

Chromium speciation and fractionation in ground and surface waters in the vicinity of chromite ore processing residue disposal sites

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Chromium concentrations of up to 91 mg l⁻¹ were found by ICP-OES for ground water from nine boreholes at four landfill sites in an area of S.E. Glasgow/S. Lanarkshire where high-lime chromite ore processing residue (COPR) from a local chemical works had been deposited from 1830 to 1968. Surface water concentrations of up to 6.7 mg l⁻¹ in a local tributary stream fell to 0.11 mg l⁻¹ in the River Clyde. Two independent techniques of complexation/colorimetry and speciated isotope dilution mass spectrometry (SIDMS) showed that Cr was predominantly (>90%) in hexavalent form (Cr^{VI}) as CrO₄²⁻, as anticipated at the high pH (7.5–12.5) of the sites. Some differences between the implied and directly determined concentrations of dissolved Cr^{III}, however, appeared related to the total organic carbon (TOC) content. This was most significant for the ground water from one borehole that had the highest TOC concentration of 300 mg l⁻¹ and at which <3% of Cr was in the form of Cr^{VI}. Subsequent ultrafiltration produced significant decreases in Cr concentration with decreasing size fractions, e.g. <0.45 μm, <100 kDa, <30 kDa and <1 kDa by the tangential-flow method. As this appeared related more to concentrations of humic substances than of TOC *per se*, horizontal bed gel electrophoresis of freeze-dried ultrafilter retentates was carried out to further characterise the Cr^{III}-organic complex. This showed for the main Cr-containing fraction, 100 kDa–0.45 μm, that the Cr was associated with a dark brown band characteristic of organic (humic) matter. Comparison of gel electrophoresis and FTIR results for ultrafilter retentates of ground water from this borehole with those for a borehole at another site where Cr^{VI} predominated suggested the influence of carboxylate groups, both in reducing Cr^{VI} and in forming soluble Cr^{III}-humic complexes. The implications of this for remediation strategies (especially those based on the addition of organic matter) designed to reduce highly mobile and carcinogenic Cr^{VI}O₄²⁻ to the much less harmful Cr^{III} as insoluble Cr(OH)₃ are discussed.

Introduction

From 1830 to 1968, over 2 million tonnes of chromite ore processing residue (COPR) were used as landfill at various locations in S.E. Glasgow, including Rutherglen and Cambuslang in what is now South Lanarkshire.^{1,2} The Cr content of this residue is high at 3–4% w/w but, more significantly, elevated concentrations as high as ~1% w/w of highly toxic and carcinogenic hexavalent Cr, which takes the form of chromate (Cr^{VI}O₄²⁻) at the prevailing high pH of 9–12 characteristic of high-lime COPR residue, have been measured in the solid phase at the contaminated sites.^{1,2} Although, until recently,^{3–5} the specific mineral phases and mechanisms responsible for its retention and release were not fully understood, Cr^{VI} continues to leach in significant quantities from the COPR disposal sites, with the result that receiving ground and surface waters in the area are contaminated at concentrations of up to ~150 mg l⁻¹ and ~10 mg l⁻¹, respectively, about 200–3000 times greater than Environmental Quality Standards.^{1,2,6–8}

In the course of a larger study aimed at the assessment and modelling of the behaviour, transport and impact of Cr at these sites,^{1,3–5,9–15} we have obtained data, reported here, on the speciation of Cr in receiving waters, involving not only determination of Cr^{VI}O₄²⁻ by the conventional diphenylcarbazide (DPC)-UV/VIS spectrometric method¹⁶ but also by speciated isotope dilution mass spectrometry (SIDMS), using ICP-MS.^{17–19}

These approaches also permit the inferred (by difference from the ICP-OES-determined total Cr) and direct measurement, respectively, of the much less toxic trivalent species Cr³⁺. Observed discrepancies at one location between total Cr (using ICP-OES) and the sum of Cr^{VI}O₄²⁻ and Cr³⁺ concentrations (using SIDMS/ICP-MS), along with significant reductions in the total Cr concentration upon acidification, led us to postulate the presence of Cr^{III}-organic complexes in ground water at this location.^{3,10}

Although the existence of such complexes in the aqueous environment has been suggested previously, there has been only limited success in terms of their specific characterisation.^{20–36} Here, as Cr^{III}-organic complexes may be important, not only to understanding the behaviour of Cr in receiving waters at some locations, but also with respect to the potential application of remediation methods based on the reduction of Cr^{VI} using, or stimulated by, organic matter,^{37–46} this study has incorporated further analytical investigation *via* techniques such as ultrafiltration, gel electrophoresis, FTIR and SEM-EDX. We have recently shown gel electrophoresis to be of value in the investigation of actinide-humic complexes in soils.⁴⁷ The findings of this Cr study, reported here along with a comprehensive presentation of Cr speciation and other relevant data for these COPR-contaminated sites, may also be significant with respect to Cr behaviour and the remediation of Cr-contaminated sites elsewhere in the world.^{38,48–50}

Experimental

Sampling

Four former COPR disposal sites, Duke's Road Playing Fields (Site 2), Rutherglen Glencairn Football Club (Site 4), Rosebery Park (Site 7) and Myrtle Park (Site 14) (Fig. 1), were used for the collection of ground water samples. Site 2 (6.5 ha), formerly a quarry but now comprising former football pitches, a playground and open space, consists of made ground overlying sandy clay overlying Carboniferous Coal Measures, with chemical waste infill material to depths of 2–10 m and groundwater at 3–11 m below ground level. Site 4 (2.5 ha), adjacent to the former J.J. White's chemical works, comprises a completely grassed football pitch, football club building, football terraces (formed from COPR) and open spaces, with made ground overlying sands, clays and silts overlying Carboniferous Coal Measures. Apart from the pitch, the remainder of the site is unsealed or sparsely vegetated and, although mostly flat-lying, there is a steep embankment sloping down to railway lines. With groundwater levels at 1.7–7.4 m from the surface, borehole (BH) 401 is adjacent to the terraces and BH 402 is at the top of the slope leading down to the railway line. Site 7 (1.5 ha) is an infilled clay pit, now comprising a disused football ground, terraces and stands, with made ground overlying alluvial sands and clays above Carboniferous Coal Measures. Groundwater lies at approximately 2 m below the ground level and the Malls Mire Burn is 200 m east of the site. Site 14 (3.5 ha) is an infilled clay pit with made ground overlying silty clays and glacial till overlying Carboniferous Coal Measures. Groundwater lies at 1–2 m below ground level and the Malls Mire Burn culvert is 200 m to the east of the site.²

Groundwater samples, collected from boreholes (BH) 201, 202, 204 (Site 2), 401, 402 (Site 4), 702 (Site 7), 1403, 1485 and 1490 (Site 14) during field trips on 10/8/98, 6/10/98, 13/10/99, 11/2/00 and 30/6/00, were obtained using a 1-l polyethylene bailer (Geotechnical Instruments Ltd., UK). Each borehole was purged by removing three well volumes of water before collection of a representative sample. Where time permitted, 125 ml of collected sample was immediately filtered on site through a 0.45 µm membrane filter (Pall Gelman, UK) into an acid-washed polyethylene bottle. A further 1 l of unfiltered sample was also retained for subsequent filtration in the laboratory. The colour of the ground water samples was yellow for boreholes (BH) 201, 204, 702, 1403, 1485 and 1490, orange for BH 202 and brown for BH 401 and BH 402.

In addition, at Sites 2, 4 and 7 on 15/10/98, 20/10/99 and 30/6/

00, COPR was collected from 20–50 cm below the ground surface, double-bagged and transported to the laboratory for storage at 4 °C prior to separation of pore water from ~200 g material by centrifugation through Whatman 40 filter paper (<8 µm) and storage in a polyethylene bottle the following day.

Surface water samples were collected from two locations on the Malls Mire Burn, MMB 1 and MMB 2, and the River Clyde (Fig. 1) on the 6/10/98, 11/2/00 and 30/6/00 field trips by submerging a 1-l polyethylene bottle or plastic bucket on a rope. Filtration of 125 ml of collected sample through a 0.45 µm membrane filter (Pall Gelman, UK) into an acid-washed polyethylene bottle was carried out immediately. A further 1 l of unfiltered sample was also retained for subsequent filtration in the laboratory. The colour of the Malls Mire Burn samples was pale yellow while that of the River Clyde was clear.

Physical pre-treatment in the laboratory

Groundwater samples collected from BH 202, BH 204, BH 401 and BH 402 on 11/2/00 and stream water samples collected from MMB 2 and MMB 1 on 11/2/00 were filtered through an 8 µm filter paper (Whatman 540), 0.45 µm and 0.2 µm hydrophilic polyethersulfone membrane filters (Supor[®], Pall Filtron, UK) and, finally (for a 15 ml aliquot), a centrifugal ultrafilter (1 kDa molecular weight cut-off), consisting of a modified polyethersulfone on a polyethylene substrate (Omega[™] membrane) in a Macrosep[®] centrifugal concentrator (Pall Filtron, USA), at 3000 rpm (MSE Mistral 3000, Sanyo Gallenkamp plc, UK) for 1 h.

Groundwater samples collected from BH 202, BH 204, BH 402 and BH 1403 on 30/6/00 were filtered through 1.2 µm (Versapor[®], Pall Filtron, USA) and 0.45 µm membrane filters (Supor[®], Pall Gelman, UK) and finally a centrifugal ultrafilter (100 kDa molecular weight cut-off, Omega[™] membrane, Macrosep[®], Pall Filtron, USA). As these <100 kDa solutions would not pass through 30 kDa centrifugal ultrafilters that had been washed using the manufacturer's recommended procedure, some of the <0.45 µm fraction (100–400 ml) for each was subsequently subjected to tangential flow ultrafiltration (Mini-ultrasette[™], Pall Filtron, USA), employing molecular weight cut-offs of 100, 30 and 1 kDa (Omega[™] membrane bonded to a polyolefin substrate) and a 500 ml UltraPump II[™] pump and reservoir system operating with a back pressure of 25 psi (Pall Filtron, USA). Portions of the filtered/ultrafiltered ground water samples from BH 202, BH 402 and BH 1403 collected on 30/6/00 were freeze-dried using an E-C Modulyo (E-C Apparatus Inc, USA) freeze-drier operated at -45 °C and <0.1 mbar.

Analysis

pH

The pH of samples was determined using a Jenway 3305 pH meter (Jenway Ltd., UK).

ICP-OES

Total concentrations of analyte elements, including Cr, in filtered and ultrafiltered samples were determined by ICP-OES, using a TJA IRIS instrument (ThermoElemental, USA) at 1350 W and with coolant, auxiliary and nebuliser Ar gas flows of 15, 0.5 and 0.7 l min⁻¹, respectively, and a pump flow rate of 1 ml min⁻¹. Multi-element calibration standards in the concentration range 0.01–200 mg l⁻¹ were used and emission intensity measured at appropriate wavelengths (nm) for Cr 205.5, Al 396.1, Ca 317.7, Fe 259.9, Mg 383.3, Mn 257.6, Na 588.9 and S 182.0, for which detection limits were 0.1, 0.03, 0.003, 0.003, 0.1, 0.001, 0.1 and 0.2 mg l⁻¹, respectively. For all elements, analytical precision was typically ± 1% for individual

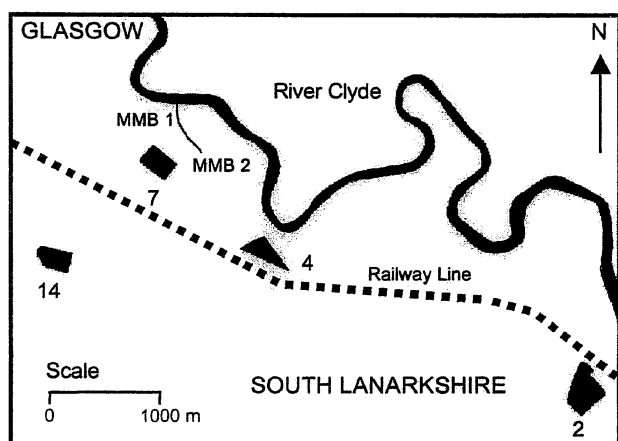


Fig. 1 Map of sampling sites, showing Site 2 (Duke's Road Playing Fields), Site 4 (Rutherglen Glencairn Football Club), Site 7 (Rosebery Park), Site 14 (Myrtle Park), MMB1 and MMB2 (Malls Mire Burn) and the River Clyde.

aliquots and $\pm 3\text{--}5\%$ (RSD) for multiple aliquots of samples. Two methods were used for speciation of Cr, namely the traditional diphenylcarbazide (DPC) complexation-UV/VIS spectrophotometric procedure for Cr^{VI} ,¹⁶ with Cr^{III} calculated as the difference between the ICP-OES and DPC measurements, and the recently introduced speciated isotope dilution mass spectrometric (SIDMS) procedure for Cr^{III} and Cr^{VI} , using anion-exchange chromatography coupled to ICP-MS.^{17–19}

DPC-UV/VIS

In the DPC-UV/VIS method,¹⁶ 2.5 ml of reagent (prepared from 0.38 g 1,5-diphenylcarbazide dissolved in 100 ml acetone, 120 ml H_3PO_4 and 280 ml H_2O) was added to typically 0.1–5.0 ml sample, adjusting the pH to 2. The solution was agitated gently, covered and left for 20 min to allow colour development. The solution was made up to 25 ml and the absorbance of the complex measured at 540 nm using a Unicam UV2-100 spectrophotometer (ThermoSpectronic, UK), employing calibration standards (prepared from 10 mg l^{-1} $\text{K}_2\text{Cr}_2\text{O}_7$) in the range 0.04–2.0 mg l^{-1} . The detection limit for Cr^{VI} in samples was 0.01 mg l^{-1} and analytical precision was typically $\pm 1\%$ (RSD).

SIDMS

In the SIDMS method,⁵¹ samples (0.05–50 ml) were spiked first with $^{53}\text{Cr}^{\text{VI}}$ and then, after adjustment of the pH to 1.7–2.0, with $^{50}\text{Cr}^{\text{III}}$ and the volume made up to 100 ml, to yield an approximate final concentration of 50 $\mu\text{g l}^{-1}$ of ^{52}Cr from the sample and 50 $\mu\text{g l}^{-1}$ of $^{53}\text{Cr}^{\text{VI}}$ and 20 $\mu\text{g l}^{-1}$ of $^{50}\text{Cr}^{\text{III}}$ from the spike. An injection valve (Rheodyne, USA) enabled the introduction of 20 μl of spiked sample into the pumped stream of eluent (0.05 M HNO_3 , 0.3 ml min^{-1}) entering an ANX4605Cr anion exchange column (Cetac Inc., USA) coupled to a VG PlasmaQuad 3 ICP-MS (ThermoElemental, UK) at 1350 W and with coolant, auxiliary and nebuliser Ar gas flows of 13.1, 0.81 and 0.84 l min^{-1} , respectively. Concentrations of individual Cr species were calculated using the appropriate isotope dilution equations.⁵¹ The detection limit for each species in samples was 0.01 mg l^{-1} and analytical precision was typically $\pm 1\%$ and $< \pm 10\%$ (RSD) at concentrations of 50 and 5 mg l^{-1} , respectively.

Anions and TOC

Anions (Cl^- , F^- , NO_3^- , SO_4^{2-}) were determined on filtered ($< 0.45\ \mu\text{m}$) samples using a Dionex DX500 system (Dionex, USA) with a GP40 pump, ED40 electrochemical detector and an IonPac AS9-HC 4 mm column with 9 mM Na_2CO_3 as eluent. Total organic carbon (TOC) was determined on filtered and ultrafiltered samples *via* non-dispersive IR spectrometric measurement of CO_2 from sodium persulfate oxidation of the carbon remaining after initial acidification with phosphoric acid, using a Model 700 Total Organic Carbon Analyser (O. I. Analytical, USA). Detection limits were 0.1 mg l^{-1} and analytical precision was typically $\pm 1\%$ (RSD).

UV/VIS spectrophotometry

The UV/VIS absorbance of selected filtered and ultrafiltered samples was recorded at 252 nm (as a measure of organic matter) and at 452 and 652 nm (as a measure of humic substances)⁵² using a Unicam UV2-100 spectrophotometer (ThermoSpectronic, UK).

Gel electrophoresis

Aliquots ($\sim 10\text{--}20\text{ mg}$) of several freeze-dried tangential-flow ultrafilter retentates (BH 202, 100 kDa–0.45 μm ; BH 402,

100 kDa–0.45 μm and 30–100 kDa) for ground water samples collected on 30/6/00 were each dissolved in 1.2 ml of 0.05 M Tris-HCl (pH 8.5) and added to the sample well of a M β P Horizontal Mega-Gel System 8300 Series 19 \times 25 cm gel electrophoresis system (Molecular Bio-Products Inc., USA) containing agarose gel (1% w/v, 250 ml 0.045 M Tris-borate). The running buffer was 0.045 M Tris-borate (pH 8.5). The system was operated at 20 mA fixed current (150 V, 3 W) for 65 min. Visual observations were recorded under both ordinary and UV light, the latter at 302 nm using a Transilluminator Model M-20 UCP Bio-Doc-It System (UVP, USA). Gels were sectioned on the basis of observed colour and fluorescence characteristics into 12–20 0.5 cm-wide strips, which were digested with 10 ml of 8 M HNO_3 on a hotplate for 2 h, evaporated to 1–2 ml and then made up to 10 ml with 2% v/v HNO_3 for subsequent analysis by ICP-OES.

FTIR

Aliquots ($\sim 0.7\text{ mg}$) of freeze-dried tangential-flow ultrafilter retentates were mixed with 100 mg KBr to produce discs for analysis by FTIR, using a Paragon 1000 FTIR spectrometer (PerkinElmer, UK), scanning from 4000 to 400 cm^{-1} .

SEM-EDX

Freeze-dried tangential-flow ultrafilter retentates of different size fractions and bulk ground water samples ($< 0.45\ \mu\text{m}$) were examined under a Philips XL20 scanning electron microscope equipped with an Oxford Instruments energy dispersive micro-analysis system. The samples were glued to the SEM stubs using conductive C adhesive strips and coated with Au/Pd to reduce sample charging.

Results and discussion

Concentrations in pore, ground and surface waters at the different locations (Tables 1 and 2)

At sites 2, 4 and 7, with the high pH (respectively 11.7, 11.9 and 12.3) typical of high-lime COPR disposal sites, pore waters contained high concentrations of total Cr (7.38–125 mg l^{-1}), predominantly (64–98%) in the form of Cr^{VI} (Table 1).

Table 2 shows that the highest total Cr concentrations in filtered ($< 0.45\ \mu\text{m}$) ground waters occurred at BH 202 (20.4–91.4 mg l^{-1}), BH 402 (6.55–15.2 mg l^{-1}) and BH 1403 and BH 1485 (30.8–33.8 mg l^{-1}). Whereas Cr^{VI} constituted $> 90\%$ of total Cr at BH 202 and BH 1403 and BH 1485 (and indeed at the boreholes with lower Cr concentrations of $< 0.01\text{--}7.43\ \text{mg l}^{-1}$, *i.e.* BH 201, BH 204, BH 401, BH 702 and BH 1490), the corresponding figure for BH 402 was $< 10\%$. While ground water from BH 202, BH 402 and BH 1403 and BH 1485 exhibited the high pH (respectively 7.7–9.0, 10.5–12.5 and 11.7–12.2) and major ion composition characteristic of high-lime COPR, the TOC at BH 402 (156–300 mg l^{-1}) was much higher than at BH 202 (29.2–39.0 mg l^{-1}) and BH 1403 and BH 1485 (8.8 mg l^{-1}).

Concentrations of total Cr, all in the form of Cr^{VI} , in the Malls Mire Burn decreased slightly from the point of emergence above ground (MMB 2, 1.58–6.28 mg l^{-1}) to the point of entry (MMB 1, 0.45–3.17 mg l^{-1}) to the River Clyde, where a significant decrease to 0.11 mg l^{-1} was observed (Table 2).

Chromium concentrations and speciation in size fractions of ground and surface waters (Tables 3, 4 and 5)

It should be noted that excellent agreement was obtained throughout between the two methods used for Cr^{VI} determination

Table 1 Concentrations (mg l^{-1}) of chromium, Cr^{VI} and other chemical entities in filtered ($<0.45 \mu\text{m}$) and cross-flow ultrafiltered pore waters at COPR-contaminated sites in SE Glasgow and South Lanarkshire (1998–2000)

Location	Date	Filter	pH	Total Cr	Cr^{VI}	Al	Ca	Fe	Mg	Mn	Na	Cl^-	F^-	NO_3^- (N)	SO_4^{2-}	TOC
Site 2 Duke's Road	15/10/98	$<0.45 \mu\text{m}$	11.7	24.6	17.8	5.4	119	0.049	1.2	0.027	6	n.a.	n.a.	n.a.	n.a.	n.a.
Site 4 R.G.F.C.	15/10/98	$<0.45 \mu\text{m}$	11.9	125	79.5	0.95	316	<0.003	<0.1	<0.001	5	n.a.	n.a.	n.a.	n.a.	n.a.
	20/10/99	$<0.45 \mu\text{m}$	12.0	30.2	28.9	0.42	212	<0.003	<0.1	<0.001	13	n.a.	n.a.	n.a.	n.a.	26.1
		$<0.45 \mu\text{m}$	11.1	13.7	13.0	0.48	80	<0.003	0.5	<0.001	4	n.a.	n.a.	n.a.	n.a.	27.2
		$<0.45 \mu\text{m}$	11.8	7.38	7.01	3.6	139	<0.003	<0.1	<0.001	9	n.a.	n.a.	n.a.	n.a.	19.3
	30/06/00	$<0.45 \mu\text{m}$	12.1	50.1	47.8	0.35	248	0.005	<0.1	<0.001	56	n.a.	n.a.	n.a.	n.a.	29.2
Site 7 Rosebery Park	15/10/98	$<100 \text{ kDa}$	12.1	49.4	48.2	0.33	254	0.005	<0.1	<0.001	56	n.a.	n.a.	n.a.	n.a.	34.2
		$<0.45 \mu\text{m}$	12.3	16.7	12.1	1.6	401	<0.003	<0.1	<0.001	6	10	0.4	13.2	5	n.a.

but that important differences were found between the inferred (ICP-DPC) and directly measured (SIDMS) results for Cr^{III} (Table 3). As discussed below, these concentration differences, with (ICP-DPC) $>$ SIDMS, appear related to the organic carbon content of the samples, perhaps through retention of Cr^{III} -organic complexes on the anion-exchange column preceding the ICP-MS.

Site 2. For ground water from BH 202, there was a decrease in Cr concentration with decreasing size fraction (Tables 4 and 5). The largest decline was from 86.3 mg l^{-1} ($<0.45 \mu\text{m}$) to 56.3 mg l^{-1} ($<1 \text{ kDa}$) in the tangential-flow ultrafiltration data for 30/6/00 (Table 5), accompanied by a corresponding fall in TOC from 34.8 to 8.0 mg l^{-1} . For all size fractions on all sampling occasions, however, Cr^{VI} still constituted $>90\%$ of total Cr (Tables 4 and 5), but there was a difference, the extent of which decreased with decreasing size fraction, between the (ICP-DPC) and SIDMS results for Cr^{III} (Table 3).

In contrast, at BH 204, where Cr (with Cr^{VI} $>90\%$) and TOC concentrations were much lower, at $\sim 5 \text{ mg l}^{-1}$ and $\sim 3 \text{ mg l}^{-1}$, respectively, there was no change in Cr

concentration with size fraction (Table 4) and no significant difference between (ICP-DPC) and SIDMS results for Cr^{III} (Table 3).

Site 4. At BH 401, where Cr (with Cr^{VI} $>90\%$) and TOC concentrations were low, at $\sim 1 \text{ mg l}^{-1}$ and $\sim 4 \text{ mg l}^{-1}$ respectively, there was no change in Cr concentration with size fraction (Table 4) and no significant difference between (ICP-DPC) and SIDMS for Cr^{III} (Table 3).

At BH 402, however, where TOC concentrations were as high as $\sim 300 \text{ mg l}^{-1}$, there was a decrease in Cr concentration with decreasing size fraction (Tables 4 and 5). The tangential-flow ultrafiltration data exhibited a decline from 11.4 mg l^{-1} ($<0.45 \mu\text{m}$) to 0.03 mg l^{-1} ($<1 \text{ kDa}$) (Table 5), accompanied by a corresponding fall in TOC from 136 to 10.1 mg l^{-1} , and there were similar decreases in Cr concentration from 6.55 mg l^{-1} ($<0.45 \mu\text{m}$) to 0.16 mg l^{-1} ($<1 \text{ kDa}$) and from 8.58 mg l^{-1} ($<0.45 \mu\text{m}$) to 1.47 mg l^{-1} ($<100 \text{ kDa}$) for the cross-flow ultrafiltration data for 11/2/00 and 30/6/00, respectively (Table 4). Cr^{VI} constituted only $<3\%$ of total Cr (Tables 4, 5) and there was a significant difference, the extent of

Table 2 Concentrations (mg l^{-1}) of chromium, Cr^{VI} and other chemical entities in filtered ($<0.45 \mu\text{m}$) ground (BH) and surface waters at or near COPR-contaminated sites in SE Glasgow and South Lanarkshire (1998–2000)

Location	Depth/ m	Water depth/ m	Date	pH	Total Cr	Cr^{VI}	Al	Ca	Fe	Mg	Mn	Na	Cl^-	F^-	NO_3^- (N)	SO_4^{2-}	TOC
Site 2 Duke's Road BH 201	13	3.2	10/08/98	7.2	3.04	3.23	0.15	122	<0.003	47	<0.001	n.a.	39	3.6	9.5	90	n.a.
			06/10/98	7.1	2.39	2.45	0.18	121	<0.003	45	0.019	n.a.	32	0.3	12.2	71	n.a.
BH 202	17.7	9.1	10/08/98	7.7	30.0	29.4	0.14	82	<0.003	61	0.016	n.a.	58	3.2	7.7	208	n.a.
			06/10/98	8.6	20.4	20.4	1.3	81	0.80	52	0.044	n.a.	59	0.8	10.7	280	n.a.
			13/10/99	8.5	50.5	48.2	<0.03	46	0.20	57	0.026	336	n.a.	n.a.	n.a.	n.a.	29.0
			11/02/00	8.9	91.4	81.9	0.26	40	0.24	67	0.010	656	25	1.7	4.8	351	29.2
			30/06/00	9.0	86.4	80.0	0.27	20	0.75	58	0.037	609	n.a.	n.a.	n.a.	n.a.	39.0
BH 204	16.8	10.1	10/08/98	7.1	3.35	3.35	0.15	128	<0.003	61	<0.001	n.a.	76	3.1	8.1	133	n.a.
			13/10/99	7.1	3.92	3.77	<0.03	101	0.008	52	0.003	86	n.a.	n.a.	n.a.	n.a.	5.9
			11/02/00	7.7	3.44	3.57	0.20	139	<0.003	62	0.001	66	61	0.2	9.4	103	2.3
			30/06/00	7.3	5.94	5.40	0.14	111	<0.003	54	0.002	87	n.a.	n.a.	n.a.	n.a.	2.9
			10/08/98	7.7	<0.01	<0.01	0.07	58	<0.003	66	0.43	n.a.	44	3.1	7.3	52	n.a.
Site 4 R.G.F.C. BH 401	4.9	1.3	13/10/99	7.4	<0.01	0.16	<0.03	59	0.03	64	0.28	34	n.a.	n.a.	n.a.	n.a.	15.1
			11/02/00	8.5	0.96	0.92	0.09	47	0.011	54	0.001	11	25	0.3	2.4	16	4.0
			30/06/00	7.4	0.07	0.03	0.12	78	0.31	67	0.36	46	n.a.	n.a.	n.a.	n.a.	11.2
BH 402	6.2	2.5	10/08/98	12.5	15.2	1.63	9.6	34	3.5	0.2	0.12	n.a.	32	5.6	7.5	35	n.a.
			13/10/99	11.0	6.78	0.23	2.2	16	0.84	0.6	0.027	201	n.a.	n.a.	n.a.	n.a.	181
			11/02/00	10.5	6.55	0.11	3.0	24	2.5	0.4	0.082	395	n.a.	n.a.	n.a.	n.a.	300
Site 7 Rosebery Park BH 702	14.5	3.0	30/06/00	10.6	8.58	<0.01	3.8	19	2.3	0.1	0.093	419	n.a.	n.a.	n.a.	n.a.	156
			10/08/98	7.5	<0.01	<0.01	0.20	146	<0.003	30	0.67	n.a.	58	3.4	6.9	38	n.a.
Site 14 Myrtle Park BH 1403	5.0	2.7	06/10/98	11.7	30.8	31.0	2.7	105	<0.003	0.1	<0.001	n.a.	18	0.2	2.9	15	n.a.
			30/06/00	11.7	33.8	30.7	2.9	71	<0.003	<0.1	<0.001	52	n.a.	n.a.	n.a.	n.a.	8.8
BH 1485	3.5	1.3	06/10/98	12.2	32.1	33.3	1.0	353	<0.003	0.2	<0.001	n.a.	29	0.4	7.9	10	n.a.
BH 1490	5.5	2.3	06/10/98	11.5	7.43	7.72	3.4	20	0.036	0.1	<0.001	n.a.	73	0.2	3.9	15	n.a.
Malls Mire			06/10/98	8.0	6.28	6.51	0.18	84	<0.003	13	0.17	n.a.	7	n.d.	0.6	19	n.a.
Burn MMB 2			11/02/00	8.2	1.58	1.56	0.10	59	0.023	9	0.026	52	55	0.2	7.9	71	3.6
			06/10/98	7.8	3.17	3.40	0.12	64	0.054	12	<0.001	n.a.	47	0.2	8.1	122	n.a.
MMB 1			11/02/00	8.2	1.54	1.52	0.12	59	0.020	9	0.032	54	59	0.2	8.0	71	3.2
			30/06/00	7.8	0.45	0.40	0.08	50	0.044	15	0.002	39	n.a.	n.a.	n.a.	n.a.	5.5
River Clyde (near MMB 1)			06/10/98	7.9	0.11	0.16	0.10	42	0.23	12	0.058	n.a.	29	0.3	12.5	49	n.a.

Table 3 Comparison of the concentrations (mg l^{-1}) of chromium and chromium species, as determined by ICP(OES), DPC and (ICP-MS) SIDMS, in filtered and cross-flow ultrafiltered pore, ground (BH) and surface waters at or near COPR-contaminated sites in S.E. Glasgow and South Lanarkshire (1999–2000)

Location	Depth/ m	Water depth/m	Date	Filter	pH	Total Cr ICP	Cr ^{VI} DPC	Cr ^{III} ICP-DPC	Cr ^{VI} SIDMS	Cr ^{III} SIDMS	TOC
Site 2 Dukes Road BH 202	17.7	(9.1) ^a	13/10/99	<0.45 μm	8.5	50.5	48.2	2.3	48.3	1.7	29.0
				<0.45 μm	8.9	91.4	81.9	9.5	n.a.	1.1	29.2
			30/06/00	<0.2 μm		91.2	84.0	7.2	95.2	2.2	28.4
				<1 kDa		87.1	85.6	1.5	88.8	1.0	n.a.
				<1.2 μm	9.0	87.5	80.5	7.0	78.9	5.8	42.2
				<0.45 μm		86.4	80.0	6.4	80.7	5.8	39.0
BH 204	16.8	(10.1) ^a	13/10/99	<0.45 μm	7.1	3.92	3.77	0.15	3.98	0.27	5.9
				<0.45 μm	7.3	5.94	5.40	0.54	5.77	0.34	2.9
			30/06/00	<1.2 μm		5.90	5.46	0.44	5.70	0.32	2.6
				<0.45 μm		5.84	5.81	0.03	5.75	0.34	4.2
				<100 kDa		80.5	80.5	<0.01	80.5	<0.01	26.1
				<0.45 μm	11.1	13.7	13.0	0.7	13.0	0.4	n.a.
Site 4 R.G.F.C. Pore waters	4.9	(1.3) ^a	20/10/99	<0.45 μm	12.0	30.2	28.9	1.3	28.7	0.6	n.a.
				<0.45 μm	11.8	7.38	7.01	0.37	6.77	0.26	n.a.
			30/06/00	<0.45 μm	12.1	50.1	47.8	2.3	48.9	2.6	29.2
				<100 kDa	12.1	49.4	48.2	1.2	47.8	3.1	34.2
				<0.45 μm	7.4	<0.01	0.16	<0.01	<0.01	0.05	15.1
				<0.45 μm	11.0	6.78	0.23	6.55	0.06	1.6	181
BH 401	6.2	(2.5) ^a	13/10/99	<0.45 μm	11.0	6.78	0.23	6.55	0.06	1.6	181
				<0.45 μm	10.5	6.55	0.11	6.44	<0.01	0.71	300
			11/02/00	<0.2 μm		4.90	0.06	4.84	<0.01	0.81	n.a.
				<1 kDa		0.16	<0.01	0.16	<0.01	0.04	n.a.
				<1.2 μm		65.6	<0.01	65.6	<0.01	4.2	231
				<0.45 μm	10.6	8.58	<0.01	8.58	<0.01	0.95	156
Malls Mire Burn MMB 1	4.9	(1.3) ^a	11/02/00	<0.45 μm	8.2	1.54	1.52	0.02	1.70	0.13	3.2
				<0.2 μm		1.56	1.53	0.03	1.32	0.10	3.6
			11/02/00	<1 kDa		1.30	1.24	0.06	1.38	0.10	n.a.
				<0.45 μm	8.2	1.54	1.52	0.02	1.70	0.13	3.2
				<0.2 μm		1.56	1.53	0.03	1.32	0.10	3.6
				<1 kDa		1.30	1.24	0.06	1.38	0.10	n.a.

^aBrackets around water depths indicate that they are nominal.

Table 4 Concentrations (mg l^{-1}) of chromium, Cr^{VI} and other chemical entities in filtered and cross-flow ultrafiltered ground (BH) and surface waters at or near COPR-contaminated sites in S.E. Glasgow and South Lanarkshire (2000)

Location	Depth/ m	Water depth/m	Date	Filter	pH	Total Cr	Cr ^{VI}	Al	Ca	Fe	Mg	Mn	Na	S	TOC
Site 2 Dukes Road BH 202	17.7	(9.1) ^a	11/02/00	<8 μm		99.3	n.a.	2.5	43	2.1	70	0.042	674	128	35.0
				<0.45 μm	8.9	91.4	81.9	0.26	40	0.24	67	0.010	656	115	29.2
			30/06/00	<0.2 μm		91.2	84.0	0.08	40	0.009	67	<0.001	653	117	28.4
				<1 kDa		87.1	85.6	0.08	38	<0.003	65	0.002	631	117	n.a.
				<1.2 μm	9.0	87.5	80.5	0.35	20	0.91	58	0.038	601	126	42.2
				<0.45 μm		86.4	80.0	0.27	20	0.75	58	0.037	609	127	39.0
BH 204	16.8	(10.1) ^a	11/02/00	<8 μm		3.56	n.a.	0.21	145	<0.003	65	0.001	68	33	1.8
				<0.45 μm	7.7	3.44	3.57	0.20	139	<0.003	62	0.001	66	32	2.3
			30/06/00	<0.2 μm		3.45	3.59	0.22	139	<0.003	62	0.001	65	33	2.5
				<1 kDa		3.42	3.53	0.12	56	<0.003	63	0.001	64	35	n.a.
				<1.2 μm	7.3	5.90	5.46	0.16	112	<0.003	55	0.002	88	29	2.6
				<0.45 μm		5.94	5.40	0.14	111	<0.003	54	0.002	87	29	2.9
Site 4 R.G.F.C. BH 401	4.9	(1.3) ^a	11/02/00	<8 μm		1.01	n.a.	0.28	50	0.12	56	0.002	12	2.9	4.0
				<0.45 μm	8.5	0.96	0.92	0.09	47	0.011	54	0.001	11	3.1	4.0
			11/02/00	<0.2 μm		0.96	0.94	0.09	46	<0.003	52	0.001	12	3.7	4.1
				<1 kDa		0.93	0.92	0.10	48	<0.003	55	0.001	14	5.6	n.a.
				<8 μm	10.5	56.4	n.a.	62	72	58	10	1.5	422	12	315
				<0.45 μm		6.55	0.11	3.0	24	2.5	0.4	0.082	395	9.3	300
BH 402	6.2	(2.5) ^a	11/02/00	<0.2 μm		4.90	0.06	2.6	23	1.8	0.4	0.060	397	9.3	n.a.
				<1 kDa		0.16	<0.01	0.51	4	0.051	0.1	0.002	115	2.0	n.a.
			30/06/00	<1.2 μm		65.6	<0.01	27.9	55	43.6	3.8	1.16	418	15	231
				<0.45 μm	10.6	8.58	<0.01	3.8	19	2.3	0.1	0.093	419	7.7	156
				<100 kDa		1.47	<0.01	3.1	13	0.33	0.1	0.016	424	6.3	137
				<8 μm		1.61	n.a.	0.13	60	0.089	9.4	0.004	53	22	3.4
Malls Mire Burn MMB 2	4.9	(1.3) ^a	11/02/00	<0.45 μm	8.2	1.58	1.56	0.10	59	0.023	9.2	0.026	52	22	3.6
				<0.2 μm		1.58	1.56	0.13	59	0.004	9.3	0.001	52	23	3.6
			11/02/00	<1 kDa		1.35	1.32	0.12	55	0.004	8.9	0.002	51	22	n.a.
				<8 μm		1.59	n.a.	0.13	61	0.11	9.6	0.006	55	22	3.4
				<0.45 μm	8.2	1.54	1.52	0.12	59	0.020	9.3	0.032	54	22	3.2
				<0.2 μm		1.56	1.53	0.11	59	<0.003	9.4	0.001	55	23	3.6
MMB 1	6.2	(2.5) ^a	11/02/00	<1 kDa		1.30	1.24	0.13	56	0.003	9.1	0.002	51	21	n.a.
				<8 μm		1.59	n.a.	0.13	61	0.11	9.6	0.006	55	22	3.4
			11/02/00	<0.45 μm	8.2	1.54	1.52	0.12	59	0.020	9.3	0.032	54	22	3.2
				<0.2 μm		1.56	1.53	0.11	59	<0.003	9.4	0.001	55	23	3.6
				<1 kDa		1.30	1.24	0.13	56	0.003	9.1	0.002	51	21	n.a.
				<8 μm		1.59	n.a.	0.13	61	0.11	9.6	0.006	55	22	3.4

^aBrackets around water depths indicate that they are nominal.

Table 5 Concentrations (mg l^{-1}) of chromium, Cr^{VI} and other chemical entities in filtered and tangential-flow ultrafiltered ground waters (BH) at or near COPR-contaminated Sites in S.E. Glasgow and South Lanarkshire (2000). Some concentrations ($<0.45 \mu\text{m}$) may differ from those cited for the same samples ($<0.45 \mu\text{m}$) in earlier tables due to re-filtration and/or re-analysis.

Location	Depth/ m	Water depth/m	Date	Filter	pH	Total Cr	Cr^{VI}	Al	Ca	Fe	Mg	Mn	Na	S	TOC
Site 2 Dukess Road BH 202	17.7	(9.1) ^a	30/06/00	<0.45 μm	9.0	86.3	79.9	0.23	19	0.43	55	0.018	571	124	34.8
				<100 kDa	9.0	79.8	75.1	0.06	17	0.043	50	0.004	535	114	23.4
				<30 kDa	9.0	72.8	68.1	0.04	15	<0.003	46	0.002	501	103	19.8
				<1 kDa	9.0	56.3	53.6	0.04	12	<0.003	37	0.003	448	77	8.0
Site 4 R.G.F.C. BH 402	6.2	(2.5) ^a	30/06/00	<0.45 μm	10.1	11.4	0.05	4.0	22	4.2	0.3	0.16	408	12	136
				<100 kDa	10.1	0.89	0.03	2.1	14	0.17	0.2	0.013	384	11	110
				<30 kDa	9.9	0.32	<0.01	1.7	10	0.050	0.2	0.005	340	8.2	65.8
				<1 kDa	9.9	0.03	<0.01	1.1	4	0.004	0.2	0.001	267	3.4	10.1
Site 14 Myrtle Park BH 1403	5.0	(2.7) ^a	30/06/00	<0.45 μm	11.4	30.9	29.8	3.4	69	0.003	<0.1	<0.001	49	5.8	9.5
				<100 kDa	11.4	28.6	28.4	3.1	60	<0.003	<0.1	<0.001	46	5.4	7.9
				<30 kDa	11.1	26.8	26.5	2.9	40	<0.003	<0.1	<0.001	45	5.0	7.1
				<1 kDa	11.0	16.4	16.9	2.1	23	0.004	<0.1	<0.001	40	3.1	6.1

^aBrackets around water depths indicate that they are nominal.

which decreased with decreasing size fraction (*e.g.* $\sim 90\%$ at $<0.45 \mu\text{m}$ to $\sim 75\%$ at $<1 \text{ kDa}$), between the (ICP-DPC) and SIDMS results for Cr^{III} (Table 3).

Site 14. At BH 1403, where the TOC was lower than at both BH 402 and BH 202, there was a decrease in the Cr concentration from 26.8–30.9 mg l^{-1} for the larger size fractions ($<0.45 \mu\text{m}$, $<100 \text{ kDa}$ and $<30 \text{ kDa}$) to 16.4 mg l^{-1} for the $<1 \text{ kDa}$ fraction, accompanied by a slight fall in TOC from 7.1–9.5 mg l^{-1} to 6.1 mg l^{-1} (Table 5). No data are available for the (ICP-DPC) comparison with SIDMS for Cr^{III} but Cr^{VI} constituted 96–103% of total Cr for the size fractions in any case (Table 5).

Malls Mire Burn. For MMB 1 and MMB 2, where the TOC was low ($<4 \text{ mg l}^{-1}$), there was only a slight decrease in Cr concentration from $\sim 1.6 \text{ mg l}^{-1}$ ($<0.45 \mu\text{m}$) to 1.3 mg l^{-1} ($<1 \text{ kDa}$), with $>95\%$ as Cr^{VI} for all size fractions (Table 4) and no significant difference in Cr^{III} by the two methods.

Comparison of tangential-flow ultrafiltration data for ground waters from BH 202, BH 402 and BH 1403 (Table 5, Figs. 2, 3)

The tangential-flow ultrafiltration data for ground waters from BH 202, BH 402 and BH 1403 (Table 5) are displayed in terms of distribution of Cr and other elements among the different ultrafilter retentates in Fig. 2. There is no obvious direct correlation between the Cr concentration and the TOC concentration, *e.g.* at BH 202 the $<1 \text{ kDa}$ fraction accounted for 65% of the total ($<0.45 \mu\text{m}$) Cr concentration but only 23% of the corresponding TOC concentration; at BH 1403 the $<1 \text{ kDa}$ fraction accounted for 53% of the total ($<0.45 \mu\text{m}$) Cr concentration and 64% of the corresponding, but much lower, TOC concentration; while at BH 402 the major Cr-containing fraction was 100 kDa– $0.45 \mu\text{m}$, which accounted for 92% of the total ($<0.45 \mu\text{m}$) Cr concentration (predominantly in the form of Cr^{III}) but only 19% of the corresponding TOC concentration.

On the basis of visual, FTIR and, especially, UV/VIS evidence, however, the concentration of the humic substance component of the organic matter in the ultrafilter retentates

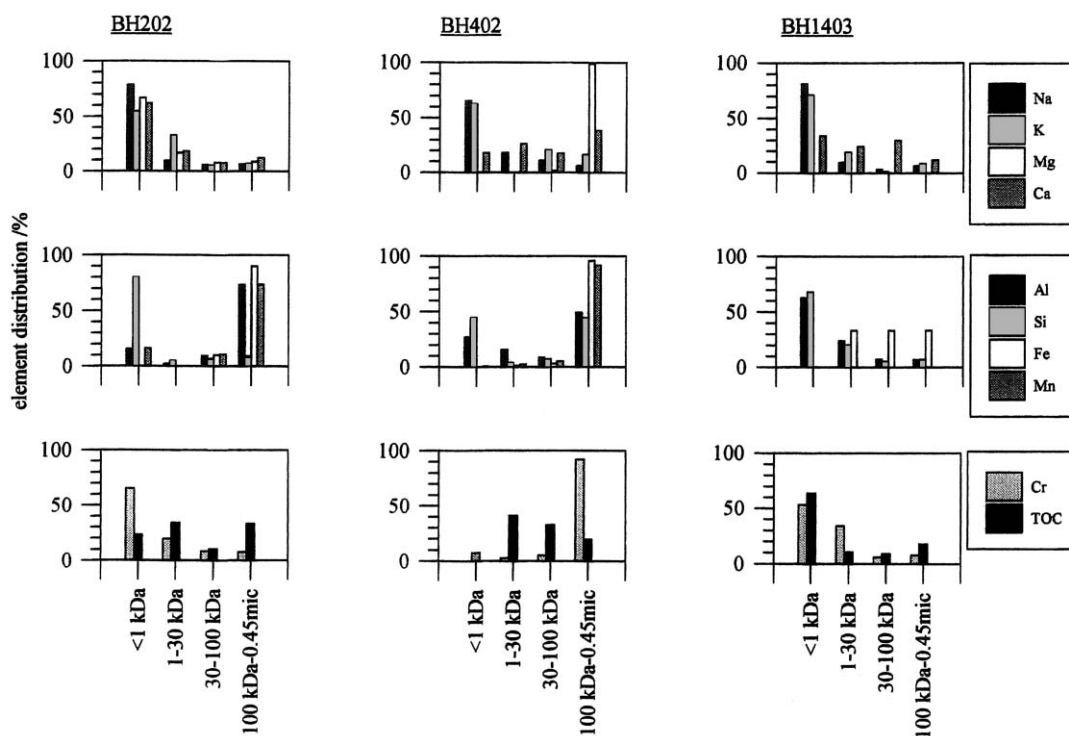


Fig. 2 Elemental and total organic carbon (TOC) distribution (%) amongst the tangential-flow ultrafiltration size fractions obtained from ground water at BH 202, BH 402 and BH 1403.

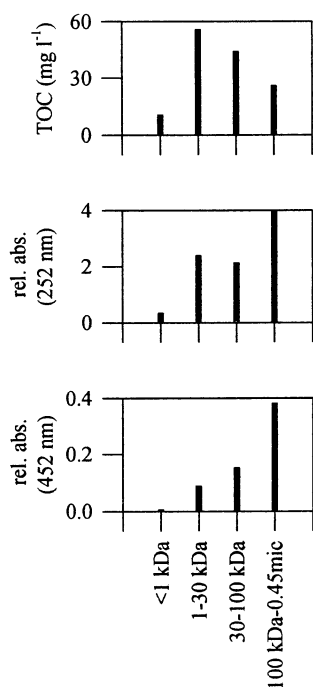


Fig. 3 Total organic carbon (TOC) concentration and relative UV/VIS absorbance (252 nm, organic matter; 452 nm, humic substances) for tangential-flow ultrafiltration size fractions obtained from ground water at BH 402. UV/VIS absorbances could not so be used for BH 202 because of the influence of the high concentrations of chromate, which absorbs at 272 nm and 372 nm.

increased with increasing size range for both BH 202 and BH 402 (Fig. 3). As the distributions of Al, Si, Fe and Mn were also skewed to larger size fractions (Fig. 2), however, it was not possible to determine the role of organic matter on the basis of the ultrafiltration data alone. Gel electrophoretic fractionation of the ultrafilter retentates was required to investigate further the role of organic matter in Cr complexation, especially for BH 402.

Gel electrophoresis of ultrafilter retentates of ground waters from BH202 and BH402 (Figs. 4, 5)

The ultrafilter retentates subjected to gel electrophoresis were 100 kDa–0.45 μm for BH 202 and 30–100 kDa and 100 kDa–0.45 μm for BH 402. For BH 202 100 kDa–0.45 μm , four electrophoretic bands (tailing F1, dark brown F2, fluorescent F2–8, yellow F6–18) were identified, in contrast to only three bands (tailing F1–2, dark brown F3–4, fluorescent F5–8) for BH 402 100 kDa–0.45 μm and three bands (tailing F1–4, dark brown F5–6, and fluorescent F6–10) for BH 402 30–100 kDa (Fig. 4). The yellow band in BH 202 100 kDa–0.45 μm is attributable to the presence of uncomplexed residual chromate in the ultrafiltration procedure (see below) but the other differences between BH 202 and BH 402, *i.e.* in the location of the tailing, dark brown and fluorescent bands, reflect the contrasting nature of the organic matter in the ultrafilter retentates for these two locations.

The greater electrophoretic mobility implied by the position of the dark brown band for BH 402 100 kDa–0.45 μm relative to that for BH 202 100 kDa–0.45 μm suggests that the BH 202 humic molecules have lower net negative charge. This charge, at the pH (8.5) of the gel electrophoresis, is likely to be from predominantly carboxylate groups. Hence it is concluded that the humic material from BH 202 has fewer carboxylate groups than the material from BH 402, consistent with a much stronger presence in the FTIR spectra of carboxylate bands⁵² at 1400 and 1032 cm^{-1} for the latter. The greater migration of the dark brown band for the 30–100 kDa fraction relative to

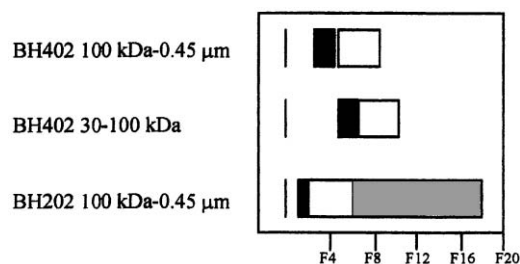


Fig. 4 Schematic diagram showing the relative positions of the dark brown (dark shading), fluorescent (white) and (for BH 202) chromate (light shading) bands obtained by horizontal bed gel electrophoresis fractionation of freeze-dried material from tangential-flow ultrafiltration size fractions of ground water from BH 202 and BH 402. In each case, the tailing band (not shown) extended between the gel well and the dark brown band.

that for the 100 kDa–0.45 μm fraction of BH 402 is consistent with the anticipated size-related mobility.

The contrasting nature of the electrophoretic distributions of Cr from the ultrafilter retentates for the two locations is shown in Fig. 5. For BH 202 100 kDa–0.45 μm , Cr occurred predominantly over F6–18, in contrast to F3–4 and F4–6 for BH 402 100 kDa–0.45 μm and 30–100 kDa fractions, respectively.

For BH 202 the 100 kDa–0.45 μm fraction is the one with the highest humic concentration. Figs. 4 and 5, however, show that the Cr in the 100 kDa–0.45 μm fraction is not associated with humic substances, a finding consistent with the general predominance of Cr^{VI} , in the form of anionic chromate, at this location (Tables 2–5). The Cr^{VI} has migrated much more rapidly under electrophoresis, yielding a distinct yellow band, than the humic substances constituting the dark brown and fluorescent bands. The presence of Cr (predominantly Cr^{VI}) in the 100 kDa–0.45 μm fraction, which constitutes only a minor

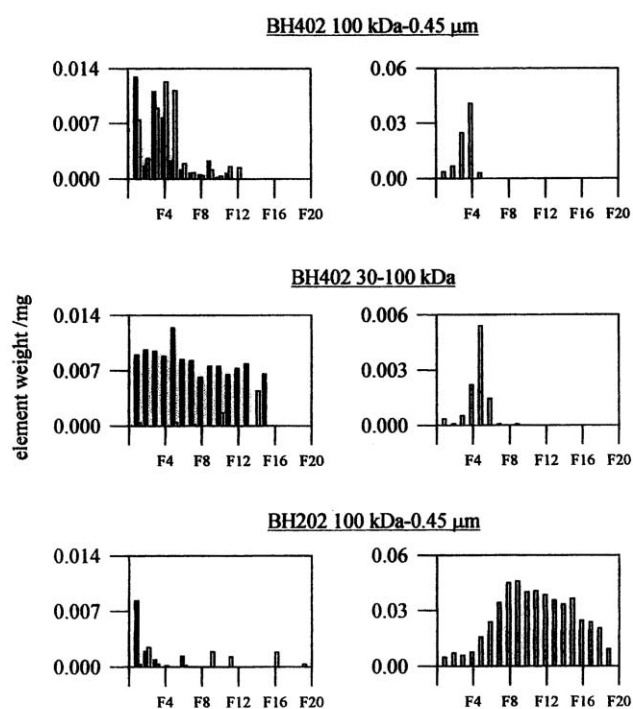


Fig. 5 The weight of Al (black shading), Fe (white) and Cr (light shading) in each gel electrophoretic fraction (0.5 cm width) obtained from freeze-dried material (20 mg) from tangential-flow ultrafiltration size fractions of ground water from BH 202 and BH 402. Although some freeze-dried material containing Al, Fe and Cr remained in the gel well, a subsequent experiment using 1 ml of non-freeze-dried material from BH 402 100 kDa–0.45 μm , which enabled all of the material to enter the gel, confirmed that the Cr peak coincided with the dark brown band.

component (~7%) of the total Cr concentration at this location, is probably a 'carry-over' artefact of the ultrafiltration procedure. It may be concluded that the humic material at this location, although comparatively high in concentration, is unable to reduce Cr^{VI} to Cr^{III}. This is probably a consequence of its lower functionality, especially with respect to carboxylate groups.

For BH 402 it is known that Cr is predominantly in the form of Cr^{III} (Tables 2–5). Fig. 5 shows that it was much less mobile under electrophoresis than the Cr at BH 202. For the 100 kDa–0.45 µm fraction, the Cr peak coincided with the position of the dark brown (organic matter) band, where Fe and Al peaks also occurred (Fig. 5). For the 30–100 kDa fraction, where the Fe concentration was very low, the Cr peak also coincided with the position of the dark brown band and so this can be unambiguously interpreted as complexation of Cr^{III} by humic substances. It is suggested, therefore, that Cr in the 100 kDa–0.45 µm fraction, where both Cr and humic concentrations are highest, is also directly complexed by humic material. The distribution of organic matter between the two size fractions may be influenced by the formation of aggregates involving Fe (hydr)oxides and humic material, for which there is limited SEM-EDX evidence. On the basis of ultrafiltration, gel electrophoresis, UV/VIS, FTIR and SEM-EDX data, it can be concluded that the organic matter at this location is capable of reducing Cr^{VI} to Cr^{III}, thereby forming Cr^{III}–humic complexes.

Implications

Although Cr was present mainly as Cr^{VI} in the high-pH ground water at most of the locations investigated, it occurred predominantly as Cr^{III}, shown here to be in association with organic material of high molecular weight, at one location (BH 402). Thus, site-specific conditions can play an important role in the speciation/fractionation of dissolved Cr. The implied reduction here of Cr^{VI} by humic substances, perhaps *via* carboxylate groups,³⁰ and the formation of Cr^{III}–humic complexes^{29,35} suggests the possible existence of a natural remediation process,³³ at least in terms of Cr^{VI} reduction in pore and ground waters. However, it also provides a means of retention of Cr^{III} in solution in preference to either precipitation of Cr(OH)₃ or reoxidation to Cr^{VI} under the prevailing alkaline conditions.³² In addition, the organically bound Cr^{III} may also preferentially sorb to and desorb from organic portions of suspended particulates.³² This behaviour could be especially important in remediation strategies based on stimulation of the reduction of Cr^{VI} by the addition of organic matter^{53,54} and should also be considered in the modelling of both the environmental chemistry of Cr and the remediation of environmental Cr contamination.

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