THE MONITORING OF Cr(III) AND Cr(VI) IN NATURAL WATER AND SYNTHETIC SOLUTIONS: AN ASSESSMENT OF THE PERFORMANCE OF THE DGT AND DPC METHODS

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Abstract. The technique of diffusive gradients in thin films or diffusive gradient in thin films (DGT) has been used in this work for the *in situ* measurement of labile Cr(III) and Cr(VI) species. Direct measurement of Cr(VI) was also carried out in parallel with a field-based colourimetric technique based on the EPA 7196 diphenyl-carbohydrazide (DPC) method. The efficiency of the DGT and DPC methods were tested (a) in the laboratory, using synthetic solutions in the presence of realistic concentrations of Cr, humic substances (HS), and ethylenediaminetetraacetic acid (EDTA), and (b) in the field, in river water affected by effluents discharged by the tannery industry. The main advantage of the DGT method is that it allows the *in situ* separation of labile species of Cr(III) and Cr(VI), though there are still uncertainties about its performance in field conditions. The DPC method proved to be a fast, accurate, and relatively economical option for the field-based determination of Cr(VI). Sample acidification and ageing of unacidified samples from contaminated aquatic environments, produced significant errors in the determination of 'dissolved' Cr. The concentration of Cr(VI) determined by either the DGT or the DPC method exceeds recommended international guidelines.

Keywords: Cr(III), Cr(VI), DGT, diphenyl-carbohydrazide (DPC), EDTA, humic substances, river water

1. Introduction

On the basis of thermodynamic considerations, in oxidising natural water of low organic matter content and of a pH $>$ 5, chromium (Cr) should be present in the hexavalent state (Nriagu and Nieboer, 1988; Palmer and Wittbrodt, 1991). However, Cr in natural waters is often present in the trivalent oxidation state. Mathematical modelling (Lin, 2002) indicates that due to the slow kinetics of Cr(III) oxidation to Cr(VI) by inorganic oxidants, Cr(III) species are more stable in typical natural waters, unless Fe(II) and S(IV) are absent. Insoluble Cr(III) compounds tend to form unless the trivalent species are kept in solution by complex formation with natural or synthetic ligands (James and Bartlett, 1983). Cr(III) can be slowly oxidised to Cr(VI) by oxidants such as dissolved oxygen, MnO_2 (Rai *et al.*, 1989) and H_2O_2 (Pettine and Millero, 1990). In turn, Cr(VI) is reduced to Cr(III) by microorganisms

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and reductants such as organic matter, sulphides, and Fe(II) (e.g. Saleh *et al*., 1989; Pettine *et al*., 1998; Gaberell *et al*., 2003).

In acidic waters (pH $<$ 6.3), the main Cr(III) species are $CrOH^{2+}$ and Cr^{3+}, whereas $Cr(OH)_3$ and $Cr(OH)_4^-$ are more common at higher pH level. For Cr(VI), the dominant species in the two pH ranges are $HCrO_4^-$ and CrO_4^{2-}, respectively. According to Hem (1977), the Cr(III) solution concentrations in equilibrium with Cr_2O_3 are less than 5 ppb at pH $>$ 4, whereas Cr(III) solution concentrations in equilibrium with $Cr(OH)_3$ vary from about 50 ppb to 500 ppm in the pH range of 5–9. The formation of (Cr, Fe)$(OH)_3$, a solid phase of very low solubility, would limit the soluble Cr(III) concentration in natural aquatic environments (Rai *et al*., 1989).

Chromium(III) is known to form complexes with many inorganic (e.g. ammonia, fluoride, cyanide, sulphate) and organic (e.g. carboxylic acids, EDTA) ligands (Baes and Mesmer, 1977; Srivastava *et al*., 1999). Theoretically, Cr(VI) can be present in relatively high concentrations in surface and groundwater due to a lack of solubility constraints and to low adsorption of Cr(VI) anionic species to oxihydroxides in neutral and alkaline conditions (Nriagu and Nieboer, 1988), though reduction to Cr(III) species is likely to keep the concentration of Cr(VI) to levels that are well below 50 ppm. Chromium(VI) does not commonly form complexes with inorganic or organic ligands (Langård, 1980).

In biological systems, Cr(III) is essential in trace amounts whereas Cr(VI) is considered to be toxic at very low concentrations (United States Environmental Protection Agency, 1998). In view of the contrasting effects of Cr species and of the possible changes of Cr oxidation state, a limit for 'total dissolved Cr' in natural water has been set at 50 ppb by the US, the EU, Canada, Russia, Japan, and many other countries. In addition, environmental standards have been developed (Hunt and Hedgecott, 1994) for Cr(VI) species in water. These range from the 4-day mean of 11 ppb in freshwater in the USA to the Canadian standards of 1 ppb in freshwater and 8 ppb for irrigation water (Pawlisz *et al*., 1996), thus requiring the measurement of Cr species.

Dissolved Cr concentrations in unpolluted freshwater are normally $<$2 ppb (Achterberg *et al*., 1997; Pettine and Millero, 1990; Pawlisz *et al*., 1996). Higher concentrations are reported in rivers affected by municipal and industrial discharges (Pawlisz *et al*., 1996). The main anthropogenic sources of Cr are electroplating, anodising, dipping, and tannery operations. The production of leather requires a series of stages involving the use of a wide range of chemical substances, including Cr(III) as chromium sulphate $[Cr_4(SO_4)_5(OH)_2]$ and, in the past, Cr(VI) as sodium dichromate ($Na_2Cr_2O_7$). In some parts of the world Cr(VI) is still used for dying furs and pelts. In Italy, one of the highest concentrations of leather tanneries is located in the Veneto region, especially along the tributaries of the Fratta-Gorzone River (Figure 1).

The main outfall of treated or partially treated tannery effluent is located at site 9 (Figure 1), although additional discharges take place further upstream. For

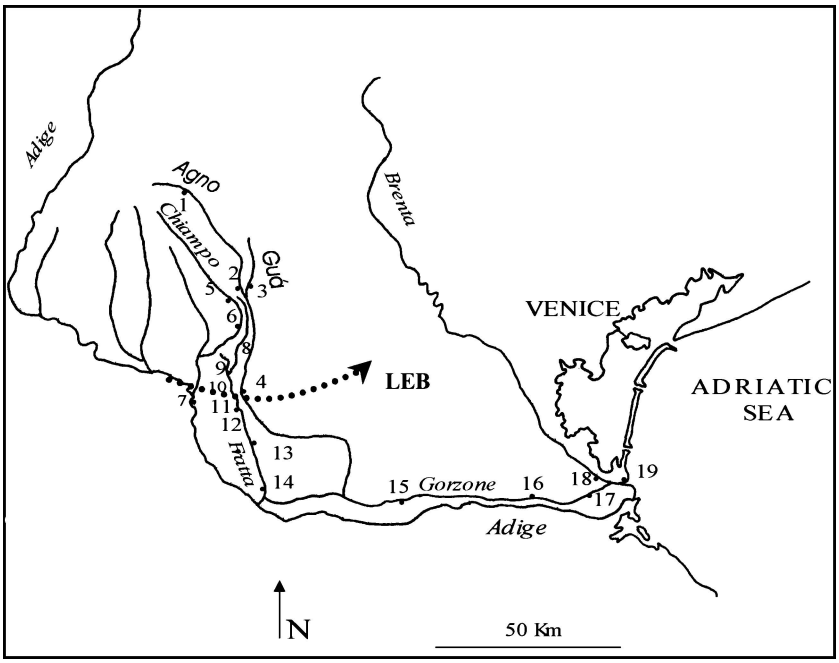

Figure 1. Simplified map of the study area, showing the main river systems and the sampling sites. The rivers flow in a southeasterly direction towards the Adriatic Sea. The dotted arrow shows the LEB canal that distributes water withdrawn from the Adige River to the Fratta River, to the Gua' River and to other streams draining this region. Site 9 is the location of the main tannery effluent discharge. The Fratta River becomes the Gorzone River after site 14. The Brenta River joins the Gorzone a few kilometres upstream of its delta, south of the Venetian Lagoon.

many years, these effluents have been responsible for the poor quality of surface water in an area where irrigation is of vital importance for the local agricultural activities. Despite the introduction of effluent treatment technology by some of the local industry and the input of dilution water from the River Adige via the LEB canal (between sites 10 and 11, Figure 1), the load of pollutants is still quite high. During a survey of the Fratta-Gorzone River system (Barakat and Giusti, 2003), 'dissolved' Cr was found to decrease from about 500 ppb near the main effluent discharge to 43 ± 22 ppb at site 14 (about 16 km further downstream). The recommended water quality standard (50 ppb Cr) are thus exceeded along this river stretch. Preliminary speciation studies carried out by the authors in 2000 indicated that the levels of Cr(VI) greatly exceeded recommended environmental quality standards. Therefore, this aquatic system required more detailed monitoring. Table I shows an example of water chemistry data obtained from sites 8, 9, 9b, and 10, during a one-day sampling session in October 2002.

A considerable number of Cr speciation methods have been developed and reviewed (Kotas and Stasicka, 2000; Marques *et al.*, 2000). Many of these methods

TABLE I
Water chemistry of selected sites monitored along the Fratta River system in October 2002

	Site 8	Site 9	Site 9b	Site 10
Distance from site 8 (km)	0	0.21	0.87	7.23
pH	7.25	7.90	7.10	7.02
T (°C)	16.1	16.0	17.0	18.5
Cond (μS cm^{-1})	771	5990	3510	2406
DO (mg L^{-1})	6.4	6.7	5.9	6.3
BOD_5 (mg L^{-1})	2.2	1.6	1.1	4.1
COD (mg L^{-1})	37.6	104.3	44.3	70.9
Na (ppm)	99.1	600	669	423
K (ppm)	46.5	27.7	16.5	11.4
Ca (ppm)	44.8	137.7	116	106.7
Mg (ppm)	45.2	42.5	34.1	31.9
Cl^- (ppm)	100.1	905.0	893.8	414
HCO_3^- (ppm)	363	470	500	430
SO_4^{2-} (ppm)	120.5	25.6	14.5	452.2
NO_3^- (ppm)	20.0	49.4	39.1	33.7
F (ppm)	0.5	3.8	2.4	1.1
Si (ppm)	4.1	2.9	3.3	4.8
Mn (ppb)	94	112	70	90
Fe (ppb)	86	90	70	80
Cr (ppb)	2.2	514	167.2	132.2

Source. Barakat (2004).

can be very useful when dealing with pristine or slightly polluted environments or in controlled conditions in the laboratory. Unfortunately, some of the commonly used techniques (e.g. organic extractions, co-precipitation with metal flocs, ion pairing reversed phase HPLC) suffer from a number of shortcomings when applied to water contaminated with tannery effluent, mostly as a result of interferences caused by the presence of organic material (Walsh and O'Halloran, 1996). The determination of dissolved Cr(III) based on the difference between the so-called 'total Cr' and Cr(VI) is no longer adequate because Cr(III)-organic complexes can be mistaken for Cr(VI) species (Menden *et al*., 1990). The determination of Cr(VI) using diphenyl-carbohydrazide (DPC) spectrometry was recommended by Rutland *et al*. (1991) and Walsh and O'Halloran (1996) as the least affected by Cr(III)-organic complexes. This method is also presently used by the Italian environment agency (ARPAV) operating in the study area. More recently, additional approaches to the measurement of Cr oxidation states have been proposed, such as the diffusive gradient in thin films (DGT) method (Davison and Zhang, 1994; Ernstberger *et al*., 2002). As explained in more detail in Section 2.2, this method can be used for the *in*

situ measurement of time-averaged concentrations of labile Cr(III) species. Also, it is possible to use the same DGT unit to determine the concentration of CrVI present in the DGT diffusive gel layer.

Independently from the sensitivity and selectivity of laboratory techniques, a major source of error in Cr speciation studies is associated with a lack of appropriate methods of sampling, sample preparation and storage. In some of the published literature, it is assumed that the integrity of the samples is not significantly affected during the time elapsed between field collection and laboratory analysis, especially if the samples have been acidified. This may be the case in waters that are not receiving high inputs of Cr and that have reached a state of equilibrium (Comber and Gardner, 2003), but very unlikely to apply to waters that are impacted by fresh inputs of Cr-laden wastewater effluent, as in the case of the Fratta River. Speciation analysis cannot be carried out after sample acidification. Acidification affects the size of colloidal particles present in the sample (filtered or unfiltered) and alters the oxidation state of Cr, with Cr(VI) likely to be quickly reduced to Cr(III) (Sirinawin and Westerlund, 1997).

In our study, we selected speciation techniques that allow either the direct determination of Cr(VI) in the field (the DPC method) or the separation of Cr(III) and Cr(VI) *in situ* (the DGT method). Cathodic stripping voltammetry (Galimowski *et al*., 1985; Korolczuk, 2000) and the Sephadex ion exchange method (Hiraide and Mizuike, 1989; Beaubien *et al*., 1994) were also tested but were not used on a routine basis as they are more time consuming and require a mobile laboratory. Also, our laboratory experiments with natural samples indicated a very low recovery by Sephadex of the colloidal Cr fraction.

1.1. Aims and objectives

The main aims and objectives of this work included the following.

(i) An assessment of the efficiency and accuracy of *in situ* and field-based speciation methods in the measurement of dissolved Cr, Cr(III) and Cr(VI) in river water affected by tannery effluent. Emphasis was given to the simplicity of deployment and measurement, contamination issues, and the use of methods that do not suffer from large interferences of organic Cr(III) complexes in the determination of Cr(VI). Particular efforts were made to assess the usefulness of the *in situ* DGT technique developed by Davison and Zhang (1994).

(ii) A parallel study of the efficiency of the DGT technique in controlled laboratory conditions using synthetic solutions of increasing complexity containing realistic concentrations of Cr(III) and Cr(VI) species, humic substances, and EDTA.

(iii) An evaluation of the occurrence and distribution of Cr(III) and Cr(VI) species in freshwater of a river system that has been adversely affected by discharges of the tannery industry for many decades.

2. Materials and Methods

2.1. Field sampling and monitoring

At each sampling site, 1 L of water was collected and filtered (0.45 μm GF/C Whatman) using a Nalgene portable filtration unit and pump. A sub-sample was acidified to about pH 2.0 with HNO_3. 'Dissolved' Cr was measured in all samples by electrothermal atomic absorption spectrometry (ETAAS) (Unicam, Thermoelemental UK) after 3 days (i.e. the time normally required to fly the samples from Italy back to the UK laboratory) and after 10 days from sample collection. Examples of data sets are shown in Figure 2. The filtered samples were used for the immediate determination of Cr(VI) concentrations using a field-based portable colourimetric method (HI 93749 Hanna ion meter, Hanna Instruments, Bedfordshire, UK) based on the EPA 7196 method. This method depends on the reaction of Cr(VI) with diphenyl-carbohydrazide (DPC) to form a purple colour in the sample. A silicon photocell detects the light emitted through the sample by a light-emitting diode at 555 nm and allows the measurement of absorbance, which is related to concentration. The meter detects Cr(VI) concentrations from 0 to 300 ppb**.** At each site, two pre-prepared DGT units purchased from DGT Research Ltd., were deployed in streamwater for about 24 h. The two DGT units were tied (back to back) with a fishing line to one end of a bamboo stick whilst the other end was hammered securely into the river bed or into the river bank, depending on local conditions. *In situ* water monitoring and collection of samples for laboratory work was carried out during five field sessions over a period of 2 years (2001–2002). Once the first monitoring sessions revealed which part of the river system was most impacted by Cr inputs (i.e. the 16 km stretch downstream of site 9), water sampling, DGT deployment, and Cr(VI) measurement in the field with the DPC method were carried out more frequently at sites 8–14 than elsewhere in the catchment.

2.2. The DGT method

This technique is based on (i) the diffusion of labile Cr species from the aqueous medium through a polyacrylamide gel and (ii) the binding of Cr(III) in a gel layer containing the ion-exchange resin Chelex-100. Labile Cr(III) species are those that can diffuse and dissociate (if bound to a complex/molecule) through the gel and bind to the resin gel. The concentration (C_{DGT}) of Cr(III) determined with the DGT deployed in solution can be calculated taking into account the mass (M) of Cr accumulated in the resin gel, the thickness (Δg) of the diffusion layer, the diffusion coefficient (D) for Cr, the area (A) exposed to the solution, and the time (t) of deployment:

$$C_{\mathrm{DGT}} = \frac{M\,\Delta g}{D\,A\,t}.$$

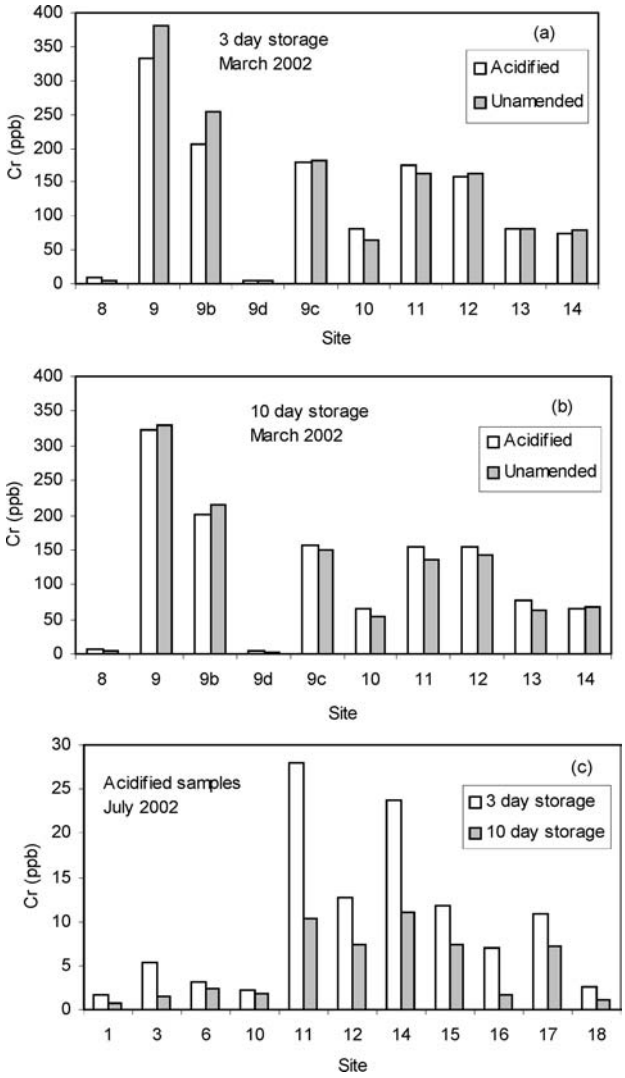

Figure 2. Comparison of the concentration of 'dissolved' Cr after (a) 3-day storage and (b) 10-day storage of acidified and unamended samples collected in March 2002. Part (c) shows the variations of Cr concentration with time of storage of the acidified samples collected in July 2002.

This value represents the time-averaged metal concentration in the solution of interest over the period of deployment. As Cr(VI) equilibrates in the diffusive gel, it can be monitored *in situ* in parallel with Cr(III). In the pH range of 3–5, the DGT method allows the measurement of the simple monomeric Cr(III) species (i.e. Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_2^+$) that are in labile equilibrium with the Cr(III) present in the bulk solution. The monomeric hydrolysis products of Cr(III) are in rapid, dynamic equilibrium with Cr^{3+} due to proton exchange reactions on a microsecond

timescale. At pH > 5, the method can potentially measure polynuclear Cr(III) species. Kinetically inert complexes are excluded from measurement (Ernstberger *et al.*, 2002). Whereas the DGT response to Cr(III) species is based on diffusive mass transport, dissociation constants, and size of the diffusing species, the response to Cr(VI) species is based on equilibration. Equilibration is reached when the concentration of Cr(VI) in the diffusive gel equals the concentration in solution. Cr(III) compounds and complexes can only be measured if they dissociate in the diffusive gel and reach the resin gel surface on a timescale of a few minutes. Such complexes include those formed with fulvic acids but exclude very stable ones such as those formed with EDTA.

Two types of DGT units were used in the laboratory experiments: DGT containing an acrylamide monomer cross-linked with a patented agarose derivative (APA DGT) and DGT containing an acrylamide monomer cross-linked with bisacrylamide (RG DGT) (Zhang and Davison, 2000). The latter are supposed to have smaller pore sizes in the gel than those of the regular APA DGT. The resin gels were eluted with the recommended 1 M HNO_3 leaching procedure. Selected units were additionally eluted with boiling 16 M HNO_3.

2.3. Laboratory experiments

In the laboratory, Cr(VI) species were detected by the DPC method in synthetic solutions (de-ionised water and 0.005 M $NaNO_3$) containing either Cr(VI) alone or both Cr(III) and Cr(VI) species. Also, DGT units were used for the simultaneous detection of Cr(VI) and Cr(III) in synthetic solutions with or without additions of humic substances (HS) and EDTA. Solutions were prepared in deionised water and 0.005 M $NaNO_3$ (Fisher Scientific, Loughborough, UK) with standard Cr(III) (1004 ± 5 μg mL^{-1} in 0.5 M HNO_3) and Cr(VI) (995 μg mL^{-1} in 0.28 M HCl) solutions (Sigma Aldrich, Dorset, UK). Standard solutions were freshly prepared for every ETAAS run. Solutions and reagents were kept cold (1–4 °C) in a refrigerator. Details of the ETAAS method are given in Table II.

TABLE II
ETAAS instrumental parameters and furnace programme

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar gas flow
Graphite atomiser				
Drying	120	20	20	Medium
Pyrolysis	1650	20	10	Medium
Atomisation	2500	0	5	Off
Cleaning	2650	0	2	Medium

Spectrometer: wavelength: 357.9 nm; spectral bandpass: 0.5 nm; background correction: Zeeman; Cuvette type: pyrolytically coated, L'vov platform; matrix modifier: $Mg(NO_3)_2$; mode: peak area.

2.4. QUALITY CONTROL

All reagents used were of ultrapure grade. Labware and plasticware were washed according to the method of Laxen and Harrison (1981). Blanks were run with each sample batch. Contamination from reagents, containers, the atmosphere, and the DGT units (total-method blank) was usually found to be in the range of 0.8–2.1 ppb Cr, with the DGT blank determined in de-ionised water normally accounting for 0.2–0.6 ppb Cr. Also, the humic substances used in the controlled experiments (extracted from Laurentian soil, purchased from Fredriks Research Ltd., Amsterdam, The Netherlands) were found to contain traces of Cr. The HS contribution of Cr in synthetic solutions was normally 0.8 ppb Cr. Chromium concentrations were determined by ETAAS in synthetic and natural samples, blanks, and certified reference materials (SRM 1943d, LGC 6011). The detection limit of ETAAS was normally 0.015 ppb. Magnesium nitrate matrix modifier was used in all ETAAS determinations. EDTA salt (BDH, Leicester) used in synthetic solutions did not contain any detectable Cr.

As some of the water samples collected had a high salinity and contained organic material, potential interferences on Cr detection (by ETAAS) caused by humic substances (HS) and Cl were investigated and were found to have no significant effect on the analytical measurements. Also, the DPC measurements were not found to be affected by significant interferences associated with the presence of NaCl, EDTA, or HS. The experiments were carried out in de-ionised water and in 0.005 M $NaNO_3$ solutions containing 20 ppb Cr with concentrations of NaCl or HS ranging from 0 to 25 ppm, and up to 10 ppm EDTA.

The potential loss of Cr from solution due to adsorption on the filter, and/or changes in Cr oxidation state subsequent to filtration, were assessed by measuring Cr(VI) concentrations with the DPC method before and after filtration of synthetic solutions and natural samples (Table III). In the field, the membrane filters were washed by filtering 100 mL of natural water which were discarded before the

TABLE III

Effect of sample filtration with GF/C Whatman filters on 'dissolved' Cr (ppb) and on Cr oxidation state, measured by the DPC methods

Cr in sample	pH	Before filtration	After filtration	*n*
Standard solutions				
20 ppb Cr(VI)	5.9	19.4 ± 1.2	20.7 ± 2.3	6
20 ppb Cr(III)	5.7	0.7 ± 1.1	Not detected	6
Natural samples				
A	7.6	nd	nd	4
B	7.6	26.7 ± 1.2	24.3 ± 2.1	3
C	7.6	22.7 ± 1.5	24.3 ± 2.1	3

nd means not detected.

collection of samples. Filter blanks were negligible or undetectable. GF/C filters were used because the filtration of natural water samples is faster than with membrane filters and because they allow the collection of suspended solids from a large volume of water.

The accuracy of ETAAS measurements of Cr was assessed by the analysis of certified reference materials LGC 6011 (soft drinking water) and SRM 1643d (surface water); the percentage of Cr recovery was 98.7 ± 14.2 ($n = 8$) and 100.7 ± 7.9 ($n = 14$), respectively. The accuracy of ETAAS and DPC measurements was also assessed in additional experiments where synthetic Cr(VI) solutions were analysed with both methods. A strong correlation ($r = 0.998$) was found between measured ETAAS concentrations of Cr(VI) and expected Cr(VI) concentrations. Also, a strong correlation ($r = 0.982$) was found between DPC measurements of Cr(VI) and expected Cr(VI) concentrations in standard solutions.

2.5. Modelling

To gain further insight into the speciation of Cr in the presence of humic substances, we input (i) the composition of the synthetic solutions used in our laboratory experiments, and (ii) the composition of the natural water from the Fratta-Gorzone River to Windermere Humic Aqueous Model (WHAM) /Model VI of Tipping (1998). This is an electrostatic, discrete-site model of cation–humic substances interactions combined with a simple inorganic speciation code for aqueous solutions. The model operates over the pH range of 3–11 and the ionic strength of 0.001–1 M. Model parameters were derived by fitting published data and calculations of molecular geometry. The database includes only one Cr oxidation state, i.e. Cr(III).

Our computer simulations with WHAM 6.0 were carried out for the pH range of 4–10, for Cr concentrations ranging from 20 to 500 ppb, and assuming a total concentration of humic substances of 10 mg L^{-1}, with humic acids (HA) to fulvic acid (FA) ratios ranging from 1:9 to 9:1. The ionic strength of the synthetic solutions was 0.005 M. The river water had an ionic strength ranging from about 0.010 to 0.047 M.

The most recent version of the chemical speciation code WATEQ4F of Ball and Nordstrom (2001) was used to compute major and trace element (including Cr(III)) speciation and mineral saturation for the synthetic solutions used in our experiments and for the river water investigated.

3. Results and Discussion

3.1. Ageing of streamwater samples and the effect of sample treatment

Figure 2 shows examples of analyses of 'dissolved' Cr in filtered (0.45 μm) river water carried out 3 and 10 days after collection. The sets of samples collected during

the March 2002 field session (Figures 2a and 2b) showed significant deterioration at sites (9 and 9b) close to the main effluent discharge. In July 2001, Cr losses of up to 71% (Figure 2c) were detected in acidified samples containing relatively low Cr concentration (<30 ppb). Filtration and acidification affected the concentration of 'dissolved' Cr especially in the case of samples characterised by relatively higher levels of COD (104–206 mg L^{-1}). The observed reduction in 'dissolved' Cr after sample acidification may be explained by the aggregation and settling of colloidal particles. Similar findings were reported for 'dissolved' aluminium by McFaralane *et al*. (1992) and later confirmed by Smith *et al*. (1996).

3.2. Cr(III) AND Cr(VI) MEASUREMENTS IN SYNTHETIC SOLUTIONS BY DGT

Examples of labile Cr measurements by APA DGT in de-ionised water with 30 ppb Cr(VI) or 30 ppb Cr(III) are shown in Figure 3. Measurements of Cr(III) in 0.005 M $NaNO_3$ solutions with and without humic substances (Figure 4) and with EDTA (Figure 5) were also obtained.

In de-ionised water of pH 5.8, the DGT recovery of Cr(III) decreased to 86% (Figure 3a) in the presence of 5 ppm HA, whereas the recovery of Cr(VI) (Figure 3b)

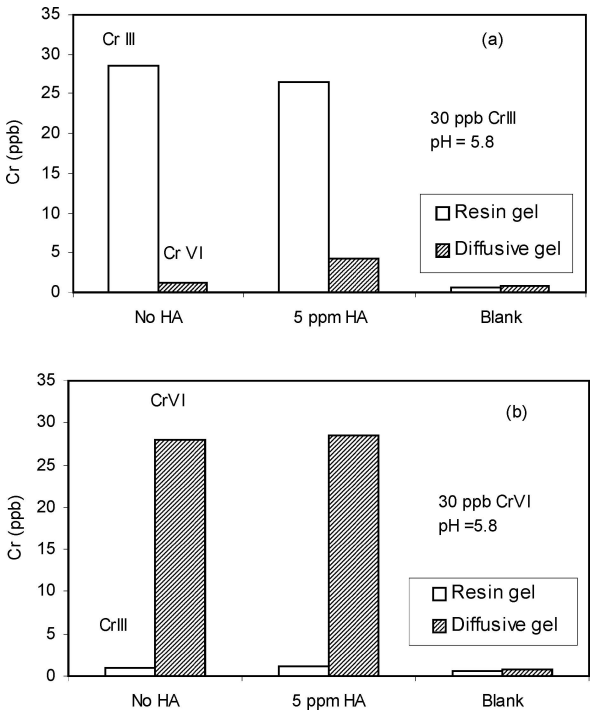

Figure 3. DGT recovery of (a) Cr(III) and (b) Cr(VI) in deionised water solutions with 30 ppb Cr(III) or 30 ppb Cr(VI).

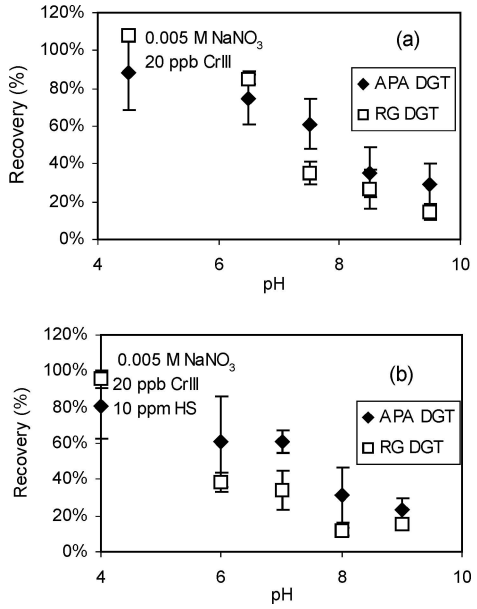

Figure 4. Cr(III) recovery in 0.005 M $NaNO_3$ solutions by RG DGT and APA DGT (a) in the absence, or (b) presence of 10 ppm of humic substances. The initial Cr(III) concentration was 20 ppb.

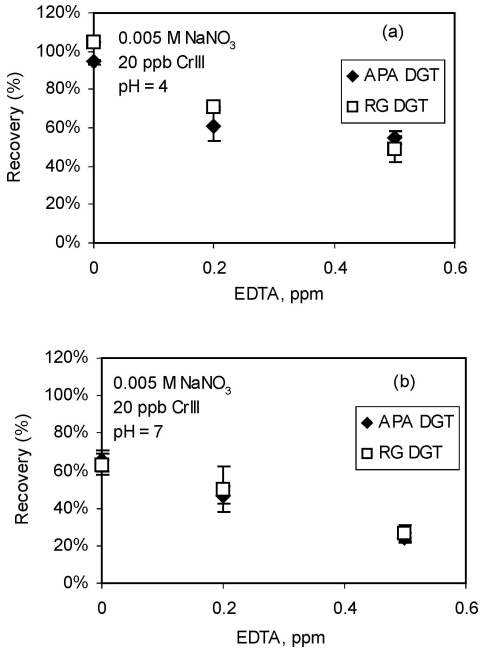

Figure 5. Cr(III) recovery by RG DGT and APA DGT in 0.005 M $NaNO_3$ solutions of (a) pH 4.0 and (b) pH 7.0 containing EDTA.

was less affected (94%). Small amounts of the Cr(VI) used in the experiments were detected as Cr(III) (Figure 3b) in the resin gel, whereas some Cr detected (Figure 3a) in the diffusive gel is actually Cr(III) that has not managed to reach the resin gel. After DGT deployment, sufficient time must elapse before elution of both resin gel and diffusive gel. This is to allow all Cr(III) to reach the resin gel. However, it is possible that slow-dissociating Cr(III)-HA complexes may end up trapped in the hydrogel layer. The presence of Cr(VI) in the resin gel may be due to the diffusion of Cr(VI) species into the gel interstices present between the resin beads (Zhang, 2003, personal communication).

The DGT recovery of Cr(III) from the resin gel (deployed for 24 h in 0.005 M $NaNO_3$ solutions containing 20 ppb Cr(III)) decreased with increasing pH of the solution (Figure 4a) to about 40–60% at pH 7.0–8.0, i.e. the pH typically found in the stream investigated. In 0.005 M $NaNO_3$ solutions containing 10 mg L^{-1} HS (1 mg L^{-1} HA and 9 mg L^{-1} FA) from Laurentian soil, less Cr(III) was recovered from the DGT resin gel than in the absence of HS (Figure 4b).

According to the WHAM 6.0 database, nearly 100% of the Cr(III) present in our DGT experiments with synthetic solution should bind to HS when these are present in concentrations totalling 10 ppm, over the pH range considered. In our experiments, the decrease in Cr(III) recovery with the DGT was not as low as expected and not consistent with the degree of complexation predicted by WHAM 6.0. This may indicate that some of the HS-Cr complexes present in solution diffuse, though less freely, through the DGT gel, or that the Cr binding with HS may be weak so that at least some of the metal becomes labile during the diffusion through the gel. Also, the humic substances may not have fully equilibrated in solution. Another important point is that the Cr-HS data in the WHAM 6.0 database is limited to the fitting of data from the study of Fukushima *et al*. (1995) in which the Cr(III)-HA binding constants are based on correlations with other metals as no experimental data were available. Finally, WHAM 6.0 omits significant redox reactions, which are particularly important in the case of Cr. The discrepancies between the computer model predictions (WHAM 6.0) and DGT data obtained in solutions containing HS were found to decrease with increasing pH, possibly due to the declining competition of H^+ ions for binding sites. Also, the diffusive gel is known to swell as pH increases (Zhang and Davison, 1999) and this may enhance the diffusion of the Cr(III)-HS complexes.

The $\log_{10}$ IAP/$K_{sp(T)}$ values for synthetic solutions containing 0.005 M $NaNO_3$, 20–500 ppb Cr(III), and any combination of HA and FA totalling up to 10 mg L^{-1}, increased from about 0 at pH 4 to about 10 in the pH range 7–10 for Cr_2O_3 (eskolaite), and remained negative below pH 6 for $Cr(OH)_{3(cr)}$ and below pH 7 for $Cr(OH)_{3(a)}$. This means that the solutions should have became supersaturated with respect to these solid phases as pH increased, thus contributing to the observed reduction in the concentration of labile Cr(III) eluted from the DGT, especially at pH $\geq$ 6. WATEQ4F did not predict changes in Cr solubility in the presence of up to 10 mg L^{-1} of HA or FA.

Preliminary experiments on Cr(III) recovery in de-ionised water solutions (Barakat, 2004) revealed poor DGT performance, due to the effect of low ionic strength on metal recovery (Alfaro-De la Torre *et al*., 2000; Sangi *et al*., 2002). The effect of EDTA on the DGT uptake of Cr(III) in 0.005 M $NaNO_3$ solutions (Figure 5) is significant (a drop of 80% at pH 7.0 with up to 0.5 ppm EDTA). The DGT data for sites located immediately downstream of the main tannery effluent (site 9) will reflect the chelation of Cr(III) by EDTA as this was found to be present in relatively high concentrations (0.7–0.8 ppm) (Barakat, 2004). The drop in Cr(III) uptake by the DGT is due to the increasing non-liability of the Cr-EDTA complex as pH increases. The formation and stability of the Cr-EDTA complex depends on the formation constant of the complex, the initial concentrations of Cr(III) and EDTA, and the pH of the solution. The complex does not form readily but, given enough time for equilibration and/or sample heating, the complex becomes stable. The strength of binding increases with pH and it is not affected much by photolysis at the timescale of the experiments (Garvan, 1964). There is presently very little information on the effect of environmental variables on the fate of Cr-EDTA complexes.

If the pore size of the restricted gel excludes the majority of the organic species and allows inorganic species to diffuse, it could estimate the inorganic species *in situ* with low interferences from fulvic and humic acids and other organic ligands. Unfortunately, this could also be a drawback. It has generally been assumed that the formation of EDTA-metal complexes (and of other metal complexes) reduces the toxicity of free heavy metal ions. However, there is increasing evidence that EDTA complexes can be more toxic than free metals (Oviedo and Rodríguez, 2003). The non-liability of Cr-EDTA complexes mean that the DGT method may not necessarily be able to selectively accumulate all the bioavailable and more toxic fraction of Cr species.

3.3. Cr(III) AND Cr(VI) MEASUREMENTS IN NATURAL SAMPLES BY DGT

The levels of Cr(III) determined by DGT in the Fratta River were in the range of 0.5–97.5 ppb with maximum levels found at the effluent discharge site (9). Despite the dilution brought about by inputs of water from the LEB canal (which in turn derives its water from the Adige River) 'dissolved' Cr levels remain considerably high after dilution.

The ratio of Cr(VI)/'total Cr' determined by DGT and DPC for sites 8–14 is shown in Figure 6a. The Cr(VI)/Cr(III) ratio by DGT for sites 8–14 is shown in Figure 6b. Assuming that no additional significant inputs of Cr(VI) exist along this river stretch, the trend found for Cr(VI) downstream of the main effluent discharge (site 9) indicates a possible oxidation of Cr(III) to Cr(VI)**.** A drop in Cr(III) is very likely to be due to the transfer of Cr(III) to the colloidal/particulate phase, to the formation of Cr-EDTA complexes and to the binding of Cr(III) to humic substances, all factors that reduce the amount of Cr(III) measured by the DGT method.

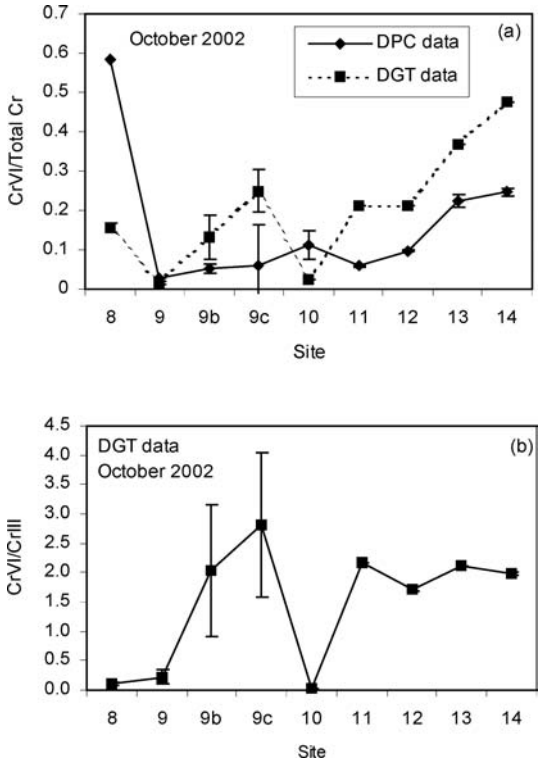

Figure 6. (a) Cr(VI)/total Cr ratios and (b) Cr(VI)/Cr(III) ratios in water samples from field sites downstream of the effluent discharge. The term 'total Cr' refers to the sum of Cr(III) and Cr(VI), as often reported in the literature.

The fact that Cr(III) concentrations measured by DGT are time-averaged over a period of many hours makes the comparison with DPC data quite difficult. Also, the DGT data for Cr(VI) is based on equilibration and refers to the last 10–20 min of DGT deployment in the river.

The saturation index ($SI = \log_{10} IAP/K_{sp(T)}$) was calculated with WATEQ4F for the stream water investigated. Given the circumneutral pH of the water at the sites monitored, supersaturation was found with respect to Cr_2O_3 (eskolaite), $FeCr_2O_4$, and $Cr(OH)_{3(cr)}$. The water approached saturation for $Cr(OH)_{3(a)}$. However, these calculations do not take into account that complexation with organic compounds may prevent the precipitation of chromium oxides and hydroxides.

3.4. DGT REPRODUCIBILITY IN FIELD CONDITIONS

The ability to reproduce the DGT measurements was tested by deploying multiple units at each river site. The mean difference between DGT pairs for multiple measurements was about $23.6 \pm 18.1\%$ for Cr(III) and $16.5 \pm 12.6\%$ for Cr(VI)

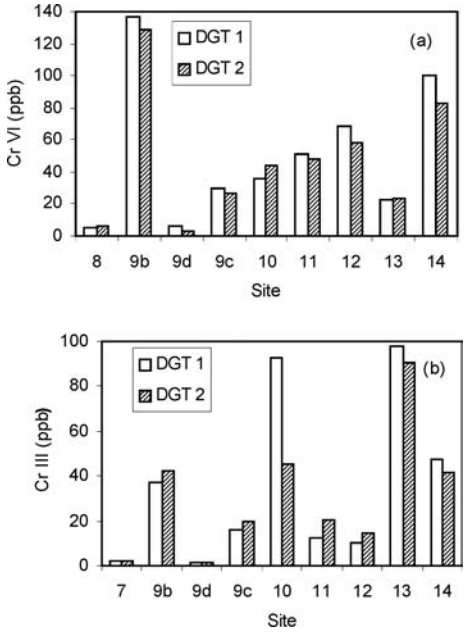

Figure 7. Reproducibility of (a) Cr(VI) and (b) Cr(III) measurements by DGT units deployed *in situ*.

(Barakat, 2004). Figure 7 shows an example of DGT data reproducibility for Cr(VI) (Figure 7a) and Cr(III) (Figure 7b) in March 2002.

The cases of a low replication of *in situ* DGT measurements in streamwater can be caused by (i) fouling, and (ii) the magnification of errors resulting from the pre-concentration effect in the resin followed by dilution before analysis. Sangi *et al*. (2002) suggested that another cause could be small variations of the thickness of the gel layer in DGT units from different batches. The gel we used was from the same batch (Zhang, 2004, personal communication). It is possible that small variations of the diffusion layer thickness of the DGT may be caused by variations of the diffusive boundary layer under different hydrodynamic conditions in the river.

3.5. DGT RECOVERY OF Cr(III) IN NATURAL SAMPLES AND SYNTHETIC SOLUTIONS, AS OBTAINED FROM RESIN ELUTION WITH ACID OF DIFFERENT MOLARITY

After deployment in the field, the digestion of DGT resins in hot 16 M HNO_3 after the conventional 1 M HNO_3 leach showed that up to 90% of the Cr bound by the resin can remain in the resin gel after the initial leaching procedure (Figure 8). In the case of synthetic solutions, the overall Cr recovery obtained with this two-step leaching procedure was close to 100% (Table IV). Higher recoveries can be explained by the solution blank and DGT blank. Since the conventional 1 M HNO_3 leaching

TABLE IV

Examples of Cr(III) extraction from DGT resin gels using a two-step procedure, i.e. 1 M HNO_3 followed by hot 16 M HNO_3

Sample	pH	Initial Cr(III) concentration in solution (ppb)	Cr(III) leached with 1 M HNO_3 (ppb)	Cr(III) leached with hot 16 M HNO_3 (ppb)	Total mass of Cr(III) leached (ppb)
A	4	17.0	14.9	7.9	22.8
B	4	18.5	11.4	9.6	21.0
C	6	18.4	12.2	5.4	17.5
D	6	20.8	12.2	10.0	22.2
E	7	19.5	5.9	13.2	19.1
F	8	17.3	7.3	12.5	19.8
G	8	18.2	2.5	17.4	19.9
H	9	15.5	2.3	12.8	15.1

DGT blanks in 0.005 M $NaNO_3$: 0.8–2.1 ppb.
DGT blanks in de-ionised water: 0.2–0.6 ppb.

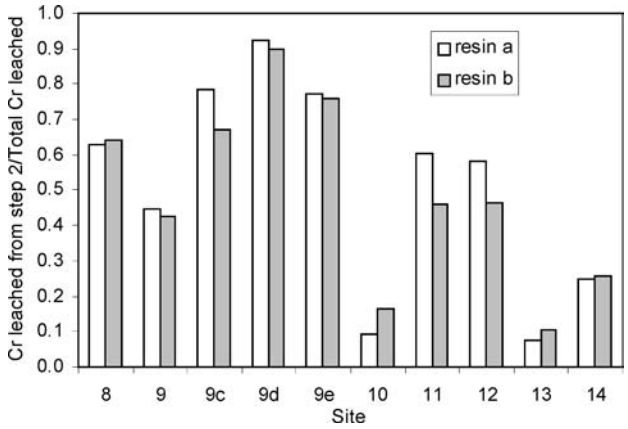

Figure 8. Ratio of Cr leached by boiling DGT resin gels in 16 M HNO_3 (step 2) over total Cr leached by both 1 M HNO_3 (step 1) and 16 M HNO_3 (step 2).

procedure is tailored for the labile monomeric Cr(III) species, the formation of small colloidal and/or polymeric Cr species that elute less efficiently could explain the incomplete recovery by the conventional elution procedure.

3.6. Cr(VI) MEASUREMENTS BY DPC IN SYNTHETIC AND NATURAL SOLUTIONS

Table III indicates that sample filtration did not change the Cr species detected by the DPC method. No significant variations in Cr(VI) were caused by filtration of

natural samples. If samples are not filtered, the presence of a high concentration of suspended solids produce inaccurate results. Our tests indicated that in this case the Cr readings vary depending on the lapse of time between collection and measurement. This is due to the fact that suspended particles interfere with the light emitted by the photocell of the portable instrument.

In synthetic solutions (de-ionised water and 0.005 M $NaNO_3$), good agreement was found between ETAAS data and DPC measurements of Cr(VI). The presence of up to 20 ppb Cr(III) in solution did not have any effect on the Cr(VI) readings.

Though the DPC method has been shown not to be affected by HS and EDTA in our laboratory experiments, Walsh and O'Halloran (1996) found that up to 15.0 ± 4.0 ppb of the 5 ppm Cr present in solution as organic complexes (especially Cr(III)-casein) were detected as Cr(VI) by DPC spectrophotometry.

In natural samples, the DPC method gave different Cr(VI) readings than the DGT diffusive gel (Figure 9). DGT values were generally higher than DPC readings, especially in samples collected downstream of the main effluent discharge (e.g. site 9b). In March 2002, the concentrations of Cr(VI) determined by DGT and DPC at site 9b (660 m downstream of site 9) were typically 133 ± 5.7 and 50.0 ± 29.3 ppb, respectively. In October 2002, Cr(VI) was 29.9 ± 10.6 and 12.0 ± 0.0 ppb, respectively. It is possible that some of the organic or inorganic Cr(III) complexes

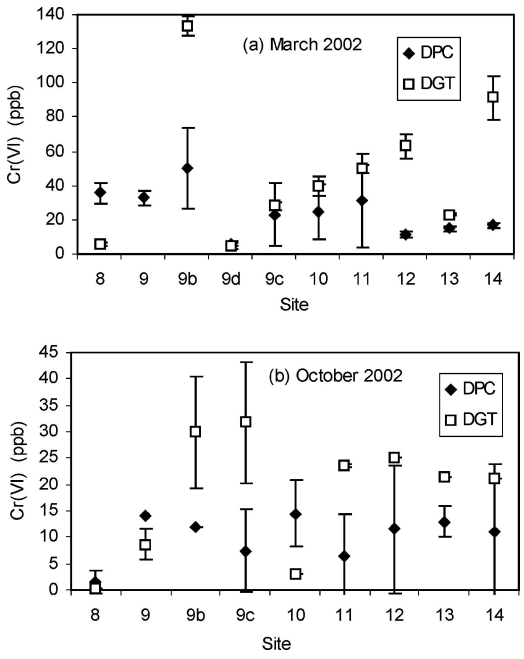

Figure 9. Comparison of Cr(VI) measurements obtained by DGT and DPC in (a) March 2002 and (b) October 2002. The standard deviation bars shown for DPC measurements refer to separate measurements carried out during 24 h and reflect the variations of Cr levels in the stream.

present along this river stretch dissociate slowly in the diffusive gel and this fraction of Cr(III) is thus incorrectly measured as Cr(VI). However, the DGT and DPC data are not directly comparable as DGT measurements refer to the Cr(VI) concentration in the diffusive gel that has equilibrated with Cr(VI) in solution 10–20 min prior to DGT retrieval, whereas the DPC data refers to the metal concentration at the time of measurement. Interferences in the DPC determination of Cr(VI) are known to occur in the presence of concentrations of Fe (>1 ppm) higher than those found in the river water analysed. Possible interferences with vanadium are removed 10 s after reaction with diphenyl-carbohydrazide. In our measurements, the standard reaction time was 6 min. The presence of Cr(V) complexes, which are stable for several hours in aqueous solutions, cannot be ruled out. They are reported to be detected as Cr(VI) by the DPC method (Eckert *et al*., 1991).

4. Conclusions

This work highlights the very high Cr contamination in the Fratta-Gorzone River system and the importance of implementing *in situ* monitoring of Cr and especially of the Cr(VI) species. Careful consideration must be given to the sampling protocol and to the analytical methods to be adopted when carrying out a Cr speciation study. Treatment (filtration, acidification) or storage of natural water samples can cause significant errors in the determination of 'dissolved' Cr. *In situ* or field-based Cr speciation techniques should be preferred to those that require sample storage or manipulation before analysis.

The field-based DPC method proved to be a relatively economic and fast way of measuring Cr(VI) with a good degree of accuracy. The DGT technique looks promising as it allows the simultaneous analysis of Cr(III) and Cr(VI) (in addition to the labile species of other elements) after *in situ* element pre-concentration. Also, the DGT time-integrated metal concentration over the period of deployment takes into account variations of effluent and river water quality at times (e.g. overnight, weekend) when conventional monitoring does not normally take place. This allows a more accurate assessment of compliance with existing regulation/legislation. However, there are still uncertainties about (i) the type of species that are not removed from the resin gel by the conventional leaching with 1 M HNO_3, (ii) the extent of separation that the different types of DGT can achieve between labile Cr species and Cr species chelated by EDTA or bound to HS, and (iii) the replication of measurements in natural waters, especially at contaminated sites. Given the complex chemistry of tannery effluent, more studies are required to assess the performance of the DGT technique in solutions of composition similar to those found in contaminated waters.

The Cr(VI) data obtained with both speciation methods (DGT and DPC) appear to contradict the commonly accepted assumption that Cr(VI) species are easily reduced in typical conditions found in river water. The increase in Cr(VI)/Cr(III)

values downstream of the main wastewater discharge is very likely to be caused by the reduced detection of Cr(III) by the DGT method caused by the formation of non-labile Cr species. At the circumneutral pH of the streamwater investigated, the presence of humic substances and chelate ligands such as EDTA means that the free cation Cr^{3+}, or monomeric species such as $Cr(OH)^{2+}$ are very unlikely to represent a high percentage of the Cr species, as can be predicted with chemical speciation codes. The solution chemistry of Cr is likely to be controlled by the presence of colloidal species and by the formation of organic complexes. This could be one of the factors causing the lower Cr(VI) levels detected by the DPC method as opposed to those obtained with the DGT, particularly at sites that are known to be impacted by wastewater discharges.

We found large discrepancies between computer model predictions (WHAM 6.0) and DGT data obtained from solutions containing humic substances. These differences can be caused by many factors. Unlike ions of other heavy metals (e.g. Cu, Zn, Ni, Pb) that are present in solution as hydrated divalent cations, the dissolved species for Cr(III) change depending on pH conditions (e.g. Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$, $Cr(OH)_4^-$,). The WHAM model is based on equilibrium reactions involving protons, metal ions, and their first hydrolysis products only, and assumes that the same intrinsic equilibrium constants apply to the aquo ion and its first hydrolysis product. The inorganic reactions listed in the database are restricted to monomeric metal complexes, the assumption being that polymeric species do not bind to humic material. The important role that polymeric species and colloidal particles may have in aquatic systems is thus overlooked. The binding constants contained in the model database should be validated with experimental studies. Finally, there is no provision in WHAM 6.0 for the presence of Cr(VI) species and of the effect of redox conditions on Cr speciation.

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