# Behaviour of chromium and chromium isotopes during estuarine mixing in the Beaulieu Estuary, UK

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## Abstract

Rivers are the principal source of chromium (Cr) to seawater and the Cr isotopic signatures of ancient marine sediments are widely considered to provide a record of the presence or absence of oxidative weathering processes on land. This assumes, however, that the $\delta^{53}$Cr value of river water is faithfully transferred to the oceans and is not modified in the estuarine mixing zone. To test this assumption we have determined the concentration and $\delta^{53}$Cr values of inorganic Cr (Cr(III)+Cr(VI)), and also Cr speciation for water samples collected within the estuarine mixing zone of the Beaulieu River, UK. The $\delta^{53}$Cr values of dissolved inorganic Cr ranged from -0.59 to 1.68‰, Cr(VI) concentrations from 0.39 to 1.83 nmol kg$^{-1}$ and Cr(III) concentrations from 0.11 to 3.21 nmol kg$^{-1}$. Both Cr(VI) concentrations and $\delta^{53}$Cr values increased linearly as a function of salinity, while Cr(III) concentrations decreased linearly with salinity. Thus $\delta^{53}$Cr, Cr(III) and Cr(VI) all showed conservative behaviour in the estuarine mixing zone, and the $\delta^{53}$Cr signature of Beaulieu River water was modified only by mixing between the river and seawater endmembers. The calculated average $\delta^{53}$Cr value of the river water endmember (-0.39 ± 0.08‰) was, however, lower than the range that has been observed in other rivers, which we attribute to input of organically-bound Cr(III) released by anoxic weathering processes. This is supported by the fact that Cr recovered by UV irradiation was found to have low $\delta^{53}$Cr values (-0.11 to -0.75‰). While input of Cr from anoxic weathering processes is unlikely to be an important source of Cr to the oceans today, this suggests that processes other than oxidative weathering may have an influence on the $\delta^{53}$Cr values of estuarine and coastal waters on the local scale. The $\delta^{53}$Cr value of the coastal seawater endmember (1.6 ± 0.4‰) was also higher than the range observed in the deep open ocean, due to *in situ* biogeochemical cycling of Cr. These factors need to be considered in the interpretation of marine sedimentary $\delta^{53}$Cr records.

**Keywords:** chromium isotopes, chromium speciation, chromium cycling, estuarine mixing, anoxic weathering

## 1. Introduction

Chromium (Cr) is a redox sensitive element with two stable oxidation states, Cr(VI) and Cr(III), at Earth surface conditions. It has four stable isotopes, $^{50}$Cr, $^{52}$Cr, $^{53}$Cr and $^{54}$Cr, which can fractionate during oxidation and reduction reactions (Zink et al., 2010; Døssing et al., 2011; Kitchen et al., 2012). Most ground water and seawater samples analysed to date are enriched in heavy Cr isotopes (i.e. they have relatively high $\delta^{53}$Cr values, where $\delta^{53}\text{Cr}=\left(\frac{(^{53}\text{Cr}/^{52}\text{Cr})_{\text{sample}}-(^{53}\text{Cr}/^{52}\text{Cr})_{\text{NBS979 standard}}}{(^{53}\text{Cr}/^{52}\text{Cr})_{\text{NBS979 standard}}}\right)\times1000$; Ellis et al. 2002; Bonnand et al. 2013; Scheiderich et al. 2015; Holmden et al. 2016; Paulukat et al. 2016; Pereira et al. 2015; Goring-Harford et al. 2018; Moos and Boyle 2018; Bruggmann et al. 2019) compared to crustal rocks ($\delta^{53}$Cr = -0.12 ± 0.10‰; Schoenberg et al. 2008). This has been attributed to the preferential release of heavy Cr isotopes during the oxidative weathering of Cr(III), followed by transfer of the Cr(VI) that forms to the oceans *via* rivers (Frei et al. 2009), and to the preferential removal of light Cr isotopes during biologically-mediated redox reactions in seawater (Scheiderich et al., 2015; Goring-Harford et al., 2018; Moos and Boyle, 2018).

Records of ancient seawater $\delta^{53}$Cr values, preserved in the authigenic fraction of marine sediments, are considered to provide evidence for the evolution of atmospheric oxygen, and consequently life, on Earth (e.g. Frei et al. 2009; Crowe et al. 2013; Planavsky et al. 2014). Critically, this interpretation relies on the assumption that the oxidative weathering signal is faithfully transferred from rivers to seawater, as rivers are the main source of Cr to the oceans (>90% of the total Cr input; Jeandel and Minster 1987; Bonnand et al. 2013; Reinhard et al. 2013; McClain and Maher 2016; Sun et al. 2019). The $\delta^{53}$Cr range previously reported for unpolluted river water is -0.3 to 1.7‰ (n=49; Figure 1; Frei et al. 2014; D'Arcy et al. 2016; Wu et al. 2017; Andronikov et al. 2019), which is similar to that of seawater (0.02 to 1.7‰; n=156; Bonnand et al. 2013; Scheiderich et al. 2015; Holmden et al. 2016; Paulukat et al. 2016; Pereira et al. 2015; Goring-Harford et al. 2018; Moos and Boyle 2018; Bruggmann et al. 2019). However, the mean value for river water (0.49 ± 0.45‰) is higher than the mean value for seawater (1.07 ± 0.35‰), which implies that $\delta^{53}$Cr values may be altered after oxidative weathering occurs, for example by redox reactions of Cr in surface ocean waters (Scheiderich et al., 2015; Goring-Harford et al., 2018; Bruggmann et al., 2019). Although other potential mechanisms for Cr isotope fractionation in natural waters have yet to be investigated in detail, it is likely that refinements to the model proposed by Frei et al. 2009 are required to properly employ Cr as a proxy for atmospheric oxygenation (see also Toma et al. 2019).

Fractionation of Cr isotopes during transport from rivers to the ocean has the potential to significantly modify $\delta^{53}$Cr values before preservation in marine sediments (Bonnand et al., 2013; Paulukat et al., 2015; D'Arcy et al., 2016). Rivers typically contain between 2nM and 20nM of dissolved Cr (e.g. Bonnand et al. 2013 and references therein), though rivers draining mafic lithologies or land contaminated with industrial waste can contain much higher levels (100-2000nM; McClain and Maher 2016; Novak et al. 2014; Paulukat et al. 2015). Chromium(VI) is the thermodynamically stable form of Cr in oxygen-replete waters (Elderfield, 1970), but rivers commonly contain both Cr(III) and Cr(VI) in varying proportions (Cranston and Murray, 1980; Dolamore-Frank, 1984; Kieber and Helz, 1992; Abu-Saba and Flegal, 1995; Gardner and Ravenscroft, 1996; Comber and Gardner, 2003; Saputro et al., 2014; McClain and Maher, 2016), likely due to complexation of Cr(III) with organic molecules, which stabilises it in solution (Dolamore-Frank, 1984; Kaczynski and Kieber, 1994; Abu-Saba and Flegal, 1995; Buerge and Hug, 1998; Icopini and Long, 2002). Chromium(VI) shows conservative behaviour in many estuaries, meaning its concentration is simply determined by the relative proportion of freshwater to seawater (Cranston and Murray, 1980; Mayer and Schick, 1981; Dolamore-Frank, 1984). However, in some estuaries Cr(VI) appears to be partially reduced to Cr(III) in the presence of organic molecules or photochemically produced Fe(II) (Kieber and Helz, 1992; Saputro et al., 2014; D'Arcy et al., 2016). The Cr(III) that is produced can be removed (i) at low salinities due to the flocculation of organic materials (Cranston and Murray, 1980; Mayer and Schick, 1981; Campbell and Yeats, 1984), or (ii) by adsorption onto sedimentary particles (Mayer and Schick, 1981; Abu-Saba and Flegal, 1995; Jonas and Millward, 2010). As Cr(III) is expected to be enriched in lighter isotopes (Ellis et al., 2002; Zink et al., 2010; Døssing et al., 2011; Kitchen et al., 2012), this may drive $\delta^{53}$Cr values in the remaining Cr(VI) that is delivered to the oceans to higher values (Bonnand et al., 2013; Paulukat et al., 2015; D'Arcy et al., 2016).

To date, Cr isotope behaviour has only been studied in the Connecticut estuary, USA (Sun et al., 2019). This study revealed that there were no systematic variations in $\delta^{53}$Cr (or Cr concentration) as a function of salinity, although Cr speciation was not determined. Given the diverse range of Cr reactions that can occur in estuarine mixing zones, further investigation is needed to assess their potential for modification of $\delta^{53}$Cr. This study reports the results of a systematic investigation of $\delta^{53}$Cr values and Cr speciation with respect to salinity in the Beaulieu River and estuary (UK).

## 2. Sampling location

The Beaulieu River is located in the New Forest National Park (UK), and drains into the strait between mainland England and the Isle of Wight known as the Solent (Figure 2). The protected status of the National Park means that its catchment is sparsely populated and there is little industry, so levels of pollution in the Beaulieu River are minimal compared to most UK rivers.

The New Forest primarily consists of heathlands, woodlands, bogs and wetlands. Surficial deposits are predominantly the Paleogene Barton and Headon Group sands, although Quaternary alluvia, clays and silts are found around the river and promote the growth of forest patches (Gilkes 1968). There are also tidal flats around the mouth of the estuary. The upper limit of the estuary is marked by a sluice gate, upstream of which is a small lake (the Mill Dam; Figure 2) that sometimes contains a small component of seawater. The depth of the river does not usually exceed ~1m whereas the depth of the estuary changes considerably with the state of the tide, varying between ~0.1 and 4m. The freshwater residence time in the estuary is ~7 days (Fang, 1995), which is similar to the residence time of water in the Solent (~6.25 days; Dyer and Lasta King 1975).

Concentrations of dissolved oxygen are high (up to 370µmol $L^{-1}$) throughout the river, and pH varies between 6.5 and 7.8 (Hopwood et al. 2014). Due to the nature of the vegetation in the catchment, the river waters have high levels of dissolved organic carbon (DOC), and estuarine waters can have DOC concentrations of >1mg $L^{-1}$ even at high salinities (*S* = >24) (Moore et al. 1979). Concentrations of dissolved iron (dFe) in the river are highly variable (8-21µM), and they fall significantly as the river water mixes with seawater, because Fe is incorporated into organic flocculates or forms Fe oxyhydroxide precipitates (Holliday and Liss, 1976; Fang, 1995; Hopwood et al., 2014). Up to ~50% of Fe at low salinities (*S* = <5) is present as Fe(II) (Hopwood et al., 2014), which is an effective reductant for Cr(VI) (Døssing et al., 2011; Kitchen et al., 2012).

The total dissolved concentration of Cr in the Solent adjacent to the Beaulieu estuary (also known as Southampton Water) is ~1.3-1.8nM (Bonnand et al., 2013), although higher concentrations (up to 5nM) have been recorded in the Beaulieu River itself (Dolamore-Frank, 1984). In a previous study, dissolved Cr appeared to behave conservatively during estuarine mixing, although loss of Cr(VI) from solution was suggested at high salinities, possibly as a result of reduction of Cr(VI) by DOC and removal of the Cr(III) that formed (Dolamore-Frank, 1984). Nevertheless, concentrations of particulate Cr were low even though dissolved concentrations of Cr(III) were relatively high, indicating that adsorption of this Cr(III) onto particulate material was not an important process in the estuary (Dolamore-Frank, 1984). The $\delta^{53}$Cr value of total dissolved Cr in Southampton Water at salinities of 30 and higher appears to be consistent over time at 1.50 ± 0.02‰, (n = 7; Bonnand et al. 2013; Goring-Harford et al. 2018) though the Cr isotopic compositions of river and estuarine waters of the Beaulieu have not hitherto been measured.

## 3. Methods

### 3.1. Sampling

All containers and sampling/filtration equipment were acid cleaned before use. A river water endmember sample was taken from the King's Hat Enclosure on 20th March 2016 and the estuary was sampled around high tide on 22nd March 2016 from the R.V. *Bill Conway*. A rigid-inflatable boat (RIB) was used to access the shallowest waters, but the low to intermediate salinities (*S* = 1-14) were inaccessible due to low rainfall in the preceding week, and the rapid mixing between freshwater and seawater at the sluice gate. A second set of samples targeting a lower salinity range was therefore taken on 5th October 2016 from the river, Mill Dam and upper part of the estuary waters during the early stages of the flood tide. Rainfall in the week preceding each sampling date were 0.0mm for March and 8.8mm for October (measured by a Davis Vantage Pro Plus weather station; http://www.tottonweather.co.uk/data-summary/).

All samples were recovered from 0.1-0.5m depth below the surface using a 1L bottle either by hand or by deploying a weighted metal free bottle holder. The 1L aliquots were homogenised in a larger container (5-6L total sample volume) and a subsample of this was taken immediately to measure salinity, pH and temperature (WTW Measurement Systems Inc. 340i handheld multimeter).

River sediment pore waters were sampled by inserting 80mm diameter plastic core liners into the river bed at King’s Hat Enclosure in April 2017. Cores were immediately transported back to the National Oceanography Centre Southampton (NOCS) and placed in a constant temperature laboratory at 10°C (to approximately match the temperature of the river water) before processing.

### 3.2. Determination of Cr concentration and Cr isotopic composition of river and estuarine waters

All acids used in sample processing were thermally distilled, while the other chemicals were Romil UpA, Fluka TraceSELECT Ultra, or Aristar® Ultra grade and contributed negligible Cr to the total procedural blank.

Water samples were filtered within 24 hours of collection in a class 100 clean laboratory using pre-rinsed Sartorius Sartobran 300 capsule filters (0.45µm). A $^{50}$Cr+$^{54}$Cr(III) double spike was added to samples being processed for isotopic analysis to account for any fractionation incurred during sample processing (full details of the spike are given in Goring-Harford et al 2018). At least 100ng of Cr, at a concentration of ~30 ppb in the analyte, was required for isotopic analysis. Because the Cr concentration of river waters and seawater is much lower (typically ~0.1ppb), it was necessary to pre-concentrate Cr. To do this we employed a Fe(II) co-precipitation method (Bonnand et al. 2013; Scheiderich et al. 2015; Goring-Harford et al. 2018). Samples collected in March 2016 were preserved by acidification to pH <2 using 2ml $L^{-1}$ of sub-boiled HCl prior to Fe(II) precipitation (except for the aliquots taken for Cr(III) analysis). The October 2016 samples were precipitated with Fe(II) on the day of filtration (within ~8 hours). Both approaches are expected to successfully capture all inorganic Cr, as Cr(III) adsorption to container walls is prevented both by low pH conditions prior to spiking and by prompt co-precipitation after collection; adsorption is not thought to be important for Cr(VI) (Gaillardet et al. 2003).

The pH of the river water samples (~3L volume) was adjusted to pH 8-9 approximately 24 hours after the double spike was added. Total dissolved inorganic chromium ($Cr_T$, defined as Cr(III) + Cr(VI)) was then removed from solution using an Fe(II) hydroxide precipitate (made from 2mM ammonium Fe(II) sulphate, Sigma-Aldrich batch 04728LI, 10ml $L^{-1}$ of sample) that converts any Cr(VI) to Cr(III) and quantitatively removes the Cr(III) in the form of a Fe(III)-Cr(III) precipitate (Shigematsu et al., 1977; Cranston and Murray, 1978; Dolamore-Frank, 1984; Jeandel and Minster, 1984). The precipitate was then separated by vacuum filtration using acid cleaned Millipore Omnipore filters (1 μm). A two-stage ion exchange chromatography procedure was carried out to remove the Fe and residual salts using the Biorad AG1-X8 and AG50-X12 resins respectively (Bonnand et al., 2013), and any remaining organic material was oxidised using $H_2O_2$. The Cr isotopic composition of the purified Cr sample-spike mixture was determined using a Thermo Fisher Neptune multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) in medium resolution mode. Newton-Raphson deconvolution and isotope dilution calculations were used to calculate

$\delta^{53}Cr_T$ and $Cr_T$ respectively. Raw data were corrected for instrumental drift and the total procedural blank contribution, which mainly came from the Fe precipitate and typically constituted <10% of the total Cr analysed (blank $\delta^{53}Cr_T$ = -0.34 ± 0.32‰ 2SD, n = 6). Repeat analyses of the NBS979 standard, normalised to the daily average NBS979 value, yielded an analytical reproducibility of ±0.04‰ (n = 344, 2SD). The external reproducibility of co-precipitated samples, determined from multiple analyses of the OSIL salinity standard (n = 6), was better than ±0.11‰ (Goring-Harford et al., 2018).

It is important to note that this technique is not expected to collect organically bound dissolved Cr ($Cr_{ORG}$), as this fraction is thought to be resistant to reduction and adsorption (Nakayama et al., 1981; Abu-Saba and Flegal, 1995). By contrast, previously published analyses of $\delta^{53}Cr$ in river waters have been obtained from samples that were pre-concentrated by evaporation; a technique considered to capture $Cr_{T+ORG}$ (Frei et al., 2014; Paulukat et al., 2015; D'Arcy et al., 2016). Nevertheless, a wide range of organic complexes with different binding strengths are present in the Beaulieu River (Hopwood et al., 2015), and our Fe co-precipitation method may capture weakly complexed $Cr_{ORG}$, thus $Cr_T$ values reported in this study are considered to be operationally defined. Filtered aliquots of two samples (B1 and B2) were analysed after UV irradiation for ~3 hours in LDPE bottles using a UV box containing 4 × G20T10 lamps, in an attempt to oxidise any $Cr_{ORG}$ and assess the potential contribution of this fraction to the total dissolved Cr pool.

### 3.3. Determination of Cr speciation in river and estuarine waters

Dissolved Cr(III) concentrations were measured using a modified version of the Fe co-precipitation technique, wherein Fe(III) hydroxide was used in place of Fe(II) hydroxide to collect Cr(III) only. Cr(III) is strongly adsorbed to Fe(III) hydroxide, whereas Cr(VI) is not, allowing effective separation of the two species (Shigematsu et al., 1977; Cranston and Murray, 1978; Dolamore-Frank, 1984; Jeandel and Minster, 1984). As for $Cr_T$, Cr(III) values are considered operationally defined because there is potential to collect some weakly bound $Cr_{ORG}$. A 500 mL sub-sample for Cr(III) analysis was taken from the bulk 5-6L sample and filtered, spiked and treated with the Fe(III) hydroxide precipitate (3 mL) either in a class 100 clean laboratory at NOCS or on board the R.V. *Bill Conway*. The Fe(III) solution was prepared in the same manner as the Fe(II) solution described in Section 3.2, except it was allowed to oxidise for 1 week with occasional shaking. As the proportions of Cr(III) and Cr(VI) in natural water samples may change rapidly after sample collection (Kingston et al., 1998), co-precipitation was done within 4 hours of sample collection. Blank solutions of Milli-Q water were processed alongside the samples.

The $^{50}$Cr+$^{54}$Cr double spike was replaced with a $^{53}$Cr(III) single spike for Cr(III) analysis and isotope dilution calculations were made using the $^{52}$Cr/$^{53}$Cr ratio. The lowest analytical error occurs when the $^{52}$Cr/$^{53}$Cr ratio is 0.1 - 3.5 (Bedson, 2007); all samples had ratios of of 0.1 - 1.1. Despite the lack of isobaric interferences on $^{52}$Cr and $^{53}$Cr, large quantities of residual Fe and salts will interfere with ICP-MS analysis so an ion exchange procedure similar to that described above was used to purify the Cr fraction. $^{52}$Cr/$^{53}$Cr ratios were then measured on an Element 2 ICP-MS. The accuracy of this procedure was tested by processing Cr(III) standards (NBS979) and mixed Cr(III) + Cr(VI) standards (NBS979 and potassium chromate, Fluka TraceCERT®) in the same way as samples. Cr(VI) concentrations were subsequently calculated by subtracting Cr(III) from $Cr_T$.

### 3.4. Analysis of dissolved iron concentrations

Total dissolved iron concentrations in the <0.45μm fraction were measured using the ferrozine method (Stookey, 1970). Approximately 5mL of each sample was filtered through pre-cleaned 0.45μm syringe filters (Millipore Millex) within 4 hours of collection. 3mL aliquots of the filtered water were immediately pipetted into vials pre-loaded with 0.2mL of 5mM ferrozine and 0.2mL of 10mM ascorbic acid. A series of Fe standards (0-50μM, made with ammonium Fe(II) sulphate) were treated in the same way. Under these conditions all Fe (Fe(II) + Fe(III)) is converted to Fe(II) that reacts to form a purple complex with ferrozine. The method collects inorganic Fe as well as organically complexed Fe, except for the most strongly bound Fe complexes (Hopwood et al., 2014). Fe concentrations were determined using a Unicom 8625

UV/Visible spectrometer set to measure absorbance at 562nm. A 4cm cell was used to maximise sensitivity and the detection limit was 0.13μM.

### 3.5. Processing of push cores and sampling of pore waters

Profiles of dissolved oxygen were measured for two of the four push cores using an optical oxygen meter (Pyroscience FirestingO2 with OX50 needle-type sensor) mounted on a micromanipulator (Pyroscience MU1). The uppermost 5cm of sediment from each core was then centrifuged to extract the pore water. Pore waters were combined and centrifuged once more; co-precipitation with Fe was not necessary. The pore waters were then vacuum filtered through pre-cleaned 0.45μm membrane filters (Whatman Polycarbonate). Organic material was oxidised by addition of 0.2mL $H_2O_2$ and refluxing in 1mL of aqua regia at 130°C for ~24 hours. Any precipitate was digested by refluxing in 0.5mL of hydrogen fluoride at 170°C for 4 days. The samples were then dissolved in 3mL of 7M HCl and dried before being passed through the ion chromatography procedure. The total procedural blank was ~3 ng, almost entirely contributed by the filter (2.4 ± 0.8 ng, n = 3). This is less than 1% of the Cr processed and is therefore considered negligible.

## 4. Results

### 4.1. Method validation

It is essential that equilibration between natural Cr in the sample and Cr in the spike is achieved in order to produce accurate data, because the yield of Cr is <100% (9 – 60% in samples with $S \leq 10$, and 60 - 85% in samples with $S \geq 10$). Equilibration is effective in seawater samples (Jeandel and Minster, 1984; Bonnand et al., 2013; Scheiderich et al., 2015; Goring-Harford et al., 2018), but to verify that this was also the case for low salinity samples, we tested an archived Beaulieu river water sample ($S = 0$) that had not been acidified for $Cr_T$, Cr(III) and $Cr_{T+ORG}$ using the $^{53}Cr$ spike, yielding concentrations of 0.63 nmol $kg^{-1}$, 0.37 nmol $kg^{-1}$ and 0.73 nmol $kg^{-1}$ respectively. To obtain an independent $Cr_{T+ORG}$ value, two more aliquots were simply dried down and treated with $H_2O_2$ to eliminate organic matter before analysis on the Element 2. The $Cr_{T+ORG}$ values of these samples (0.71 ± 0.09 nmol $kg^{-1}$ 2SD, n=2) were within error of the spiked and co-precipitated sample. Thus, this investigation demonstrates that: (i) spike equilibration is effective in low salinity waters containing a mixture of Cr(III) and Cr(VI); (ii) $Cr_{ORG}$ is effectively released by UV irradiation; and (iii) all Cr species have been determined by our analyses. Apart from its atomic mass, the $^{50+54}Cr$ spike is identical to the $^{53}Cr$ spike, so it is reasonable to assume that spike equilibration was also effective for $Cr_T$ and $\delta^{53}Cr_T$ analyses.

For speciation analyses, the average total procedural blank for the samples that were partly processed on board the R.V. *Bill Conway* was 0.08 ± 0.02nmol (2SD, n=2). This is within error of our long term total procedural blank for samples processed in the clean laboratory (0.09 ± 0.06nmol 2SD; n=13), implying that the samples were not compromised by handling outside of the clean laboratory. Several authors have shown that Fe(III) co-precipitation is an effective technique for measuring Cr(III) in natural waters, with or without employing an isotopic spike (Shigematsu et al., 1977; Cranston and Murray, 1978; Dolamore-Frank, 1984; Jeandel and Minster, 1984). To check that the method is capable of producing accurate Cr(III) concentrations with our $^{53}Cr$ spike, Cr(III) and mixed Cr(III) + Cr(VI) standards in Milli-Q water were tested (Table 2). The Cr(III) standards gave values within ±4% of the expected value, demonstrating that little Cr(III) was lost to container walls before sample-spike equilibration occurred. Mixed Cr(III) + Cr(VI) standards had a slightly higher uncertainty of ±10% (Table 1). The higher uncertainty of the mixed standards may reflect speciation changes prior to addition of the Fe precipitate, as this was not done until ~24 hours after spiking. In an effort to circumvent this issue, the Fe precipitate was added to river water and estuary samples within 4 hours of sample collection; nevertheless, the uncertainty of Cr(III), Cr(VI) and $Cr_T$ measurements are conservatively reported in this study as ± 10%. In support of this, sample B13 was processed twice and yielded an average Cr(III) concentration of 0.25nmol $kg^{-1}$ ± 7%.

### 4.2. Cr and $\delta^{53}Cr_T$ variation in estuarine waters

The range of $Cr_T$ values for samples collected in March 2016 (1.64 to 1.89 nmol $kg^{-1}$; Table 2) was similar to that measured previously for this location (1.64 to 5.05nmol $kg^{-1}$; Bonnand et al.

2013; Dolamore-Frank 1984), whereas the October samples had very low $Cr_T$ (0.66 to 1.03 nmol $kg^{-1}$). On both sampling dates $Cr_T$ decreased slightly with salinity. A negative correlation was observed between Cr(III) and salinity (Figure 3C; $R^2 = 0.95$, $p < 10^{-7}$ for March, $R^2 = 0.57$, $p < 0.1$ for October), whereas Cr(VI) showed a positive correlation (Figure 3D; $R^2 = 0.87$, $p < 10^{-5}$ for March, $R^2 = 0.24$, $p < 0.4$ for October). Approximately 15% of $Cr_T$ was found to be present as Cr(III) in high salinity waters (*S* = >29), compared with up to 55% in low salinity waters (*S* = <5). The $\delta^{53}Cr_T$ values (-0.59 to 1.68‰) increased linearly with increasing salinity (Figure 3E; $R^2 = 0.98$, $p < 10^{-10}$ for March, $R^2 = 0.84$, $p < 0.02$ for October). Assuming that the relationship between salinity and $\delta^{53}Cr_T$ is linear, even at very low salinity (see Section 5.1), then the extrapolated $\delta^{53}Cr_T$ value of the river endmember at *S* = 0 was the same in March ($\delta^{53}Cr_{T\text{-CALCULATED}}$ = -0.43 ± 0.06‰) and October ($\delta^{53}Cr_{T\text{-CALCULATED}}$ = -0.34 ± 0.13‰).

### 4.3. Cr associated with organic material

Tests performed using the $^{53}Cr$ single spike method demonstrated that UV irradiation did not contribute any significant Cr to the total procedural blank, as the average UV irradiated blank (0.06 ± 0.03nmol, n = 3) was within error of the long term procedural blank (0.09 ± 0.06nmol; n=13).

Water samples B1 and B2 irradiated with UV light had higher dissolved Cr concentrations ($Cr_{T+ORG}$) compared to non-irradiated aliquots, indicating that at least 18% of the Cr in low to mid salinity waters was organically bound (Table 3). The UV-irradiated samples also had lower $\delta^{53}Cr_{T+ORG}$ compared to $\delta^{53}Cr_T$ in non-irradiated samples, which implies that the $Cr_{ORG}$ fraction has a lower $\delta^{53}Cr$ composition than the $Cr_T$ fraction. The $\delta^{53}Cr$ value of $Cr_{ORG}$ is given by:

$$\delta^{53}\mathrm{Cr_{ORG}} = \frac{\left(\delta^{53}\mathrm{Cr_{T+ORG}} - \ (\mathrm{F_T} \text{ x } \delta^{53}\mathrm{Cr_T})\right)}{\mathrm{F_{ORG}}}$$

Where $F_T = Cr_T/Cr_{T+ORG}$ and $F_{ORG} = Cr_{ORG}/Cr_{T+ORG}$. B1 and B2 yield $\delta^{53}Cr_{ORG}$ values of -0.75‰ and -0.11‰, respectively (Table 3).

### 4.4. Cr concentration and Cr isotopic composition of river sediment pore waters

The sediment core-top waters contained 230-260μM of dissolved $O_2$, and the pH was 6.9 at approximately 1cm depth below the river bed (measured in one core only). Oxygen profiles (Figure 4) revealed a shallow oxygen penetration depth of 2.9 ± 1.7mm (2SD) below the sediment-water interface. $Cr_T$ concentrations of pore waters from the two cores were 100 and 120nmol kg$^{-1}$ and $\delta^{53}Cr_{T+ORG}$ values were 0.06 ± 0.05‰ and 0.13 ± 0.05‰ respectively. These analyses included any $Cr_{ORG}$ in the pore waters as the Fe co-precipitation method was not used.

## 5. Discussion

### 5.1. Behaviour of Cr and Cr isotopes during estuarine mixing

Concentrations of $Cr_T$ in samples collected in October were significantly lower than in March, and compared to previous measurements (Dolamore-Frank, 1984). Dilution of surface water Cr may have played a part as there was more rainfall (8.8 mm) in October, however this cannot explain a reduction of ~50% in $Cr_T$. Another explanation is that a greater proportion of dissolved Cr(III) was contained in the organic fraction (which is not captured by our Fe co-precipitation method) due to the release of dissolved organic material in the autumn following the decomposition of deciduous tree leaves; this would have affected even the high salinity sample (B20, $S$ = 29.6) because it was taken from a well vegetated part of the river (Figure 2). Organic molecules from leaf litter leachates have been shown to strongly bind copper in the early stages of decomposition because microbes transform or consume the most effective organic ligands (proteins and polyphenol-like compounds) over time (Cuss and Gueguen, 2012). It is possible that a similar situation applies to Cr. In support of this, large amounts of foam were observed on the river surface in October, suggesting that concentrations of organic surfactants were high.

Figure 3A provides evidence for the removal of dissolved iron at low salinities in the Beaulieu Estuary as observed in previous studies (Holliday and Liss, 1976; Fang, 1995), which is thought to reflect the incorporation of Fe into flocculated organic particles (Sholkovitz et al., 1978; Moore et al., 1979; Hopwood et al., 2014). However, no relationship was observed between $Cr_T$ and dFe concentrations at low salinities ($R^2 = 0.01$ for October), suggesting that inorganic Cr species were unaffected by the flocculation of organic material during the transition from river to estuary.

Concentrations of Cr(VI), Cr(III) and $\delta^{53}Cr_T$ exhibited linear relationships with salinity on both sampling dates, whilst $Cr_T$ showed little variation with salinity because the river and seawater endmembers had similar $Cr_T$ concentrations (Figure 3B-E). Re-release of Cr from particulate material at high salinities has previously been observed in both the Beaulieu estuary (Dolamore-Frank, 1984) and the Connecticut estuary (Sun et al., 2019), but there was no increase in $Cr_T$ that would suggest a similar mechanism in this case. Furthermore, the relationship between $\delta^{53}Cr_T$ and salinity was much stronger ($R^2 = 0.98$ and 0.84 for March and October respectively; Figure 3E) than that between $\delta^{53}Cr_T$ and $Cr_T$ ($R^2 = 0.24$ and 0.00 for March and October respectively; Figure 3F), strongly suggesting that salinity, rather than reduction and removal of isotopically light Cr(III), exerts the main control on $\delta^{53}Cr_T$. The distributions of Cr(VI), Cr(III) and $\delta^{53}Cr_T$ in the Beaulieu estuary are therefore thought to be principally controlled by simple mixing between a high Cr(III)/low Cr(VI), low $\delta^{53}Cr_T$ river water endmember and a low Cr(III)/high Cr(VI), high $\delta^{53}Cr_T$ seawater endmember. This is supported by our mixing model (Figure 5; see Sections 5.2 and 5.3), where river and seawater endmember values for Cr(III), Cr(VI) and $\delta^{53}Cr_T$ for March have been calculated by linear extrapolation, and intermediate values calculated by adding the proportions contributed by the endmembers; there is good agreement between model and measured values. These findings contrast with those from the Connecticut estuary, where Cr removal onto suspended particulate material and into sediments at low to moderate salinities appeared to be associated with Cr isotope fractionation (Sun et al., 2019).

It is possible that removal of Cr(III) and/or Cr(VI) occurs at very low salinities (<0.5), because sample B1 (which was taken from further upstream than the other samples), had a much higher $Cr_T$ concentration (5.05nmol $kg^{-1}$) than the other samples. Reduction of Cr(VI) and subsequent removal of the Cr(III) that forms would drive the $\delta^{53}Cr_T$ composition of the remaining dissolved Cr to a higher value because the fractionation factors for Cr(VI) reduction by Fe(II) or DOC, the most abundant reductants in the Beaulieu River system, are large ($\Delta_{Cr(VI)-Cr(III)}$ = 3.6 to 4.2‰ and 3.1‰ respectively; Døssing et al. 2011; Kitchen et al. 2012). Figure 5A models the $\delta^{53}Cr_T$ value of remaining dissolved Cr in the Beaulieu estuary for March, assuming that all of the Cr(III) in sample B1 (3.21nmol kg$^{-1}$, 64% of the $Cr_T$) was produced by reduction of Cr(VI), and that this Cr(III) was subsequently removed at *S* = <0.5, followed by conservative mixing at higher salinities. It is clear that this would result in much higher $\delta^{53}Cr_T$ values than those observed in the estuary, which instead fall along a conservative mixing line with a river water endmember $\delta^{53}Cr_{T\text{-}CALCULATED}$ value of -0.39‰ (see Section 5.2). Therefore, if Cr removal does occur, it must be associated with no, or minimal, isotopic fractionation.

### 5.2. Controls on the Cr concentration and Cr isotopic composition of the river water endmember

The variation in $Cr_T$ and $\delta^{53}Cr_T$ values is higher in the lower salinity samples that were collected from upstream of the sluice gate (*S* = ≤14.5; Figure 3). In particular, samples B1 and B17 have high $\delta^{53}Cr_T$, high $Cr_T$ and a low proportion of Cr(III) relative to samples of similar salinity that may be indicative of input of Cr from a different source. Nevertheless, overall there is a linear relationship between $\delta^{53}Cr_T$ and salinity, so the average $\delta^{53}Cr_T$ value of the river water endmember can be estimated by extrapolating the regression line to *S* = 0. The estimated $\delta^{53}Cr_T$ value of the river water endmember, based on both the March and October data, is -0.39 ± 0.08‰, lower than the range determined for most other rivers to date (Figure 1). It is also lower than the $\delta^{53}Cr$ value of crustal rocks (-0.12 ± 0.10‰; Schoenberg et al. 2008), and the $\delta^{53}Cr_{T+ORG}$ values of pore waters in Beaulieu River bed sediments (0.06 to 0.13‰). Although Cr isotope fractionation during oxidative weathering is poorly characterised, it is expected to produce aqueous Cr(VI) that has a higher $\delta^{53}Cr$ value than the crustal value (e.g. Frei et al. 2014; D'Arcy et al. 2016), thus oxidative weathering cannot be the principal control on the $\delta^{53}Cr_T$ value of the Beaulieu River.

Chromium can also be released into solution *via* dissolution of sedimentary Fe-Cr (oxy)hydroxides under anoxic conditions (Rigaud et al., 2013). The oxic-anoxic boundary is located close to the sediment-water interface in the Beaulieu River (Figure 4), thus given the high concentration of dissolved $Cr_{T+ORG}$ in the sediment pore waters (100-120nmol $kg^{-1}$), diffusion of dissolved Cr(III) derived from the dissolution of Fe-Cr (oxy)hydroxides could be an important source of Cr into the Beaulieu river. Chromium contained in (oxy)hydroxides is expected to be enriched in lighter Cr isotopes (Døssing et al., 2011; Kitchen et al., 2012), so this mechanism may also account for the low $\delta^{53}Cr_T$ values in the Beaulieu river endmember. Analyses of sediment pore waters from the Beaulieu do not support this scenario, however, as their $\delta^{53}Cr_{T+ORG}$ values (0.06‰ and 0.13‰) were higher than that of the river water endmember ($\delta^{53}Cr_{T\text{-}CALCULATED}$ = -0.39‰; measured values as low as -0.59‰). Instead, we suggest that the $\delta^{53}Cr_T$ value of Beaulieu River water is primarily controlled by the presence of organic ligands (Figure 6). Mobile organic Cr(III) species are likely to form in the soil solution (Icopini and Long, 2002; Beck et al., 2008; Rigaud et al., 2013), and may be released into river waters. Formation of these organic Cr(III) complexes can occur *via* inorganic or biological reduction of Cr(VI), which may be derived from oxidation of Cr(III) in the uppermost oxic sediments, or from Cr(VI) that has formed *via* the diffusion and oxidation of dissolved Cr(III) originating from the underlying anoxic zone. Reduction of Cr(VI) by both mechanisms is associated with large isotopic fractionation factors ($\Delta_{Cr(VI)\text{-}Cr(III)}$ = 1.8 - 4.5‰ for various bacteria and 3.1‰ for organic molecules; Sikora et al. 2008; Han et al. 2012; Kitchen et al. 2012; Basu et al. 2014). Thus, organic Cr(III) complexes produced in this way are likely to have a low $\delta^{53}Cr$ value, consistent with our findings for $\delta^{53}Cr_{ORG}$ in the Beaulieu (-0.8 to -0.1‰; Table 3). Dissociation of these low $\delta^{53}Cr(III)$ bearing complexes by photochemical reactions (Kieber and Helz, 1992) would also explain why $\delta^{53}Cr_T$ values were low and the proportion of dissolved Cr(III) was high in low salinity waters, and particularly as we sampled very shallow waters on clear, sunny days. In support of this hypothesis, it is notable that the $\delta^{53}Cr_{T+ORG}$ value of the UV irradiated sample B1 (0.06‰) was very similar to that of the pore waters (0.06-0.13‰) that were sampled in very close proximity; it appears that the river water directly reflects the pore water Cr source when $Cr_{ORG}$ is taken into account. The changing proportion of Cr released into solution *via* this process *versus* Cr released due to oxidative weathering may also explain the higher scatter in the data at low salinities.

### 5.3. Controls on the Cr concentration and Cr isotopic composition of the seawater endmember

The estimated $\delta^{53}Cr_T$ value of the coastal seawater endmember at *S* = 35 (1.6 ± 0.4‰; calculated using March and October data) is similar to those previously measured in shelf waters (typically 1.3 to 1.5‰, *S* = 30 to 34; Bonnand et al. 2013; Scheiderich et al. 2015; Goring-Harford et al. 2018), but higher than the values typically measured in oxic deep water masses (1.0 to 1.2‰; Bonnand et al. 2013; Scheiderich et al. 2015; Goring-Harford et al. 2018). This likely reflects internal cycling of Cr within coastal and shelf waters, e.g. the reduction of Cr(VI) to Cr(III) in surface waters followed by removal onto biogenic particles, and the release of Cr from sedimentary sources (Scheiderich et al., 2015; Goring-Harford et al., 2018), Because the volume of the Beaulieu River is far smaller than that of Southampton Water and its $Cr_T$ is low, the low $\delta^{53}Cr_T$ of the Beaulieu River does not have a significant impact Southampton Water $\delta^{53}Cr_T$ values. In other estuarine systems, however, high salinity shelf waters (which typically have similar Cr concentrations to Southampton Water, ~2 nM; Scheiderich et al. 2015; Goring-Harford et al. 2018) may be significantly impacted by riverine $\delta^{53}Cr_T$ if there is a larger riverine Cr input. Figure 7 shows how $\delta^{53}Cr_T$ values in high salinity waters would be modified by a river with similar $\delta^{53}Cr_T$ to the Beaulieu and a higher $Cr_T$ of 15nM (similar to, for example, the Humber River; Comber and Gardner 2003). In this situation, the riverine input would still be significantly impacting $\delta^{53}Cr_T$ at *S* = 34 (1.18‰), causing it to be over 0.4‰ lower than the seawater endmember (*S* = 35, $\delta^{53}Cr_T$ = 1.60‰), whereas for a river like the Beaulieu (with much lower $Cr_T$), the difference is <0.1‰. Thus, rivers with high $Cr_T$ may influence the $\delta^{53}Cr$ value of high salinity estuarine waters, and possibly even the adjacent continental shelf waters if the river and seawater endmembers also have very different $\delta^{53}Cr$ values.

### 5.4. Implications for the $\delta^{53}$Cr redox proxy

Whilst our data provide no insight as to the behaviour of organically bound Cr in estuaries, significant quantities of $Cr_{ORG}$ are unlikely to be transferred to the open ocean because DOC concentrations are extremely low in the open ocean (~40-100μmol C $L^{-1}$, compared to up to ~5mmol C $L^{-1}$ in the Beaulieu River; e.g. Miller and Zepp 1995; Hansell and Carlson 1998). Furthermore, organically bound Cr in the Beaulieu River is <20% of the total Cr, even though it has far higher DOC concentrations than most other rivers (Moore et al., 1979). Thus, Cr is most likely to be transferred to the ocean in its inorganic forms, with the composition of the dissolved Cr(III) and Cr(VI) species controlling the 'baseline' $\delta^{53}$Cr value of seawater on a global scale (though modifications will occur in the ocean itself; Scheiderich et al. 2015; Goring-Harford et al. 2018; Bruggmann et al. 2019). Our study shows that inorganic forms of dissolved Cr behave conservatively during estuarine mixing in the Beaulieu and that Cr(VI) is not reduced to Cr(III). If this were true for all estuaries, the global average riverine $\delta^{53}$Cr value would be faithfully transferred to the ocean. However, our study also reveals that anoxic, rather than oxidative, weathering processes are likely to be the principal source of Cr to the Beaulieu River, and that the $\delta^{53}$Cr value of the river water endmember is controlled by complexation with organic ligands. The operation of fractionating processes beside oxidative weathering potentially complicates the interpretation of seawater $\delta^{53}$Cr values in terms of the level of atmospheric oxygenation, although we note that on a global scale, the input of Cr from oxidative weathering in mafic catchments is likely to be far more important source of Cr to the oceans than from organic rich, non-mafic catchments (McClain and Maher, 2016).

Finally, in a scenario where riverine $\delta^{53}$Cr values are dissimilar to those of seawater, and especially where the riverine Cr concentration is high, $\delta^{53}$Cr values of shelf waters may be significantly influenced by input of riverine Cr (Figure 7). As a result, shelf sediments are likely to be poor candidates for redox proxy studies, because $\delta^{53}$Cr values will reflect a mixture of local and global scale processes.

## 6. Conclusions

In contrast to most river systems that have relatively high $\delta^{53}$Cr values due to release of Cr(VI) by oxidative weathering processes, dissolved Cr in the Beaulieu River is characterised by low $\delta^{53}Cr_T$ values (-0.59 to 0.24‰). We suggest that in this DOC-rich river system, pore water Cr(VI) is partly back-reduced to Cr(III) by organic or Fe(II) reductants, and the formation of organic complexes keeps the Cr(III) in solution. Our results also demonstrated that Cr(III), Cr(VI) and Cr isotopes behave conservatively in the estuarine mixing zone and, even in the presence of high concentrations of dFe and DOC, we found no evidence for reduction of Cr(VI) to Cr(III).

Knowledge of the behaviour of Cr and Cr isotopes in rivers and during estuarine mixing is essential for the interpretation of the Cr isotope redox proxy. We have shown that oxidative weathering is not the only source of dissolved Cr in organic-rich river systems, and that input of Cr from anoxic weathering processes contributes Cr with a distinctly lower $\delta^{53}$Cr value (~ -0.4‰). At the global scale, however, such organic-rich rivers are unlikely to be an important source of dissolved Cr to the oceans. While inorganic riverine $\delta^{53}$Cr values appear to be unmodified during estuarine mixing, the estimated $\delta^{53}$Cr value of the seawater endmember (1.6 ± 0.4‰) is higher than the range reported to date for most deep water masses (1.0-1.2‰), which supports existing evidence that cycling of Cr within coastal and shelf seas may modify the $\delta^{53}$Cr value of seawater (Scheiderich et al., 2015; Goring-Harford et al., 2018). Internal biogeochemical cycling of oceanic Cr therefore needs to be taken into consideration in the interpretation of the seawater $\delta^{53}$Cr record preserved in authigenic marine sediments in terms of oxidative weathering. We also show that even in estuaries where Cr behaves conservatively, $\delta^{53}$Cr values of shelf waters can be modified by input of riverine Cr. The sedimentary record of seawater $\delta^{53}$Cr in these settings may therefore reflect local, rather than global, processes.

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## References

Abu-Saba, K.E. and Flegal, A.R. (1995) Chromium in San Francisco Bay: superposition of geochemical processes causes complex spatial distributions of redox species. *Mar. Chem.* **49**, 189-199.

Andronikov, A.V., Novak, M., Borodulina, G.S., Efremenko, N.A., Andronikova, I.E., Chesalina, G.L., Levichev, M.A., Subetto, D.A., Sebek, O. and Zobkova, M.V. (2019) One river, two streams: chemical and chromium isotopic features of the Neglinka River (Karelia, northwest Russia). *Hydrological Sciences Journal*.

Basu, A., Johnson, T.M. and Sanford, R.A. (2014) Cr isotope fractionation factors for Cr(VI) reduction by a metabolically diverse group of bacteria. *Geochim. Cosmochim. Acta* **142**, 349-361.

Beck, M., Dellwig, O., Schnetger, B. and Brumsack, H.-J. (2008) Cycling of trace metals (Mn, Fe, Mo, U, V, Cr) in deep pore waters of intertidal flat sediments. *Geochim. Cosmochim. Acta* **72**, 2822-2840.

Bedson, P. (2007) Guidelines for achieving high accuracy in isotope dilution mass spectrometry (IDMS). Royal Society of Chemistry, Cambridge, GBR.

Bonnand, P., James, R.H., Parkinson, I.J., Connelly, D.P. and Fairchild, I.J. (2013) The chromium isotopic composition of seawater and marine carbonates. *Earth. Planet. Sci. Lett.* **382**, 10-20.

Bruggmann, S., Scholz, F., Klaebe, R.M., Canfield, D.E. and Frei, R. (2019) Chromium isotope cycling in the water column and sediments of the Peruvian continental margin. *Geochim. Cosmochim. Acta* **257**, 224-242.

Buerge, I.J. and Hug, S.J. (1998) Influence of organic ligands on chromium(VI) reduction by iron(II). *Environ. Sci. Technol.* **32**, 2092-2099.

Campbell, J.A. and Yeats, P.A. (1984) Dissolved Chromium in the St. Lawrence Estuary. *Estuar. Coast. Shelf Sci.* **19**, 513-522.

Comber, S. and Gardner, M. (2003) Chromium redox speciation in natural waters. *J. Environ. Monit.* **5**, 410-413.

Cranston, R.E. and Murray, J.W. (1978) The determination of chromium species in natural waters. *Anal. Chim. Acta* **99**, 275-282.

Cranston, R.E. and Murray, J.W. (1980) Chromium species in the Columbia River and estuary. *Limnol. Oceanogr.* **25**, 1104-1112.

Crowe, S.A., Døssing, L.N., Beukes, N.J., Bau, M., Kruger, S.J., Frei, R. and Canfield, D.E. (2013) Atmospheric oxygenation three billion years ago. *Nature* **501**, 535-538.

Cuss, C. and Gueguen, C. (2012) Impacts of Microbial Activity on the Optical and Copper-Binding Properties of Leaf-Litter Leachate. *Frontiers in Microbiology* **3**, 166.

D'Arcy, J., Babechuk, M.G., Døssing, L.N., Gaucher, C. and Frei, R. (2016) Processes controlling the chromium isotopic composition of river water: Constrains from basaltic river catchments. *Geochim. Cosmochim. Acta* **186**, 296-315.

Dolamore-Frank, J.A. (1984) The analysis, occurrence and chemical speciation of zinc and chromium in natural waters. University of Southampton, UK.

Døssing, L.N., Dideriksen, K., Stipp, S.L.S. and Frei, R. (2011) Reduction of hexavalent chromium by ferrous iron: A process of chromium isotope fractionation and its relevance to natural environments. *Chem. Geol.* **285**, 157-166.

Dyer, K.R. and Lasta King, H. (1975) The Residual Water Flow through the Solent, South England. *Geophysical Journal International* **42**, 97-106.

Elderfield, H. (1970) Chromium speciation in seawater. *Earth. Planet. Sci. Lett.* **9**, 10-16.

Ellis, A.S., Johnson, T.M. and Bullen, T.D. (2002) Chromium isotopes and the fate of hexavalent chromium in the environment. *Science* **295**, 2060-2062.

Fang, T.-H. (1995) Studies of the behaviour of trace metals during mixing in some estuaries of the Solent region. University of Southampton.

Frei, R., Gaucher, C., Poulton, S.W. and Canfield, D.E. (2009) Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes. *Nature* **461**, 250-253.

Frei, R., Poiré, D. and Frei, K.M. (2014) Weathering on land and transport of chromium to the ocean in a subtropical region (Misiones, NW Argentina): A chromium stable isotope perspective. *Chem. Geol.* **381**, 110-124.

Gaillardet, J., Viers, J. and Dupré, B. (2003) 5.09 - Trace elements in river waters, in: Holland, H.D., Turekian, K.K. (Eds.), Treatise on Geochemistry. Pergamon, Oxford, pp. 225-272.

Gardner, M.J. and Ravenscroft, J.E. (1996) Determination of chromium(III) and total chromium in marine waters. *Fresenius J. Anal. Chem.* **354**, 602-605.

Gilkes, R.J. (1968) Clay Mineral Provinces in the Tertiary Sediments of the Hampshire Basin. *Clay Minerals* **7**, 351-361.

Goring-Harford, H.J., Klar, J.K., Pearce, C.R., Connelly, D.P., Achterberg, E.P. and James, R.H. (2018) Behaviour of chromium isotopes in the eastern sub-tropical Atlantic Oxygen Minimum Zone. *Geochim. Cosmochim. Acta* **236**, 41-59.

Han, R., Qin, L., Brown, S.T., Christensen, J.N. and Beller, H.R. (2012) Differential isotopic fractionation during Cr(VI) reduction by an aquifer-derived bacterium under aerobic versus denitrifying conditions. *Appl. Environ. Microbiol.* **78**, 2462-2464.

Hansell, D.A. and Carlson, C.A. (1998) Deep-ocean gradients in the concentration of dissolved organic carbon. *Nature* **395**, 263-266.

Holliday, L.M. and Liss, P.S. (1976) The behaviour of dissolved iron, manganese and zinc in the Beaulieu Estuary, S. England. *Estuarine and Coastal Marine Science* **4**, 349-353.

Holmden, C., Jacobson, A.D., Sageman, B.B. and Hurtgen, M.T. (2016) Response of the Cr isotope proxy to Cretaceous Ocean Anoxic Event 2 in a pelagic carbonate succession from the Western Interior Seaway. *Geochim. Cosmochim. Acta* **186**, 277-295.

Hopwood, M.J., Statham, P.J. and Milani, A. (2014) Dissolved Fe(II) in a river-estuary system rich in dissolved organic matter. *Estuar. Coast. Shelf Sci.* **151**, 1-9.

Hopwood, M.J., Statham, P.J., Skrabal, S.A. and Willey, J.D. (2015) Dissolved iron(II) ligands in river and estuarine water. *Mar. Chem.* **173**, 173-182.

Icopini, G.A. and Long, D.T. (2002) Speciation of Aqueous Chromium by Use of Solid-Phase Extractions in the Field. *Environ. Sci. Technol.* **36**, 2994-2999.

Jeandel, C. and Minster, J.F. (1984) Isotope dilution measurement of inorganic chromium(III) and total chromium in seawater. *Mar. Chem.* **14**, 347-364.

Jeandel, C. and Minster, J.F. (1987) Chromium behaviour in the ocean: Global versus regional processes. *Global Biogeochem. Cycles* **1**, 131-154.

Jonas, P.J.C. and Millward, G.E. (2010) Metals and nutrients in the Severn Estuary and Bristol Channel: Contemporary inputs and distributions. *Mar. Pollut. Bull.* **61**, 52-67.

Kaczynski, S.E. and Kieber, R.J. (1994) Hydrophobic C18 bound organic complexes of chromium and their potential impact on the geochemistry of chromium in natural waters. *Environ. Sci. Technol.* **28**, 799-804.

Kieber, R.J. and Helz, G.R. (1992) Indirect photoreduction of aqueous chromium(VI). *Environ. Sci. Technol.* **26**, 307-312.

Kingston, H.M., Huo, D., Lu, Y. and Chalk, S. (1998) Accuracy in species analysis: speciated isotope dilution mass spectrometry (SIDMS) exemplified by the evaluation of chromium species. *Spectrochim. Acta, Part B* **53**, 299-309.

Kitchen, J.W., Johnson, T.M., Bullen, T.D., Zhu, J. and Raddatz, A. (2012) Chromium isotope fractionation factors for reduction of Cr(VI) by aqueous Fe(II) and organic molecules. *Geochim. Cosmochim. Acta* **89**, 190-201.

Mayer, L.M. and Schick, L.L. (1981) Removal of hexavalent chromium from estuarine waters by model substrates and natural sediments. *Environ. Sci. Technol.* **15**, 1482-1484.

McClain, C.N. and Maher, K. (2016) Chromium fluxes and speciation in ultramafic catchments and global rivers. *Chem. Geol.* **426**, 135-157.

Miller, W.L. and Zepp, R.G. (1995) Photochemical production of dissolved inorganic carbon from terrestrial organic matter: Significance to the oceanic organic carbon cycle. *Geophys. Res. Lett.* **22**, 417-420.

Moore, R.M., Burton, J.D., Williams, P.J.L. and Young, M.L. (1979) The behaviour of dissolved organic material, iron and manganese in estuarine mixing. *Geochim. Cosmochim. Acta* **43**, 919-926.

Moos, S.B. and Boyle, E.A. (2018) Determination of accurate and precise chromium isotope ratios in seawater samples by MC-ICP-MS illustrated by analysis of SAFe Station in the North Pacific Ocean. *Chem. Geol.* **511**, 481-493.

Nakayama, E., Kuwamoto, T., Tsurubo, S., Tokoro, H. and Fujinaga, T. (1981) Chemical speciation of chromium in sea water: Part 1. Effect of naturally occurring organic materials on the complex formation of chromium(III). *Anal. Chim. Acta* **130**, 289-294.

Novak, M., Chrastny, V., Cadkova, E., Farkas, J., Bullen, T.D., Tylcer, J., Szurmanova, Z., Cron, M., Prechova, E., Curik, J., Stepanova, M., Pasava, J., Erbanova, L., Houskova, M., Puncochar, K. and Hellerich, L.A. (2014) Common occurrence of a positive δ53Cr shift in central European waters contaminated by geogenic/industrial chromium relative to source values. *Environ. Sci. Technol.* **48**, 6089-6096.

Paulukat, C., Døssing, L.N., Mondal, S.K., Voegelin, A.R. and Frei, R. (2015) Oxidative release of chromium from Archean ultramafic rocks, its transport and environmental impact – A Cr isotope perspective on the Sukinda valley ore district (Orissa, India). *Appl. Geochem.* **59**, 125-138.

Paulukat, C., Gilleaudeau, G.J., Chernyavskiy, P. and Frei, R. (2016) The Cr-isotope signature of surface seawater — A global perspective. *Chem. Geol.* **444**, 101-109.

Pereira, N.S., Voegelin, A.R., Paulukat, C., Sial, A.N., Ferreira, V.P. and Frei, R. (2015) Chromium-isotope signatures in scleractinian corals from the Rocas Atoll, Tropical South Atlantic. *Geobiology* **14**, 54-67.

Planavsky, N.J., Reinhard, C.T., Wang, X., Thomson, D., McGoldrick, P., Rainbird, R.H., Johnson, T., Fischer, W.W. and Lyons, T.W. (2014) Low Mid-Proterozoic atmospheric oxygen levels and the delayed rise of animals. *Science* **346**, 635-638.

Reinhard, C.T., Planavsky, N.J., Robbins, L.J., Partin, C.A., Gill, B.C., Lalonde, S.V., Bekker, A., Konhauser, K.O. and Lyons, T.W. (2013) Proterozoic ocean redox and biogeochemical stasis. *Proceedings of the National Academy of Sciences* **110**, 5357-5362.

Rigaud, S., Radakovitch, O., Couture, R.-M., Deflandre, B., Cossa, D., Garnier, C. and Garnier, J.-M. (2013) Mobility and fluxes of trace elements and nutrients at the sediment–water interface of a lagoon under contrasting water column oxygenation conditions. *Appl. Geochem.* **31**, 35-51.

Saputro, S., Yoshimura, K., Matsuoka, S., Takehara, K., Narsito, Aizawa, J. and Tennichi, Y. (2014) Speciation of dissolved chromium and the mechanisms controlling its concentration in natural water. *Chem. Geol.* **364**, 33-41.

Scheiderich, K., Amini, M., Holmden, C. and Francois, R. (2015) Global variability of chromium isotopes in seawater demonstrated by Pacific, Atlantic, and Arctic Ocean samples. *Earth. Planet. Sci. Lett.* **423**, 87-97.

Schoenberg, R., Zink, S., Staubwasser, M. and Blanckenburg, F.v. (2008) The stable Cr isotope inventory of solid Earth reservoirs determined by double spike MC-ICP-MS. *Chem. Geol.* **249**, 294-306.

Shigematsu, T., Gohda, S., Yamazaki, H. and Nishikawa, Y. (1977) Spectrophotometric Determination of Chromium (III) and Chromium (VI) in Sea Water. *Bull. Inst. Chem. Res.* **55**, 429-440.

Sholkovitz, E.R., Boyle, E.A. and Price, N.B. (1978) The removal of dissolved humic acids and iron during estuarine mixing. *Earth. Planet. Sci. Lett.* **40**, 130-136.

Sikora, E.R., Johnson, T.M. and Bullen, T.D. (2008) Microbial mass-dependent fractionation of chromium isotopes. *Geochim. Cosmochim. Acta* **72**, 3631-3641.

Stookey, L.L. (1970) Ferrozine---a new spectrophotometric reagent for iron. *Anal. Chem.* **42**, 779-781.

Sun, Z., Wang, X. and Planavsky, N. (2019) Cr isotope systematics in the Connecticut River estuary. *Chem. Geol.* **506**, 29-39.

Toma, J., Holmden, C., Shakotko, P., Pan, Y. and Ootes, L. (2019) Cr isotopic insights into ca. 1.9 Ga oxidative weathering of the continents using the Beaverlodge Lake paleosol, Northwest Territories, Canada. *Geobiology* **17**, 467-489.

Wu, W., Wang, X., Reinhard, C.T. and Planavsky, N.J. (2017) Chromium isotope systematics in the Connecticut River. *Chem. Geol.* **456**, 98-111.

Zink, S., Schoenberg, R. and Staubwasser, M. (2010) Isotopic fractionation and reaction kinetics between Cr(III) and Cr(VI) in aqueous media. *Geochim. Cosmochim. Acta* **74**, 5729-5745.

## Figure captions

Figure 1. $\delta^{53}$Cr data for unpolluted rivers that drain into the ocean ([1]D'Arcy et al. 2016; [2]Wu et al. 2017; [3]Frei et al. 2014). Horizontal grey bar shows $\delta^{53}$Cr values for silicate crust; orange bar shows typical $\delta^{53}$Cr and Cr concentration of seawater (Bonnand et al., 2013; Scheiderich et al., 2015; Paulukat et al., 2016).

Figure 2. Sampling locations. Darker blue areas are intertidal flats.

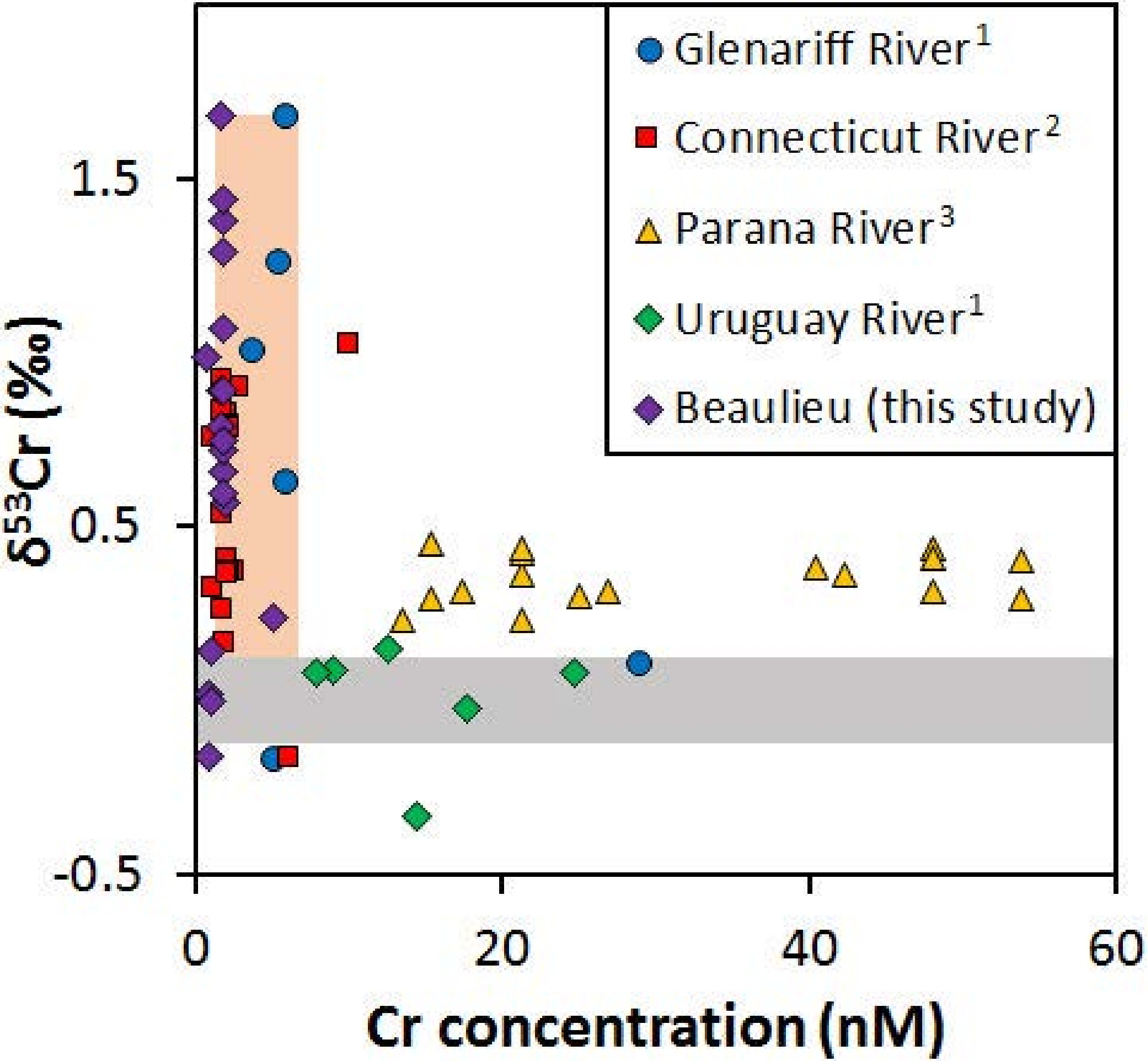
Figure 3. Relationship between salinity and (A) dFe, (B) $Cr_T$, (C) Cr(III) concentration, (D) Cr(VI) concentration, and (E) $\delta^{53}Cr_T$ (where error bars represent the external reproducibility; 0.11‰). (F) Relationship between $Cr_T$ and $\delta^{53}Cr_T$. Error bars for $Cr_T$, Cr(VI) and Cr(III) are 10%. The March 20th sample (B1) is excluded from A and from the trend lines in B-E because it is thought to be an outlier (see text for details).

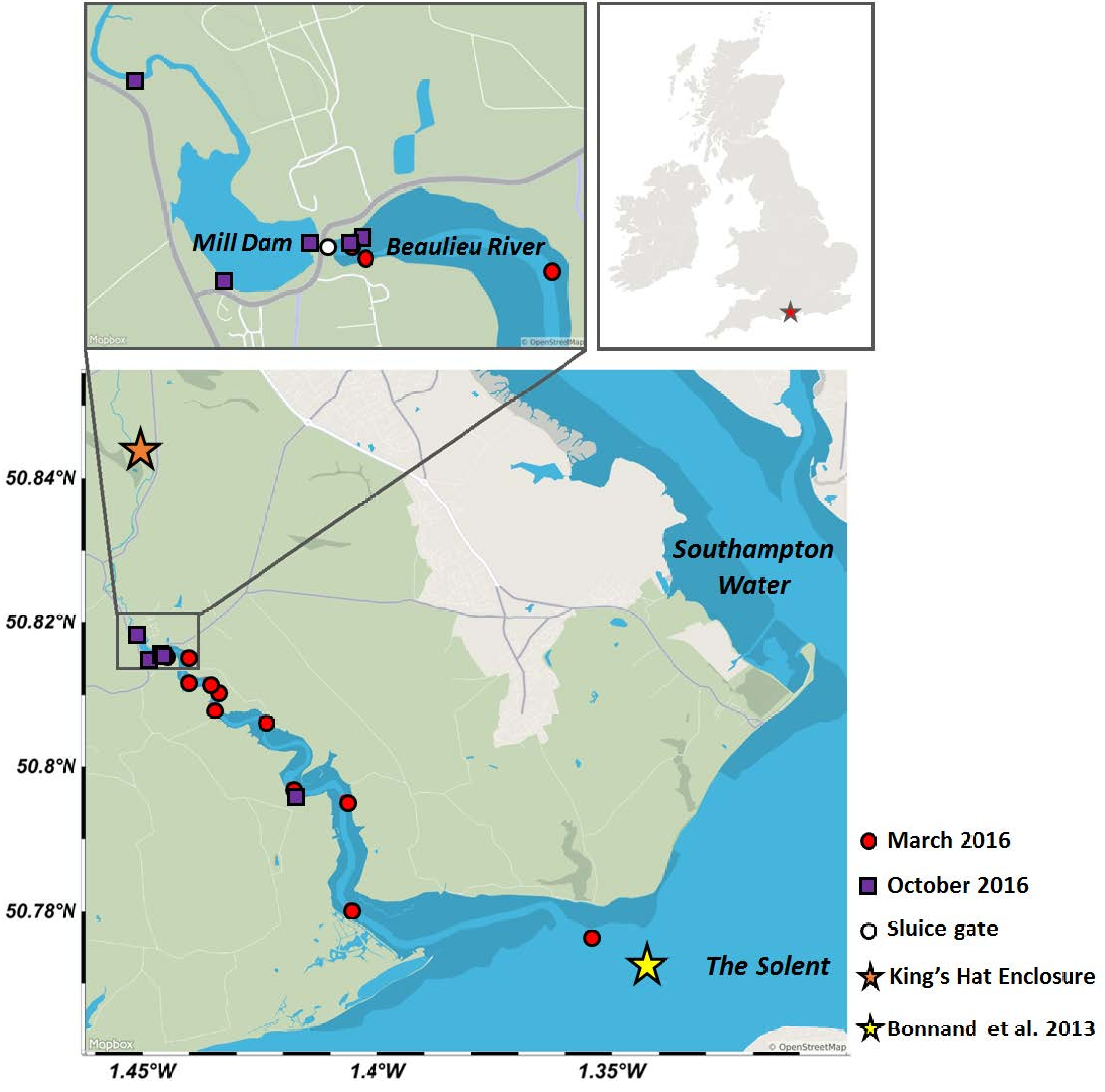
Figure 4. Combined $O_2$ profile for river sediment push cores (n=3). Solid horizontal lines show the standard deviation from the mean value (none for -2.0 to -0.2mm as only one set of measurements taken). Dotted line is the sediment-water interface and dashed line is the average oxic-anoxic boundary depth.

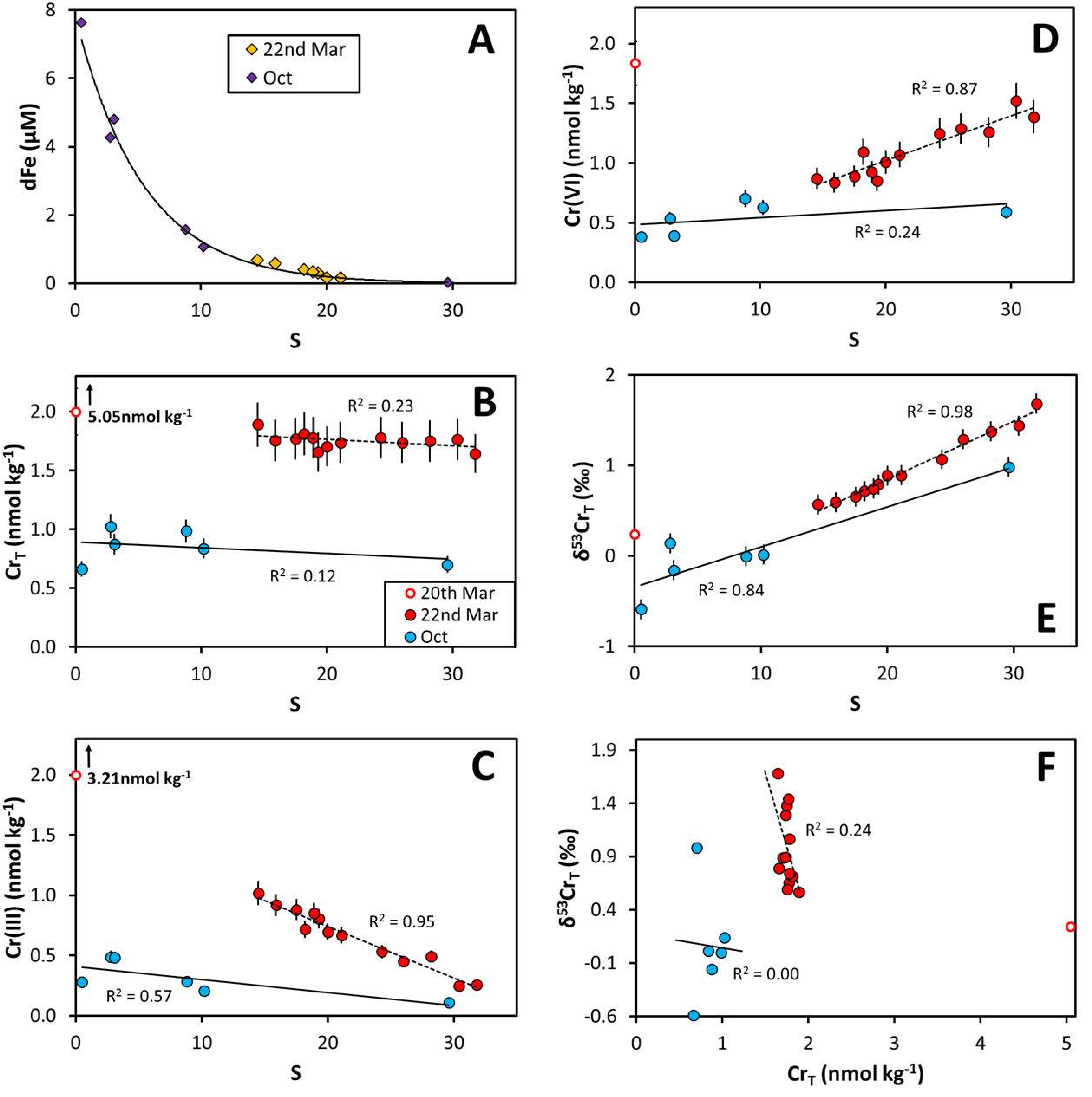
Figure 5. (A) Modelled evolution of the $\delta^{53}$Cr value of Cr remaining in solution after reductive removal of Cr(VI) in sample B1 at $S$ = <0.5, as a function of salinity. Sample B1 and B14 $\delta^{53}$Cr and $Cr_T$ values used to represent river and seawater endmembers respectively. River endmember $\delta^{53}$Cr for conservative mixing line = -0.39‰ (see text for details). (B) Modelled evolution of Cr(VI)/Cr(III) for conservative mixing. River ($S$ = 0) and seawater ($S$ = 35) endmember Cr(VI) and Cr(III) values extrapolated from March data.

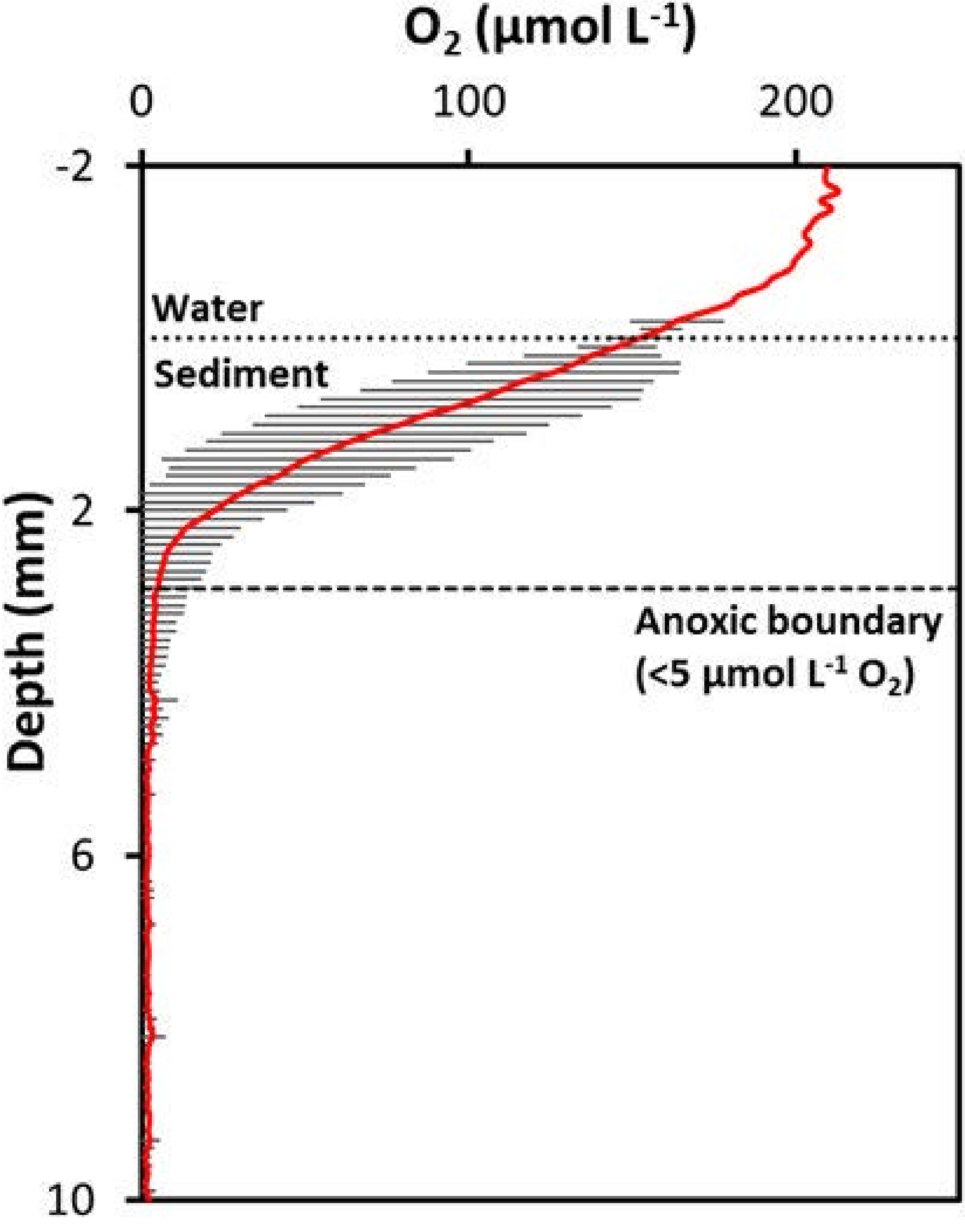
Figure 6. Schematic diagram showing potential mechanisms for Cr release and redox transformations within sediments/soils in the Beaulieu River catchment ([1]Frei et al. 2014; [2]D'Arcy et al. 2016; [3]Wu et al. 2017).

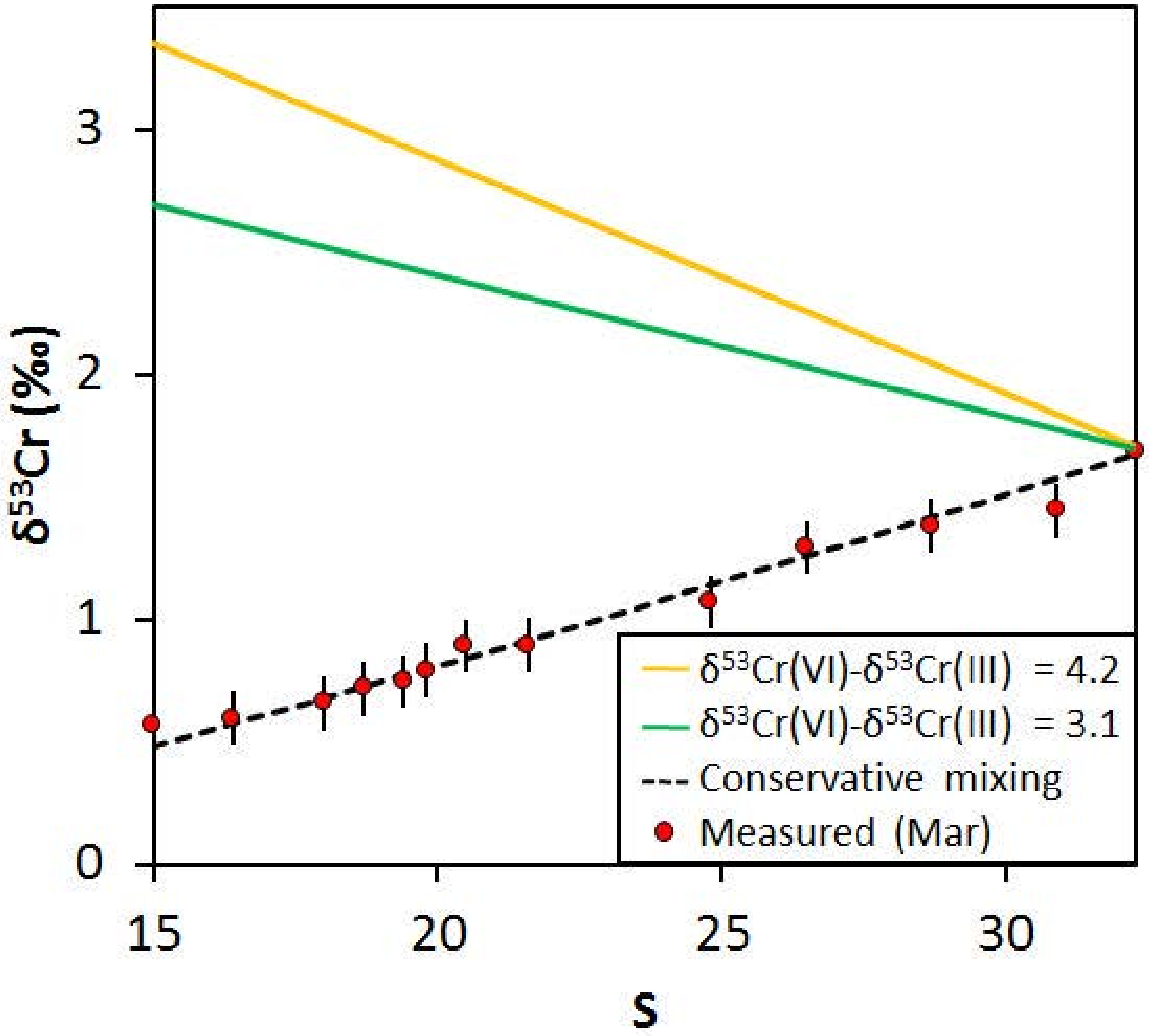
Figure 7. Modelled evolution of the $\delta^{53}$Cr value of Cr during conservative mixing between a seawater endmember with $Cr_T$ = 1.6 nM and $\delta^{53}$Cr = 1.6‰, and river water endmembers with various $Cr_T$ and $\delta^{53}$Cr values.

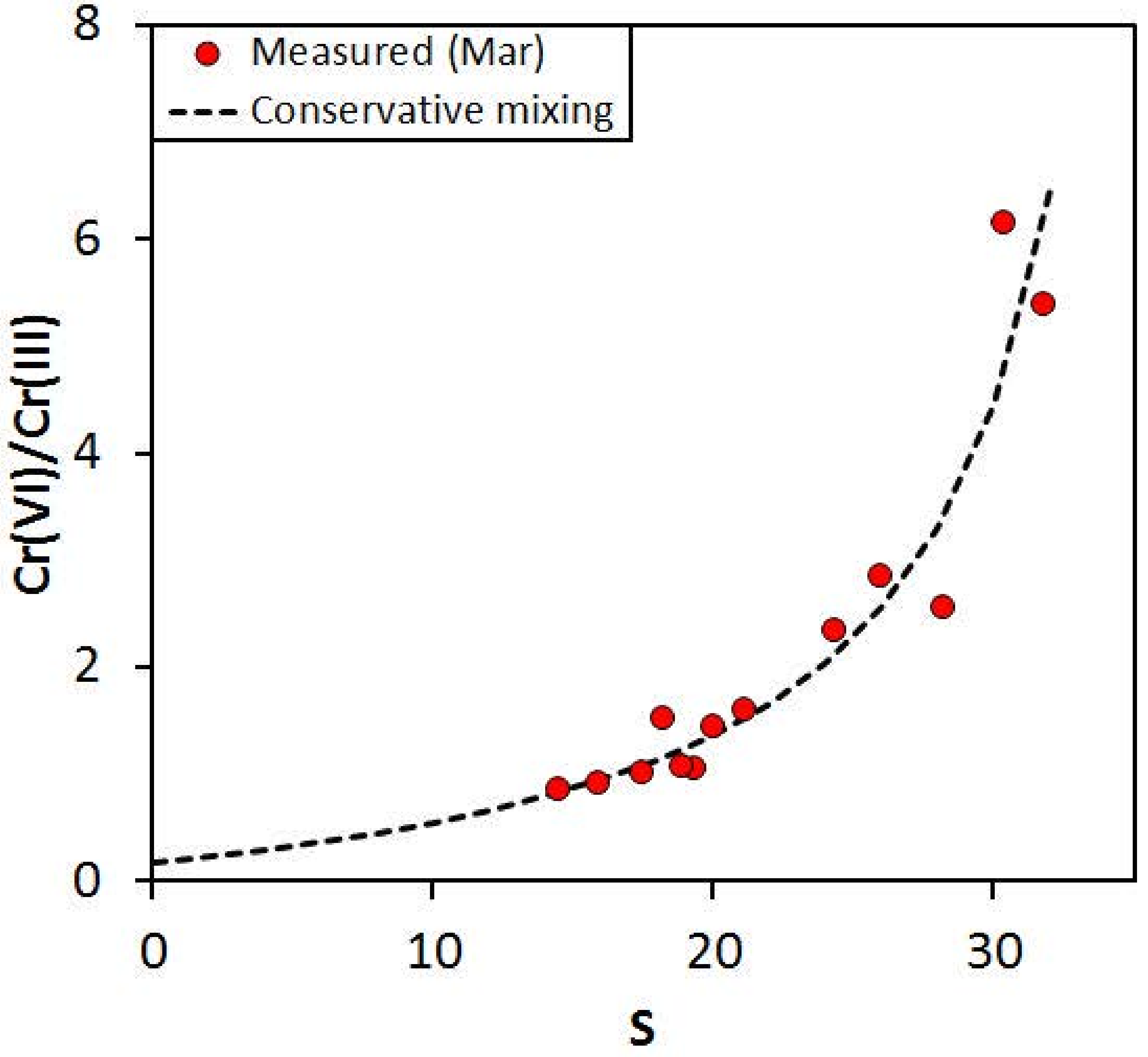

Glenariff River[1]
Connecticut River[2]
Parana River[3]
Uruguay River[1]
Beaulieu (this study)
$\delta^{53}$Cr (‰)
1.5
0.5
-0.5
0
20
40
60
Cr concentration (nM)

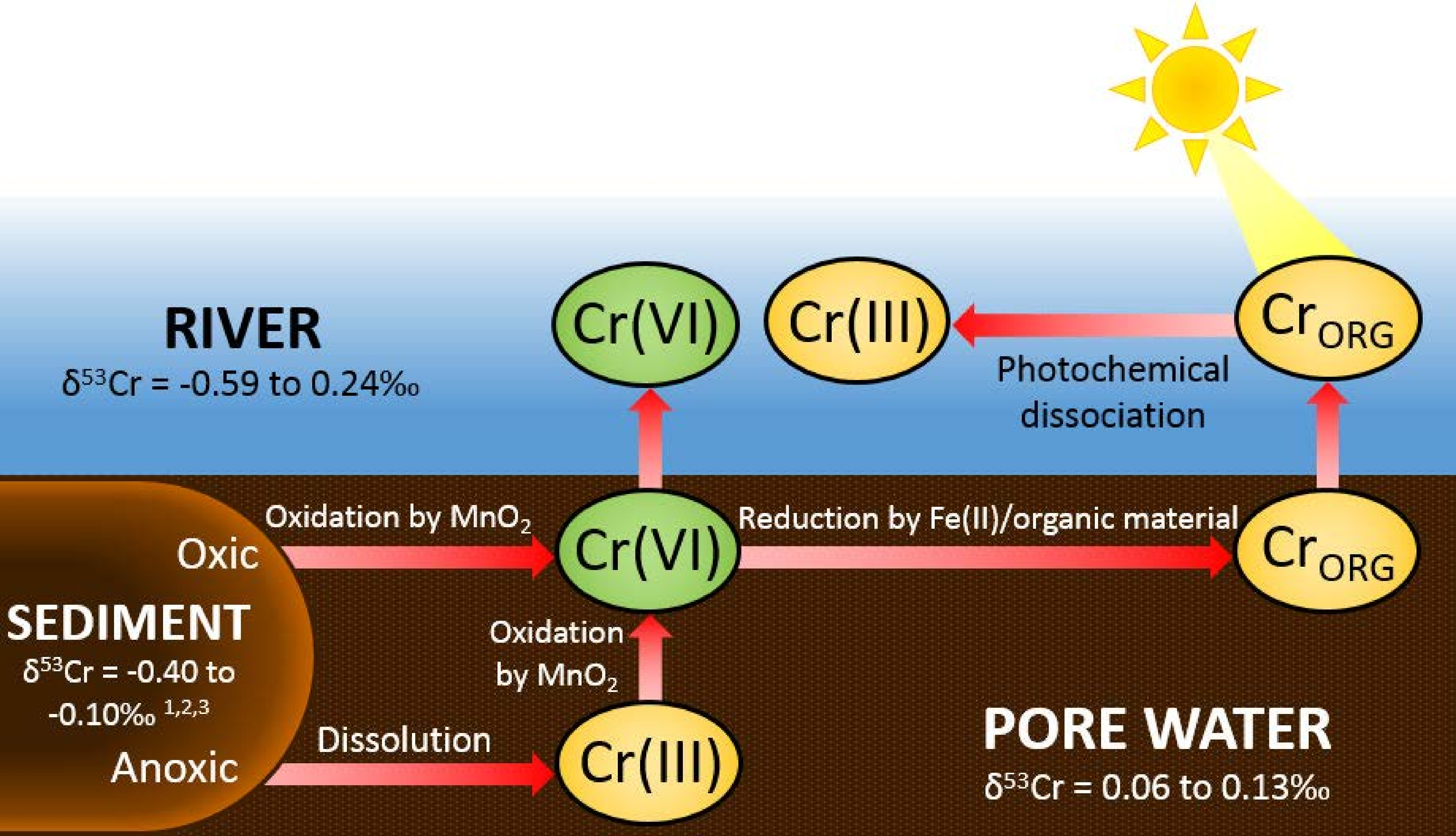

Mill Dam
Beaulieu River
Mapbox
© OpenStreetMap
Southampton Water
The Solent
50.84°N
50.82°N
50.8°N
50.78°N
1.45°W
1.4°W
1.35°W
● March 2016
■ October 2016
○ Sluice gate
★ King's Hat Enclosure
★ Bonnand et al. 2013


A
22nd Mar
Oct
dFe (µM)
S
D
Cr(VI) (nmol kg-1)
R2 = 0.87
R2 = 0.24
S
B
5.05nmol kg-1
R2 = 0.23
R2 = 0.12
CrT (nmol kg-1)
20th Mar
22nd Mar
Oct
S
E
δ53CrT (‰)
R2 = 0.98
R2 = 0.84
S
C
3.21nmol kg-1
R2 = 0.95
R2 = 0.57
Cr(III) (nmol kg-1)
S
F
δ53CrT (‰)
R2 = 0.24
R2 = 0.00
CrT (nmol kg-1)


$O_2$ (µmol $L^{-1}$)
0
100
200
-2
2
6
10
Depth (mm)
Water
Sediment
Anoxic boundary
(<5 µmol $L^{-1}$ $O_2$)


δ53Cr (‰)
3
2
1
0
15
20
25
30
S
δ53Cr(VI)-δ53Cr(III) = 4.2
δ53Cr(VI)-δ53Cr(III) = 3.1
Conservative mixing
Measured (Mar)


Cr(VI)/Cr(III)
8
6
4
2
0
0
10
20
30
S
Measured (Mar)
Conservative mixing


RIVER
δ53Cr = -0.59 to 0.24‰
Cr(VI)
Cr(III)
CrORG
Photochemical dissociation
Oxidation by MnO2
Oxic
Cr(VI)
Reduction by Fe(II)/organic material
CrORG
SEDIMENT
δ53Cr = -0.40 to -0.10‰ 1,2,3
Oxidation by MnO2
Dissolution
Anoxic
Cr(III)
PORE WATER
δ53Cr = 0.06 to 0.13‰

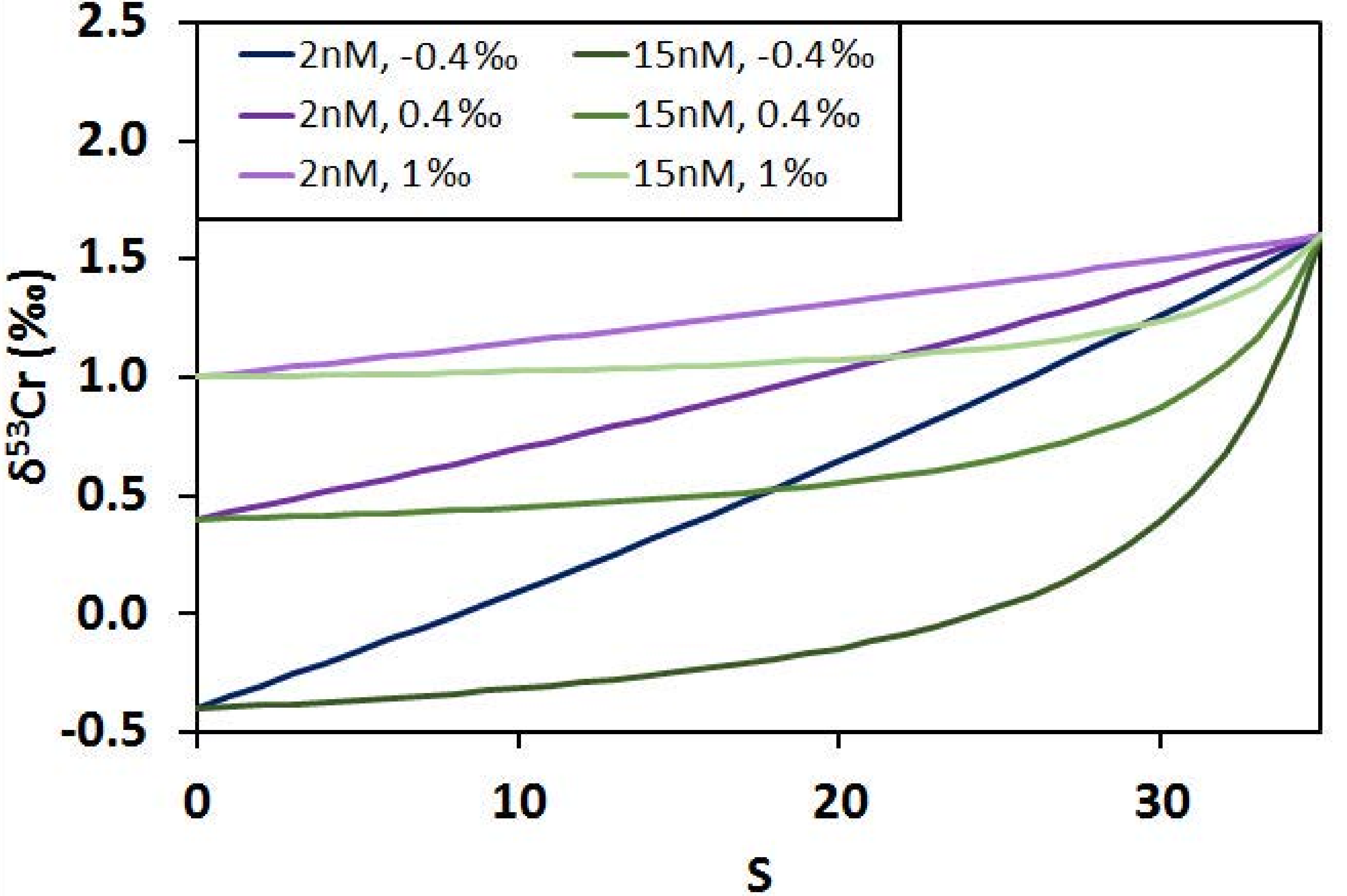

2nM, -0.4‰
2nM, 0.4‰
2nM, 1‰
15nM, -0.4‰
15nM, 0.4‰
15nM, 1‰
$\delta^{53}$Cr (‰)
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
10
20
30
S

Table 1. Results of analysis of Cr(III) concentration by Fe(III) pre-concentration and addition of $^{53}$Cr-enriched spike.

| **Standard type** | **Calculated Cr(III) (nmol kg$^{-1}$)** | **Measured Cr(III) (nmol kg$^{-1}$)** | **Difference (%)** |
|---|---|---|---|
| Cr(III) only | 11.00 | 11.23 | 2.0 |
| | 10.77 | 11.19 | 3.8 |
| | 10.58 | 10.48 | -2.0 |
| | 10.04 | 10.44 | 1.9 |
| | 10.49 | 10.78 | +2.8 |
| | 10.45 | 10.23 | -2.1 |
| Cr(III) + Cr(VI) | 4.75 | 5.19 | 8.6 |
| (1:1 mix) | 4.81 | 5.23 | 8.0 |
| | 5.77 | 5.25 | -9.7 |
| | 5.77 | 5.23 | -10.0 |

Table 2. Composition of water samples from the Beaulieu River and Beaulieu estuary. BDL = Below Detection Limit.

| **Sampling date** | **Sample** | **Salinity (*S*)** | **pH** | **Temperature (°C)** | **$\delta^{53}$Cr (‰)** | **2SD** | **$Cr_T$ (nmol $kg^{-1}$)** | **Cr(III) (nmol $kg^{-1}$)** | **Cr(VI) (nmol $kg^{-1}$)** | **dFe (µM)** |
|---|---|---|---|---|---|---|---|---|---|---|
| 20th March 2016 | B1 | 0.0 | 7.68 | 8.6 | 0.24 | 0.02 | 5.05 | 3.21 | 1.83 | 12.63 |
| 22nd March 2016 | B2 | 14.5 | 7.81 | 10.4 | 0.57 | 0.04 | 1.89 | 1.02 | 0.87 | 0.68 |
|  | B3 | 17.5 | 7.95 | 9.6 | 0.66 | 0.01 | 1.77 | 0.88 | 0.89 | 0.17 |
|  | B4 | 20.0 | 8.10 | 11.3 | 0.89 | 0.00 | 1.70 | 0.70 | 1.01 | 0.30 |
|  | B5 | 19.3 | 8.09 | 10.2 | 0.79 | 0.06 | 1.66 | 0.81 | 0.85 | 0.17 |
|  | B6 | 21.1 | 8.09 | 10.3 | 0.89 | 0.02 | 1.74 | 0.67 | 1.07 | 0.59 |
|  | B7 | 15.9 | 7.97 | 11.1 | 0.59 | 0.04 | 1.76 | 0.92 | 0.84 | 0.39 |
|  | B8 | 18.2 | 8.05 | 10.3 | 0.72 | 0.02 | 1.81 | 0.72 | 1.09 | 0.34 |
|  | B9 | 18.9 | 8.05 | 11.4 | 0.74 | 0.06 | 1.78 | 0.85 | 0.92 | BDL |
|  | B10 | 24.3 | 8.11 | 10.7 | 1.07 | 0.11 | 1.78 | 0.53 | 1.25 | BDL |
|  | B11 | 26.0 | 8.08 | 10.3 | 1.29 | 0.06 | 1.74 | 0.45 | 1.29 | BDL |
|  | B12 | 28.2 | 8.12 | 10.3 | 1.38 | 0.04 | 1.75 | 0.49 | 1.26 | BDL |
|  | B13 | 30.4 | 8.14 | 10.3 | 1.44 | 0.02 | 1.77 | 0.25 | 1.52 | BDL |
|  | B14 | 31.8 | 8.14 | 9.9 | 1.68 | 0.04 | 1.64 | 0.26 | 1.39 | BDL |
| 5th October 2016 | B15 | 10.2 | 7.40 | 14.7 | 0.02 | 0.06 | 0.84 | 0.21 | 0.63 | 1.37 |
|  | B16 | 0.5 | 7.04 | 13.3 | -0.59 | 0.05 | 0.66 | 0.28 | 0.38 | 7.55 |
|  | B17 | 2.8 | 7.68 | 14.7 | 0.14 | 0.01 | 1.03 | 0.49 | 0.54 | 4.22 |
|  | B18 | 3.1 | 7.31 | 13.7 | -0.16 | 0.07 | 0.87 | 0.48 | 0.39 | 4.76 |
|  | B19 | 8.8 | 7.37 | 15.7 | 0.00 | 0.01 | 0.99 | 0.28 | 0.70 | 1.57 |
|  | B20 | 29.6 | 8.17 | 17.1 | 0.98 | 0.04 | 0.70 | 0.11 | 0.59 | BDL |

Table 3. Results for UV irradiated samples.

| **Sample** | **$Cr_T$ + $Cr_{ORG}$ (nmol $kg^{-1}$)** | **$Cr_{ORG}$ (nmol $kg^{-1}$)** | **$Cr_{ORG}$ (%)** | **$\delta^{53}Cr$ $Cr_T$ + $Cr_{ORG}$ (‰)** | **2SD** | **$\delta^{53}Cr$ $Cr_{ORG}$ calculated (‰)** |
|---|---|---|---|---|---|---|
| B1 | 6.17 | 1.13 | 18 | 0.06 | 0.01 | -0.75 |
| B2 | 2.52 | 0.63 | 25 | 0.40 | 0.01 | -0.11 |