Abiotic reduction of Cr(VI) by humic acids derived from peat and lignite: kinetics and removal mechanism

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Abstract
Hexavalent chromium contamination of groundwater is a worldwide problem caused by anthropogenic and natural processes. We report the rate of Cr(VI) removal by two humic acids (extracted from Miocene age lignite and younger peat soil) in aqueous suspensions across a pH range likely to be encountered in terrestrial environments. Cr(VI) was reduced to Cr(III) in a first-order reaction with respect to Cr(VI) concentration, but exhibited a partial order (~ 0.5) with respect to [H+] . This reaction was more rapid with the peat humic acid, where Cr(VI) reduction was observed at all pH values investigated (3.7 ≤ pH ≤ 10.5). 13C NMR and pyrolysis GC-MS spectroscopy indicate that the reaction results in loss of substituted phenolic moieties and hydroxyl groups from the humic acids. X-ray absorption spectroscopy indicated that at all pH values the resulting Cr(III) was associated with the partially degraded humic acid in an inner-sphere adsorption complex. The reaction mechanism is likely to be controlled by ester formation between Cr(VI) and phenolic/hydroxyl moieties, as this initial step is rapid in acidic systems but far less favourable in alkaline conditions. Our findings highlight the potential of humic acid to reduce and remove Cr(VI) from solution in a range of environmental conditions.

Keywords Humic substances - Humic acids - Chromium - Contaminated land - Groundwater

Introduction
Chromium is a strategically important metal that is produced commercially from the chromite ore as sodium dichromate and similar chemicals (Wilbur et al. 2000; Jacobs and Testa 2005; Kogel et al. 2006). It is widely used in alloys, electroplating, leather tanning, timber treatment, wax, chromate pigments, refractories, ceramics, catalysts and organic acids (Barnhart 1997; Darrie 2001; Jacobs and Testa 2005; International Chromium Development Association 2016). Chromium has two environmentally stable oxidation states: Cr(III) and Cr(VI) (Pourbaix 1966; Brito et al. 1997). Cr(III) is an essential trace element for living organisms that has an influence on the biological function of the humans and animals (Lukaski 1999) and has a role in lipid, carbohydrate and glucose metabolism (Vincent 2000; Cefalu and Hu 2004). In contrast, Cr(VI) is toxic to plants (Chandra and Kulshreshtha 2004; Shanker et al. 2005), animals and humans (Costa 1997) and is classified as a mutagenic and carcinogenic material (Leonard and Lauwerys 1980; Kondo et al. 2003; Holmes et al. 2008).
Occasionally the manufacture and industrial use of chromium can lead to contamination of groundwater and soils (Burke et al. 1991; Puls et al. 1999; Geelhoed et al. 2002; Whittleston et al. 2011; Ding et al. 2016; Izbicki and Groover 2016; Matern et al. 2016). Natural processes have also lead to elevated chromium concentrations in groundwater above the World Health Organisation maximum for drinking water (50 μg/L; (WHO 2003)) at numerous locations around the world (Robertson 1991; Fantoni et al. 2002; Ball and Izbicki 2004; Steinpress 2005). For example, ultramafic rocks can have high Cr contents (Stueber and Goles 1967; Schwertmann and Latham 1986; Becquer et al. 2003), which is mainly in Cr(III) in the parent minerals, but can be oxidised to Cr(VI) during weathering, particularly by manganese (IV) oxides (Bartlett and James 1979; Eary and Rai 1987; Fendorf and Zasoski 1992). While Cr(VI) release can result from many processes, some of the most intractable environmental problems are associated with poor disposal of chromite ore processing residue (COPR) from the high-lime process. While this is an obsolete method for producing chromate chemicals, it is only now being phased-out in newly industrialised countries (e.g. India, China and Bangladesh; Darrie2001; Gao and Xia 2011; Matern et al. 2016). As a result, there are numerous problematic legacy sites from this technology around the world (Higgins et al. 1998; Geelhoed et al. 2002; Stewart et al. 2007; Whittleston et al. 2011; Matern et al. 2017; Zhou et al. 2018). Water in contact with high-lime COPR has a pH > 12 and can have aqueous Cr(VI) concentrations in excess of 1 mM (Higgins et al. 1998; Stewart et al. 2010; Matern et al. 2017). When such water inevitably escapes from abandoned waste piles into the geosphere, it produces Cr(VI) plume where the pH varies from hyperalkaline values close to source towards the natural soil value in the far field.

Due to its toxicity and potential mobility (as soluble anionic aqueous species such as CrO$_4^{2-}$, HCrO$_4^{-}$ and Cr$_2$O$_7^{2-}$; Pourbaix 1966; Brito et al. 1997), the accidental release of Cr(VI) into terrestrial ecosystems is a significant cause for concern. In oxidising environments, surface complexation reactions with iron and aluminium oxide minerals can remove Cr(VI) from solution at acidic pH (Rai et al. 1989); however, at neutral and alkaline pH, adsorption to soil minerals is generally weak due to the presence of net negative surface charge at mineral surfaces (Rai et al. 1989; Langmuir 1997). Cr is far less mobile in reducing soil environments because aqueous Fe(II), Fe(II)-containing minerals and reduced sulphur compounds can rapidly reduce Cr(VI) to Cr(III) (Eary and Rai 1988; Rai et al. 1989; Eary and Rai 1991; Palmer and Wittbrodt 1991). Once reduced, Cr(III) will precipitate as Cr(OH)$_3$ in circumneutral conditions (Pourbaix 1966) or, when reduced by Fe(II), as (Cr$_x$ Fe$_{1-x}$)(OH)$_3$ (Sass and Rai 1987; Eary and Rai 1988; Rai et al. 1989).

Most soils contain organic matter, which plays an important role in the cycling of many elements in the environment (Gustafsson et al. 2001). Humic substances (the majority of soil organic matter; International Humic Substances Society 2007) are the dark-coloured, heterogeneous organic compounds produced by the decay and transformation of plant and animal residues by bacteria and fungi (Stevenson 1994; Swift 1999; Sutton and Sposito 2005; Brookes et al. 2008). The main humic precursor molecules are formed by depolymerisation and oxidation of plant biopolymers and proteins to produce molecules that contain unaltered polymer segments and phenolic, hydroxyl, carboxyl and amino residues (Wershaw 1986; Stevenson 1994; Swift 1999; Aro et al. 2005). However, there is still debate about how humic substances subsequently form. The traditional ‘polymer model’ assumes that the precursors are microbiologically synthesised into large randomly coiled polymeric macromolecules (Swift 1999), whereas recent evidence suggests that humic substances are supramolecular associations (Wershaw 1994; Kögel-Knabner 2000; Sutton and Sposito 2005).

Amphiphilic precursor molecules cluster together into micelle-like particles (Wershaw 1999; Kögel-Knabner 2000), and other biomolecules from plant degradation become associated with either hydrophobic or hydrophilic domains (Piccolo et al. 1996; von Wandruszka 1998; Zang et al. 2000; Piccolo 2001; Simpson et al. 2002; Fan et al. 2004). While most evidence now supports this ‘micelle model’, it does not preclude development of polymer-type bonds, particularly as humic substances can potentially age and degrade over millions of years (Burdon 2001; Knicker et al. 2002; Sutton and Sposito 2005).

Cr(VI) can be reduced to Cr(III) by reaction with organic matter that contains phenolic, hydroxyl and aldehyde moieties (Lee and Stewart 1967; Wiberg and Schafer 1967; Elovitz and Fish 1995; Chen et al. 2015). The reaction with such moieties is thought to involve a chromate ester intermediate that can form with monomeric aqueous H$_2$CrO$_4$ and HCrO$_4^{-}$ species, with the redox step occurring during ester decomposition (Lee and Stewart 1967; Wiberg and Schafer 1967; Elovitz and Fish 1995). Reduction of Cr by this mechanism is rapid in acidic systems, but the rate decreases markedly with increasing pH (Lee and Stewart 1967; Elovitz and Fish 1995; Wittbrodt and Palmer 1997). Usually, it is assumed that Cr(VI) reduction by alcohol, phenolic and aldehyde moieties is negligible when ≥ pH 6 because chromate ester formation is less favourable with the CrO$_4^{2-}$ dianion, which is the dominant Cr(VI) species at high pH (Elovitz and Fish 1995). However, investigations of Cr(VI) mobility at sites contaminated with hyperalkaline (pH > 12) chromium ore processing residue leachate have observed Cr accumulation in organic-rich soils at ~ pH 10.5 (Higgins et al. 1998; Whittleston et al. 2011; Ding et al. 2016), indicating that high pH interactions may occur under field conditions and timescales not observed in short-term laboratory studies.
Although Cr(VI) reduction by humic substances has been well studied in acidic to neutral systems (Wittbrodt and Palmer 1995; Wittbrodt and Palmer 1997; Jardine et al. 1999; Huang et al. 2012), far less is known about potential reactions in the neutral to alkaline pH range relevant to COPR disposal sites. This knowledge gap is important because humic matter are one of the key soil component controlling Cr(VI) mobility in oxic near-surface environments. Further, the introduction of humic matter at a suitable pH point in a Cr(VI) plume could be the basis for groundwater treatment that mitigates environmental damage at otherwise intractable waste disposal sites. This study therefore investigates the reaction between aqueous Cr(VI) and humic acids derived from two sources (peat and lignin) over the range of pH values representative of an environment where an alkaline plume slowly buffers towards the natural pH value of the host soil. The objectives were to (i) investigate the rate at which Cr is removed from aqueous solution by the humic acids using batch exposure tests, (ii) to determine the oxidation state and local bonding environment of resulting solid-associated Cr using X-ray absorption spectroscopy (XAS) and (iii) identify changes humic acid functionality that resulted from the reaction using both 13C nuclear magnetic resonance (NMR) spectroscopy and pyrolysis-gas chromatography-mass spectrometry (PyGCMS). Together, these new data were used to develop a new understanding of the Cr(VI) reduction mechanism occurring with humic substances in the neutral to alkaline pH range.

Materials and methods

Humic acids

Humic acid is the humic fraction that is soluble at pH 12, but progressively precipitated as the pH is buffered to pH 2 (Stevenson 1994; Wershaw 1994; Sutton and Sposito 2005). Aldrich humic acid (AHA), a lignite derived humic acid (Poynton 2016), was acquired as a sodium salt (Sigma-Aldrich Company Ltd. UK). Control samples were prepared using a 1 M HCl or NaOH. Samples were intermittently shaken, and the pH was adjusted until the pH value was stable for at least 1 day. The suspensions were then autoclaved at 121 °C for 15 min to ensure that the subsequent long-duration experiments were abiotic. After cooling, autoclaved DIW was added to each bottle to make up the volume to 96.7 mL, and the pH was readjusted, if necessary, to each target value. Air was flushed from the experiments by bubbling nitrogen through the suspensions. Finally, 3.3 mL of potassium chromate solution (1/30 M K2CrO4; Fluka, Germany) was added for a 100 mL final volume ([Cr(VI)] = 1100 μmol L⁻¹). Bottles were sealed with butyl rubber stoppers with aluminium crimps (Sigma-Aldrich Company Ltd. UK). Control samples were prepared using the potassium chromate solution and autoclaved, N2 purged, DIW. Bottles were incubated in the dark at 20 ± 1 °C and periodically sampled aseptically for geochemical analysis. During sampling, bottles were shaken and 2 mL of suspension was extracted using N2 gas-filled syringes. Samples were divided for Cr(VI) and pH determination. Subsamples for Cr(VI) analyses were passed through a 3-kDa filter (Amicon ultra 0.5 centrifugal filter).

After testing (~ 50 days), further aqueous subsamples were taken for Cr(VI) and pH analysis, as described above, then an equal volume of aluminium sulphate solution (Al₂(SO₄)₃.16H₂O; 5 g/L) was added to the remaining sample to coagulate colloidal humic acid (HA) (two volumes were added to the pH 11 sample). The mixtures were shaken manually for a few seconds then centrifuged at 3226g for 1 min, and the supernatant was immediately separated. The solid phase was then washed three times with DIW and centrifuged. Half the solid sample was air-dried in an anaerobic cabinet and retained for XAS analysis. The other half was oven-dried at 100 °C. The supernatant and oven-dried solid samples were analysed for total Cr analysis as described below.

Cr(VI)-humic acid batch experiments

Hhumic acid powder (1 g) was added to DIW (90 mL) in 120-mL glass serum bottles (AHA was used as supplied whereas PHA came from the last step of the extraction protocol). Triplicate suspensions were equilibrated at pH values 3, 5, 7, 8.5, 9 and 11 using either 1 M HCl or NaOH. Samples were intermittently shaken, and the pH was adjusted until the pH value was stable for at least 1 day. The suspensions were then autoclaved at 121 °C for 15 min to ensure that the subsequent long-duration experiments were abiotic. After cooling, autoclaved DIW was added to each bottle to make up the volume to 96.7 mL, and the pH was readjusted, if necessary, to each target value. Air was flushed from the experiments by bubbling nitrogen through the suspensions. Finally, 3.3 mL of potassium chromate solution (1/30 M K2CrO4; Fluka, Germany) was added for a 100 mL final volume ([Cr(VI)] = 1100 μmol L⁻¹). Bottles were sealed with butyl rubber stoppers with aluminium crimps (Sigma-Aldrich Company Ltd. UK). Control samples were prepared using the potassium chromate solution and autoclaved, N2 purged, DIW. Bottles were incubated in the dark at 20 ± 1 °C and periodically sampled aseptically for geochemical analysis. During sampling, bottles were shaken and 2 mL of suspension was extracted using N2 gas-filled syringes. Samples were divided for Cr(VI) and pH determination. Subsamples for Cr(VI) analyses were passed through a 3-kDa filter (Amicon ultra 0.5 centrifugal filter).

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Similar AHA and PHA samples were prepared with an excess of Cr(VI) (8000 μmol Cr(VI)/g HA) to provide solid-phase samples for 13C NMR and PyGCMS analysis. The samples were prepared at pH 3 and allowed to equilibrate for 31 days before the solid phase was separated from the solution by filtration (control samples of AHA and PHA were equilibrated at pH 3).

Aqueous Cr(VI) concentrations were determined colourimetrically (method 7196A; USEPA 1992). Total Cr associated with the humic acid was determined after acid digestion (method 3050B; USEPA 1996). Total Cr in aqueous solutions and acid digestions were determined by inductively coupled plasma optical emission spectrometry (Thermo Scientific iCAP 7400 radial ICP-OES).

X-ray absorption spectroscopy

Cr K-edge XAS spectra were collected from selected humic acid samples recovered from the low concentration Cr(VI) batch experiments (the ‘Cr(VI)-humic acid batch experiments’ section) on beamlines I18 and B18 at the Diamond Light Source, UK. Reference spectra were also collected for standard laboratory chemicals and precipitated Cr-hydroxide (Saraswat and Vajpe 1984). X-ray absorption near edge (XANES) spectra were summed and normalised using Athena v0.9.24 (Ravel and Newville 2005), and background subtracted extended X-ray absorption fine structure (EXAFS) spectra were fitted to model coordination environments using Artemis v0.9.24 (see SI sections S1.2 and S1.3 for details).

Cross-polarisation magic-angle-spinning 13C-NMR spectroscopy

Humic acid samples were disaggregated and homogenised and packed into 4 mm diameter zirconium rotor tubes. Cross-polarisation magic-angle-spinning (CP/MAS) 13C-NMR spectra were obtained on a Bruker 400 MHz Avance II spectrometer, with a double-bearing magic-angle-spinning probe head (BL4 type) and a Bruker MAS II control unit (see SI for details). Chemical shifts were calibrated using an alpha-glycine spectrum (calibrated on the glycine peak at 43.5 ppm).

Pyrolysis-gas chromatography-mass spectrometry

PyGCMS analysis was performed using a CDS 5000 series pyrolyser (CDS Analytical Inc., Oxford, PA, USA) connected to a Shimadzu QP2010 GC-MS (Shimadzu Corporation, Kyoto, Japan). Samples of approximately 2–3 mg of finely ground and homogenised humic acid were placed between quartz wool plugs in a quartz pyrolysis tube and pyrolysed at a heating rate of 20 °C per millisecond to 500 °C. The pyrolysates were initially trapped on a TENAX adsorbent trap before being desorbed into an Rtx 1701 capillary column (see SI section S1.5).

Results

Characterisation of humic acids

Aldrich humic acid produces 10× more ash upon ignition than PHA (27% and 2%). Refining AHA by alkali extraction/acid precipitation reduces the ash content to 18%. The principle inorganic elements in both humic acids are Al, Si, K, Fe and Ca (SI Table S2: Na is not detectable by ED-XRF), and these form ~18% of AHA by elemental mass, whereas these are about 0.5% of PHA by elemental mass. The detailed properties of AHA, rAHA and PHA are reported in full in the Supplementary Information (Table S1 and S2).

The C, H, N, S and O elemental compositions of rAHA and PHA are very similar. AHA contains proportionally more O than rAHA and PHA (assumed to be associated with the fraction removed by refining), but had a similar H/C ratio. The total acidity values of rAHA and PHA determined by the barium hydroxide method were 6.4 and 6.7 meq/g, respectively. The carboxylic acidities determined by the calcium acetate method were 3.1 and 2.6 meq/g, respectively, suggesting the phenolic acidities of rAHA and PHA were 3.3 and 4.1 meq/g, respectively. The carboxylic and phenolic acidities of rAHA and PHA determined from the base titrations were 3.7 and 3.3 meq/g (carboxylic) and 1.9 and 2.1 meq/g (phenolic), respectively (Table 1, SI Fig. S1).

Aqueous Cr speciation and Cr(VI) removal rates determined after contact with humic acid

The rate at which Cr(VI) was removed from free solution by AHA was dependent on the pH of the suspension (Fig. 1). The pH value of these systems changed slightly during the first 24 h, but quickly stabilised at the value used to name the systems. At pH 4.1 Cr(VI) was removed from solution over a period of about 15 days, whereas Cr(VI) removal at pH 6.2 took ~50 days. At pH 7.8 and pH 8.6, only partial Cr(VI) removal was observed after ~50 days (~40% and ~10% removal, respectively), with no detectable Cr(VI) removal above pH 9.

The rate at which Cr(VI) was removed from free solution by PHA was also dependent on the pH of the suspension. However, the reaction was significantly faster with PHA than with AHA (e.g. complete Cr(VI) removal at pH 5.8 took ~2 days), and the Cr(VI) removal was observed in all tests (85% and 55% of Cr(VI) were removed after ~50 days at pH 8.8 and pH 10.4, respectively).

After 51 days, the partitioning of Cr between the free solution and the humic acid and the oxidation state of free aqueous Cr varied with the pH of the systems (Fig. 2). At pH 4.1 in the AHA system ~90% of the Cr(VI) initially in solution was transferred to the humic acid, and no free aqueous Cr(VI) was detected (the small amount of Cr remaining in free
Table 1  Carboxylic, phenolic and total acidity of the humic acids (meq/g)

| Functional groups                                      | rAHA       | PHA       |
|--------------------------------------------------------|------------|-----------|
| Total acidity—Ba(OH)₂ method (1)                        | 6.4 ± 0.4  | 6.7 ± 0.1 |
| Carboxyl acidity—Ca-acetate method (2)                  | 3.1 ± 0.1  | 2.6 ± 0.0 |
| Phenolic acidity (difference between (1) and (2) above) | 3.3        | 4.1       |
| Carboxyl acidity—titration method (3)                   | 3.7        | 3.3       |
| Phenolic acidity—titration method (4)                   | 1.9        | 2.1       |
| Total acidity—titration method (sum of (3) and (4) above)| 5.6        | 5.4       |

Note: Carboxylic and phenolic acidity were calculated from the base titrations following Ritchie and Purdue (2003)

Fig. 1  a, b Cr(VI) removal from free aqueous solution by AHA and PHA, respectively, at various initial pH values (C/C₀ is the normalised Cr(VI) concentration; [Cr(VI)]₀ = 1100 μM and [HA] = 1 g/100 mL); c, d solution pH of the AHA and PHA systems, respectively; e, f pseudo-first-order rate plots for the Cr(VI)-AHA and Cr(VI)-PHA reactions, respectively
solution was attributed to aqueous Cr(III)). A similar pattern was observed at pH 6.2, although ~ 5% of the Cr remained as aqueous Cr(VI). At pH 7.8, about 60% of the Cr remained as aqueous Cr(VI). Above pH 8.5, there was very little Cr associated with the humic acid, and > 90% remained in the solution as Cr(VI).

In the presence of PHA, most of the Cr(VI) initially in free solution was transferred to the humic acid at pH < 8, and no free aqueous Cr(VI) was detected in these systems (although about 10% of the Cr remained in free solution at pH 3.7 presumably as Cr(III)). In the pH 8.6 and pH 8.8 PHA systems, most of the Cr was associated with the humic acid after 51 days, but ~ 5% and ~ 15% of Cr remained in solution as Cr(VI), respectively. However, at pH 10.5, there was more variation in the behaviour of the PHA system, so six replicates were tested. After 51 days, some Cr was associated with the humic acid in all replicates, but the amount of Cr(VI) remaining in free solution varied between 0 and 90% (average 45%).

AHA and PHA samples that were prepared with excess Cr(VI) for subsequent 13C NMR and PyGCMS analysis buffered the solution from pH 3 to ~ pH 7 in the long-term. AHA removed ~ 500 μmol Cr(VI)/g from solution. PHA removed ~ 1400 μmol Cr(VI)/g from solution.

**X-ray absorption spectroscopy**

XANES spectra collected from both AHA and PHA samples that had been exposed to Cr(VI) lacked any evidence of the characteristic Cr(VI) pre-edge peak at 5994 eV (Peterson et al. 1996), indicating that only Cr(III) was present in solids regardless of the solution pH during the reaction (S.I. Fig. S2). The XANES spectra from both AHA and PHA sample were qualitatively similar and most closely resemble those collected from the Cr(III) aqueous or poorly crystalline hydrous Cr(OH)3 standards, lacking the detailed structure of the crystalline Cr2O3 standard (the absence of structure associated with Cr2O3 is probably indicative of Cr(III) binding with HA functional groups, since there is no Cr(III) observed in solution). EXAFS fitting revealed that all samples were best fit by single-scattering and multiple-scattering pathways associated with the Cr(III)O6 octahedra (i.e. 6 O atoms at 1.96–1.97 Å) and by the inclusion of additional Cr-C pathways at 3.0–3.1 Å produced final fits with unrealistically long Cr-Cr pathway lengths (3.3–3.9 Å) and the large Debye-Waller factors (0.009–0.010; indicative of overfitting) compared to other pathways and failed to improve the overall fit quality. Therefore, the data provided no evidence for Cr(OH)3 polymerisation that has been observed previously for some Cr(III)-humic acid associations (Gustafsson et al. 2014).

**Cross-polarisation magic-angle-spinning 13C NMR spectroscopy**

Comparison of the 13C-NMR spectra of AHA and PHA indicates differences between the two materials (Table 2 and Fig. 4). Nearly 50% of the AHA spectrum is in the chemical shift range usually associated with alkyl C (0–45 ppm; carbon centres singly bonded to either C or H; Golchin et al. 1997; Kögel-Knabner 2000), with about 1/3 of the PHA spectrum occupying the same range. Conversely, ~ 25% of the PHA spectrum is in the range associated with alkyl C bonded singly to O (45–110 ppm), yet < 5% of the AHA spectrum is in this range. Approximately 40% of the AHA spectrum is in a range associated with alkene and aromatic C (110–160 ppm), whereas ~ 30% of the PHA spectrum is in this range. However, ~ 10% of both spectra are in the sub-range associated with carboxyl C (160–220 ppm), and in both cases, this is mainly in the sub-range characteristic of carboxylic and ester moieties (160–185 ppm) (Knicker et al. 2005). Both humic acids have ~ 10% of their spectra associated with carboxyl C (160–220 ppm), and in both cases, this is mainly in the sub-range characteristic of carboxylic and ester moieties (160–185 ppm) (Knicker et al. 2005).

The 13C-NMR spectra of AHA and PHA both show changes due to the reaction with Cr(VI) in acidic solution (Table 2 and Fig. 4). The proportion of spectra usually associated with aromatic C has decreased by ~ 5% and ~ 10%, respectively. PHA also exhibits a ~ 10% decrease in the proportion of the spectrum associated with alkyl C bonded singly to O (from ~ 25 to ~ 15%), whereas AHA shows little change. In both cases, the proportion of the spectra usually associated with alkyl C (0–45 ppm) has increased by ~ 5% and ~ 20%, respectively.
respectively. Neither material appears to exhibit any increase in the proportion of the spectrum associated with carbonyl C after reaction with Cr (160–220 ppm), but this may be the result of the shielding that occurs due to electron redistribution when carbonyl groups form complexes with Cr(III) (Zhang et al. 2017).

**Pyrolysis-gas chromatography-mass spectrometry**

Direct quantitative comparison of functionality between the humic acid samples from PyGCMS is inappropriate due to the difference in detector response from different chemical fragments. However, examination of the pyrograms show differences before and after reaction with excess Cr(VI) in acidic solution and thus indicate the changes in humic acid functionality that resulted from the reaction. The reaction of PHA with excess Cr(VI) resulted in a large decrease in the relative size of peaks from products containing phenolic fragments and an increase in the relative size of peaks associated with long-chain aliphatic fragments (Fig. 5 and SI Fig. S3c, d). Peaks for methoxy-phenolic and other substituted phenolic compounds exhibited the largest decrease in relative size. The pyrograms for AHA were less well resolved (possibly a result of the higher ash content), but these also showed a decrease in the relative size of peaks associated with aromatic fragments (SI Fig. S3a, b).

**Discussion**

**Relative differences in reactive sites in lignite and peat derived humic acids**

Both the barium hydroxide and direct base titration methods indicate that rAHA and PHA have similar total acidity (per unit mass of the total material). However, the direct base titration and the difference between the barium hydroxide and calcium acetate methods indicate that PHA has 10–25% greater phenolic acidity than rAHA. More importantly, the ash remaining after a loss on ignition (18% in rAHA and 2% in PHA) is often a result of amorphous silica and aluminosilicate impurities present in the humic acid (Tan 1977). Such minerals can buffer pH

**Table 2** Proportion of humic acid carbon in the different bonding environments before and after reaction with excess Cr(VI) determined by CP MAS 13C-NMR (spectra were operationally divided into characteristic chemical shift regions (Golchin et al. 1997; Kögel-Knabner 2000))

| Type of organic carbon (% of total area) | AHA | PHA |
|----------------------------------------|-----|-----|
| Before reaction | After reaction | Difference | Before reaction | After reaction | Difference |
| Alkyl C (0–45 ppm) | 47.1 | 52.0 | +4.9 | 33.9 | 53.5 | +19.6 |
| O-alkyl C (45–110 ppm) | 2.1 | 2.5 | +0.4 | 24.8 | 14.7 | −10.0 |
| Aromatic C (110–160 ppm) | 38.7 | 33.9 | −4.8 | 27.8 | 17.7 | −10.0 |
| Carbonyl C (160–220 ppm) | 12.1 | 11.5 | −0.5 | 13.5 | 14.0 | +0.5 |
| Aromaticity* (%) | 44.0 | 38.4 | −5.6 | 32.1 | 20.6 | −11.5 |

*aAromaticity is defined as (aromatic C)/(alkyl C + O-alkyl C + Aromatic C)*
during a titration producing ‘acidity’ in the phenolic range, and when allowance is made for the ash removed by refining (AHA is 27% ash), it is clear that the actual phenolic acidity of PHA is likely to be higher than that of AHA.

Chemical shift regions of the $^{13}$C NMR spectra indicate AHA and PHA contain similar proportions of carbonyl C centres associated with either carboxylic acid or ester groups (160–185 ppm). The $^{13}$C NMR spectra also indicate that the two HAs contain similar proportions of aromatic/alkene C centres in the range normally associated with aromatic C–O centres (140–160 ppm). $^{13}$C NMR cannot differentiate aromatic C bonded to O in phenolic moieties from those associated with an ether linkage (i.e. it cannot differentiate between Ph–O–H from Ph–O–C), but the differences in the phenolic acidity together with lower reactivity with Cr(VI) suggest that a larger proportion of the aromatic C–O centres in AHA may be associated with less reactive ether linkages (characteristic of phenolic polymers) than in PHA. AHA was extracted from Miocene age lignite (6–26 Ma; Germany), whereas PHA was extracted from Holocene age peat (< 12 ka, Ireland). As lignite is essentially compressed and heated peat, the differences in functionality of the two humic acids are probably associated with changes that occur during ageing of the parent materials. This is likely to have involved the formation of linking bonds between phenolic and other aromatic moieties (i.e. reactions similar to the polyphenol pathway assumed in the polymer model of humic substance formation; Stevenson 1994), as oxidative polymerisation of hydroxyphenols and toluenes can be catalysed by enzymes found in plants, fungi and bacteria (Martin and Haider 1980).
Controls on the rate of Cr(VI) reduction with humic acid

XANES analysis indicates that the interaction of Cr(VI) with these humic acids resulted in a reduction to Cr(III) at all pH values tested. Also, the similarity of spectral details suggests that Cr(III) produced by reaction with humic acids resides in the same chemical environment regardless of the pH of the system. Changes in the 13C NMR spectra indicate that both HAs suffered a loss of aromatic/alkene C during the reaction with Cr(VI) in acid solution. PyGCMS pyrograms confirm that both HAs suffered a loss of aromatic and an increase in aliphatic moieties during the reaction with Cr(VI) in acid solution. 

Humic acid samples for 13CNMR and pyrolysis GC-MS analysis were reacted with an excess of Cr(VI), and as a result, they buffered the pH from 3 to ~7 (indicating the reaction between Cr(VI) and HA in acidic systems). These samples indicate that AHA can reduce ~500 μmol Cr(VI)/g and PHA ~1400 μmol Cr(VI)/g when the pH ≤7. Thus, in the longer term batch tests which were conducted with 110 μmol Cr(VI)/g, HA was available in excess when the pH ≤7. In this pH range, the rate of Cr(VI) removal by both HAs is first order with respect to the concentration of Cr(VI) species (Fig. 1e, f). The reaction may still be first order with respect to Cr(VI) concentration at pH >7. At pH 7.8, AHA reduced only ~40 μmol/g Cr(VI) after 51 days, but the reaction exhibits an approximately linear relationship between log([Cr(VI)]) and time (r² = 0.78; see SI Table S6). The reaction with PHA exhibited a linear relationship between log([Cr(VI)]) and time at pH 8.6 and 8.8 (r² = 0.99 and 1.00, respectively).

The rates at which AHA and PHA reduced Cr(VI) is dependent on [H⁺], which decreases with the increasing pH. The rapidity of Cr(VI) removal from a solution made an accurate rate determination difficult at pH ≤4; however, least squares fitting of Eq. (1) to data where pH ≤9 yields the values of the exponent, a, of 0.48 for AHA and 0.40 for PHA (see SI Fig. S4).

$$k_{obs} = k_0 [H^+]^a \quad (1)$$

This is consistent with the trend observed by Wittbrott and Palmer (Wittbrodt and Palmer 1995; Wittbrodt and Palmer 1997), who found that the rate of Cr(VI) reduction by soil fulvic acid and soil humic acid were both proportional to [H⁺]0.45 when pH ≤7.

Mechanism of Cr(VI) reduction with humic acid

Cr(VI) reduction by humic acid requires that Cr(VI) is first adsorbed in manner that facilitates electron transfer. Experimental studies using simple alcohols and phenolic compounds highlight the formation of a chromate ester as the first step in Cr(VI) reduction (Lee and Stewart 1967; Wiberg and Schafer 1967; Elovitz and Fish 1995). As alcohol and phenolic functional groups are common in humic acid, it is reasonable to expect similar interactions will occur in the experiments reported here, as illustrated in Fig. 6. Humic acids can contain vicinal diols (two hydroxyl groups attached to adjacent carbon atoms), like those found in the humic precursors.
caffeic, gallic and tannic acid (Nakayasu et al. 1999; Deiana et al. 2007), and these can also form cyclic chromate ester with Cr(VI) as illustrated in Fig. 6 (Wiberg 1965).

Chromate ester formation is rapid and reversible in acidic conditions (methylphenol reaches equilibrium in < 60 s at pH ≤ 5; Elovitz and Fish 1995). It occurs primarily with monomeric Cr(VI) species and is far more favourable with chromic acid and bichromate species than with the dianionic chromate species (Wiberg 1965; Lee and Stewart 1967; Wiberg and Schafer 1967; Elovitz and Fish 1995), probably because the Cr centre is more electrophilic in the monovalent bichromate than in the divalent chromate anion. Therefore, the rate at which Cr(VI) is reduced by alcohol and phenolic moieties declines sharply when pH ≥ 6 (Elovitz and Fish 1995). However, data presented here shows that Cr(VI) reduction proceeds slowly at alkaline pH, with the same eventual fate for the Cr(III) across the pH range (Fig. 3). This suggests that, while less favourable due to increased electrostatic repulsion, chromate ester formation occurs between deprotonated humic acids and the dianionic chromate species, with the result that Cr(VI) is reduced by humic acids at alkaline pH values on long timescales.

Reduction of Cr(VI) must have resulted in oxidation of the humic acids, but 13C NMR did not identify the functional groups produced. Oxidation of phenolic and alcohol groups by Cr(VI) usually produces ketones and carboxylic acids (Wiberg 1965; Rocek and Riehl 1967; Deiana et al. 2007), and thus, an increase in carbonyl range of the 13C NMR spectra would be anticipated. However, Zhang et al. (2017) showed that Cr(III) sorption to humic acids results in the formation of carbonyl-Cr(III) complexes, and shielding associated with electron redistribution causes a decrease in the 13C NMR signal from carbonyl groups. Thus, it is likely that Cr(VI) reduction by AHA and PHA resulted in the formation of additional carbonyl groups, but these were not detected by 13C NMR due to such shielding. This explanation is compatible with our Cr EXAFS data which suggests that the Cr(III) formed an inner-sphere adsorption complex with two C atoms.

The reduction of Cr(VI) by the humic acids was first order with respect to [Cr(VI)], so the rate-limiting step likely involves a single Cr-containing species. This step is probably chromate ester decomposition (Lee and Stewart 1967; Elovitz and Fish 1995; Wittbrodt and Palmer 1997), which can then result in transfer of one or two electrons to the chromate ion resulting in the production of either Cr(V) or Cr(IV) moieties (Wiberg 1965; Lee and Stewart 1967; Haight et al. 1971; Elovitz and Fish 1995). The reduction is also mixed order with respect to [H+] which is compatible with Cr(VI)-ester decomposition proceeding concurrently by multiple pathways (with 4-methylphenol ester decomposition can proceed concurrently by proton-activated pathways and a proton-independent pathway; Elovitz and Fish 1995), but it may also indicate that the equilibrium constant for the ester formation may be increasingly less favourable with $\text{H}_2\text{CrO}_4$, $\text{HCrO}_4^-$ and $\text{CrO}_4^{2-}$ species.

Metal reduction by vicinal diols can result in cleavage of the intervening C–C bond (Wiberg 1965; Deiana et al. 1992; Deiana et al. 1995; Deiana et al. 2007). Such ‘ring opening’ phenomena are consistent with the loss of aromatic and methoxy-phenolic groups observe by NMR and PyGCMS in this study. Cr(IV) moieties produced by electron transfer are unstable and will rapidly disproportionate to form Cr(III) and Cr(V), and Cr(V) can react with alcohol and phenolic groups via the chromate ester in much the same way as Cr(VI) (Wiberg 1965; Haight et al. 1971; Bruckner 2002). Therefore, through several cycles of absorption, ester formation, reduction and disproportionation steps, the Cr(VI) is likely to be eventually converted to the Cr(III) end product. Cr(III) formed from reduction of Cr(VI) remains associated with the partially degraded humic acid at all pH values, although with samples where pH < 4, small amounts of Cr(III) are also present in solution due to the protonation of humic acid surface sites which results in lower sorption of Cr(III) under acidic pH. The lack of Cr-Cr pathways in the Cr-humic acid inner-sphere adsorption complexes points to little or no aqueous Cr(III) accumulation after reduction, such that few Cr(III)-Cr(III)}
interactions occur during adsorption, and the formation of the Cr(III) dimers observed by Gustafsson et al. (2014) at high pH is not favoured.

**Implications**

Cr(VI) is reduced to Cr(III) by reaction with humic substances over a wide range of pH values found in the environment. This reaction is rapid in acid and neutral conditions, and therefore, natural soil organic matter will reduce Cr(VI) transport through groundwater when it is present. Also, Cr(VI) contaminated groundwater could be treated by deploying humic substances within an engineered treatment scheme (such as a permeable reactive barrier). Reduction reduces Cr toxicity, and the resulting Cr(III) is strongly held by inner-sphere bonding with humic acids, which significantly reduces the opportunity for the spread of Cr(III) or reoxidation into mobile Cr(VI) species.

The rate at which Cr(VI) is reduced and the total capacity for Cr(VI) reduction are both proportional to the reactivity of the humic acid used and particularly the density of phenolic and hydroxyl sites in the humic substances. Thus, it is important to choose younger sources of organic matter (e.g. sewage sludge, compost), which contain more labile humic substances, to maximise treatment efficiency and longevity in real applications. This choice will be particularly important when pH > 7, where reaction rates are lower.

Treatment of Cr(VI) contaminated groundwater by permeable reactive barrier (PRB) is challenging in alkaline conditions as the reactive materials conventionally deployed within PRBs are not durable in this pH range (e.g. ZVI is passivated at high pH and Fe(II) containing substances, such as green rusts and ferric sulphate solutions, have very short active lifetimes). The reaction of Cr(VI) with humic acids will also not be easy to exploit within a conventional PRB, as it takes place on a timescale of weeks. However, a different remediation strategy may be appropriate, as humic acids become increasingly soluble as the pH rises and a large proportion of humic acids are mobile at high pH. Thus, humic acids will migrate with the groundwater until the pH is sufficiently buffered by reactions with soil minerals for precipitation, creating a diffuse reactive zone downstream of the intervention point.

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**References**

Aro N, Pakula T, Penttilä M (2005) Transcriptional regulation of plant cell wall degradation by filamentous fungi. FEMS Microbiol Rev 29: 719–739

ASTM (2010) Standard test methods for moisture, ash, and organic matter of peat and other organic soils. ASTM International, West Conshohocken, pp D2974–D207a

Ball JW, Izbicki J (2004) Occurrence of hexavalent chromium in ground water in the western Mojave Desert, California. Appl Geochem 19: 1123–1135

Barnhart J (1997) Occurrences, uses, and properties of chromium. Regul Toxicol Pharmacol 26:S3–S7

Bartlett R, James B (1979) Behavior of chromium in soils: III. Oxidation. J Environ Qual 8:31–35

Becker T, Quantin C, Sicot M, Boudot JP (2003) Chromium availability in ultramafic soils from New Caledonia. Sci Total Environ 301:251–261

Brito F, Ascanio J, Mateo S, Hernández C, Araujo L, Gili P, Martín-Zarza P, Domínguez S, Mederos A (1997) Equilibria of chromate(VI) species in acid medium and ab initio studies of these species. Polyhedron 16:3835–3846

Brookes PC, Cayuela ML, Contin M, De Nobili M, Kemmitt SJ, Mondini C (2008) The mineralisation of fresh and humified soil organic matter by the soil microbial biomass. Waste Manag 28:716–722

Bruckner R (2002) Advanced organic chemistry: reaction mechanisms. Harcourt/Academic Press, San Diego

Burdon J (2001) Are the traditional concepts of the structures of humic substances realistic? Soil Sci 166:752–769

Burke T, Faglione J, Goldoft M, Hazen RE, Iglewicz R, McKee T (1991) Cromite ore processing residue in Hudson County, New Jersey. Environ Health Perspect 92:131

Cefalu WT, Hu FB (2004) Role of chromium in human health and in diabetes. Diabetes Care 27:2741–2751

Chandra P, Kulshreshtha K (2004) Chromium accumulation and toxicity in aquatic vascular plants. Bot Rev 70:313–327

Chen ZF, Zhao YS, Li Q (2015) Characteristics and kinetics of hexavalent chromium reduction by gallic acid in aqueous solutions. Water Sci Technol 71:1694–1700

Costa M (1997) Toxicity and carcinogenicity of Cr (VI) in animal models and humans. Crit Rev Toxicol 27:431–442

Darrie G (2001) Commercial extraction technology and process waste disposal in the manufacture of chromium chemicals from ore. Environ Geochem Health 23:187–193

Deiana S, Gessa C, Manunza B, Marchetti M, Usai M (1992) Mechanism and stoichiometry of the redox reaction between iron(III) and caffeic acid. Plant Soil 145:287–294

Deiana S, Gessa C, Manunza B, Rausa R, Solinas V (1995) Iron(III) reduction by natural humic acids: a potentiometric and spectroscopic study. Eur J Soil Sci 46:103–108

Deiana S, Premoli A, Senette C (2007) Reduction of Cr(VI) by caffeic acid. Chemosphere 67:1919–1926

Ding W, Stewart DI, Humphrey PN, Rout SP, Burke IT (2016) Role of an organic carbon-rich soil and Fe(III) reduction in reducing the toxicity and environmental mobility of chromium(VI) at a COPR disposal site. Sci Total Environ 541:1191–1199

Eary LE, Rai D (1987) Kinetics of chromium (III) oxidation to chromium (VI) by reaction with manganese dioxide. Environmental Science & Technology 21:1187–1193

Eary L, Rai D (1988) Chromate removal from aqueous wastes by reduction with ferrous ion. Environmental Science & Technology 22: 972–977

Eary L, Rai D (1991) Chromate reduction by subsurface soils under acidic conditions. Soil Sci Soc Am J 55:676–683

Elovitz MS, Fish W (1995) Redox interactions of Cr (VI) and substituted phenols: products and mechanism. Environ Sci Technol 29:1933–1943
Fan TM, Lane A, Chekmenev E, Witteborn R, Higashi R (2004) Synthesis and physico-chemical properties of peptides in soil humic substances. J Pept Res 63:253–264
Fantoni D, Brozzo G, Canepa M, Cipolli F, Marini L, Ottonello G, Zuccolini M (2002) Natural hexavalent chromium in groundwaters interacting with ophiolitic rocks. Environ Geol 42:871–882
Fendrov SE, Zasoski RJ (1992) Chromium(III) oxidation by δ-MnO2. 1. Characterization. Environ Sci Technol 26:79–85
Gao Y, Xia J (2011) Chromium contamination accident in China: viewing environmental policy of China. Environ Sci Technol 45:8605–8606
Geelhoed JS, Meeussen JC, Hillier S, Lumsdon DG, Thomas RP, Farmer JD, Huang S-W, Chiang P-N, Liu J-C, Hung J-T, Kuan W-H, Tzou Y-M, Langmuir D (1997) Aqueous environmental geochemistry. Prentice Hall, Upper Saddle River
Golchin A, Clarke P, Baldock J, Higashi T, Skjemstad J, Oades J (1997) The effects of vegetation and burning on the chemical composition of soil organic matter in a volcanic ash soil as shown by 13C NMR spectroscopy. I. Whole soil and humic acid fraction. Geoderma 76:155–174
Gustafsson JP, Mark-och v K, Tidigare I (2001) Modeling the acid-base properties and metal complexation of humic substances with the Stockholm Humic Model. J Colloid Interface Sci 244:102–112
Gustafsson JP, Persson I, Oromieh AG, van Schaik JWJ, Sjostedt C, Kleja DB (2014) Chromium(II) complexation to natural organic matter: mechanisms and modeling. Environ Sci Technol 48:1753–1761
Haigh G, Huang TJ, Shakhashiri B (1971) Reactions of chromium (IV). J Inorg Nucl Chem 33:2169–2175
Higgins TE, Halloran AR, Dobbins ME, Pattignton AJ (1998) In situ reduction of hexavalent chromium in alkaline soils enriched with chromium ore processing residue. J Air Waste Manage Assoc 48:1100–1106
Holmes AL, Wise S, Wise JP Sr (2008) Carcinogenicity of hexavalent chromium. Indian J Med Res
Huang S-W, Chiang P-N, Liu J-C, Hung J-T, Kuan W-H, Tzou Y-M, Wang S-L, Huang J-J, Chen C-C, Wang M-K (2012) Chromate reduction on humic acid derived from a peat soil–exploration of the activated sites on HAs for chromate removal. Chemosphere 87:587–594
International Chromium Development Association (2016) Uses of chrome
International Humic Substances Society (2007) What are humic substances?
Izbicki JA, Groover K (2016) A plan for study of hexavalent chromium. CR (VI) in groundwater near a mapped plume, Hinkley, California. US Geological Survey
Jacobs JA, Testa SM (2005) Overview of chromium(VI) in the environment: background and history. In: Guertin J, Jacobs JA, Avakian CP (eds) Chromium(VI) handbook. CRC Press, Boca Raton
Janos P, Křiženecká S, Madronová L (2008) Acid–base titration curves of solid humic acids. React Funct Polym 68:242–247
Jardine PM, Fendorf SE, Hayes MA, Larsen IL, Brooks SC, Bailey WB (1999) Fate and transport of hexavalent chromium in undisturbed heterogeneous soil. Environ Sci Technol 33:2939–2944
Knicker H, Totsche KU, Almendros G, González-Vila FJ (2005) Condensation degree of burnt peat and plant residues and the reliability of solid-state VACP MAS C-13 NMR spectra obtained from pyrogenic humic material. Org Geochem 36:1359–1377
Kogel KE, Trivedi NC, Barker JM, Krukowsky ST (2006) Industrial minerals & rocks: commodities, markets, and uses., 7th edition ed. Society for Mining, Metallurgy, and Exploration
Schwertmann U, Latham M (1986) Properties of iron oxides in some new caledonian oxisols. Geoderma 39:105–123
Shanker AK, Cervantes C, Loza-Tavares H, Avudainayagam S (2005) Chromium toxicity in plants. Environ Int 31:739–753
Simpson AJ, Kingery WL, Hayes MH, Spraul M, Humpfer E, Dvortsak P, Kerssebaum R, Godejohann M, Hofmann M (2002) Molecular structures and associations of humic substances in the terrestrial environment. Naturwissenschaften 89:84–88
Steinpress MG (2005) Naturally occurring chromium (VI) in groundwater, including the presidio of San Francisco case study. In: Guertin J, Jacobs JA, Avakian CP (eds) Chromium (VI) handbook. CRC Press, Boca Raton, Fla, pp 93–141
Stevenson FJ (1994) Humus chemistry: genesis, composition, reactions, 2nd edn. Wiley, New York
Stewart DI, Burke IT, Mortimer RJ (2007) Stimulation of microbially mediated chromate reduction in alkaline soil-water systems. Geomicrobiol J 24:655–669
Stewart DI, Burke IT, Hughes-Berry DV, Whittleston RA (2010) Microbially mediated chromate reduction in soil contaminated by highly alkaline leachate from chromium containing waste. Ecol Eng 36:211–221
Stueber AM, Golew GG (1967) Abundances of Na, Mn, Cr, Sc and Co in ultramafic rocks. Geochim Cosmochim Acta 31:75–93
Sutton R, Sposito G (2005) Molecular structure in soil humic substances: the new view. Environ Sci Technol 39:9009–9015
Swift RS (1999) Macromolecular structure of soil humic substances: fact, fiction, and opinion. Soil Sci 164:790–802
Tan KH (1977) Infrared spectra spectra of humic and fulvic acids, containing silica, metal ions, and hygroscopic moisture. Soil Sci 123:235–240
USEPA (1992) SW-846 manual: method 7196A. Chromium hexavalent (colorimetric)
USEPA (1996) Method 3050B: acid digestion of sediments sludges and soils (revision 2)
Vincent JB (2000) The biochemistry of chromium. J Nutr 130:715–718
von Wandruszka R (1998) The micellar model of humic acid: evidence from pyrene fluorescence measurements. Soil Sci 163:921–930
Wershaw RL (1986) A new model for humic materials and their interactions with hydrophobic organic chemicals in soil-water or sediment-water systems. J Contam Hydrol 1:29–45
Wershaw RL (1994) Membrane-micelle model for humus in soils and sediments and its relation to humification. US Geological Survey
Wershaw RL (1999) Molecular aggregation of humic substances. Soil Sci 164:803–813
Whittleston RA, Stewart DI, Mortimer RJ, Tilt ZC, Brown AP, Geraki K, Burke IT (2011) Chromate reduction in Fe (II)-containing soil affected by hyperalkaline leachate from chromite ore processing residue. J Hazard Mater 194:15–23
WHO (2003) Chromium in drinking-water background document for development of WHO Guidelines for drinking-water quality
Wiberg KB (1965) Oxidation by chromic acid and chromyl compounds. In: Wiberg KB (ed) Oxidation in organic chemistry. Academic Press, New York
Wiberg KB, Schaffer H (1967) Direct observation of intermediates in the chromic acid oxidation of secondary alcohols. J Am Chem Soc 89:455–457
Wilbur SB, United States. Agency for toxic, S., Disease, R., Corporation, S.R (2000) Toxicological profile for chromium
Wittbrodt PR, Palmer CD (1995) Reduction of Cr(VI) in the presence of excess soil fulvic acid. Environ Sci Technol 29:255–263
Wittbrodt PR, Palmer CD (1997) Reduction of Cr(VI) by soil humic acids. Eur J Soil Sci 48:151–162
Zang X, van Heemst JD, Dria KJ, Hatcher PG (2000) Encapsulation of protein in humic acid from a histosol as an explanation for the occurrence of organic nitrogen in soil and sediment. Org Geochem 31:679–695
Zhang J, Chen L, Yin H, Jin S, Liu F, Chen H (2017) Mechanism study of humic acid functional groups for Cr(VI) retention: two-dimensional FTIR and 13C CP/MAS NMR correlation spectroscopic analysis. Environ Pollut 225:86–92
Zhou B, Huang D, Wu J, Zhu Q, Zhu H (2018) Horizontal and vertical distributions of chromium in a chromate production district of South Central China. Int J Environ Res Public Health 15:571