-scale oxidation of Cr(III) to Cr(VI) is unlikely to occur in the Salford Quays
417 sediment. However, this may not be the case in other Cr-contaminated urban water
418 bodies and careful investigation of the environmental processes that might drive Cr
419 transformation is needed in order to comprehensively evaluate environmental risk.
420 The formation of soluble Cr(III) species due to the dissolution of Cr(III) minerals and
421 adsorbed species is the most likely mechanism by which Cr may mobilise from the
422 sediments. The solubility of chromium hydroxide [Cr(OH)₃] is low between pH 6 and
423 12 and under reducing and mildly oxic conditions (Takeno 2005). As long as anoxic
424 conditions remain, Cr-bearing Fe oxides may also exist as insoluble sulphide
425 minerals or, more likely, incorporated into the phosphate mineral vivianite. However,
426 most Cr in the aquatic sediment was found to be associated with glass grains.
427 Furnace-derived glasses in contaminated soils and sediments are known to be prone
428 to chemical dissolution at sub-neutral pH due to organic acid generation as part of
429 early sediment diagenesis (Lottermoser 2002; Parsons et al. 2001). Taylor and Boulton
430 (2007) found evidence from petrographic observations of chemical dissolution
431 occurring in Fe-rich glass grains and associated contaminant metal (Zn) release.
432 However, Cr concentrations in pore waters were not measured so it remains
433 unknown as to whether chemical dissolution may affect the cycling of Cr in urban
434 aquatic sediment sinks. Evidence from the chemical extractions performed in the
435 present study suggests Cr(III) has limited mobility and is not easily leached
436 compared to other trace and toxic metals. However, the timeframe of exposure to
437 low pH may be an important factor. Aqueous Cr species (e.g. Cr²⁺, Cr³⁺) can
438 generally only exist at pH below 4 and while such low pH levels can occur in acidic
439 soils, they are rarely encountered in sediments. Therefore, the release of organic
440 acids during early diagenetic organic matter oxidation may not impact upon glass
441 solubility and Cr mobility. However, it must be acknowledged that the presence of
442 glass slag phases as major hosts of Cr is not reflected in grain-specific sequential
443 chemical extraction methodologies (including BCR).

5. Conclusions

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

448 Chromium has been found to exist primarily in two major grain types in urban
1 449 particulate matter from the major urban conurbation of Manchester, UK. Chromium is
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3 450 mainly associated with Fe oxides and industrial glass grains in urban aquatic
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5 451 sediment. XANES analysis suggests this Cr exists primarily as the relatively non-
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7 452 toxic Cr(III) species. The predominant anoxic and neutral pH of the Salford Quays
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9 453 sediments suggests that this Cr(III) may be stable as long as these environmental
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11 454 conditions are maintained. While oxidation of the sediments may occur under a
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13 455 variety of scenarios, it is unlikely that sediment pH can be maintained at a high
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15 456 enough level, in conjunction with oxic conditions, to mobilise Cr(III) as more soluble
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17 457 and toxic Cr(VI). Of course, this may not be the case in other urban aquatic sediment
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19 458 sinks that exhibit different environmental conditions to the Salford Quays. Aside from
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21 459 the issue of speciation, geochemical analyses have shown that most Cr is
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23 460 incorporated within the crystalline structure of industrial glass grains in the aquatic
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25 461 sediment and therefore exhibits limited environmental mobility in comparison to other
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27 462 trace metals. These glass grains may be prone to chemical dissolution at low pH;
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29 463 however, it is unlikely that sediment pH can reach a low enough level to mobilise
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31 464 aqueous Cr species. Industrial glass grains are a major component of urban
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33 465 sediment worldwide suggesting most Cr within the urban sediment cascade may be
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35 466 resistant to environmental processes that could mobilise more bioavailable forms.
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37 467 Future research should, through experiments and geochemical modelling, address
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39 468 this potential mobility under a variety of environmental scenarios. These data would
40
41 469 facilitate the development of environmental risk models for Cr mobility and cycling in
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43 470 urban environments.
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46
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48
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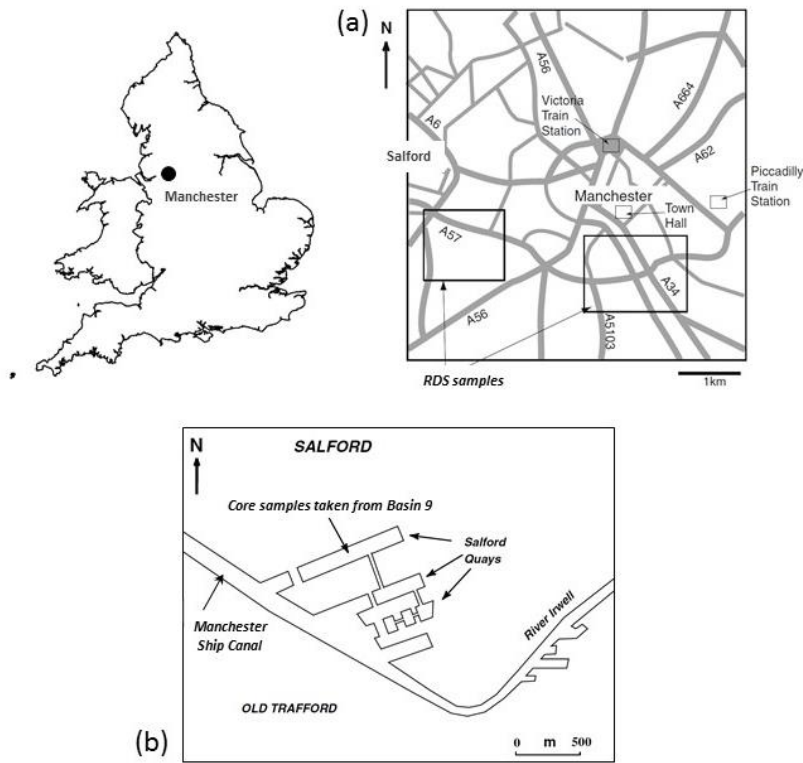
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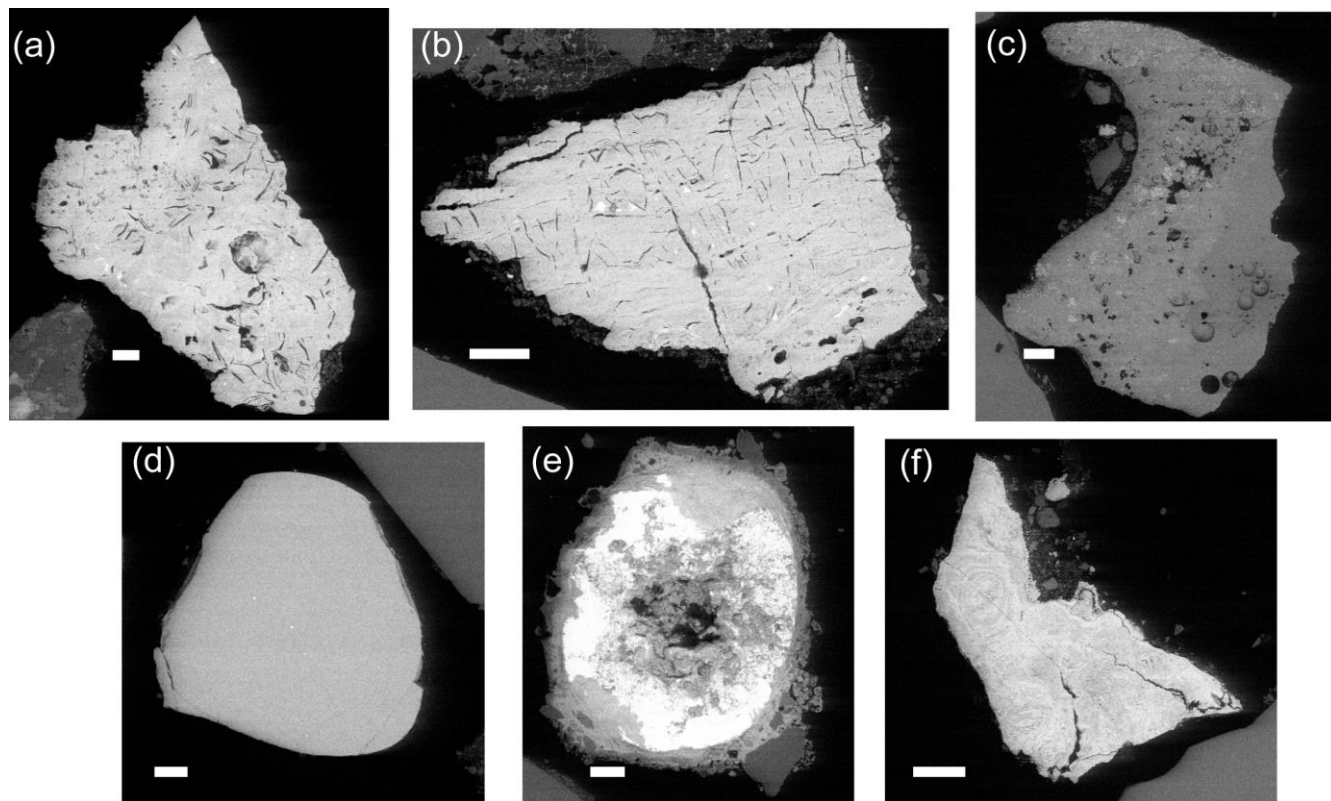
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661 Figure 1. Location of Manchester showing (a) RDS sampling sites in Manchester city centre
662 and (b) aquatic sediment sampling site in the Salford Quays.

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

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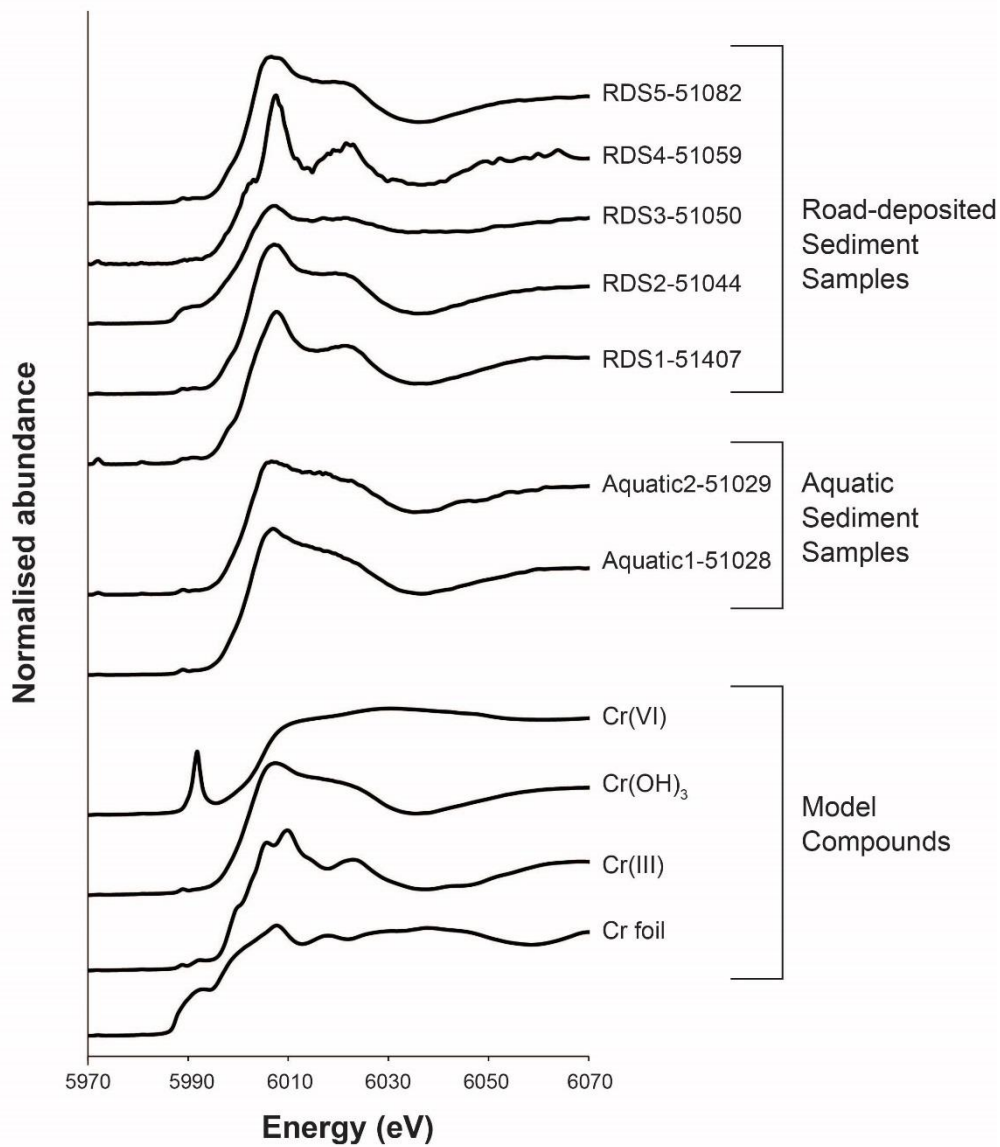
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695 Figure 3. Representative Cr K-edge XANES spectra for sediment particulates and Cr K-edge
696 XANES spectra for model compounds. Note the dominance of Cr(III) and only small
697 amounts of Cr(VI) in aquatic sediment particulates.

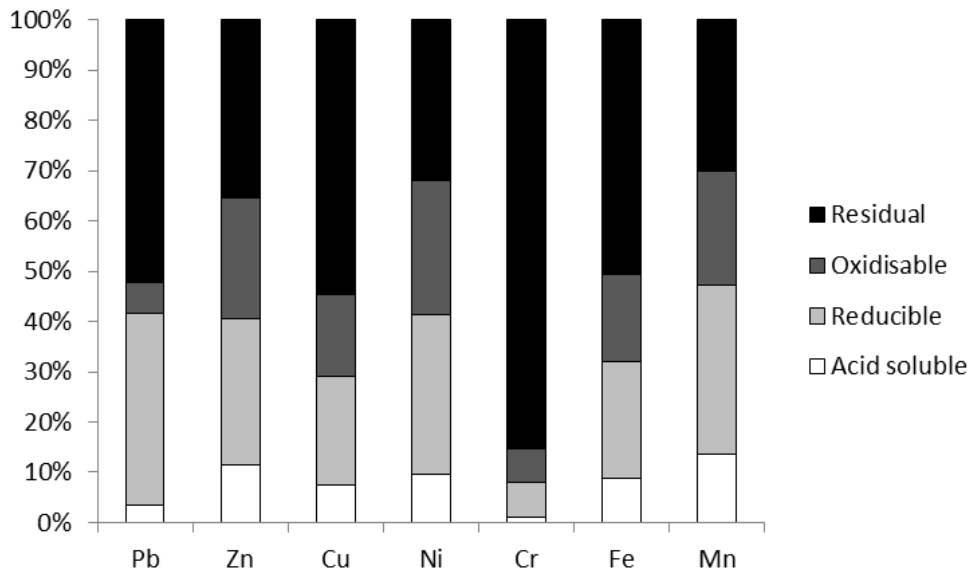
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703 Figure 4. Mean sequential extraction and residual Pb, Zn, Cu, Ni, Cr, Fe and Mn
704 concentrations ($n = 3$) from glass grains. Results are shown as percentages associated with
705 each phase.

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722 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 ₂ O ₃ (wt. %)	MgO (wt. %)	CaO (wt. %)	MnO (wt. %)	FeO [^] or Fe ₂ O ₃ [*] (wt. %)	Na ₂ O (wt. %)	K ₂ O (wt. %)	Cr (ppm)
<i>Salford Quays aquatic sediment</i>										
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
<i>Manchester road-deposited sediment</i>										
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

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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

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724 " The total of 149 wt. % is too high for Fe₂O₃, so we assume that this is iron metal (Fe).
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728 Table 2. Mean concentrations ($\mu\text{g g}^{-1}$) of metals in industrial glass particles from Salford Quays sediment ($n = 3$). Results are shown for pseudo-
729 total metals and each geochemical phase of the sequential extraction.

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

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731 * Environment Agency of England and Wales draft Threshold Effect Level (TEL) guidelines ($\mu\text{g g}^{-1}$) for total metals in freshwater sediments (Environment Agency, 2008).
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733 Table 3: Energy values of pre-edge resonances, shoulder, absorption edge, edge crest and multi-resonance structures in XANES spectra at
734 chromium *K*-edge for model compounds and environmental samples (values reported on eV).

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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 ₂ O ₃ _{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 ₂ Cr ₂ O ₇ _{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		

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