



Limitations on the role of the hyporheic zone in chromium natural attenuation in a contaminated urban stream



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ABSTRACT

The urban hyporheic zone may offer natural attenuation potential for contaminants. This potential is contaminant-specific and may be spatially and temporally variable. The aim of this study was the assessment of the natural attenuation potential of the hyporheic zone of an urban stream receiving hexavalent chromium (Cr)-rich effluents from the historical land disposal of chromite ore processing residue (COPR) in Glasgow, Scotland. The evidence based approach involved the use of a network of multilevel piezometers for best capturing potential anoxic field conditions and fine-scale spatial gradients in solute concentrations of surface water and porewater. In-situ porewater sampling was integrated with sediment sampling and reach-scale monitoring of stream water quality. The results show a sharp decrease of total dissolved (filtered <0.45 μm) Cr concentrations at the surface water – sediment boundary in all profiles, from Cr mean values of 1100 μg l⁻¹ in surface water to 5 μg l⁻¹ in porewater. Chromium speciation analysis indicates that no Cr(VI) was detectable in the neutral pH, moderately reducing porewater, while it was the dominant species in surface water. Evidence of historical COPR detrital grains contributed to the total Cr concentrations (size fraction <150 μm) up to 8800 mg kg⁻¹ in the streambed sediment. The abundance in the porewater of Fe (mean value = 1700 μg l⁻¹), mainly as Fe(II), a natural electron donor for Cr(VI) reduction to Cr(III), indicates a high natural attenuation potential of the hyporheic zone for downwelling dissolved Cr, through Cr(VI) reduction to Cr(III) and the formation of Cr(III) solids of low solubility. Authigenic Cr-rich rims on particles also documented active Cr precipitation from solution in the fine sediments. Large short-term changes of stream stage and stream water composition were not reflected in the hyporheic conservative (chloride) and reactive solute composition. This result indicates only limited surface water infiltration and suggests that small advective exchange might limit the effectiveness of the hyporheic zone for enhancing Cr surface water quality at the reach-scale. This is supported by further evidence from preliminary surface water quality synoptic sampling which shows only moderate to low downstream decrease in surface water Cr concentrations. The surface water investigation needs to be supported by combined water quality-flow monitoring and to be extended to a wider range of temporal and spatial scales to corroborate the reach-scale findings.

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1. Introduction

Awareness of the opportunity offered by the incorporation of the hyporheic zone into stream management for improving water quality and supporting biodiversity in urban areas is increasing

(Gessner et al., 2014; Lawrence et al., 2013; Ward et al., 2011). In order to improve the confidence in incorporating the hyporheic zone into urban water management, a better understanding of the natural contaminant attenuation capacity of the hyporheic zone in urban environments is needed (Smith et al., 2008). The hyporheic zone, a zone of exchange between the stream and the shallow subsurface, has the potential to mitigate diffuse pollution in urban streams. Yet, for some of the lowland streams with very fine and organic rich bed sediments, unfavourable hydraulic conditions,

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limiting flow exchange between streambeds and surface water, are considered to constrain the efficiency of contaminant removal in the hyporheic zone (Herzog et al., 2015). Also largely unexplored, is the overall significance of the hyporheic zone attenuation potential in light of the large variability in stream flow regime and solute composition that urban watercourses may experience (e.g. as a result of storm runoff from impervious surfaces and variable wastewater effluent discharges). These variables can significantly affect the size and composition of the hyporheic zone, and the biogeochemical processes associated with it (Boulton et al., 1998; Mueller Price et al., 2015; Siergieiev et al., 2014; Zimmer and Lautz, 2013), and therefore, the contaminant attenuation capacity of the hyporheic zone.

Chromium (Cr) is a common historical contaminant in the urban environment due to its widespread use in industrial applications such as tanning, metallurgy and plating. Tons of chromite ore processing residue (COPR) have in the past been landfilled in urban areas (e.g. Hudson County, New Jersey, USA (Burke et al., 1991) and Glasgow, United Kingdom (Farmer et al., 1999)). Natural attenuation may be a viable option for remediation of Cr contaminated sites under certain settings (Palmer and Puls, 1996). Chromium attenuation in water is due to the reduction of Cr(VI), present as mobile and toxic chromate (CrO_4^{2-}) and dichromate (HCrO_4^-) anions, to Cr(III), whose solubility is limited by the formation of $\text{Cr}(\text{OH})_3$, Cr(III) co-precipitated with iron oxy-hydroxides or adsorbed to mineral phases (Ball and Nordstrom, 1998).

Several studies (Hellerich and Nikolaidis, 2005; Henderson, 1994; Higgins et al., 1998; Wadhawan et al., 2013; Whittleston et al., 2011) have reported Cr attenuation in groundwater, wetlands, estuarine sediments and soils. However, investigations within urban settings are lacking. Given their peculiarities, as described above, additional studies in urban streams are needed. Because of the strong dependence of Cr solubility and toxicity on Cr oxidation state, the hyporheic zone of some urban lowland streams with organic-rich silty-clay sediments, might have a high attenuation potential for Cr. In this study we investigated the occurrence and behaviour of Cr in the hyporheic zone of a Cr contaminated urban stream, the Polmadie Burn, a tributary of the river Clyde, Glasgow, UK, where Cr(VI) enriched waters have discharged into the stream channel for many decades. The catchment of the Polmadie Burn includes areas impacted by the historical disposal of chromite ore processing residue (COPR). Our goal was i) to provide a field-based evaluation of the hypothesis that Cr(VI) contaminated waters will not persist in the hyporheic zone of a stream characterised by fine sediments. Included in our evaluation was ii) a preliminary assessment of the impact of short-term stream stage fluctuations and compositional changes on hyporheic Cr water quality and iii) the importance at the reach-scale of the hyporheic zone as a Cr natural attenuation zone. By understanding the processes in the shallow hyporheic zone of the study site we aim to provide lines of evidence to complement the assessment of the linkage between urban land, groundwater and river contamination and the potential role of the hyporheic zone for enhancing water quality and improving aquatic habitats in an urban setting, to justify consideration in restoration work.

2. Study area

The Polmadie Burn (National Grid Reference [NGR] NS 60160 63255) (Fig. 1), is located within the Oatlands area of Glasgow, UK, approximately 3 km to the south-east of the city centre. It drains into the River Clyde in the study area and its catchment includes areas impacted by the historical disposal of COPR that originated from White's Chemical Works (operational between 1810 and 1967) in Shawfield in the immediate vicinity of the study site. The

chrome, derived from the processing of chromite ore, was supplied as chromium oxide from 1919 to 1945 and then as dichromate salts. Historical land uses of the catchment area ranged from farmland and residential to a colliery, railway sidings, industrial works and clay pits. Although the burn is situated upstream of the Clyde Tidal Weir at Glasgow, which is designed to stabilise the upstream banking of the River Clyde by maintaining a fixed water level, a tidal response in the groundwater levels was considered plausible. The stream levels respond rapidly to culverted drainage upstream of the study area.

Chromium concentrations in surface water up to 6.3 mg l^{-1} have been measured by Farmer et al. (2002). Existing UK water Environmental Quality Standards (EQS) for the protection of freshwater organisms range from 5 to $50 \text{ } \mu\text{g l}^{-1}$ total dissolved Cr. In a regional geochemical survey of the Clyde catchment, Fordyce et al. (2004) reported 3550 mg kg^{-1} Cr in bed sediments (<150 μm fraction) sampled from Polmadie Burn, largely exceeding the Canadian sediment quality guideline for Cr of 111 mg kg^{-1} (Macdonald et al., 2000). The Canadian standards rather than UK standards are considered in this study, as established sediment quality guidelines for metals in river and marine sediments are not available for the UK.

The bedrock geology beneath the Polmadie Burn comprises the Scottish Middle Coal Measures Formation, overlain in the south-east by the Scottish Upper Coal Measures Formation (British Geological Survey, 1993). These formations are Carboniferous in age and comprise cyclic alternations of mudstone, siltstone and sandstone with seat clay, seat earth and coal seams at some levels. The bedrock geology is overlain by superficial sequences of Quaternary River Terrace Deposits. These are covered by extensive sandy, silty, alluvial deposits laid down where local depressions coincide with the course of the modern river system, including the Polmadie Burn. The superficial geology of low permeability clays and silts (alluvium) and/or cohesive glacial till were considered to represent a barrier to significant deep groundwater flow gains or losses along the stream. The focus of the hyporheic zone investigation was, therefore, on the relationship between stream water and the upper ~50 cm of the streambed.

There are extensive areas of infilled and made ground to the south and south-east of the open section of the Polmadie Burn. Borehole evidence (records held by the BGS National Geoscience Data Centre) indicates that the alluvium extends to at least 20 m depth. More specifically, a borehole at National Grid Reference NGR NS 60036 63051 was taken to 15.0 m depth, but did not fully penetrate the alluvium. It encountered 4.50 m of made ground underlain by interbedded silty sand and sandy clay with silt on its parting.

The depth of incision of the Polmadie Burn is in the order of 3 m. This is elevated relative to that of the River Clyde. The channel has been canalised. In the lower, northerly flowing reach (site A, Fig. 1) the valley side slopes are about 17° and a small terrace of 1.0–1.5 m width has formed approximately 0.9 m above the valley floor on both sides of the valley. In the upper, north-westerly flowing reach (site B, Fig. 1), the valley sides are steeper, such that the profile takes more of a "U"-shape form and terrace development is minimal. The bed of the Polmadie Burn comprises a dark brown to dark grey organic-rich silty-clay. The presence of large debris (shopping trollies, waste, rugs, bricks) was also noticeable.

3. Methods

The multiple lines of evidence approach combined in-situ monitoring, hydraulic testing, sampling and geochemical/mineralogical characterisation of hyporheic water, surface water and streambed sediments, to analyse stream-subsurface interactions

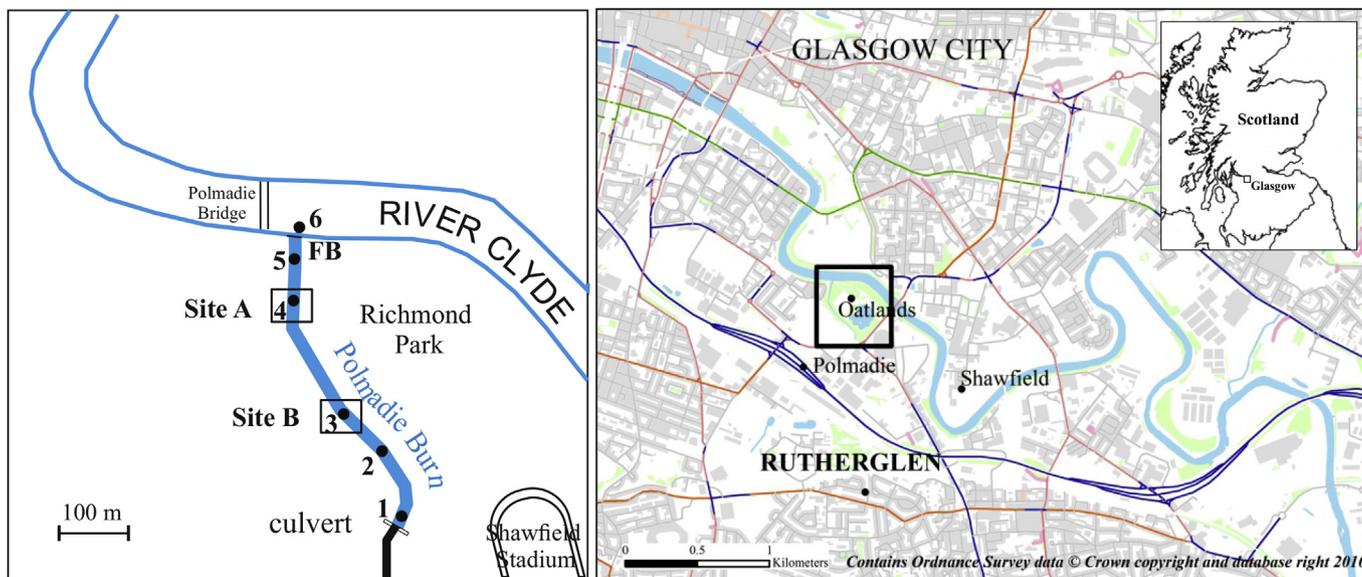


Fig. 1. Study area with location of Site A and Site B for hyporheic zone sampling and 1–6 sampling points for synoptic water quality sampling (FB: footbridge; point 6: River Clyde).

and explain the critical factors and underlying mechanisms affecting Cr behaviour and speciation. The fieldwork was conducted in 2012 during two periods: the first in February enabled sampling of water from the hyporheic zone and stream during an apparent large short-term variation in stream depth, with temporary exposure of river bed sediments, whereas the second field data collation period in September enabled data collation in more constant hydraulic conditions in the Pomadie Burn. Additional synoptic surface water quality sampling was carried out to provide qualitative evidence of the whole-stream contaminant attenuation to which the hyporheic zone may contribute.

3.1. Surface water and porewater sampling and analysis

The spatial variation of the shallow hyporheic zone was addressed by sampling two stream stretches with a network of multilevel piezometers in order to resolve vertical porewater chemistry differences across the stream section. Site A (Fig. 2) was sampled in February 2012 (21/02/2012) with two multilevel piezometers spaced ~ 2 m, one (ML A-I) close to the river banks (sampling sediment-depth interval 20–50 cm below riverbed) and the other (ML A-II) towards the centre of the stream (sampling sediment-depth interval 0–40 cm below riverbed). Site B was sampled in September 2012 (26/09/2012) with four multilevel piezometers (ML B-I, ML B-II, ML B-III, ML B-IV) installed on a cross channel transect along the bed to provide a number of vertical depth profiles covering an interval 0–90 cm below riverbed (Fig. 2). At each piezometer point a depth-integrated sample of the Polmadie Burn surface water was also collected at the time of the hyporheic zone porewater sampling; obtained vertical profiles of natural geochemical tracers (e.g. Cl) were used to estimate infiltration amounts and flow patterns.

A first assessment of the impact of short-term stream stage variations on the hyporheic zone was undertaken by repeated sampling of the ML A-I multilevel sampler and overlying water, planned at site A, so that times of stream stage highs and lows were captured during a spring tidal cycle (Fig. S1). On 21/02/12 ML A-I porewater samples were taken during very low river stage (16:30), while the streambed was exposed and the surface water was taken from the middle channel (Fig. S2). ML A-I was further sampled on

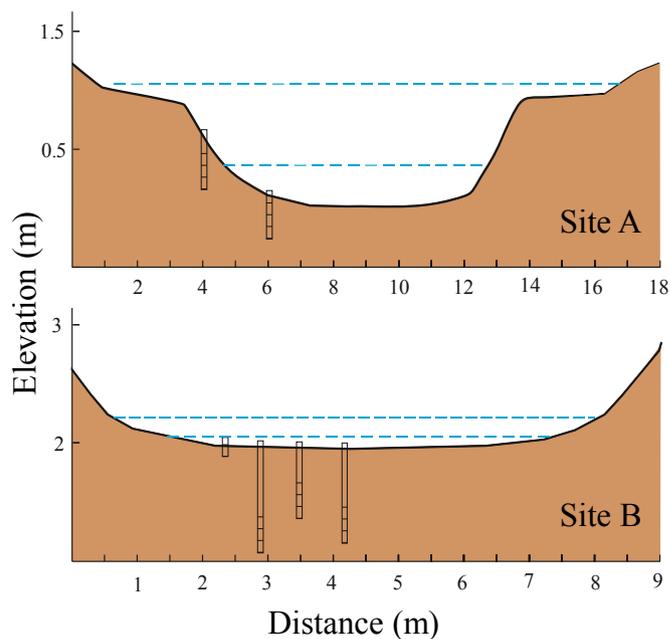


Fig. 2. Stream cross sections of site A (upper) and site B (lower), as located on Fig. 1. Broken lines indicate surface water level (stage) variation range observed at the time of sampling.

the 23/02/2012, three times throughout the day at 11.30 (rep 1), 13.15 (rep 2) and 17.10 (rep 3), in correspondence of a sequence of relatively low (ML A-I -rep 1) – high (ML A-I rep 2) – low stream (ML A-I rep 3) stage (Fig. S1).

The multilevel piezometer design was based on that used by Rivett et al. (2008) and described in Palumbo-Roe and Dearden (2013). A stabilization period >12 h was allowed between piezometer installation and the start of sampling so as to minimise the after-effects of installation on water chemistry. Water samples were drawn using a low-flow multichannel peristaltic pump that enabled simultaneous sampling of the four ports (at 10 cm intervals) of the multilevel samplers at an approximate flow rate of 4 ml/min. The sample tubes were purged before sampling by

collecting and discarding 3 times the volume of water present in the sample tube. Samples of ~50 ml were then collected in acid-rinsed 60 ml polyethylene bottles. Upon completion of the water sampling, pH and Eh were measured using a flow-through cell and the Pt electrode Eh measured values were corrected to the Standard Hydrogen Electrode. The Eh probe was tested in the laboratory prior to the fieldwork against a Zobell's standard solution with measurements within 5 mV of the Zobell's Eh at ambient temperature.

Filtration of the collected surface water and porewater samples through a 0.45 μm filter was carried out immediately upon sampling. Alkalinity was determined by titrating 25 ml filtered water against H_2SO_4 , using a bromocresol green indicator solution. For colorimetric Fe(II) analysis of a sample subset, 15 ml of the filtrate was added to 1.5 ml of a pre-made reagent containing the colour-forming agent 2,2' dipyridyl. Samples for the analysis of major and trace anions, and Non Purgeable Organic Carbon (NPOC) were refrigerated with no further preservation and samples for the analysis of major and trace cations were preserved via acidification with 1% HNO_3 prior to refrigeration.

Determination of Cl, SO_4 and F was by ion chromatography (IC) and major and trace elements were determined by inductively-coupled plasma mass spectrometry (ICP-MS), with independent QC checks providing $96 \pm 3\%$ accuracy (in-house QC solution) and $98 \pm 4\%$ accuracy (NIST SRM 1643e). The NPOC content was determined using a Shimadzu TOC-V CPH analyser with an associated ASI-V auto-sampler.

Concentrations of major and trace elements determined in procedural blanks were negligible when compared with the reported data. Repeatability of the field measurements estimated from the results of surface water duplicate (D) determinations and reported as relative percent difference $\text{RPD} = (D_1 - D_2)100 / [(D_1 + D_2) / 2]$ was <25% for non-purgeable organic carbon (NPOC), <15% for bicarbonate (HCO_3^-), sulphate (SO_4) and chloride (Cl), and Eh, < 10% for iron (Fe), <5% for manganese (Mn), <4% for Cr. Field duplicates for the hyporheic porewater at various depths had higher RPD, as has been observed by other authors (Nagorski and Moore, 1999).

3.2. Speciation analysis of chromium in water

The measurement of trivalent Cr(III) and hexavalent Cr(VI) forms in water samples was achieved through the coupling of a High Performance Liquid Chromatograph (HPLC, Dionex AS-50, GP40) consisting of a gradient pump and an autosampler, to an Inductively Coupled Plasma Spectrometer (ICP-MS, Agilent 7500cx). The 0.45 μm -filtered unacidified water samples were placed in an oven at 70 °C for 1.5 h with 15 mM EDTA, to complex Cr(III) and ensure separation of it from Cr(VI) on the anion exchange column (Hamilton PRP X-100, 250 mm \times 4.6 mm, 5 μm). Samples complexed with 15 mM EDTA were injected (100 μl) onto the HPLC anion exchange column and separated according to their affinity for the column and the mobile phase, which consisted of a gradient elution program using 4 mM and 60 mM NH_4NO_3 (with 5 mM EDTA), adjusted to pH 9.3 with ammonia. The eluent from the column was directly aspirated into the ICP-MS, which monitored the m/z ratio of Cr-52, using helium in the collision cell to minimise interferences on m/z 52. The analysis of each sample was completed within 9 min. Total Cr was measured on each sample acidified to 1% HNO_3 /0.5% HCl. The comparison of Cr speciation results by HPLC-ICP-MS to total Cr by ICP-MS generally provided good agreement of $112 \pm 4\%$ ($[\text{Sum of Cr species} \times 100] / \text{total Cr}$).

3.3. Sediment sampling and characterisation

Sampling of sediment depth profiles was undertaken with a

hand-auger at a time of very low tide at sites A and B in February 2012. Composite sediment samples were generated from five consecutive auger flights, spatially distributed across a 5 m line, collected in a plastic bucket and homogenised with a spatula. They were typically silty-clay sediments. Lithological descriptions were made and are reported in the [Supplementary Information Tables S1 and S2](#).

Chemical analysis of the freeze-dried <150 μm sediment fraction was carried out using mixed acid digestion ($\text{HF}/\text{HClO}_4/\text{HNO}_3$) and ICP-MS. The pH was analysed by a CaCl_2 /slurry method, organic matter content by loss on ignition (LOI) at 450 °C, and mineralogical analysis using X-ray diffraction (XRD).

Sub-samples of the bed sediment were examined by scanning electron microscopy (SEM) and Energy Dispersive X-ray Microanalysis (EDS) to determine the type of Cr-bearing phases found in sediments from the study area. Grains were mounted in epoxy resin blocks that were then ground using SiC abrasive discs and polished down to 1 μm using diamond-embedded polishing cloths, followed by coating with a thin layer of vacuum evaporated carbon. To observe the morphology and texture using the secondary electron (SE) imaging signal, grains were mounted onto sample holders and then sputter-coated with Pt metal.

During the February 2012 visit drive-in piezometers were installed in the east and west banks at site A. They were used for slug testing (rising head) to estimate hydraulic conductivity of the bank sediments.

3.4. Surface water quality synoptic sampling

The Polmadie Burn was sampled in February (21/02/2012 at 15:00) and September 2012 (26/09/2012, at 10:30, 13:10, and 15:00), between the point where the stream emerges from the culvert into Richmond Park and its outlet into the River Clyde (Fig. 1). The River Clyde was sampled at regular intervals throughout the day during the September survey. Five sampling points evenly distributed along the stream (locations 1 to 5 in Fig. 1) were sampled for water chemical analysis, as simultaneously as possible, by 4 different people along the 500 m stream segment. This ensured that the results provide a snapshot in time of the entire stream.

3.5. Equilibrium speciation model

The equilibrium aqueous speciation of Cr and mineral saturation states of surface and porewater samples were modelled with the Geochemist's Workbench software package (Bethke and Yeakel, 2014), with the thermo.minteq thermodynamic database, with site specific data inputs, in order to assist in the interpretation of the results by indicating possible mineral/aqueous stable (equilibrium) phases in a given scenario.

4. Results and discussion

4.1. Chromium speciation in surface water and porewater

Table 1 reports the averages and range of physicochemical parameters and elemental concentrations of surface water and porewater collected in February and September 2012 (full dataset in Table S3).

The mean total dissolved (<0.45 μm) Cr concentrations in porewater was 5.04 $\mu\text{g l}^{-1}$ (N = 36), with a range from 2.5 to 12.4 $\mu\text{g l}^{-1}$. Speciation analysis indicates that no Cr(VI) was detectable above the detection limit of 0.03–0.08 $\mu\text{g l}^{-1}$ in the porewater. In contrast, the mean total dissolved Cr concentration in surface water was 1090 $\mu\text{g l}^{-1}$ (N = 32), with a range from

Table 1
Averages and range of physicochemical parameters and elemental concentrations of surface water and porewater collected in February and September 2012 in the Polmadie Burn.

	Eh (mV)		pH		Cl ⁻ (mg l ⁻¹)		SO ₄ ²⁻ (mg l ⁻¹)		NO ₃ (mg l ⁻¹)		HCO ₃ (mg l ⁻¹)		NPOC (mg l ⁻¹)		Mn (μg l ⁻¹)		Total Fe (μg l ⁻¹)		Cr (μg l ⁻¹)	
	HZ	SW	HZ	SW	HZ	SW	HZ	SW	HZ	SW	HZ	SW	HZ	SW	HZ	SW	HZ	SW	HZ	SW
Mean	161	355	7.16	7.70	45.5	41.1	9.89	43.7	1.36	6.81	430	129	7.31	3.81	1670	64.4	6180	92.6	5.04	1090
Median	147	366	-	-	41.3	29.2	6.80	41.8	0.64	6.56	401	120	7.20	3.80	1760	66.5	7010	93.5	4.75	1110
Min	120	229	6.71	7.31	33.0	20.7	0.95	14.7	0.22	4.46	235	48.8	3.52	2.90	407	33.7	173	35.0	2.50	123
Max	249	413	7.72	8.03	78.2	94.9	60.4	80.0	4.38	9.42	622	198	13.00	5.34	2680	100.0	13500	203.0	12.40	2230
N	32	32	36	32	32	32	32	32	23	32	32	32	32	32	36	32	36	32	36	32

123 μg l⁻¹ to 2228 μg l⁻¹ and most of the Cr was Cr(VI) (Table 2). Surface waters had pH ranging from 7.31 to 8.03, while porewater pH values ranged from 6.71 to 7.15. Eh measurements were higher in surface water (from 229 to 413 mV) than in the streambed porewater (from 120 to 249 mV).

4.2. Hyporheic zone geochemistry

Fig. 3 compares the physico-chemical characteristics of the porewater from the multilevel samplers and surface water. Data are from all sampling points on all sampling occasions and from multiple sample depths; the non-parametric Mann-Whitney test in Minitab was used to determine whether two population medians are significantly different at $\alpha = 0.001$. The solutes Cr, HCO₃, SO₄, NO₃, Mn, Fe and NPOC were significantly different ($p = 0.000$) between surface water and porewater. These elements behave as non-conservative elements. Their concentration and distribution in the hyporheic zone depend on the balance between the rate of the controlling biogeochemical reactions within the hyporheic substrate versus the residence time of the hyporheic flow (Harvey et al., 2013). For Cl ions there was not a significant difference at $\alpha = 0.001$ between the population medians of Cl in porewater and surface water samples, suggesting Cl conservative behaviour through the hyporheic zone. As such, measurements of conservative Cl were used for making considerations on surface water - hyporheic zone connectivity in section 4.4.

Element concentration vertical profiles in the hyporheic porewater and overlying surface water at site A (21/2/2012) and site B (27/9/2012) are illustrated in Fig. 4 and Fig. 5 to give more details on the element distributions across the surface water-subsurface zone. These are snapshots of spatial distribution of surface water and porewater chemistry at the time of sampling. For site A, at ML A-1 a decreasing surface water - porewater vertical gradient for Eh, SO₄ and partially pH was observed, coupled with an increase in HCO₃, Mn, Fe. Total dissolved Cr concentrations decreased sharply at the water-sediment interface and then steadily with sediment depth, from 12.4 to 3.1 μg l⁻¹. For ML A-2, a sediment depth concentration gradient was less obvious, but porewater concentrations were distinctively offset from surface water, especially with lower Eh, pH and SO₄ and higher HCO₃, Mn and Fe concentrations. ML A-2 porewater dissolved Cr concentrations ranged from 2.9 to 6.2 μg l⁻¹. At site B, the porewater from the multilevel piezometers across the streambed exhibited concentrations of HCO₃, Mn, Fe and NPOC increasing at depth. Concentrations of Cr were also very low, ranging from 2.5 to 5.6 μg l⁻¹. A Cr increase with depth was observed and coincided with maxima in the Fe, Mn and NPOC depth profiles (Fig. 5). Overall, similar patterns in surface water - hyporheic zone element concentration gradients were observed at each of the sampling locations, with a decrease in pH, Eh, NO₃, and SO₄ coupled with an increase in HCO₃, Mn, and Fe at the water-sediment interface and with depth. This reflects a biogeochemically reactive hyporheic zone with predominant redox

Table 2
Chromium speciation analysis.

Sample type	Site	Date	HPLC data			Total	
			CrVI	CrIII	(CrIII + VI)	Cr (F/A)	Recovery
			μg l ⁻¹	μg l ⁻¹	μg l ⁻¹	μg l ⁻¹	%
SW	Point 5	26/09/2012	470	3.23	473	477	99
SW	Point 5	26/09/2012	863	40.9	904	980	92
SW	Point 1	26/09/2012	1591	<0.05	1591	1531	104
SW	Point 2	26/09/2012	1439	0.32	1439	1404	103
SW	Point 3	26/09/2012	1429	<0.05	1429	1398	102
SW	Point 4	26/09/2012	1278	<0.05	1278	1128	113
SW	Point 4	26/09/2012	906	<0.05	906	1123	81
SW	Point 5	26/09/2012	918	<0.05	918	1140	81
SW	River Clyde	26/09/2012	<0.05	0.31	0.31	1.68	18
SW	Site A	26/09/2012	2060	<0.05	2060	2293	90
SW	Site B	26/09/2012	1890	42.7	1932	2025	95
HZ	Site A	21/02/2012	<0.04	3.89	3.85	5.93	65
HZ	Site A	21/02/2012	<0.06	3.12	3.06	3.19	96
HZ	Site A	21/02/2012	<0.07	5.59	5.52	5.61	98
HZ	Site A	21/02/2012	<0.03	4.81	4.79	5.80	83
HZ	Site A	23/02/2012	<0.03	5.37	5.34	6.66	80
HZ	Site A	23/02/2012	<0.04	5.01	4.97	7.65	65
HZ	Site A	23/02/2012	<0.08	4.36	4.28	7.95	54
HZ	Site B	26/09/2012	<0.05	0.27	0.27	1.6	17
HZ	Site B	26/09/2012	<0.05	<0.05	<0.05	2.48	-
HZ	Site B	26/09/2012	<0.05	0.28	0.28	0.8	35
HZ	Site B	26/09/2012	<0.05	0.27	0.27	1.1	24

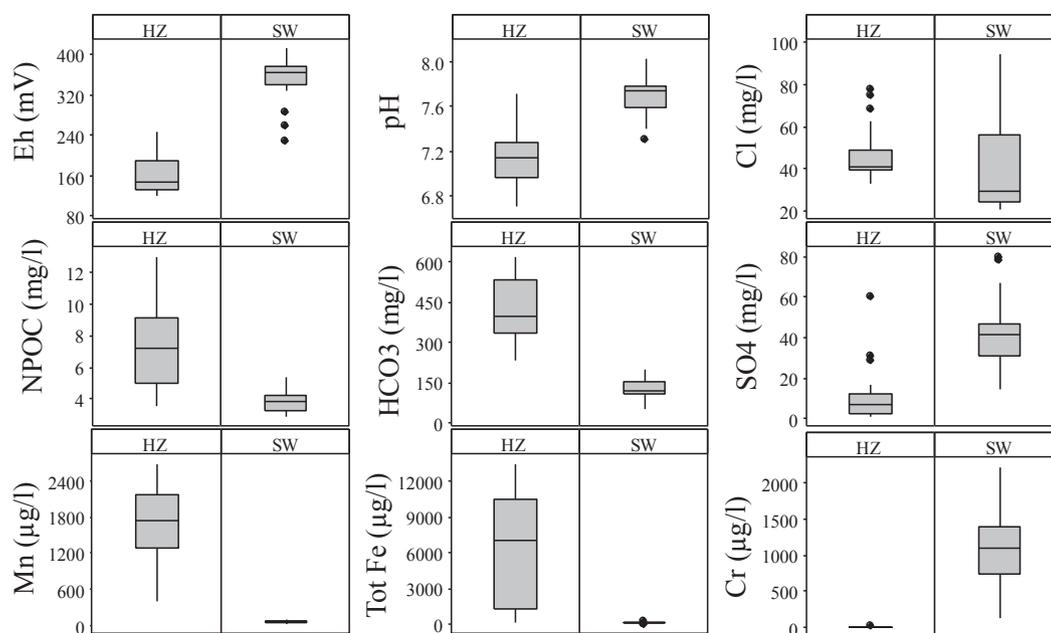


Fig. 3. Box plots comparing Eh, pH and concentrations of selected constituents in the hyporheic zone porewater (HZ) and surface water (SW) at the study area. Boxes are within the lower and upper quartile distribution and show the mean value.

processes, likely involving organic matter degradation, affecting the sediment porewater chemistry of non-conservative elements. In the sediments, during oxidation of organic matter, the thermodynamically most favourable primary electron acceptors are O_2 , followed by nitrates, manganese oxides, iron oxy-hydroxides and sulphates in order of decreasing energy release during reaction (Appelo and Postma, 2005). The hydraulic permeability of the bank sediments and representative of the stream bed sediments, as derived from slug tests performed in standpipe piezometers installed on both sides of the stream, was low, with a transmissivity (T) between 0.01 and $0.06 \text{ m}^2 \text{ day}^{-1}$. The combination of low permeable sediments and accumulation of vegetation on the bed sediments are known to reduce the surface-subsurface water exchange (Argerich et al., 2011) and could create conditions favourable for the anaerobic degradation of organic matter, thus accounting for the observed vertical trends. The reduction of nitrates was resolved close to the surface water – sediment interface. Porewaters were particularly enriched in dissolved Fe, mainly as Fe(II) (60–85% of the total Fe). The Fe concentrations in anoxic sediment porewater depends on the availability of iron oxy-hydroxides to supply Fe(II) by reduction and of sulphates to reduce and precipitate iron sulphides, and their respective reaction kinetics. The peak concentrations of Fe in porewater with depth suggested that the reduction of iron oxyhydroxides dominates over the precipitation of iron sulphides. This is either due to increased availability of reactive sedimentary iron in the sediment with depth or to the consumption of all infiltrating sulphate at shallower depths by sulphate reducers. An apparent difference between the geochemical depth profiles of ML A-1, the multilevel closer to the bank, and ML A-2, closer to the centre of the channel, suggests a more biogeochemically active hyporheic zone towards the centre of the channel.

Sediments were also sampled to identify sinks and sources for Cr in the hyporheic zone. The sediments size fraction $<150 \mu\text{m}$ contained elevated concentrations of Cr ranging from 1100 up to 8800 mg kg^{-1} (Table S4), confirming what had been highlighted by the regional geochemical survey of the Clyde catchment (Fordyce et al., 2004). Soil pH ranged from 6.53 to 7.00. Organic matter

content, determined as LOI, ranged from 9.8 to 22% w/w, with samples lower in the profiles containing less organic material. Iron ranged from $4.6 \cdot 10^3$ to $6.5 \cdot 10^3 \text{ mg kg}^{-1}$ and Mn from 570 to 1200 mg kg^{-1} . Sulphur ranged from 1270 to 6400 mg kg^{-1} and was shown to be more enriched at depth. Bulk mineralogy by XRD indicates quartz, feldspars and pyroxene as the major mineral phases with the presence of abundant amorphous material. Although XRD analysis did not show any Cr-bearing minerals, SEM analysis of sediment grains from the bed sediment revealed important insights regarding solid Cr-host phases in the sediment. Chromium was present in crystalline banded rims with the appearance of high-temperature alteration haloes on grains previously identified as COPR (Hillier et al., 2003). These crystalline haloes, composed of Ca, Fe, Cr, Al and O (Fig. 6d), possibly brownmillerite ($\text{Ca}_2(\text{Fe,Al})_2\text{O}_5$ with Cr(III) substituting for Fe, Al), are easily recognised for their very bright back-scattered electron (BSE) signal (Fig. 6a). These observations clearly indicate the presence of detrital COPR waste material in the streambed sediment, which contributes to the high Cr concentrations measured in the solid samples. However, the very low Cr concentrations in porewater suggest the mineral phases associated with the COPR were not having an important role in enhancing pore water Cr content under the study conditions. Other coatings enriched in Cr were common, the massive texture with signs of desiccation cracks suggesting the presence of hydrated material (Fig. 6b and c). EDS spectra indicate that most coatings comprised Cr, Ca, Fe, S, P and O (Fig. 6e). Similar elemental associations in grain encrustations in contaminated stream and estuarine sediments were seen by Moles et al. (2003). Fine-grained aggregates comprising Cr-rich host phases, too small to be clearly identified by SEM, were also abundant. We could not ascertain definitely whether Cr was simply detrital (residual COPR waste clasts) or also authigenic, as a result of in-situ reactions with Cr-enriched aqueous fluid and further precipitation in the hyporheic zone; however, SEM observations show coating textures that could have not survived significant transport and the presence of abundant quartz grains (not so common in the COPR material, Hillier et al., 2003) coated by Cr-rich rims; they are, therefore, considered evidence of in-situ formation. SEM analysis also showed

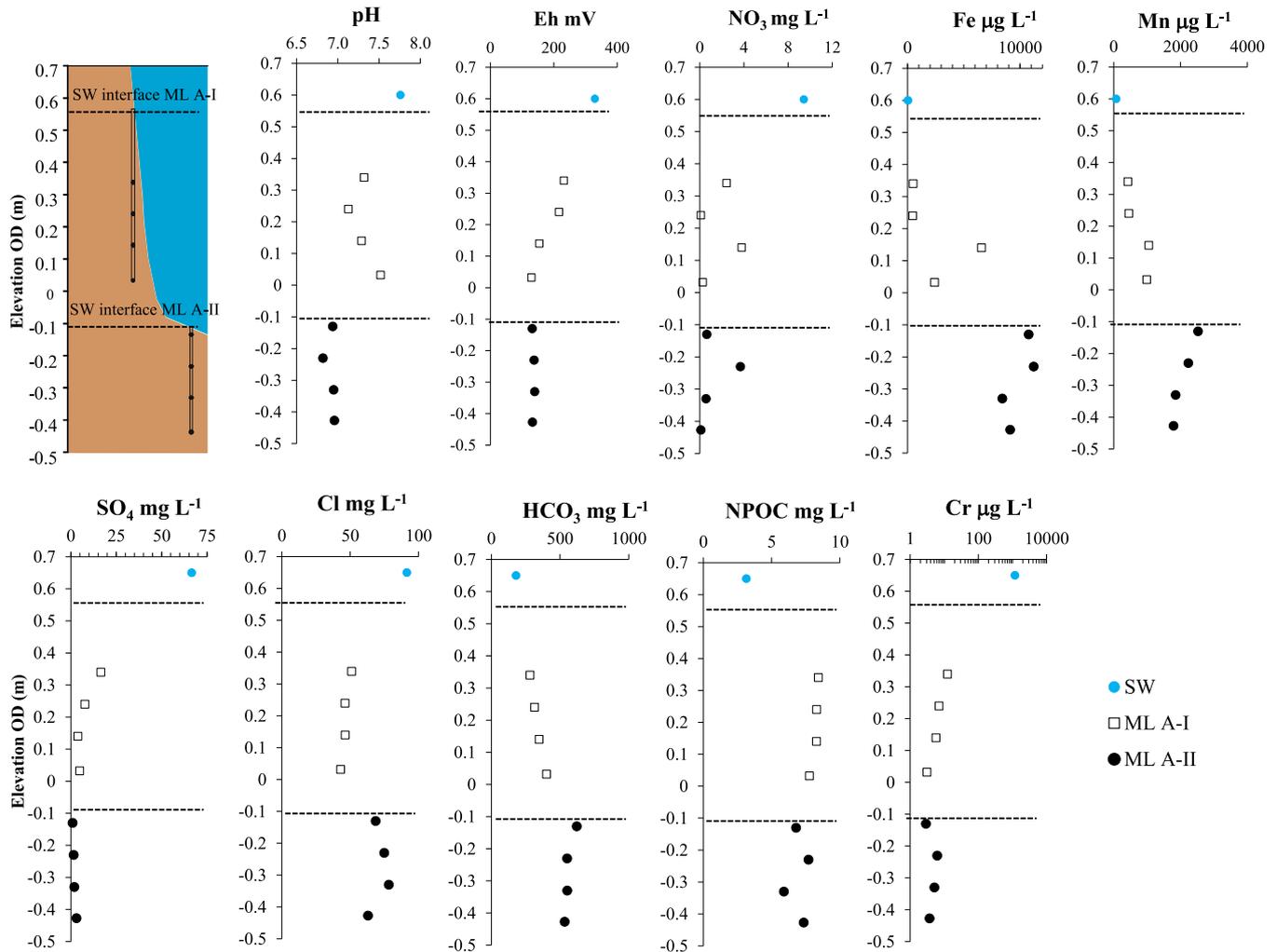


Fig. 4. Porewater vertical element concentration profiles at site A from multilevel piezometers. The multilevel piezometer ML A-I was sampled on the 21-Feb-12 (16:30) at low tide; ML A-II was sampled on the 21-Feb-12 (17:00). “SW Interface” dotted line indicates the sediment - water boundary. OD: Ordnance Datum (sea level).

several occurrences of framboidal Fe-sulphide, indicative of reducing redox conditions.

4.3. Chromium behaviour in the study hyporheic zone

The sharp decrease of total dissolved Cr concentrations from thousands to tens of $\mu\text{g l}^{-1}$ (Figs. 4 and 5) at the surface water – sediment boundary and the disappearance of Cr(VI) in the hyporheic porewater was featured in all profiles. This decrease was two orders of magnitude larger than the corresponding decrease in SO_4 , suggesting favourable conditions for the enhanced removal of Cr solute, compared to other non-conservative solutes such as e.g. SO_4 , in the hyporheic zone. Fig. 7 shows the predominance of aqueous Cr species and stability of Cr minerals as function of pH and Eh, in presence of Fe(II) at concentrations found in the porewater. Although the use of stability diagrams does not preclude the possible presence of metastable phases containing Cr(VI) subjected to kinetic controls, it is clear that all porewater samples fall in the thermodynamic stability field of $\text{Cr}(\text{OH})_3$. This supports the suggestion of natural attenuation of total dissolved Cr in the hyporheic zone by Cr(VI) reduction with subsequent precipitation of Cr(III) solid phases. Organic matter, dissolved Fe(II), various Fe(II) bearing mineral phases and dissolved sulphides are capable

of reducing Cr(VI) (Graham and Bouwer, 2009; Wadhawan et al., 2013 and references within). Fe(II) is found an effective reductant of Cr(VI) under most soil and water conditions, even in oxygenated, high-pH systems (Fendorf and Li, 1996). Furthermore, the reduction of Cr(VI) to Cr(III) by Fe(II) is rapid and can go to completion in a matter of minutes (Eary and Rai, 1989). Under the prevailing conditions at the study site, with porewater Fe (II) being so high, any Cr(VI), supplied to the porewater through COPR mineral phase dissolution or advective exchange/diffusion mechanisms at the surface water/sediment interface, is expected to be readily reduced to Cr(III), according to the general expression $\text{Cr}(\text{VI})_{(\text{aq})} + 3\text{Fe}(\text{II})_{(\text{aq})} = \text{Cr}(\text{III})_{(\text{aq})} + 3\text{Fe}(\text{III})_{(\text{aq})}$. As previously noted, the observed authigenic Cr-rich rims on particles supported active Cr precipitation from solution in the sediments. The result of Cr reduction by Fe(II) and subsequent sequestration in the form of Cr-Fe hydroxides by the sediments is likely to lead to the accumulation of Cr and Fe in the sediments. In our samples, correlation between Fe and Cr was moderate $r = 0.831$ ($p = 0.01$) (Fig. S4), possibly as a result of various contributions to the total concentrations of Cr and Fe, other than the freshly precipitated oxides. A selective or sequential extraction of the sediments to identify Cr association to solid phases would be able to indicate more clearly a relationship. Concentration depth profiles (Table S4) were instead

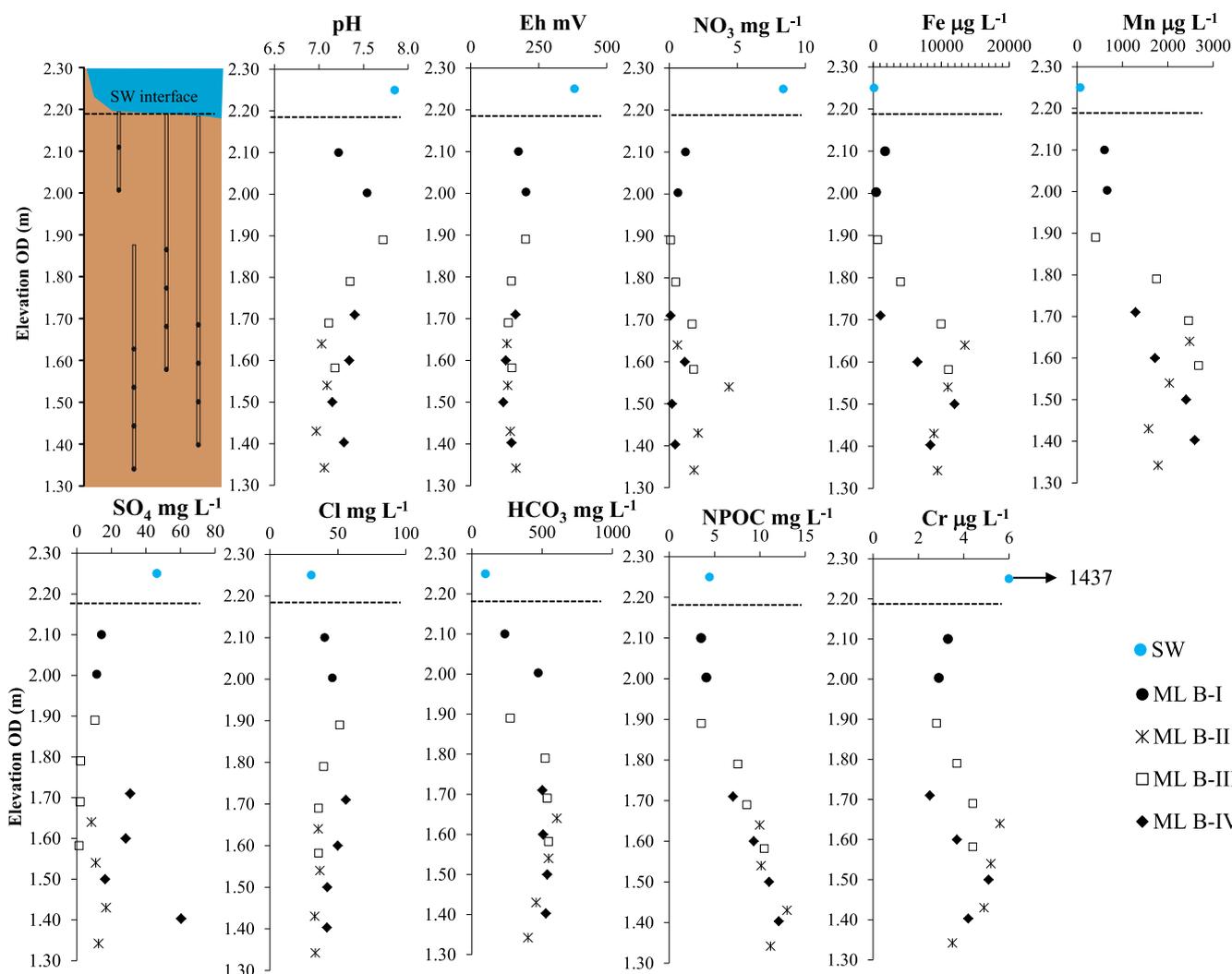


Fig. 5. Porewater vertical element concentration profiles at site B from multilevel piezometers. "SW Interface" dotted line indicates the sediment - water boundary. OD: Ordnance Datum (sea level).

inconclusive in demonstrating that the sediment accumulates Cr from surface water, as the highest level of Cr were recorded not in the uppermost layers, but between 0.20 and 0.90 m depth at site A and 0.30–0.55 m depth at Site B. This could be the result of a larger portion of detrital Cr at greater depth.

Despite the very low dissolved Cr concentrations ($<13 \mu\text{g l}^{-1}$), modelled saturation indices for porewaters indicate that they remained oversaturated in $\text{Cr}(\text{OH})_3$ and FeCr_2O_4 . Values exceeding the solubility limits could be attributable to organically complexed Cr(III) (Gustafsson et al., 2014). A contribution to the dissolved 0.45 μm fraction of the colloidal size fraction, in which Cr(III) sorbed or precipitated is transported as colloidal fraction, cannot, however, be excluded. A decrease of porewater Cr with sediment depth was accompanied by a slight increase at overall greater depths, concomitant to Fe peaks in solution (for September porewater $r_{\text{Cr-Fe}} = +0.909$ ($p < 0.001$), Fig. S3). Previous studies on marine and estuarine sediments have reported a similar pattern of total Cr concentrations increasing with depth (Brumsack and Gieskes, 1983; Douglas and Quinn, 1988). The mechanism proposed involves the reductive dissolution of Cr(III)-bearing mineral phases, likely iron oxyhydroxides, and mobilisation of Cr(III) as Cr-organic matter complexes (Brumsack and Gieskes, 1983).

4.4. Hyporheic connectivity and response to stream stage changes

Temporal sampling of multilevel ML A-I during a spring tidal cycle (Fig. S1) in the February fieldwork provided insights on: (i) the hyporheic flowpaths using natural tracers such as Cl, and (ii) the response of the hyporheic porewater composition to short-term temporal changes of stream stage and stream composition at the observation point. The sediments remained temporally exposed (on 21/02/12) and then submerged during the tidal cycle. On the basis of the observed spatial variation at site 1, ML A-I, the multilevel closer to the bank, was more likely to respond to the stream stage fluctuation.

Measurements of Cl through the hyporheic zone with respect to surface water under the different sampling times were used for making assessments of hyporheic connectivity. Assuming the conservative nature of Cl, porewater Cl concentration would reflect the surface water – porewater mixing processes (Engelhardt et al., 2011) and the vertical gradients in the streambed would vary mainly as a result of the extent of mixing. For a hyporheic zone well connected to surface water, it could be expected a uniform surface water - hyporheic porewater Cl concentration profile, with surface water compositional temporal changes mirrored in the hyporheic

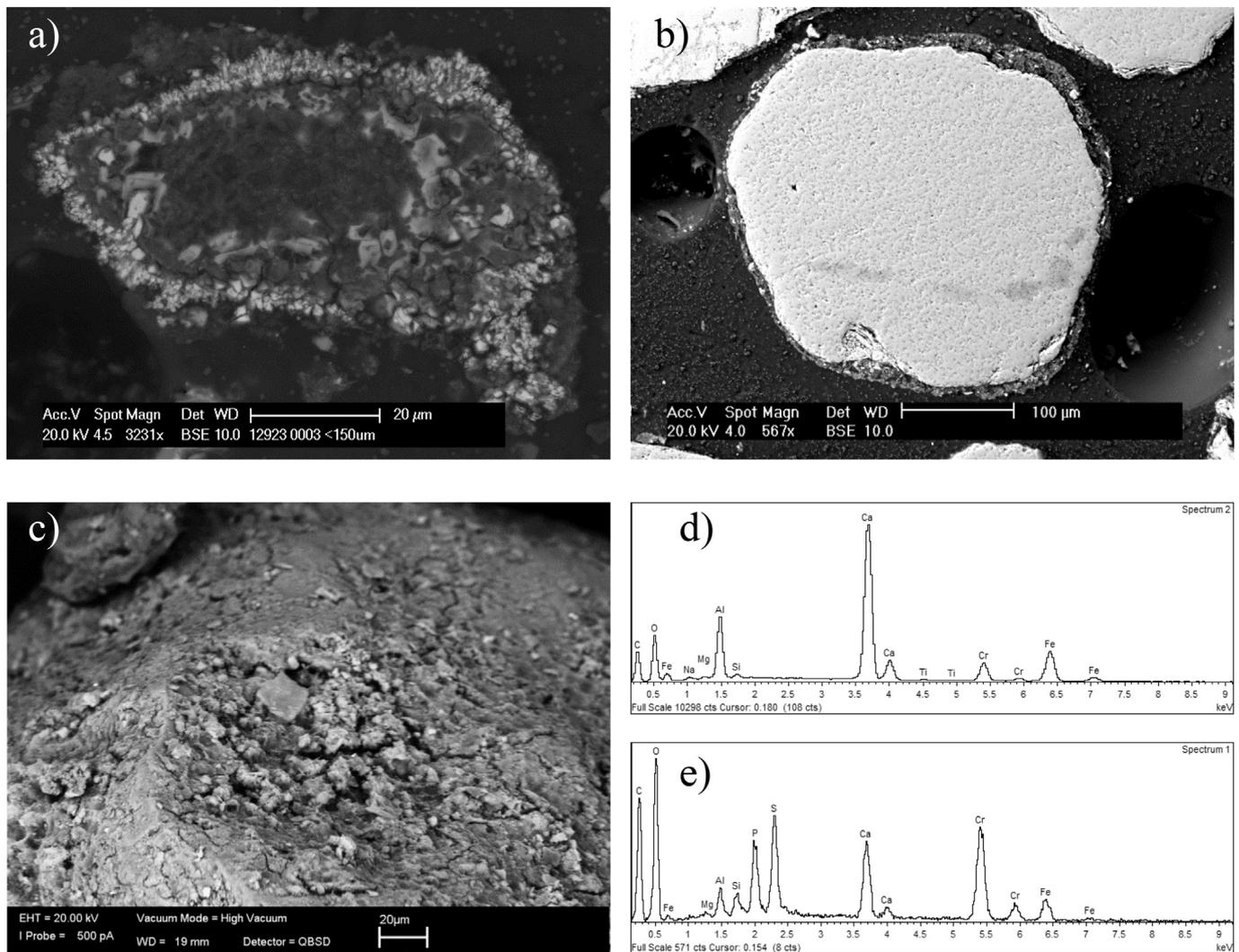


Fig. 6. Back-scattered electron (BSE) images of a) polished section of relict grain of the primary COPR with the presence of Cr in crystalline rims with the appearance of high-temperature alteration haloes; EDX spectrum of the very bright BSE external rim is shown in d); b) polished section of quartz grain with a coating enriched in Cr with a fairly constant composition shown in e); c) detail of the coating massive texture.

zone. However, the large changes in Cl concentrations measured in surface water during the tidal cycle (relative standard deviation, RSD, of 47%) were only weakly reflected in the hyporheic porewater (RSD decreasing from 10% to 4% with sediment depth, and within the field duplicate repeatability), albeit with highest and lowest Cl concentrations in the surface water occurring at the same time as in the porewater (Fig. 8). Chloride patterns were also mirrored by Eh, sulphate and Cr. The observed subtle variations at 20 cm below the sediment surface disappeared at greater depth (50 cm). These results suggest only limited advective exchange/surface water infiltration and long residence times of the hyporheic flow. This is in accordance with the low sediment hydraulic conductivity measured. As a result, the hyporheic zone composition integrates the surface water solute concentrations over time and reflects the effects of biogeochemical processes, enhanced by low resident time of the water flow. Past research in the hyporheic zone (Harvey, 2016 and references within) has shown that small changes in stream stage can affect the vertical exchange of surface water with the streambed and compositional changes in the hyporheic zone. Increases in stream stage have been shown to reverse hydraulic gradients in gaining streams allowing surface water infiltration into the streambed (Malcolm et al., 2004; Zimmer and Lautz, 2013).

Wildman et al. (2010) also demonstrated that sediment exposure and submersion during changing water levels in a reservoir shoreline may result in changes in the sediment porewater redox geochemistry. From our monitoring, it was evident that at the study location the response of the hyporheic zone geochemistry to fluctuating stream stage was instead weak, due to only limited exchange between surface water and hyporheic porewater. It is noticeable that sediments remained moderately reducing even after exposure to air and Cr porewater concentration remained low and largely unaffected by sediment exposure to air and subsequently submersion (sampling on 21/02/12 ML A-I at 16:30).

4.5. In-stream hydrological responses

The surface water level of the Polmadie Burn was influenced by both rainfall events and diurnal tidal cycles of the River Clyde, 40 m downstream. Surface water chemistry was examined in two sampling periods: one in February where the stream water levels varied significantly within the diurnal spring tidal cycles; and a second sampling period in September, where the tidal variations were lower, being within neap tidal phase; an antecedent rainfall event the day before sampling was also registered. The documented

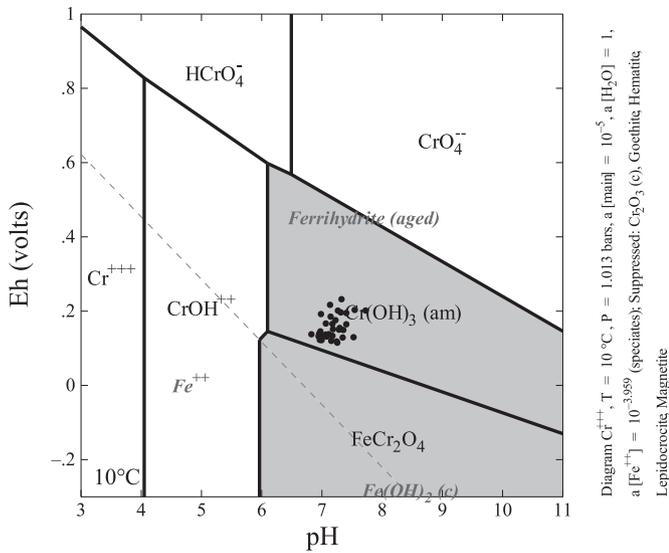


Fig. 7. Eh-pH phase diagram showing equilibrium between aqueous chromium species and chromium mineral phases (grey shaded areas) at initial tot Cr = 10^{-5} M ($519 \mu\text{g l}^{-1}$) and in presence of porewater Fe(II) = 1.1×10^{-4} M ($6200 \mu\text{g l}^{-1}$). Precipitation of thermodynamically stable Cr_2O_3 was suppressed in favour of the more reactive solid phase $\text{Cr}(\text{OH})_3$. Iron ions were allowed to speciate over x and y axes and the dashed lines delineate Fe stability fields (in italics) (suppressed magnetite, hematite, goethite and lepidocrocite in favour of ferrihydrite (aged)). Porewater samples are indicated by a solid circle.

temporal variability in stream water level and surface water chemistry during the sampling events is reported in supplementary information (Fig. S5). Spatial patterns of conservative and non-conservative solute concentrations obtained by surface water synoptic sampling of the Polmadie Burn were used to collect supporting evidence of potential whole-stream contaminant attenuation processes. Large spatial variations in Cr concentrations along the Polmadie Burn were highlighted (Fig. 9). In February a sharp decrease in Cr concentrations beyond 170 m (point 3 from Fig. 1) downstream from the “culvert” (point 1) was mirrored by a similar decrease in most of the major and trace element concentrations, including Cl (Fig. 9), Ca, Mg, Sr, Mn and Fe. The relative standard difference of Cr concentrations across the burn was 26% and at the outlet into the River Clyde (point 5) the % difference from point 1 was 41%. In September, the relative standard difference of Cr concentrations across the burn was 17%, 13%, and 9%, respectively, for the 10:30, 13:10, and 15:00 sampling times. The % difference between point 1 and point 5 was 32% (at 10:30), 28% (at 13:10), and 18% (at 15:00 sampling time). A decrease was, however, not generally observed for conservative elements such as Na, Cl. The subtle Cl concentration decrease from point 4 and 5, only for sampling time 15:00, was within the analytical error of the Cl measurements.

Under synoptic (i.e contemporaneous) sampling, the principal processes for downstream reductions of solute concentrations in stream water are i) dilution by augmented flow by tributaries and groundwater seeps (if low in those solutes), and/or ii) mass loss by

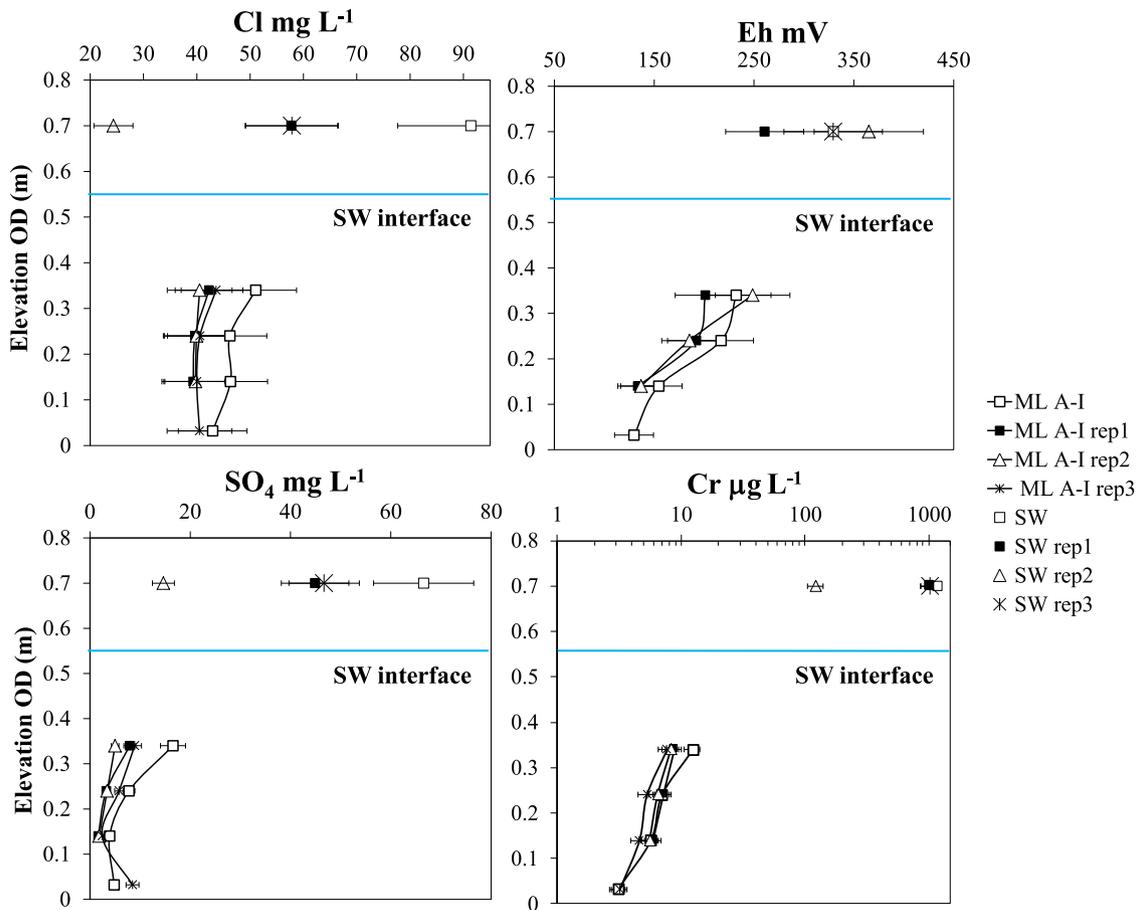


Fig. 8. Temporal variation of porewater Eh, Cl, SO_4 and Cr concentration profiles from multilevel ML A-I with respect to concentrations in surface water (error bars representing repeatability of the field measurements). OD: Ordnance Datum (sea level).

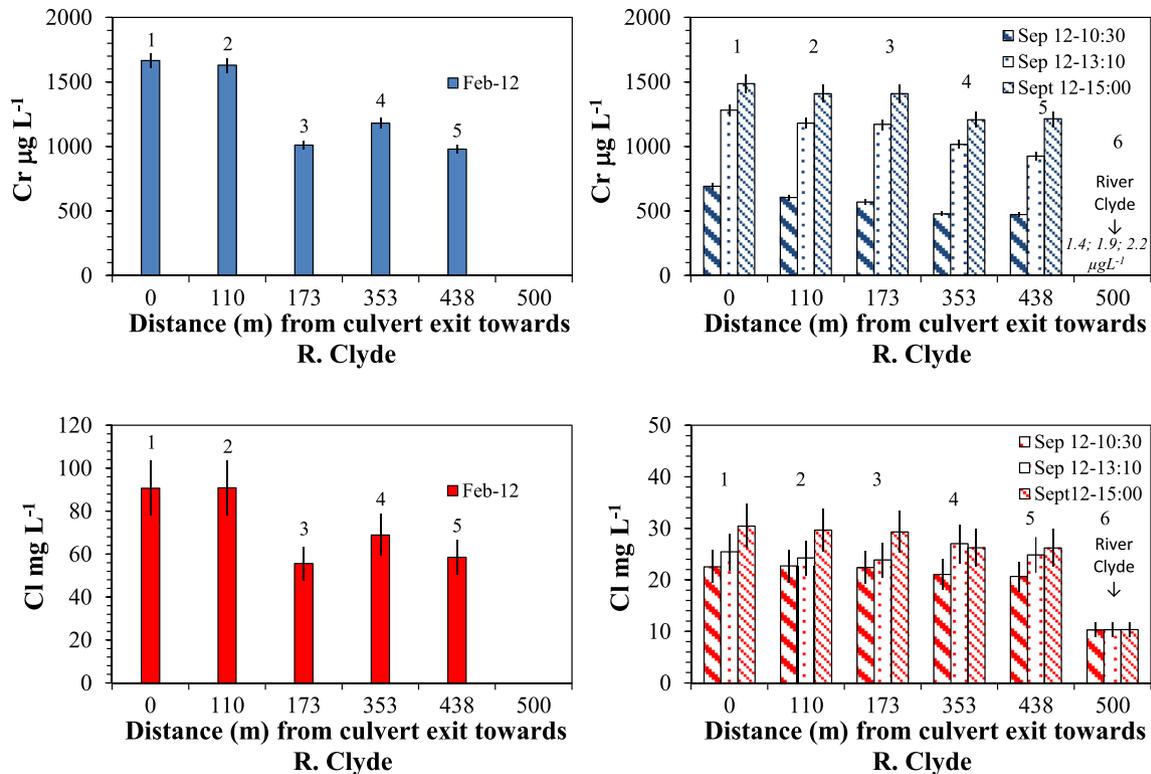


Fig. 9. Spatial variation of dissolved Cr, and Cl concentrations along the Polmadie Burn to the River Clyde during two sampling visits (standard error bars 5% for Cr and 14% for Cl). 1 to 6: sampling points as per Fig. 1.

chemical precipitation and adsorption of dissolved solutes on suspended particles or through hyporheic sediments (Chapman et al., 1983). Stream flow gauging could not be carried out at the time of the synoptic sampling. In the absence of flow measurements, in-stream Cr metal loads, sources and losses, according to the methods illustrated in Kimball et al. (2002) and Runkel et al. (2013), among others, could not be quantified in our study. Yet, on a qualitative basis, considerations of the hydrology at the time of the site survey and of the site hydrogeology were made. An inspection of the entire stream length did not reveal any evidence of flow inputs to the stream through tributaries or seepages or water diversions in the sampled reach. Low permeability clays and silts (alluvium) and/or cohesive glacial till were considered also to present a barrier to significant groundwater flow gains or losses along the stream. On this basis, we inferred little contributions or losses to the total flow along the stream during the September synoptic sampling. Then, the decrease in Cr concentration downstream from the culvert exit, not observed for conservative elements, may indicate in-stream attenuation by solute precipitation and/or adsorption. The extent of attenuation, although low to moderate, varied through the three sampling events in the day and demonstrates the temporal heterogeneity of in-stream processes in the study stream. In February, however, a tidal wave was recorded. Then, the congruent decrease of conservative and non-conservative elements downstream the culvert point in February suggests that we captured a snapshot of the rising tide moving upstream into the burn, reducing the head and therefore the flow rate in the burn; and plausibly causing dilution by mixing of the stream water with the River Clyde waters at sample points 5, 4, and possibly point 3. Overall, the significance of the September events in attenuating by mass loss Cr concentrations in the burn was, however, low and subordinate to the previously observed effect of tidal mixing/dilution during the February sampling. The specific stream

compartments (e.g. hyporheic zone, suspended sediment, vegetation) contributing to the attenuation processes are difficult to discern on the basis of stream water quality measurements only and further combined water quality-flow monitoring and use of tracer injection tests (Runkel et al., 2013) are desirable to corroborate these findings.

5. Conclusion

In this study we provided field-based evidence of Cr(VI) absence in the hyporheic zone of a Cr contaminated urban stream. The pH-neutral anoxic sediment was capable of reducing Cr(VI) to Cr(III) due to the abundance of reductants like Fe(II) within the porewater. The hydrological setting of this short length of urban stream was complex and variable, being influenced by both tidal effects and a 'flashy' catchment response to storm events. In this setting, surface water high Cr(VI) concentrations varied greatly, spatially and temporally. In contrast, results from this study indicate that the large variability in the stream flow regime and solute chemistry did not affect the composition of the hyporheic zone and Cr. Conservative Cl concentration gradients suggested limited connectivity and long residence times of solutes in the hyporheic zone to account for the observed patterns. This is consistent with the low sediment hydraulic conductivity measured. As a result of limited hyporheic exchange, the hyporheic processes may be less effective for enhancing stream water quality due to transport limitations (Harvey et al., 2013). Although not unequivocally a measure of solute loss and hyporheic solute attenuation, we measured in parallel that the downstream decrease in surface water Cr concentrations in one of the sampling event (September) was only moderate to low (18–32%). A full evaluation of the significance of what was observed at reach-scale warrants long-term monitoring, combining hydraulic and chemical characterisation of the stream system at a

wider range of temporal and spatial scales (Bencala et al., 2011). Nevertheless, our findings contribute to a better understanding of the natural attenuation capacity of the hyporheic zone in urban streams with similarities to the study site and could be used to inform remediation strategies and manage risks. In particular, river restoration design efforts are often directed towards enhancing hyporheic exchange and adjusting residence time (Harvey et al., 2013; Herzog et al., 2015) to reach optimal conditions between hyporheic flux/stream discharge and rate of reactions of chemicals. In the case of Cr, where the attenuation is due to Cr(VI) to Cr(III) reduction, consideration should be given to preserve porewater electron donors required for this, as too short hyporheic residence times might inhibit the formation of anoxic zones, depending on site specific conditions.

The streambed sediments were found to be noticeably enriched in Cr and containing COPR grains. These sediments represent a concern over the potential for Cr(VI) reoccurrence during sediment resuspension and oxygenation. Batch reaction experiments by Magar et al. (2008), aimed at assessing the reactivity to re-oxidation of Cr(III) products under processes relevant to sediment bioturbation, dredging and flood events, have shown no signs of Cr(III) oxidation for aged sediments containing Cr(III) (hydro)oxides. Instead, Cr(VI) release was observed during resuspension and aeration of reduced Cr-spiked sediments by Wadhawan et al. (2013); Cr(III) oxidation by Mn (III; IV) (hydr)oxides being the underlying mechanism. In our study we found that Cr porewater concentration remained low and largely unaffected by sediment exposure to air and subsequently submersion. This is an area that requires further investigation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apgeochem.2017.02.011>.

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