Chromium fluxes and speciation in ultramafic catchments and global rivers

C.N. McClain^{a,*} and K. Maher^a

^a*Department of Geological Sciences, Stanford University, Stanford, CA 94305, USA*

*Corresponding author E-mail addresses: cynthia.mcclain@stanford.edu,
cnmcclain@gmail.com

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^a*Department of Geological Sciences, Stanford University, Stanford, CA 94305, USA*

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cnmcclain@gmail.com

Abstract

The role of ultramafic rock weathering in global chromium (Cr) budgets and how these may be linked to changes in Earth's climate over geological time was investigated by compiling dissolved Cr speciation and fluxes in (i) 73 of the world's large rivers, representing ~35% of global river discharge to oceans, and in (ii) an ultramafic catchment (Putah Creek watershed) in the California Coast Range Mountains, USA. Weathering of ultramafic rocks creates ideal conditions for Cr release and redox cycling. Alkaline river water draining ultramafic catchments is naturally enriched in Cr (up to 582 nmol/L). Chromium concentrations increase with the extent of rock-water interaction (as indicated by correlations with Mg and HCO₃⁻ concentrations and pH), whereas Cr cycling depends on the availability of electron donors and acceptors (*e.g.* Fe(II), organics, Mn(III/IV)-oxides). Thus, dissolved Cr is exported from ultramafic watersheds as both the soluble hexavalent Cr(VI) species (MgCrO₄, CrO₄²⁻), and also as trivalent Cr(III) species (CrOH(CO₃)²⁻, Cr(OH)₃). The latter Cr(III) species were previously thought to have low solubility. Ultramafic catchments have higher area normalized Cr and major ion fluxes for a given runoff when compared to global rivers and may thus have a disproportional impact on global Cr-budgets, long-term carbon cycling and moderation of the Earth's climate over million-year timescales. Riverine export fluxes of Cr are linearly correlated with fluxes of Ca + Mg and alkalinity in both ultramafic catchments and global rivers. This suggests that silicate weathering is a key control on Cr fluxes and that major element weathering fluxes may be a useful proxy for estimating Cr and other trace element fluxes. Globally, present-day riverine dissolved Cr fluxes to oceans are spatially variable and estimated to be 1.7×10^9 mol/yr, three times higher than previously reported. However, when geochemical reactions in estuaries are considered riverine Cr fluxes may be lower. Throughout Earth history, Cr weathering fluxes also may have varied with changes in the global distribution of ultramafic rocks, Cr concentrations in continental rocks, or climatic conditions (*e.g.* atmospheric CO₂ levels or runoff). Such variation should be considered when interpreting both modern and past Cr seawater isotopic compositions and residence times.

Keywords

Chromium; chemical weathering; ultramafic rocks; river water; spring water; California

1. Introduction

Trace elements influence global biogeochemical cycling, moderate redox conditions in water and sediment, reflect human influence on the environment and may

have recorded Earth's past environmental conditions. During weathering of rocks, trace elements (*e.g.*, Al, Cr, Mn, Fe, As, Mo, U) are mobilized and transported as dissolved and particulate matter via rivers and groundwater to depositional environments such as alluvial plains and ocean basins. Chemical reactions during transport may result in changes in trace element concentration, oxidation state, and aqueous speciation, affecting isotopic composition, mobility, toxicity, bioavailability and ultimately what is recorded in the rock record. Weathering of major elements and large-scale transfer through the Earth's surface to oceans is well understood for many rock types, but the corresponding weathering fluxes of trace elements have received less attention (Gaillardet and Dupré, 2003). The behavior of chromium (Cr) in rivers is particularly important because Cr riverine fluxes constitute 76-96% of input to oceans (Bonnand et al., 2013), Cr is a possible tracer of paleoredox conditions (Frei et al., 2009), Cr is a widespread contaminant and health hazard (Chatham-Stephens et al., 2013; Oze et al., 2007), and Cr is highly sensitive to biogeochemical transformations under changing environmental conditions.

The main sources of Cr to rivers are rock weathering (crustal rocks typically have Cr concentrations of 100 mg/kg) and anthropogenic discharges (chemicals, tailings, slag, scrap), which are estimated to contribute 5×10^8 mol/yr and 2×10^9 mol/yr, respectively (Nriagu and Nieboer, 1988). For most large rivers, particles transport most of the total Cr load (*i.e.* dissolved plus particulate) (Gibbs, 1977; Kotaś and Stasicka, 2000; Pettine et al., 1992). However, the corresponding riverine dissolved Cr concentrations (herein referred to as Cr(TOT)) are crucial to quantify because of toxicity to biota (Nriagu and Nieboer, 1988) and Cr carcinogenicity to humans associated with drinking water high in Cr (Beaumont et al., 2008; World Health Organization, 2012). By extension, understanding the processes that control the dissolved Cr concentration of rivers can lead to improved estimates of metal loading to aquatic ecosystems and drinking water sources. Current estimates of riverine dissolved Cr fluxes to the ocean are based on averages calculated from < 15 rivers (Bertine, 1971; Bonnand et al., 2013; Campbell and Yeats, 1984; Gaillardet and Dupré, 2003; Jeandel and Minster, 1984; Martin and Meybeck, 1979), even though more concentration and discharge data are available (GEMS, 2015; Milliman and Farnsworth, 2011). Further, species-specific (*i.e.* Cr(VI), Cr(III)) dissolved Cr fluxes of rivers have not been estimated globally, or for individual rivers, and are necessary to improve understanding of Cr sources, local contamination, oceanic Cr cycling (Scheiderich et al., 2015; Sirinawin et al., 2000), and Cr isotopes as a paleoredox proxy (Crowe et al., 2014; Frei et al., 2009; 2011; 2014; Frei and Polat, 2013; Konhauser et al., 2011).

The majority of research on Cr geochemistry has focused on laboratory studies and individual sites, whereas very little work has focused on large-scale controls on Cr concentrations in surface waters. In rivers, both Cr(III), a vital micronutrient for animals (Nriagu and Nieboer, 1988) and Cr(VI), a toxic carcinogen (Beaumont et al., 2008; World Health Organization, 2012), are detected and thought to cycle through the environment depending on the abundance of electron donors/acceptors, sorbants, competing sorbates and Cr aqueous speciation (Abu-Saba and Flegal, 1995; Comber and Gardner, 2003; Cranston and Murray, 1980; Kaczynski and Kieber, 1993; Pankow et al., 1977; Pettine et al., 1994; Saputro et al., 2014; Shuman and Dempsey, 1977; Stefánsson et al., 2014). Chromium(III) may be oxidized to Cr(VI) by manganese oxides, oxygen or

hydrogen peroxide (Richard and Bourg, 1991), whereas Cr(VI) can be reduced under many conditions, primarily by Fe(II), but also by microbes, organic acids and sulfide (Fendorf et al., 2000). Sorption to mineral surfaces will attenuate both Cr(III) and Cr(VI) concentrations, but the extent depends on concentration, pH, specific aqueous speciation, and bulk water composition (Fendorf, 1995; Richard and Bourg, 1991). Typical regulatory limits for Cr in drinking water are 962 nmol/L (50 µg/L) for Cr(TOT) and 192 nmol/L (10 µg/L) for Cr(VI) (California, 2014; World Health Organization, 2012).

Ultramafic rocks have higher Cr concentrations (2,400 mg/kg) compared to all other rock types (Nriagu and Nieboer, 1988) and may therefore be a more important source of Cr to natural waters than volcanic, basaltic or sedimentary rocks. Ultramafic rivers (*i.e.* surface water in catchments with ultramafic bedrock) are characterized by high dissolved Cr(TOT) concentrations (13.5 to 4,807 nmol/L), which in some cases exceed drinking water limits by a factor of up to five (Farkaš et al., 2013; Gough et al., 1989; Novák et al., 2014; Taylor et al., 1998). Groundwater from aquifers containing ultramafic materials often contain high levels of naturally occurring Cr, mostly as Cr(VI), that approach or exceed the drinking water limit for Cr(TOT) of 962 nmol/L (Apollaro et al., 2011; Becquer, 2003; Dawson et al., 2008; Deverel and Millard, 1988; Fantoni et al., 2002; Godgul and Sahu, 1995; Gonzalez et al., 2005; Gray, 2003; Kaprara et al., 2014; Lelli et al., 2013; Manning et al., 2015; Moraetis et al., 2012; Robles-Camacho and Armienta, 2000; Wood et al., 2010). Ultramafic rocks currently compromise ~ 0.2% of exorheic continental area (Dai and Trenberth, 2003; Dürr et al., 2005) and are generally associated with orogenic belts or ophiolites, which are found along continental margins (Dilek, 2003; Oze et al., 2007) where erosion and weathering rates are higher than cratonic regions (Bluth and Kump, 1991; Stallard, 1988). Throughout Earth's history, the distribution of ultramafic rocks and the Cr content of these rocks has varied (Dilek, 2003; Furnes et al., 2014). Thus, over time, weathering of ultramafic rocks may be important contributors of Cr to surface and groundwater as well as depositional environments including alluvial plains, continental margins and ocean basins.

Despite high Cr concentrations, to our knowledge, no studies have quantified Cr aqueous speciation or Cr fluxes in rivers in ultramafic source regions. Soils, developed from weathering of ultramafic rocks, have been better studied than surface waters in ultramafic regions. Both Cr(VI) and Cr(III) are found to weather from ultramafic soils reaching concentrations of up to 1,000 and up to 135 mg/kg soil respectively, constituting a potential source to surface and groundwater (Becquer, 2003; Cooper, 2002; Fandeur et al., 2009; Garnier et al., 2006). However, these studies were mostly conducted in tropical weathering environments where lateritic soils retain Cr(VI) by sorption on Fe-oxides, decreasing Cr mobility. Riverine dissolved Cr concentrations and fluxes may be higher in temperate climates due to differing soil mineralogy (*e.g.* fewer Fe-oxides) and higher pH. Furthermore, more mobile and bioavailable Cr aqueous species (*e.g.* MgCrO_4 and $\text{CrOH}(\text{CO}_3)_2^{2-}$) may be present in ultramafic water due to high Mg and HCO_3^- concentrations, enhancing the solubility of $\text{Fe}_x\text{Cr}_{(1-x)}(\text{OH})_3$ minerals which are thought to govern Cr(III) concentrations in natural waters (Accornero et al., 2010; Cranston and Murray, 1980; Rai et al., 2007; Sass and Rai, 1987; Stefánsson et al., 2014).

Few studies have quantified the trace element speciation or fluxes associated with rivers draining mafic and ultramafic lithologies (as noted by Gaillardet and Dupré (2003)), despite high trace element concentrations in the rocks (Nriagu and Nieboer,

1988). Moreover, mafic and ultramafic rocks are known to be some of the most reactive materials at the Earth's surface, having elevated weathering fluxes of major ions compared to global rivers (Dupré et al., 2003; Gaillardet et al., 1999; 2011; Schopka et al., 2011). Mafic rock weathering disproportionately contributes to base cation and alkalinity fluxes (Dessert et al., 2003; Dupré et al., 2003; Gaillardet et al., 2011; Hartmann et al., 2009). However, the role of ultramafic rock weathering in setting the global trace metal and major ion weathering fluxes and impacting global geochemical cycles remains to be quantified. Because chemical weathering of Ca- and Mg-silicate rocks is one of the primary mechanisms responsible for removal of atmospheric CO₂ over geologic timescales, the weathering of ultramafic rocks may also play a key role in regulating the long-term carbon cycle and Earth's climate (Berner and Kothavala, 2001; Walker et al., 1981).

This study had four primary research objectives. First, we identified the speciation, fluxes and primary controls on dissolved Cr in surface water from an ultramafic watershed in a temperate climate. Specifically, we collected surface water and spring water samples within a well-characterized ultramafic province along the west coast of North America within the central California Coast Range Serpentine Belt, concurrently measuring discharge and water compositions. Second, we calculated contemporary riverine dissolved Cr flux to oceans by compiling a database of dissolved Cr concentrations, speciation and discharge from 73 rivers globally. Third, we determined whether ultramafic watersheds contribute proportionally to global riverine dissolved Cr fluxes to oceans and to cation and alkalinity fluxes by comparing chemical weathering fluxes from the small uplands ultramafic watershed to fluxes from other ultramafic areas, to Cr fluxes from previous studies in the San Francisco Bay/Estuary, and to Cr fluxes associated with global rivers. Finally, we investigated whether chemical weathering fluxes can be used as a proxy to estimate trace element fluxes by comparing cation and alkalinity fluxes to Cr fluxes.

2. Materials and methods

We present an analysis of two different spatial scales. First, we evaluate the controls on Cr within a small uplands watershed with uniform lithology in central California, USA, based on concentration and discharge data collected from streams and springs over several seasons. Subsequently, we evaluate global Cr concentrations in large rivers obtained from pre-existing databases. These global rivers have mixed lithology, where information is averaged over large areas, providing a complementary approach to investigating riverine Cr cycling. Below we provide an overview of the study area and sampling methods, followed by a discussion of the data sources and statistical analysis used in the global flux analysis.

2.1. Study area and sampling

This study focuses on a series of seven sub-catchments in the Hunting Creek watershed within the Putah Creek watershed, a tributary of the Sacramento River in the central California Coast Range, USA (**Fig. 1**). The Sacramento River accounts for ~80% of flow into the San Francisco Bay-Estuary, which drains into the Pacific Ocean (Conomas, 1979). The climate of this region is Mediterranean with mean annual temperature of 25°C in July and 8°C in January with seasonal precipitation averaging 620

mm/yr, where over 95% falls between October and April (WRCC, 2014). Precipitation was collected in February and March of 2012 for chemical analysis using a ball-in-funnel type collector.

The Putah Creek watershed is 184 km² with 1,436 m of relief, supports a population of approximately 80,000 people (SRWP, 2015) and is characterized by an abundance of ultramafic bedrock. Until the construction of the Monticello Dam to form Lake Berryessa in 1957, Putah Creek transported and extensively deposited Cr-bearing ultramafic sediments in alluvial plains of the southern Sacramento Valley, part of California's Central Valley (Morrison et al., 2015), which has led to regional Cr groundwater contamination (Manning et al., 2015). Additionally, Lake Berryessa supplies municipal, industrial and irrigation water to major cities in Solano county. In the Putah Creek watershed, ultramafic bodies are present as thin strips of serpentinitized peridotite (*i.e.* serpentinite) in fault contact with Great Valley group marine sedimentary deposits (largely Jurassic Knoxville Formation mudstones) and metamorphic Franciscan mélange (Blake and Jones, 1981; Goldhaber et al., 2009; Hopson et al., 2008; Ingersoll and Dickson, 1981). In places, the ultramafic bodies are overlain by or juxtaposed against andesite from the Clear Lake Volcanic field (McLaughlin Natural Reserve, 2007). In Lake and Napa counties, within the same region as our field area, two Mg-HCO₃ springs have Cr concentrations of 1,519 nmol/L to 1,750 nmol/L (Berkstresser, 1968) and within the Putah Creek watershed groundwater concentrations exceed the Cr(VI) drinking water limit of 162 nmol/L (Manning et al., 2015). Nevertheless, no studies report Cr concentrations or speciation in regional surface waters.

The Hunting Creek watershed, a subcatchment within the Putah Creek watershed, located within the University of California McLaughlin Natural Preserve, was selected for this study due to the consistent lithology and similar vegetation. Bedrock in the Hunting Creek watershed (**Fig. 1c**) consists primarily of the Berryessa Serpentinite Complex, which is composed of highly serpentinitized and sheared ultramafic rock (Hopson et al., 2008; Phipps, 1984). This complex was tectonically emplaced during Mesozoic subduction, and has been described by Phipps (1984). There is no evidence for active serpentinitization expressed at the surface (*i.e.* no high-pH Ca²⁺-OH⁻¹ springs are observed in the area (Barnes, 1969)) possibly because the bedrock is highly serpentinitized (Carnevale et al., 2011). The predominant vegetation is grassy meadows and "serpentine barrens", which have minimal vegetation including manzanita, chamise and gray pine. Due to the small amount of vegetation, the amount of organic matter in this area is limited (Morrison et al., 2015), influencing, for example, the soil types that develop and organic acid concentrations in soils and surface waters. Geomorphologically, within the serpentine barrens there is a steep-walled incised canyon, with evidence of recent landslides.

Seven ultramafic bedrock samples were collected from outcrops throughout the Hunting Creek watershed for mineralogical and chemical analysis. Field observations reveal well-drained, thin soils (< 1 m) overlying saprolite and fractured bedrock. Regionally, ultramafic soils contain chromite and secondary clay and Fe-(hydr)oxide minerals, which are all potential sources of Cr to surface water and groundwater (Morrison et al., 2015). We observe that soils, saprolite and chemically weathered bedrock fractures also contain secondary minerals such as clays and brown, black, purple, red, orange and yellow microcrystalline minerals, often coating surfaces, which we

assumed to be mixed metal-(oxy)hydroxides (Cornell and Schwertmann, 2004). Visual inspection of drill core from mineral exploration in the watershed also reveals extensive subsurface chemical weathering due to > 5 m wide zones of low-density oxidized, and reduced saprock along fractures in the serpentinite bedrock.

Within the Putah Creek watershed we collected spring and surface water samples from headwater regions (Hunting Creek) to the Sacramento Valley (**Fig. 1**). Major tributaries draining ultramafic regions in the Putah Creek watershed were sampled, including Hunting Creek, Pope Creek, and Putah Creek. Thirty-one surface water samples were collected during the dry summer season in 2010-2013, and four samples were collected in the rainy season. During 2010-2012 precipitation was similar to the mean annual precipitation for the region (~750 mm), whereas during 2013 it was ~ 6 times lower (118 mm) (WRCC, 2014). Streams are not gauged; however, where possible, surface water volumetric flow rates were determined by the velocity-area method, measuring the cross sectional area and linear flow rate using the floating object technique. Measured surface water discharge in the Putah Creek watershed ranged from 7.3 to 1,728 m³/hour, values which are assumed to represent a minimum seasonal value due to sampling in the dry season (**Table A.1**).

In headwater regions, groundwater discharging at springs is primarily responsible for stream baseflow in the summer because there is rarely precipitation between April and October (SRWP, 2015). For example, spring-fed Hunting Creek is a gaining stream as indicated by the positive relationships between discharge and upslope contributing area and discharge and relief (**Table 1**). Nine spring water samples were collected throughout the Putah Creek watershed from hillslopes and valley bottoms, targeting areas with ultramafic bedrock, during the dry summer season in 2010-2013. The samples were collected from developed pipes or from natural seeps through sediment/fractured bedrock using gravity fed plastic tubing. Volumetric flow rates were determined at 4 sampling locations. Spring discharges range from 0.01 to 0.12 m³/hr (**Table A.1**).

We also sampled the only major storage reservoir in the watershed, Lake Berryessa. In the Sacramento Valley, below the Monticello Dam and major diversions, stream flow is maintained at approximately 4,500 m³/hr for fish habitat, but flows decrease downstream because in this reach Putah Creek is a losing stream, contributing to groundwater recharge (SRWP, 2015).

Water samples were collected in HDPE bottles, filtered in the field (Geotech in-line high capacity 0.45 µm cartridges or 0.2 µm syringe PES filters), and split into the two sub-samples: un-acidified and acidified with concentrated OptimaTM nitric acid to pH less than 2. All samples were stored with no headspace, at 4°C, until chemical analysis. In this watershed, samples with sulfate concentrations above 50 mg/kg were excluded due to potential for anthropogenic influence. Field blanks were collected for quality assurance and revealed negligible contamination.

Streambeds were classified as: bedrock, mortar bed (gravel cemented by silica and carbonates, also known as “Holocene conglomerates” (Barnes and O’Neil, 1971)) or sediment laden. To infer chemical reducing potential, we recorded field observations of organic carbon sources, grain size, color and odor in riparian zones, stream banks and streambeds.

2.2. Chemical analysis

Major and trace element concentrations of acidified water samples were analyzed with a Thermo Scientific ICAP 6300 Duo View Spectrometer (ICP-OES) (B, Ba, Ca, Fe, K, Mg, Mn, Na, Rb, Si, Sr) and a Thermo Scientific XSeries II Quadrupole Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Al, Co, Cr, Cu, Ni, Pb, U) in Environmental Measurements-1 Laboratory at Stanford University. Sample duplicates were within 10%. Reproducibility was determined to be within 5%, using the external reference High-Purity Standards ICP-MS-E multi-element standard.

Chromium(VI) concentrations were determined spectrophotometrically at 540 nm on a Shimadzu UV-1601 spectrophotometer by a modified s-diphenyl carbazide (DPC) method within 48 hours of collection (Arar et al., 1994; Bartlett, 1979). The DPC reagent was made with deionized water, trace metal grade sulfuric acid and methanol. In a cuvette, 0.125 mL of DPC reagent was added to 1 mL of filtered, unacidified water sample (or standard solution), capped, gently mixed and allowed to develop the magenta color, in the dark, for 20 minutes. The detection limit was 6 nmol/L. Sample duplicates and 192 nmol/L Ricca Chemical potassium chromate replicates ($n > 4$) were within 5%.

Inorganic anions (Cl, NO₂, Br, NO₃, SO₄, PO₄) and organic acids (glycolate, <http://www.gwb.com/formate>) of unacidified water samples were quantified using a Dionex DX-500 Ion Chromatograph in Environmental Measurements-1 Laboratory at Stanford University. Inorganic acids were quantified with an AS11-HC analytic column and < 50 mmol/L sodium hydroxide eluent with a gradient elution method. Detection limits were 0.06 μ mol/L. For organic acids, an ICE-AS6 analytic column was used with 0.4 mmol/L heptafluorobutyric acid (HPFA) eluent and 5 mmol/L tetrabutylammonium hydroxide (TBAOH) regenerant. Replicates ($n=5$) were within 10% error on our in-house multi-acid standard (Inorganic Ventures) for glycolate and formate. Detection limits were 0.3 μ mol/L.

Alkalinity was determined using the Hach colorimetric method with a digital titrator. Each 25 mL unacidified water sample was titrated to a pH of 4.5 with sulfuric acid. Sample duplicates were within 10%.

Major and trace element concentrations of rock samples were determined on bulk powdered samples, analyzed by X-ray fluorescence spectrometry (XRF) on an Ametek Spectro XEPOS XRF in Environmental Measurements-1 Laboratory at Stanford University. Results were normalized on a volatile-free basis, with percent error < 5% on duplicates and a detection limit of 0.2 to 50 mg/kg for most elements. Mineralogy was determined using standard petrographic thin sections and on bulk powdered samples using X-ray diffractometry (XRD) (Rigaku Geigerflex XRD, CuK-alpha source at 35 kV and 15 mA, scan from 5° to 70° 2 θ , 0.02 step size, dwell time 1 second per step). XRD patterns were fit with Jade software (Materials Data Inc., Livermore, CA).

2.3. Geochemical modeling

Aqueous species distributions, charge balance, mineral saturation states and surface complexation were calculated with The Geochemist's Workbench 10 (Bethke, 2014), using the LLNL.v8.r6 thermodynamic database (J. E. Johnson et al., 2000) which was updated with equilibrium constants for solid and aqueous Cr species from Ball and Nordstrom (1998), Rai et al. (1988), Sass and Rai (1987), Accornero et al. (2010) and Rai et al. (2007). From the species distributions in the fluid, we calculated the fluid's saturation index with respect to minerals: $SI = \log(Q/K)$, where Q is the activity product,

and K is the equilibrium constant for a given mineral dissolution reaction. The fluid is undersaturated with respect to the mineral if $SI < 0$, supersaturated with respect to the mineral if $SI > 0$, and saturated if $SI = 0$. Sorption of Cr(VI) onto $Fe(OH)_3$ as a function of pH was calculated with the modified two-layer surface complexation model of Dzombak and Morel (1990).

2.4. Spatial analysis of watershed characteristics

To calculate watershed area, relief, and runoff in the Hunting Creek watershed (summarized in **Table 1**), the National Elevation Dataset (NED) one-third arc-second cell size digital elevation map (DEM) was processed in ArcGIS 10.2. The DEM was projected to NAD 1983 UTM Zone 10N. We used Spatial Analyst Hydrology functions to fill in sinks of the raster surface (removing imperfections in the data), calculate flow directions and flow accumulation in each cell for stream locations, move sampling locations (snap pour points) to the cell of highest flow accumulation within 20 meters, and determine the contributing area (watershed) above each sampling location. Each sample's sub-basin area ranges from 1.2 to 40.8 km².

Relief was calculated as the difference between the largest and smallest value of all the cells in the DEM raster using the ArcGIS Zonal functions to calculate the range. The Hunting Creek watershed sampling locations have relief of < 621 m. Runoff (mm/yr) is calculated by normalizing the measured volumetric discharge to the DEM-based watershed area.

2.5. Solute source determination

In the Hunting Creek watershed (**Fig. 1c**), stream chemistry is influenced primarily by weathering and atmospheric deposition. In this study, fractions of solutes from different rock types (evaporite, silicate, carbonate) were not differentiated. Therefore the weathering flux represents a combined signature of mixed lithologies, when present in the watersheds. We use a forward model with pre-assigned ratios to calculate the contribution of atmospheric versus weathering sources. These pre-assigned ratios are known to be the largest source of uncertainty in this method (Moon et al., 2014; 2007). The mass-balance equation for an element X (e.g. Mg, Ca, SO_4^{2-}) is:

$$[X]_{tot} = [X]_{rain} + [X]^*$$

where “*tot*” refers to the total concentration of X, “*rain*” refers to solutes derived from atmospheric inputs and $[X]^*$ refers to solutes derived from low-temperature chemical weathering.

The atmospheric contribution is calculated using $[Cl]_{rain}$ and pre-assigned seawater X/Cl ratios listed in **Table A.1**, such that:

$$[X]_{rain} = \left(\frac{X}{Cl} \right)_{seawater} \times [Cl]_{rain}$$

where $[Cl]_{rain}$ is the concentration measured in precipitation in this study multiplied by an evapotranspiration factor, calculated to be 4 (precipitation/runoff at the farthest downstream station, MC11-53) (after Schopka et al., 2011).

Thus, solute concentrations derived from weathering are referred to as X^* :

$$[X]^* = [X]_{tot} - [X]_{rain}$$

2.6. Chemical flux calculations

To calculate chemical denudation rates from river chemical data we first removed the atmospheric contribution to determine the solute concentrations derived from chemical weathering reactions, $[X]^*$, as described in *section 2.5.*, and then multiplied this by runoff to get a rate. We report rates as either total fluxes or area-normalized fluxes, by dividing by the watershed area. Fluxes are expected to be within ~30% error, where the largest errors originate in discharge measurements (*e.g.* Di Baldassare and Montanari, 2009). Cation weathering flux is calculated as $[Ca]^* + [Mg]^* + [K]^* + [Na]^*$. Total weathering flux is calculated as the cation weathering flux plus $[SiO_2]^*$. Reactive metal flux is calculated as $[Cr]^* + [Mn]^* + [Fe]^*$. All other fluxes are clearly named. All Cr fluxes, except Cr(TOT)* within the Hunting Creek watershed, were not corrected for potential atmospheric contributions because dissolved Cr concentrations in rainwater were below detection in this study, and are generally < 2 nmol/L in rainwater (Kieber et al., 2002).

2.7. Compilation of global river Cr concentrations and discharge

We compiled a dataset of dissolved Cr concentrations (both Cr(TOT) and Cr(VI)), watershed area, and discharge from 73 rivers worldwide. The dataset was mainly acquired from the United Nations Environmental Program Global Environmental Monitoring System (GEMS) Water program (GEMS, 2015). The GEMS/Water water quality and discharge database is compiled from GEMS/Water Global Network stations maintained by governmental or local organizations where the analytical quality was monitored by the program and subsequently published online. Discharge and Cr concentrations for each river could only be downloaded from the GEMS/Water database as means, with timespan and number of samples provided. The sampling, and thus the means reported, may not capture the overall variation in flow and concentration for a given river. There are also uncertainties associated with each measurement, and with using time-averaged discharges and concentrations instead of synchronous measurements (Moon et al., 2014). Eleven other studies where dissolved Cr concentrations were measured are also compiled (Arienzo et al., 2001; Comber and Gardner, 2003; Cortecci et al., 2009; Cranston and Murray, 1980; EnvironmentCanada, 2015; Frei et al., 2014; Gaillardet and Dupré, 2003; Lekkas et al., 2004; Mora et al., 2009; Papafilippaki and Kotti, 2008; Pettine et al., 1994). In these studies, where simultaneous watershed area and discharge measurements were not available, we used the closest (within 50 km) area and discharge values from the compilation by Milliman and Farnsworth (2011), which also introduces uncertainty. Although all regions of the world (except Antarctica) are represented in this compilation, rivers in Asia and Africa are under represented due to lack of monitoring stations and data reporting.

Only rivers discharging into the oceans were selected (no inward draining basins or tributaries). For each river, we selected the stations furthest downstream; most are upstream of estuaries that may exist. The samples span from 1977 to 2013, although the time span for data collection from each river varies. Seventy-three rivers with a total of 5,653 dissolved Cr concentration measurements satisfied these criteria. For each river, the total number of data points ranges from 1 to 395, with a median value of 52. For the Amazon we used data from Gaillardet and Dupré (2003) because there was more data available over a longer time span than in GEMS. Recognizing that the following introduces additional uncertainty, we calculated global mean Cr concentrations from our

database of mean riverine Cr concentrations, because the individual measurements for a given river, in most cases, were unavailable. The 73 rivers account for ~33% of the exorheic continental area and ~35% of global river discharge to the ocean (Dai and Trenberth, 2003).

3. Results

3.1. Putah Creek ultramafic watershed

3.1.1. Water compositions: Major elements

Chemical compositions of precipitation, surface water, and spring water samples along with water volumetric discharge in the Putah Creek watershed are given in **Table A.1**. Major element water compositions are used to determine water flow paths, to calculate chemical fluxes, and to identify Cr sources, and aqueous Cr speciation. Typical of semi-arid regions, all water samples have total dissolved solids > 500 mg/kg (except for 5 samples, which were collected either from Lake Berryessa or in January).

In the Putah Creek watershed, water composition evolves upon interaction with the two dominant bedrock lithologies in the field area: ultramafic serpentinite and sedimentary Great Valley sequence (mean chemical composition given in **Table A.2**). The geochemical signature of spring and surface water at this site is consistent with meteoric fluids interacting at low temperatures with serpentinite resulting in alkaline (pH 7.68 to 9) Mg-HCO₃ waters (**Fig. 2**). Cation concentrations decrease in the order Mg²⁺ > Ca²⁺ > Na⁺ > K⁺ > Sr²⁺, and anion concentrations decrease in the order HCO₃⁻ > SO₄²⁻ > Cl⁻ > NO₃⁻ > PO₄³⁻ (**Fig. 2, Table A.1**). Similar to ultramafic regions globally, Mg²⁺ and Ca²⁺ in spring and surface water are primarily derived from rock weathering, whereas Cl⁻, Na⁺ and K⁺ have significant contributions from rain (1-70%) (see Schopka et al., 2011 for comparison).

During rock-water interaction, serpentinite minerals (*e.g.*, serpentine, magnesite and brucite), dissolve, raising pH and Mg²⁺ and HCO₃⁻ concentrations until hydromagnesite supersaturation is reached (SI > 0) and precipitation occurs (**Fig. 3a**). In surface waters and springs, alkalinity and Mg²⁺ are positively correlated (Pearson's correlation coefficients are 0.97 and 0.41, respectively) indicating that there is a gradient in the extent of rock-water interaction (travel times) in the watershed (**Table A.3**). Calculated CO₂ fugacities (1.0134 atm, 25°C) of springs are on average ~5 times atmospheric (10⁻³) and surface waters are ~2.5 times atmospheric (10^{-2.7}). These values are similar to values reported for alpine streams (Peter et al., 2014). During subsequent equilibration with the atmosphere, CO₂ is lost by degassing and dissolved carbonate speciation changes, resulting in further pH increases. The trends of increasing hydromagnesite, calcite and brucite saturation as a function of pH (**Fig. 3**) can be explained by CO₂ degassing and brucite dissolution. Brucite remains undersaturated in all water samples, whereas calcite is close to saturation or supersaturated in samples with pH exceeding 8 (all but 2 samples). Although water samples are calculated to be supersaturated with respect to the serpentine mineral antigorite (not shown), precipitation of antigorite at ambient temperatures is unlikely, possibly due to a surface free energy barrier. Similar degrees of supersaturation are also observed for albite and K-feldspar saturation states in natural waters (Maher et al., 2009; White et al., 2009).

Dissolved SiO₂ concentrations range from 65 to 1,403 µmol/L, similar to values previously reported for other ultramafic areas (*e.g.* Schopka et al., 2011) and suggest the

fluid is undersaturated with respect to amorphous silica ($\text{SiO}_{2(\text{am})}$) (**Fig. 3d**). During weathering, more Si is retained in solid phases (likely clays), compared to Ca, Na and Mg, as shown by the high Φ ratio (*i.e.* $(\text{Na}+\text{K}+\text{Ca}+\text{Mg})/\text{Si}$) for waters compared to bedrock (**Table A.1**).

At many locations in the Putah Creek watershed, we observed field evidence of recent mineral precipitation, consistent with mineral saturation states calculated from measured water compositions. For example, stream-bed sediments in the Hunting Creek watershed are cemented by secondary carbonates and silica forming “mortar beds”, also known as “Holocene conglomerates” (Barnes and O’Neil, 1971). Additionally, at spring MC11-54 hydromagnesite precipitates (confirmed by powder X-ray diffraction, not shown) form abundant rock coatings at the source. For this spring water sample, the high charge balance error is likely due to the dissolution of carbonate colloids during alkalinity titrations resulting in a higher alkalinity value. Calculated charge balance errors (CBE) for all other samples were between -12 to 7% where Cl, Si and alkalinity were measured.

Due to differences in Na/Mg and Ca/Mg ratios between regional serpentinite bedrock, and sedimentary Great Valley bedrock (**Table A.2**), these elemental ratios in spring and surface water can be used to differentiate water derived from these lithologies. Ca/Mg ratios for all water samples do not exceed 1, due to low Ca concentrations in ultramafic bedrock, similar to findings of Karapa et al. (2014) for ultramafic waters in Greece. In springs, the elemental ratios Na/Mg and Ca/Mg (**Fig. 4**) are relatively constant and similar to the average serpentinite composition in the Hunting Creek watershed indicating that these cations are released congruently during bedrock chemical weathering. Most of the recharge area of springs lies within ultramafic bedrock and the observed scatter for springs may be due to chemical weathering of bedrock with varying degrees of serpentinization and slightly different compositions.

Spring and surface water compositions from close sampling locations are very similar, which is consistent with the observation that spring water contributes to river baseflow. In contrast to springs, surface waters show some evidence of dilution by a Ca-Na rich water (**Fig. 4**). Within the Putah Creek watershed, outside the Hunting Creek watershed, surface water elemental ratios lie along a mixing line between regional serpentinite bedrock and Great Valley bedrock end members (**Fig. 4**). This suggests that water composition may be governed by mixing between water influenced by dissolution of Great Valley rocks and serpentinite.

3.1.2. Water compositions: Trace elements

In addition to major element concentrations and ratios, trace metal abundances may also track the influence of ultramafic rocks on water compositions, and provide insight into Cr sources and Cr redox cycling. In the Putah Creek watershed, Fe, Mn, Co, Ni and Cr are all present at higher concentrations in ultramafic rocks compared to Great Valley rocks (**Table A.2**). Because in many natural settings Mn and Fe control Cr oxidation and reduction respectively, it is especially important to evaluate these elements.

Correlations between trace element concentrations were evaluated in spring and surface waters. In springs, there are positive correlations between Mn-Ni (0.94), and Pb-Rb (0.99), and a negative correlation between Fe-pH (-0.92) (Pearson’s correlation coefficients given in parentheses) (**Table A.4**). The correlation between Mn and Ni in springs could be due to ultramafic rock dissolution or the fact that Ni strongly sorbs to

Mn-(oxy)hydroxides (Kay et al., 2001). The observation of dissolved Fe concentrations decreasing with increasing pH, may be due to a faster rate of Fe oxidation and subsequent precipitation as Fe-(oxy)hydroxides at higher pH. In surface waters, there are positive correlations between Mn-Fe (0.98), Mn-Ni (0.88), Mn-Co (0.86), Fe-Ni (0.86), Fe-Co (0.87), Cr(TOT)-Mg (0.82) and, Cr(TOT)-alkalinity (0.83) (**Table A.3**). The mobility of Mn and Fe in water under reducing conditions may explain the positive correlation. In contrast, Cr is more mobile under oxidizing conditions and correlates instead with Mg and alkalinity. By extension, because Mg concentrations and alkalinity increase with the extent of weathering, the extent of rock-water interaction is an important control on Cr concentrations in this system

3.1.3. Water compositions: Chromium concentration and oxidation state

Total dissolved Cr concentrations, Cr(TOT), in the alkaline springs and surface water of this field site range from below detection to 946 nmol/L, and are similar to Cr concentrations in other ultramafic areas around the world (Berkstresser, 1968; Fantoni et al., 2002; Kaprara et al., 2014; Novák et al., 2014), but higher than regions draining different lithologies (Saputro et al., 2014; Stefánsson et al., 2014). (**Fig. 5, Table A.1**). This is likely due to higher concentrations of Cr in ultramafic bedrock. Most springs in the Putah Creek watershed have higher total Cr concentrations than surface water. No water samples exceeded the Cr(TOT) drinking water limit of 962 nmol/L.

In the Putah Creek watershed both Cr(VI) and Cr(III) are present at concentrations > 19 nmol/L in approximately half of the water samples collected (**Fig. 5**). The oxidation state of dissolved Cr has been previously studied in ultramafic springs (Kaprara et al., 2014), however, such data have not been reported for ultramafic stream waters. Hexavalent Cr concentrations in the springs from this study range from below detection to 1,010 nmol/L and are higher than springs in Greece, likely due to higher pH (Kaprara et al., 2014). Springs in this study also have higher Cr(VI) concentrations than surface waters, and a higher proportion of Cr(VI)/Cr(TOT) than surface waters (80% and 56%, respectively). Chromium(VI) concentrations exceed the California drinking water limit of 192 nmol/L in 78% of spring samples and 22% of surface water samples (**Fig. 5**). Thus, there is a higher risk to human health by ingesting spring water derived from ultramafic rocks relative to surface water from the same areas.

Surprisingly, trivalent Cr concentrations are higher (up to 270 nmol/L) in these ultramafic waters compared to those previously reported for alkaline water draining any lithology (Saputro et al., 2014) likely due to increased solubility of Cr(III) with elevated carbonate alkalinity (Rai et al., 2007). Trivalent Cr was detected in 75% of surface water samples and 55% of spring samples, although mean Cr(III) concentrations are slightly higher in spring samples. Therefore, the assumption that Cr(III) has a low solubility and there is < 19 nmol/L Cr(III) in alkaline waters, as has been suggested in recent review papers (Saputro et al., 2014), may need to be re-evaluated.

For springs and surface waters, relationships between total Cr, Cr(VI) and Cr(III), and major and trace elements differ, suggesting various processes (*e.g.* redox reactions, rock-water interaction, aqueous complexation) govern Cr aqueous geochemistry. In springs, most Cr(TOT) is in the form of Cr(VI), as indicated by the linear relationship between Cr(TOT) and Cr(VI) (**Fig. 5**) and the Pearson's correlation coefficient between Cr(TOT) and Cr(VI) (0.95) (**Table A.4**). Hexavalent Cr is also correlated with pH (0.93),

Mg (0.76) and negatively correlated with Fe (-0.89) (**Table A.4**). Trivalent Cr is positively correlated with alkalinity (0.88) (**Fig. 6, Table A.4**). In surface waters, there is a positive correlation between Cr(VI) and Cr(TOT) (0.91), alkalinity (0.8), and Mg (0.76) (**Fig. 5, Fig. 6, Table A.3**). There is also a positive correlation between Cr(III) and Cr(TOT) (0.89), alkalinity (0.73), and Mg (0.75) (**Fig. 5, Fig. 6, Table A.3**).

Within surface water samples, Cr(VI) concentrations are lower in streams with sediment-laden channels compared to bedrock channels (**Fig. 7**). Additionally, in sediment-laden streams, median Cr(III) concentrations are higher than Cr(VI). Thus, reduction of Cr(VI) in streams with sediment beds may also explain why Cr(VI) concentrations are lower in surface water than springs.

3.1.4. Elemental and chemical weathering fluxes in Hunting Creek watershed

Chemical weathering fluxes in the predominantly ultramafic Hunting Creek watershed, in the headwaters region of Putah Creek, are calculated using major and trace element water compositions and baseflow discharge/runoff values to quantify the dissolved load carried by streams at different locations within the watershed (**Table 2**). These fluxes vary based on lithology, geomorphology, climate and hydrology, among other factors. Total fluxes (mass/time) are highly dependent on the size of the watershed, whereas area-normalized fluxes (mass/area/time) allow for comparisons between catchments of different sizes. Despite low runoff, the relatively high solute loads result in area-normalized total weathering fluxes within the Hunting Creek watershed of 0.27 to 1.5×10^6 mol/km²/yr (6 to 36 t/km²/yr) (see *section 4.2.5* for comparison to global rivers). Export of cations derived from silicate weathering is 0.25 to 1.39×10^6 mol/km²/yr. Area normalized fluxes of Ca* + Mg* are 0.2 to 1.3×10^6 mol/km²/yr, primarily due to the large dissolved flux of Mg. The area-normalized bicarbonate flux due to rock weathering, is 0.2 to 1×10^6 mol/km²/yr. The highest fluxes are from the farthest downstream watershed (largest area and relief) with the highest discharge. This subcatchment is comprised of a deeply eroded “canyon”, with steep walls and evidence of recent landslides. Based on the geomorphology, this region is likely more actively incising, which may explain the higher weathering rates.

Dissolved reactive metal fluxes (sum of Cr*, Mn*, Fe*) can indicate the extent of biogeochemical cycling and moderation of redox conditions in water and sediment. In the Hunting Creek watershed these fluxes are 13 to 66 mol/km²/yr (**Table 3**). Dissolved Cr(TOT)* fluxes are 10.7 to 46 mol/km²/yr, constituting 54 to 83% of the reactive metal flux. Over half of the metal flux is from Cr, which is due to the high mobility of Cr in oxidized water compared to Fe and Mn. Chromium(VI) fluxes are 6.1 to 28 mol/km²/year and Cr(III) fluxes are 4.6 to 18.3 mol/km²/yr. Similar to major element fluxes, the highest area-normalized Cr fluxes are from the actively incising canyon watershed.

In terms of total fluxes, the Hunting Creek watershed exports both Cr(VI) and Cr(III) downstream towards the Central Valley, San Francisco Bay Estuary and Pacific Ocean. With 1.9×10^3 mol/yr of dissolved Cr(TOT)* being exported from this watershed there is a high potential for the downstream depositional areas to accumulate “high” concentrations of “reactive” Cr (either dissolved or sorbed) due to surface water recharge or sediment deposition.

3.2. Global rivers

3.2.1. Hydrology

Our compiled dataset of 73 of the world's largest rivers accounts for ~33% of the exorheic continental area and ~35% of global river discharge to the ocean (Dai and Trenberth, 2003), spanning variable runoff and basin areas (**Table 4**). Mean runoff ranges from 0.9 mm/yr (Sarno River, Italy) to 2,407 mm/year (Kiso River, Japan), and drainage basin area ranges from $1.6 \times 10^2 \text{ km}^2$ (Keritis River, Greece) to $6.1 \times 10^6 \text{ km}^2$ (Amazon River, Brazil). Because dissolved Cr concentrations are $< 2 \text{ nmol/L}$ in rainwater (Kieber, 2002), we did not subtract atmospheric concentrations from measured data before computing fluxes, thus we assume that all Cr in surface water is from rock weathering or anthropogenic inputs.

3.2.2. Chromium concentration and oxidation state

Chromium concentrations and oxidation state vary broadly across large rivers. In our compilation, mean dissolved Cr(TOT) concentrations in large rivers are given in **Table 5** and range from 4.8 nmol/L (Orinoco River, Venezuela) to 1,923 nmol/L (Panuco River, Mexico), with a global mean of 151 nmol/L. Because some rivers are influenced by anthropogenic sources, the global contemporary average concentration represents a mixed signal of natural and anthropogenic Cr. Previous reviews have shown that dissolved Cr(TOT) concentrations rarely exceed 115 nmol/L (6 $\mu\text{g/L}$) away from anthropogenic sources (Kotaš and Stasicka, 2000; Rakhunde et al., 2012; Richard and Bourg, 1991; Saputro et al., 2014). Although we did not quantify the contribution from anthropogenic Cr sources in watersheds (e.g. by comparison to population density), the highest dissolved Cr and Cr(VI) concentrations (higher than the highest measured at our ultramafic field area) are found in rivers with industrial influence (e.g. textile or tanning), agricultural pollution, or flow paths through densely populated areas (Panuco, Pinios, Kelani, Sarno, Alphios, Musi, Kiso, Cimanuk, Citarum, Barito, and Pardo Rivers).

Mean dissolved Cr(VI) concentrations in 24 global rivers are given in **Table 6** and range from 3.5 nmol/L (Ouse River, England) to 385 nmol/L (Kiso River, Japan), where the global mean is 178 nmol/L. These 24 rivers only account for ~6% of the exorheic continental area and ~4% of the global river discharge to the ocean (Dai and Trenberth, 2003), with half of the rivers located in Asia. The global average calculations assume that the database compiled in this study is representative of most rivers. However, Cr(VI) is not commonly measured unless there is known anthropogenic Cr contamination and thus the mean value proposed in this study may be higher than natural background Cr(VI) concentrations. Dissolved Cr(III) concentrations were only measured in one large river (Cranston and Murray, 1980), which does not allow for comparison among global rivers. However, eleven global rivers have both dissolved Cr(TOT) and Cr(VI) measurements, revealing a close, but not perfect, 1:1 ratio (**Fig. A.1**). For one outlier, the Kiso River, Cr(VI) and Cr(TOT) concentrations were measured decades apart, which may explain the discrepancy. Otherwise, from these eleven rivers, it appears that most, but not all, Cr(TOT) is Cr(VI) in the database of rivers we have compiled.

3.2.3. Chromium fluxes

Combining concentration, watershed area and discharge, area-normalized chemical fluxes allow for comparison of watersheds of different sizes to evaluate the efficiency of solute production and export. Area-normalized Cr(TOT) fluxes vary over four orders of magnitude, from 0.1 (Rio Grande, USA) to 4,075 $\text{mol/km}^2/\text{yr}$ (Panuco

River, Mexico), averaging 22 mol/km²/yr (**Table 5, Fig. 12**). The highest area normalized Cr(TOT) fluxes are from anthropogenically-polluted rivers (Panuco, Kelani, Musi, Citarum, Alphios and Pinios Rivers). Area-normalized Cr(VI) fluxes are lower than area-normalized Cr fluxes. They also have a wide range, from 0.8 mol/km²/yr (Ouse River, England) to 926 mol/km²/yr (Kiso River, Japan) (**Table 6, Fig. 12**). The highest area-normalized Cr(VI) fluxes are also from anthropogenically-contaminated watersheds.

Although area-normalized fluxes allow for comparison of watersheds of different sizes, total riverine fluxes document export of mass from the watershed, a requirement for computing global Cr budgets. Globally, dissolved Cr(TOT) fluxes range over 6 orders of magnitude, from 2.2 x 10² mol/yr (Sarno River, Greece) to 2.5 x 10⁸ mol/yr (Panuco River, Mexico) (**Table 5**). This range is more substantial than the variation in global silicate fluxes, which are generally within a factor of 1,000 globally (Gaillardet et al., 2003). Globally, Cr(VI) fluxes range from 7 x 10³ mol/yr (Ouse River, England) to 5.5 x 10⁷ mol/yr (Yangtze River, China) (**Table 6**).

4. Discussion

4.1. Putah Creek ultramafic watershed

4.1.1. Sources of Cr

Hydrologic and geochemical measurements from the Putah Creek watershed constitute one of the most detailed data sets yet obtained for an ultramafic watershed. We use these combined hydrologic and geochemical observations to identify regions of water-rock interaction and determine the likely sources of Cr in surface and spring waters.

In the Mediterranean climate of Putah Creek, seasonal precipitation acquires solutes, including Cr, as it infiltrates through chemically weathered porous soil and saprolite into fractured bedrock/saprock, recharging groundwater and eventually discharges at springs, contributing to stream baseflow. The correlation between Mg and alkalinity in springs and surface water indicates that either variable travel times through the subsurface or variable reactivity along flow paths, or both, have influenced the chemical composition of the water. Without additional hydrologic data to constrain water travel times, we cannot distinguish between the two controls (travel time, reactivity) on the extent of weathering (Maher, 2011). However, a surprising observation is that the Cr concentrations are strongly correlated with the extent of weathering (Mg²⁺, alkalinity, pH, Ni), suggesting that although redox processes may alter Cr levels, particularly within sediment-laden streams, weathering is a first-order control on Cr levels within the watershed.

Flow through “reactive” weathered zones such as soil and saprolite are likely source regions for the dissolution of Cr and other ions, although given the high concentrations we observe in spring waters, we cannot dismiss deeper weathering via flow through fractured bedrock (Brantley et al., 2013; Manning et al., 2013) as an additional source. Chemically weathered ultramafic rock is thought to be more reactive than unweathered bedrock because of the finer grain size, secondary minerals such as clay and oxides (Morrison et al., 2015). Thus, although some of the primary minerals may have been weathered, the higher porosity and surface area exposed to fluid may increase reactivity (e.g. Chadwick and Chorover, 2001; Lebedeva et al., 2007; Navarre-Sitchler and Brantley, 2007; White et al., 1996; 1998). Lateritic ultramafic soils,

developed in tropical regions, can act as source zones for both Cr(VI) and Cr(III) (Becquer, 2003; Cooper, 2002; Fandeur et al., 2009; Garnier et al., 2006). Ultramafic soils from this region are also known to contain soluble Cr (Morrison, 2010), which may be flushed to groundwater and surface water during infiltration. However, our observation that spring water, which generally has the highest levels of Cr, is out of equilibrium with the atmosphere based on mineral precipitates and high CO₂ fugacities in the discharge areas, suggests that long travel times, rather than variations in reactivity, may be the dominant driver of base cation, alkalinity and Cr concentrations. Future work will focus on solid phase characterization and evaluation of Cr sources in Putah Creek watershed's ultramafic soils, saprolite and bedrock.

Given that ultramafic rock weathering exerts a first order control on Cr-levels, in sections 4.1.2 – 4.1.5, we use the Putah Creek spring and surface water chemical compositions, combined with speciation calculations to examine how the availability of reductants (*e.g.* Fe(II), organics), equilibrium with Cr_xFe_(1-x)(OH)₃ minerals and sorption of Cr(VI) may determine the net flux and speciation of Cr from ultramafic watersheds.

4.1.2. Chromium aqueous speciation

The distribution of different dissolved Cr(III) and Cr(VI) complexes influences the reactivity, mobility and toxicity, and is thus important for assessing the fate and transport of Cr in watersheds. For example, aqueous speciation may impact the thermodynamics of redox reactions (Ginder-Vogel et al., 2006) and the sorption of Cr onto mineral surfaces (Rai and Zachara, 1986). Although extensive experimental work has been conducted regarding individual and in some cases composite effects of environmental conditions on Cr speciation (*e.g.* Brown et al., 2001; Reich and Koretsky, 2011; Zachara et al., 1989), relatively few studies have sought to relate these observations to field evidence in surface water.

The theoretical aqueous speciation of Cr as a function of pH and oxidation/reduction potential (eV), using values generalized from our measured water compositions, is presented in **Figure 8**. Given the vulnerability of Cr to redox transformations, stability lines for different forms of Mn and Fe, for the pH range of our samples, are also shown in **Figure 8**. We did not measure dissolved Mn or Fe speciation, but expect that, if detected, both would be present in the reduced form. If the measured concentrations of Cr(VI) and Cr(III) represent equilibrium between the two oxidation states (Wang et al., 2015), then the calculated redox potential for water samples (gray shading in **Figure 8**) is between birnessite/Mn(II)CO₃ and Fe(III)(OH)₃/Fe(II)CO₃. This illustrates how small shifts in redox potential could result in Cr oxidation or reduction as discussed in section 4.1.5.

Based on mean water compositions from the Putah Creek watershed, the expected dominant Cr(VI) aqueous species is anionic CrO₄²⁻ and dominant Cr(III) aqueous species is neutrally charged Cr(OH)_{3(aq)} (**Fig. 8**). Nevertheless, because these ultramafic waters are Mg- and HCO₃-rich and the major ion concentrations vary from sample to sample, multiple aqueous Cr(VI) and Cr(III) species are present as discussed in sections 4.1.3 and 4.1.4.

4.1.3. Controls on Cr(VI)

Although CrO_4^{2-} is the dominant Cr(VI) aqueous species in most samples from the Putah Creek watershed, CrO_4^{2-} can associate with cations such as Mg^{2+} , Ca^{2+} and Na^+ at high major ion concentrations (Accornero et al., 2010). Based on calculations in GWB using our thermodynamic database (described in *section 2.3*), CrO_4^{2-} is predicted to be the dominant Cr(VI) aqueous species for 72% of water samples and $\text{MgCrO}_{4(\text{aq})}$ for the remaining 28%, those with higher Mg concentrations (**Fig. 9a**). For all samples $\text{MgCrO}_{4(\text{aq})}$ makes up 18-55% of the Cr(VI) species and $\text{CaCrO}_{4(\text{aq})}$ makes up 1-19% of Cr(VI) aqueous species, which is consistent with the Ca/Mg ratio <1 , and the observed correlation between Cr(VI) and Mg concentrations. Apollaro et al. (2011) and Lelli et al. (2013) also found that Cr(VI) speciation in groundwater in serpentinite-rich areas was mixed between neutral solutes and charged solutes (CrO_4^{2-} , $\text{MgCrO}_{4(\text{aq})}$, $\text{CaCrO}_{4(\text{aq})}$). However, due to high detection limits for Cr(VI) in their study, these authors assumed that all Cr in Cr(TOT) measurements was Cr(VI) and thus they did not evaluate the possibility of appreciable Cr(III) concentrations.

We observe an apparent upper limit to Cr(VI) concentrations of ~ 270 nmol/L (95th percentile) in the ultramafic water samples (**Fig. 9b**). This Cr(VI) concentration is above what would be predicted in equilibrium dissolved Cr(III), in turn governed by equilibrium with $\text{Cr}_x\text{Fe}_{(1-x)}(\text{OH})_3$ minerals (see *section 4.1.4*), indicating another mechanism is likely governing Cr(VI) levels. These open systems may be in disequilibrium due to variations in availability of oxidants and reductants and relative reaction rates, resulting in variable accumulation of Cr(VI) in solution. Alternatively, secondary minerals can sequester Cr and maintain higher aqueous Cr(VI) concentrations. However, we were not able to determine which secondary Cr(VI)-bearing minerals may control aqueous Cr(VI) at our study site. For example, all water samples are undersaturated with respect to what are thought to be the most likely solubility controlling Cr(VI) minerals, $\text{Ba}(\text{CrO}_4)_x(\text{SO}_4)_{1-x}$ (where x is 0.01, 0.04 or 0.23), due to low SO_4 and Ba concentrations (Prieto et al., 2002; Rai et al., 1988). Additionally, due to low SO_4 concentrations Cr(VI) substituted jarosite is unlikely to form (Drouet et al., 2003). Chromium(VI) could be incorporated into “Holocene carbonates” resulting in a direct mineral source of oxidized Cr upon dissolution (Sánchez-Pastor et al., 2011; Tang et al., 2007). Unfortunately, no suitable data is available to perform thermodynamic calculations and we expect the concentrations would be less than a few mg/kg, below detection by spectroscopic methods.

The mobility of Cr(VI) in the environment is influenced by the charge of the aqueous species as well as the charge and composition of mineral surfaces along water flow paths. Hexavalent Cr is relatively mobile in natural waters at pH greater than ~ 7 , although sorption of Cr(VI) varies strongly as a function of pH (Rai et al., 1989) regardless of whether the aqueous species are neutrally charged ($\text{MgCrO}_{4(\text{aq})}$, $\text{CaCrO}_{4(\text{aq})}$) or anionic (CrO_4^{2-}). Anionic species sorb to positively charged mineral surfaces (*e.g.* Fe, Mn and Al-oxides), which are typically found coating exposed surfaces. Based on surface complexation modeling of one such oxide, $\text{Fe}(\text{OH})_3$, using thermodynamic data from Dzombak and Morel (1990) for Cr sorption, we found that $\sim 45\%$ of CrO_4^{2-} sorbs at pH 7.7, while only $\sim 9\%$ sorbs at pH 9. In contrast, one study found that Cr(VI) sorption on ferrihydrite increased in the pH range 7 to 9 in the presence of 2.5 mmol/L Mg, possibly due to the formation of ion pairs on the mineral surface (Rai and Zachara, 1986). Although many of our samples have pH > 8.5 , because Mg concentrations range from 0.5

to 8.3 mmol/L, sorption of Cr(VI) onto Fe-(oxy)hydroxides may actually be an important control on Cr(VI) concentrations. Additionally, CrO_4^{2-} sorption may be inhibited by other anions, including bicarbonate, due to electrostatic effects and competition for surface sites (Brown et al., 2001; van Beinum et al., 2006; Villalobos et al., 2003; Zachara et al., 1987). Therefore, the main factors that influence Cr(VI) mobility in ultramafic stream water samples are alkaline pH, and presence of iron oxides and competing anions. Additional paired spectroscopic and sorption studies under a range of conditions are required to fully evaluate the role of sorption in moderating Cr(VI) concentration and mobility in natural waters.

4.1.4. Controls on Cr(III)

The presence of Cr(III) in alkaline spring and surface water samples is a surprising finding because Cr(III) was previously thought to have low solubility (Saputro et al., 2014). These elevated concentrations may be explained by major ion chemistry of ultramafic waters influencing Cr(III) solubility and aqueous speciation. Although $\text{Cr}(\text{OH})_{3(\text{aq})}$ is predicted to be the dominant Cr(III) aqueous species in all water samples, $\text{CrOH}(\text{CO}_3)_2^{2-}$ makes up 2-31% of Cr(III) species (however, this aqueous complex has never been confirmed analytically (Rai et al., 2007)) (**Fig. 10a**). To our knowledge, this is the first study to evaluate the existence of this Cr(III)-carbonate species in natural waters by performing speciation calculations. Its presence, due to higher $\text{Fe}_x\text{Cr}_{(1-x)}(\text{OH})_3$ mineral solubility at elevated $f\text{CO}_2$ (Rai et al., 2007), may explain the elevated Cr(III) concentrations (< 270 nmol/L) compared to other natural waters (< 19 nmol/L) (Cranston and Murray, 1980; Frei et al., 2014; Saputro et al., 2014; Stefánsson et al., 2014). The observed correlation between Cr(III) and carbonate alkalinity may also be explained by the presence of $\text{CrOH}(\text{CO}_3)_2^{2-}$ (**Fig. 6**). This finding is similar to the formation of U-carbonato complexes in waters with elevated carbonate alkalinity, where the formation of inorganic neutral to anionic aqueous U species enhances mobility and thermodynamic favorability of redox reactions (Bargar et al., 1999; Ginder-Vogel et al., 2006; Maher et al., 2013; Stewart et al., 2010). Chromium(III)-organic complexation was not considered here because stability constants are only available for glutamate and citrate, which were not measured in this study (Gabriel et al., 2007; Hamada et al., 2009; Smith et al., 2004). However, because organic acids were detected in surface water samples (**Table A.1**) organic complexation may be important, especially for the transport and reactivity of Cr(III) in organic-rich surface water or soils (Buerge and Hug, 1998; Carbonaro et al., 2008; Duckworth et al., 2014; James and Bartlett, 1983a; Nakayama et al., 1981; Puzon et al., 2005; 2008).

Secondary Cr(III)-bearing minerals can sequester Cr, control aqueous Cr(III) concentrations and serve as soluble Cr sources. As shown in **Figure 10b**, Cr(III) concentrations (up to 269 nmol/L) can be partly explained by equilibrium with secondary minerals such as $\text{Cr}_x\text{Fe}_{(1-x)}(\text{OH})_3$ (where $x > 0.5$) and are higher than would be predicted for equilibrium with primary Cr minerals in the bedrock (Cr-spinels, serpentine) or lower mole fraction Cr secondary minerals (as are thought to be the solubility controlling phase in alkaline waters in Iceland; Stefánsson et al., 2014). Morrison et al. (2015) identified Cr-bearing clays and Si-Cr-bearing ferrihydrite (by transmission electron microscopy/energy-dispersive X-ray spectroscopy) in ultramafic soils from the region with Cr concentrations ranging from 0.16 to 1.16 wt%, interpreted as a secondary mineral

resulting from Cr redistribution during weathering. Our field observations of prevalent colorful secondary minerals, assumed to be mixed metal-(oxy)hydroxides, in both weathered zones (soil and saprolite) and along fracture planes in bedrock, are consistent with the findings of Morrison et al. (2015) and equilibrium with soluble secondary minerals, in the presence of elevated carbonate alkalinity, governing aqueous Cr(III) concentrations.

The mobility of Cr(III) in the environment is also influenced by the charge of the aqueous species, as well as the charge and composition of mineral surfaces. Based on laboratory studies and field observations, Cr(III) readily sorbs or precipitates at $\text{pH} > 4$, unless complexed in solution. Sorption and precipitation of Cr(III) is thought to limit concentrations to $< 9 \text{ nmol/L}$ in natural waters, based on field measurements, and speciation and solubility calculations (Carbonaro and Stone, 2005; Duckworth et al., 2014; Nakayama et al., 1981; Rai et al., 2007; Stefánsson et al., 2014). However, we observed elevated Cr(III) concentrations in ultramafic waters. This could be explained by (1) decreased sorption of Cr(III) as the two predicted predominant Cr(III) species are anionic ($\text{CrOH}(\text{CO}_3)_2^{2-}$) and neutrally charged ($\text{Cr}(\text{OH})_{3(\text{aq})}$), (2) increased solubility of Cr(III)-minerals in the presence of bicarbonate, or (3) a combined effect of both. The differences in charge and coordination between Cr(III) aqueous species also alters their reactivity and mobility in the environment. For example, the rate of Cr oxidation may decrease due to Cr(III) complexation because Cr(III) complexes are less labile than Cr(III) hydrolysis products (James and Bartlett, 1983b; Johnson and Xyla, 1991; Nakayama et al., 1981; Tzou et al., 2002). The magnitude of decrease in oxidation rate will depend on the strength of the ligand. Future laboratory studies investigating Cr(III) sorption in bicarbonate waters at $\text{pH} > 7.5$ are warranted given field evidence of mobile Cr(III) aqueous species. Because Cr(III) can be oxidized to toxic and carcinogenic Cr(VI) by chlorine during drinking water treatment (Lindsay et al., 2012; Saputro et al., 2011), the surface water in this region containing elevated Cr(III), in addition to Cr(VI), may present a human health risk.

4.1.5. Chromium cycling

The original source of Cr in the Putah Creek watershed is from the dissolution of Cr(III)-bearing minerals found in ultramafic rocks (e.g. silicates, oxides), while weathering processes may transfer Cr to new chemical and physical environments. In addition, Mn and Fe, which are also elevated above crustal levels in ultramafic rocks, are two of the primary species involved in Cr redox reactions. Thus, weathering of these rocks results in a relatively rare combination of ideal circumstances for both Cr oxidation and reduction, or Cr redox cycling (**Fig. 11**).

As primary minerals in ultramafic bedrock dissolve, Mn and Cr (among others) are released to solution. Manganese is oxidized by oxygen (aided by Mn-oxidizing bacteria) (Tebo et al., 2004) forming Mn-(oxy)hydroxides, such as black dendrites along the fracture planes that we observed in bedrock drill core. Chromium(III) is then oxidized by Mn-(oxy)hydroxides, oxygen or H_2O_2 (Eary and Rai, 1987; Pettine and Millero, 1990; Schroeder and Lee, 1975). This reaction releases Cr(VI) and Mn(II) to solution; the latter may then be re-oxidized forming Mn-(oxy)hydroxides and further catalyze the oxidation of Cr(III). The co-evolution of Mn and Cr cycling as weathering reactions proceed may

explain why Cr concentrations are correlated with the extent of weathering (*i.e.*, HCO_3^- , Mg and Ni concentrations and pH).

Mineral dissolution also alters the concentrations of solutes that affect Cr mobility. For example, as HCO_3^- concentrations increase above 8 mmol/L (up to 14 mmol/L at our site) the solubility of $\text{Cr}(\text{OH})_{3(\text{am})}$ increases due to the formation of aqueous Cr(III)-carbonate complexes (Rai et al., 2007), further driving dissolution of Cr(III) from rocks or secondary minerals. As pH increases, both the rate of Cr oxidation by oxygen and the rate of Mn oxidation (and subsequent Cr oxidation) increase (Namgung et al., 2014; Schroeder and Lee, 1975). Chromium(VI) also forms Mg and Ca complexes, which may further enhance Cr(III) oxidation and possibly suppress Cr(VI) reduction. Additionally, as pH increases along flow paths, less Cr(VI) sorbs to mineral surfaces (Izbicki et al., 2008).

The coupled weathering processes described above tend to result in enhanced mobility of Cr and may be favored in shallow weathering environments, such as soils, where oxygen is abundant. However, Cr(VI) may be reduced to aqueous Cr(III) by Fe(II), organic acids, and bacteria (among other reductants) along groundwater flow paths and in surface water forming secondary Cr(III) precipitates. Such reactions are not restricted to deeper subsurface environments further along flow paths. For example, micron-scale redox gradients (*e.g.* in soil aggregates) that allow for the co-existence of birnessite and reduced Fe could lead to redox cycling of Cr that is not fully captured by evaluation of aqueous concentrations alone, but may govern net Cr production.

In springs, Fe and Cr(VI) concentrations are negatively correlated, presenting evidence of Cr(VI) reduction by Fe(II), as we would expect dissolved Fe to be Fe(II). Upon Cr(VI) reduction to Cr(III) by Fe(II), mixed $\text{Cr}_x\text{Fe}_{(1-x)}(\text{OH})_3$ secondary minerals form (Hansel et al., 2003; Sass and Rai, 1987), which have been observed in soils (Morrison et al., 2015), and possibly on surfaces in saprolite and bedrock.

In surface water, aqueous Cr concentrations and speciation are also influenced by dilution and composition of the streambed sediments (**Fig. 7**). In this study we have not quantified the role of organics, H_2O_2 , or suspended sediment or colloids in aqueous Cr speciation, although they are also expected to be important (Gasser et al., 1994; Pettine et al., 1994; Pettine and Millero, 1990). Chromium(VI) concentrations are lower in sediment-laden stream channels, compared to bedrock channels. Sediment streambeds at this field site contain organic matter and visible redox gradients (brown-black) with sediment depth in the stream bank indicative of reducing condition and the presence of organic acids capable of Cr(VI) reduction. Stream waters in streams with sediment-laden channels have detectable Fe, Mn and organic acid concentrations (higher than in bedrock streams) and more Cr(III) than Cr(VI), providing evidence for reducing conditions, and reduction of Cr(VI) by Fe(II).

The balance between ultramafic rock weathering and elemental cycling along water flow paths in the Putah Creek watershed govern observed Cr concentrations and speciation. In ultramafic catchments, key Cr transformations take place in oxic zones (*e.g.* dissolution of Cr and re-distribution into Cr(III) solids and aqueous Cr(VI) species in soil), followed by Cr attenuation when micro- or predominantly reducing environments are accessed along flow paths or in surface water channels. The main factors controlling Cr in solution appear to be the lithology of the recharge area, degree of rock-water interaction (*e.g.* Mg^{2+} , alkalinity, pH), availability of reductants (*e.g.* Fe(II), organics),

and equilibrium with $\text{Cr}_x\text{Fe}_{(1-x)}(\text{OH})_3$ minerals and an unidentified Cr(VI)-bearing mineral. Cr redox cycling in soils, groundwater and surface water in the Putah Creek watershed may concentrate Cr in sediments (precipitated or sorbed). Both dissolved Cr (as Cr(VI and Cr(III)), and Cr in stream sediments are exported downstream to (1) floodplains in the Central Valley, leading to soils, aquifer sediments and alluvial aquifers with elevated Cr and Cr(VI) concentrations (Chung et al., 2001; Goldhaber et al., 2009; Manning et al., 2015; Mills et al., 2011; Morrison et al., 2015; 2009) and (2) the Sacramento River, San Francisco Bay-Estuary and Pacific Ocean. Thus, understanding the transformations in headwater streams is a necessary first step to understanding the subsequent distribution of Cr and other trace metals in the environment.

4.2. Comparison among global rivers and ultramafic watersheds

Weathering of ultramafic rocks contributes trace element, base cation and alkalinity fluxes to surface waters and depositional environments (e.g. continental margins, ocean basins or alluvial plains). In addition to the high trace element concentrations, ultramafic rocks are highly out of equilibrium at the Earth's surface and thus constitute the most reactive rock type undergoing chemical weathering, having the potential to influence long-term carbon cycling. To evaluate the role of ultramafic watersheds in global Cr and elemental fluxes, we compare elemental concentration data and chemical weathering fluxes from the Hunting Creek watershed to other ultramafic watersheds (Schopka et al., 2011) and global rivers (Gaillardet et al., 1999; 2011). We focus on quantifying Cr concentrations and fluxes and how they may have changed over Earth history because Cr is a widespread contaminant (Chatham-Stephens et al., 2013; Oze et al., 2007) and possible tracer of paleoredox conditions (Frei et al., 2009).

4.2.1. Controls on global riverine Cr concentration and oxidation state

We report the most comprehensive compilation of dissolved Cr(TOT) and Cr(VI) concentrations of rivers globally to date, along with revised global averages in **Tables 3 and 4** and **Figure 12**. Chromium concentrations vary widely and the sources of variation are complex including anthropogenic contamination, hydrology, equilibrium with secondary Cr-bearing minerals, and lithology.

Dissolved Cr(TOT) and Cr(VI) concentrations in rivers worldwide, and in the Hunting Creek watershed, show minimal correlation with runoff. As shown in **Figure 12**, large rivers have greater variability in Cr concentrations than the Hunting Creek watershed. However, Cr(VI) does appear to have an upper limit in concentration globally of 330 nmol/L (95th percentile) (**Fig. 12**), similar to the value for Putah Creek (270 nmol/L). Large rivers with dissolved Cr(TOT) and Cr(VI) concentrations above what is predicted for equilibrium with $\text{Cr}(\text{OH})_3$ may represent disequilibrium, due to the availability and relative rates of redox reaction couples, or equilibrium with an unidentified more soluble Cr(VI)-bearing mineral.

Dissolution of different lithologies could lead to large differences in trace element concentrations in rivers. Surface waters in ultramafic source regions (this study), where bedrock has the highest Cr concentrations of any rock type, are characterized by high dissolved Cr(TOT) concentrations (13.5 to 4,807 nmol/L), which in some cases exceed drinking water limits by a factor of up to five (Farkaš et al., 2013; Gough et al., 1989; Novák et al., 2014). However, in the global river database we have compiled, watersheds

containing ultramafic bedrock (Sacramento, Pinios, Aliakmonas, Evros, Barito, Musi) also have widespread anthropogenic influences. Thus, it is difficult to decipher whether Cr concentrations in these rivers can be attributed to anthropogenic or lithologic factors. Chromium concentrations in rivers draining volcanic and metamorphic regions have intermediate concentrations, typically < 58 nmol/L at $\text{pH} > 4$ (Frei et al., 2014; Saputro et al., 2014; Stefánsson et al., 2014). These intermediate concentrations are likely maintained by the solubility of the secondary precipitate $\text{Fe}_{0.1}\text{Cr}_{0.9}(\text{OH})_3$ (Cranston and Murray, 1980; Stefánsson et al., 2014). Lithologic controls on Cr concentrations were also investigated by Frei et al. (2014) for the basaltic Parana River catchment. These authors attribute the elevated Cr concentrations (~ 38 nmol/L) in Parana River water to basalt weathering because basalt has higher Cr concentrations than the crustal average. Without more watershed-scale studies on Cr geochemistry within a uniform lithology, away from anthropogenic influences, and over a wide range of runoff, we are unable to attribute variations in dissolved Cr concentration in river water to variations in bedrock composition.

When considering all of the global rivers in this compilation, including those with anthropogenic contamination, our estimate of 152 nmol/L Cr for the global mean riverine dissolved Cr(TOT) is higher than those previously reported by Bonnand et al. (2011) (2–15 nmol/L) and Gaillardet and Dupré (2003) (14 nmol/L) (**Table 4**). In most locations, river sampling took place post-industrialization, between 1977 and 2013. Thus, mean Cr concentrations reported in this study provide an estimate of contemporary Cr concentrations in large rivers.

4.2.2. Riverine Cr fluxes

Although concentrations provide important insight into the processes that are controlling Cr release, area-normalized chemical fluxes allow for comparison of watersheds of different sizes to evaluate the efficiency of solute production and export. Here, we evaluate the role of anthropogenic contamination, hydrology, lithology and redox state in governing area-normalized Cr fluxes, and how these fluxes may have varied over Earth history. The highest area normalized Cr and Cr(VI) fluxes are from anthropogenically-influenced rivers. Globally, and within the ultramafic Hunting Creek watershed, area-normalized Cr(TOT) and Cr(VI) fluxes increase with increasing runoff (**Fig. 12**). Chemical fluxes can be maximized when chemical equilibrium with a solid phase is maintained and minimized when fluid residence times are short or reactions slow (Maher and Chamberlain, 2014). Thus, if Cr concentrations are maximized due to mineral solubility, riverine Cr fluxes may be more dependent on water discharge: the higher the discharge the higher the Cr flux.

Anthropogenic contamination and hydrology appear to be major controls on area-normalized Cr fluxes. However, watersheds with different lithology, thus varying Cr concentrations and reactivity, have different efficiencies of Cr export. The ultramafic watersheds studied here are efficient producers and exporters of dissolved Cr(TOT) (averaging $20 \text{ mol/km}^2/\text{yr}$), having higher area-normalized Cr(TOT) fluxes compared to rivers with similar runoff. Ultramafic catchments have similar area-normalized Cr(TOT) fluxes to the average global river ($22 \text{ mol/km}^2/\text{yr}$), despite higher global average runoff. However, basalt-dominated watersheds, such as the Parana (Frei et al., 2014) which has similar runoff to Hunting Creek, appear to have lower Cr fluxes than the average global

river (we calculate area-normalized dissolved Cr(TOT) fluxes for the Parana River to be ~14 mol/km²/yr). From these two studies evaluating watershed scale riverine Cr fluxes (Hunting Creek and Parana River), one may conclude that ultramafic rocks are more efficient Cr(TOT) exporters than mafic rocks. However, there is currently insufficient data to evaluate the extent to which ultramafic rivers contribute disproportionately to the global Cr flux because this sole study of Cr fluxes in ultramafic catchments has a narrow range of runoff due to the dry climate. If Cr concentrations are consistently higher than average and do not show dilution with increasing discharge, then higher concentrations would result in consistently higher area-normalized fluxes for a given runoff compared to global rivers.

Although area-normalized fluxes enable evaluation of solute production efficiency, total riverine fluxes document export of mass from the watershed, a requirement for computing global Cr budgets. Riverine Cr fluxes are an essential component of global Cr budgets, thought to account for 76-96% of Cr inputs to oceans (Bonnand et al., 2013). Our compilation of Cr(TOT) fluxes in rivers accounts for 35% of global river discharge (Dai and Trenberth, 2003), summing to 5.8×10^8 mol Cr(TOT)/yr for this set of rivers. Assuming these fluxes are representative global rivers, by scaling up to 100% of global river discharge we estimate the global river dissolved Cr(TOT) to be 1.7×10^9 mol/yr. From smaller compilations of “natural” river systems, Bonnand et al. (2013) estimated a lower global Cr riverine flux of 0.8 to 5.6×10^8 mol/yr, and Gaillardet and Dupré (2003) estimated 5×10^8 mol/yr. Both of these estimates are from rivers selected to be free from high anthropogenic pollution. Our estimate, which is over three times larger than previous estimates may capture either a higher background or the impact of humans on the global Cr cycle: pollution may have increased riverine Cr fluxes by up to a factor of three. We calculate riverine Cr input to be > 98% of input to oceans and an oceanic Cr residence time to be ~3,000 yr, where the latter is a factor of three lower than previous estimates (MBARI, 2014; Sirinawin et al., 2000). However, if geochemical reactions taking place in estuaries are considered, estimates of riverine Cr fluxes and oceanic Cr residence times will differ as discussed in *section 4.2.3*.

A few global rivers make up a large proportion of global dissolved Cr(TOT) flux. From the rivers analyzed, total dissolved Cr(TOT) flux is highest from the Panuco River, Mexico, due to the high concentration and large discharge, accounting for 6.3% of the global Cr(TOT) riverine flux to oceans. Following are the Amazon (5%), Yangtze (3%) and Parana (1.4%) (for comparison 5% is reported for Parana in Frei et al. (2014)). This suggests that there is high spatial variability in the discharge of Cr to ocean basins, making it more challenging to separate the role of local and global variations in changing ocean chemistry. This spatial variability in riverine Cr fluxes may lead to different Cr concentrations in coastal waters and continental margin sediments (Jeandel and Minster, 1987), vertical Cr concentration gradients in oceans (*e.g.* conservative or nutrient-like) (Sirinawin et al., 2000), and ultimately differences in amount and nature of Cr recorded in the rock record in ocean basins (*e.g.* Frei et al., 2009). However, on geologic timescales, processes increasing local (catchment-scale) weathering fluxes may only have large influences on ocean chemistry if the duration is long lasting.

For Cr(VI), our compilation accounts for 4% of global river discharge (Dai and Trenberth, 2003), and we estimate riverine Cr(VI) flux is 3.5×10^9 mol/yr. This Cr(VI) flux is larger than the estimated global Cr(TOT) flux, likely an overestimate because

Cr(VI) sampling is usually conducted in polluted areas, thus the Cr(VI) fluxes we report are probably higher than most global rivers due to sampling bias. In addition, we use a relatively small number of measurements to extrapolate the total Cr(VI) flux.

Chromium weathering fluxes may have varied over Earth history because of changes in the global distribution of ultramafic rocks, Cr concentrations in ultramafic rocks, or different climatic conditions (*e.g.* $f\text{CO}_2$ or runoff). Therefore it may not be appropriate to use modern riverine Cr fluxes on geologic timescales. During Earth history, there have been periods of enhanced ophiolite genesis and emplacement, referred to as “ophiolite pulses”, due to supercontinent assembly or dismantling, and the emplacement of large igneous provinces (Dilek, 2003; Dilek and Furnes, 2011). Because a larger area of ultramafic rock was likely sub-aerially exposed at the Earth’s surface during “ophiolite pulses” of the Mesozoic Era (225 to 65 Ma) (Dilek, 2003), Cr(TOT) weathering fluxes may have been higher during this interval. However, Precambrian ophiolites tend to have higher Cr concentrations (Furnes et al., 2014), which also could have resulted in higher Cr weathering fluxes during this period in Earth history. In addition, if Cr(III) mineral solubility and Cr(III) concentrations increase with increasing $f\text{CO}_2$ (Rai et al., 2007), then Cr concentrations and corresponding fluxes may have also been elevated during periods of elevated atmospheric CO_2 levels. For example, previous interpretations of excursions in Cr concentrations in banded iron formations associated with the Great Oxidation Event (~ 2.48 Gyr ago) are attributed to due to acid rock drainage (Konhauser et al., 2011). However, if Cr-mineral solubility is a function of $f\text{CO}_2$, such assumptions may need to be re-evaluated given that $f\text{CO}_2$ levels were also elevated during this time (Konhauser et al., 2011).

4.2.3. The role of estuaries in riverine Cr budgets

Geochemical reactions taking place in estuaries may change Cr concentrations, speciation and isotope ratios and are therefore important to consider when calculating the flux of Cr to oceans from rivers in global Cr budgets. We were able to track the fate of Cr from Hunting Creek and Putah Creek, through the Sacramento River to the San Francisco Bay-Estuary and the Pacific Ocean by including data from Abu Saba et al. (1995) and (1997). The Sacramento River, when entering the San Francisco Bay-Estuary has a mixture of Cr(III) and Cr(VI) (Abu-Saba and Flegal, 1997; 1995) with our finding for the Putah Creek tributary. The Cr flux from the Sacramento River we estimate is 6.6×10^5 mol/yr, which is intermediate between Cr fluxes previously reported during low fluvial flow (1×10^5 mol/yr) and high fluvial flow (7×10^6 mol/yr) (Abu-Saba and Flegal, 1997). During high fluvial flow Sacramento River water is diverted through the Yolo Bypass, which contains sediments derived from ultramafic rocks of the Putah Creek watershed, leading to higher Cr fluxes to the San Francisco Bay-Estuary (Abu-Saba and Flegal, 1997).

As salinity increases in the San Francisco Bay Estuary, due to the mixing of river water and seawater, Cr(III) is removed from solution either by adsorption to suspended or benthic sediment particles or by flocculation (Abu-Saba and Flegal, 1995). This may result in the accumulation of Cr in estuarine sediments. In contrast to Cr(III), Cr(VI) concentrations undergo little variation, remaining roughly constant (~2 nmol/L). As river water mixes with seawater in this estuary and other estuaries globally, Cr concentration evolves towards seawater (0.9 to 7.3 nmol/L) (Bonnand et al., 2013), depending on

residence time and other factors (Campbell and Yeats, 1984; Cranston and Murray, 1980; Frei et al., 2014; Mayer et al., 1984; Pfeiffer et al., 1982). Speciation of Cr also likely evolves towards seawater where $\text{Cr}(\text{OH})_3$ and NaCrO_4^- are expected to be the dominant Cr(III) and Cr(VI) species respectively (Accornero et al., 2010). Based on the decrease in Cr concentration observed in estuaries, we calculate a lower estimate of Cr flux from the Sacramento River through the San Francisco Bay-Estuary to the ocean of 4.3×10^4 mol/yr. This strongly suggests that using dissolved Cr concentrations from upstream of estuaries to calculate riverine Cr fluxes to oceans may result in an over estimate due to geochemical reactions taking place in estuaries. If Cr(TOT) concentrations decrease to ~ 2 nmol/L when all rivers meet the ocean, global riverine dissolved Cr(TOT) fluxes may be as low as 7.5×10^7 mol/yr, over six times lower than previous estimates (Bonnand et al., 2013; Gaillardet and Dupré, 2003), and over an order of magnitude lower than our estimate. Ocean residence times may then be $\sim 70,000$ years, also an order of magnitude higher than previous estimates (e.g. MBARI, 2014; Sirinawin et al., 2000), suggesting Cr behaves more conservatively and may be more useful as a paleoredox proxy.

Measurement of riverine Cr fluxes is a crucial step in constraining not only the modern Cr budget, but also the Cr isotopic budget that is used for paleoredox reconstructions. Riverine Cr fluxes vary as a function of lithology and discharge, and we expect that Cr isotopic compositions may also differ between rivers draining different lithologies (Farkaš et al., 2013; Schoenberg et al., 2008). In addition to changes in Cr-source rock lithology, changes in Cr aqueous speciation/coordination and reactions (e.g. redox) during riverine transport and in estuaries may induce isotopic fractionation (Ellis et al., 2004; Schauble et al., 2004). Careful longitudinal sampling along rivers, with concurrent concentration, speciation, isotopic composition and discharge measurements are crucial to unraveling the modern Cr isotopic signature transferred from land to sea, and may reveal useful information about past variations in ocean redox chemistry.

4.2.4. Role of ultramafic rocks in global weathering

Major element chemical weathering fluxes in the ultramafic Hunting Creek watershed in central California are similar to global rivers (Gaillardet et al., 1999), volcanic rivers (Gaillardet et al., 2011) and the Zambales and Angat ophiolites (ultramafic rocks) in the Philippines (Schopka et al., 2011) (**Fig. 13**). Runoff and mineralogy appear to be two of the main parameters controlling weathering. Fluxes from all these rivers have a positive relationship with runoff, indicating a strong dependence on discharge. Dissolved concentrations in rivers draining ultramafic areas are higher than volcanic areas. This suggests that different mineral assemblages may be controlling the cation fluxes. Some of the highest runoff values in this compilation are from volcanic regions (many located in tropical regions). The high runoff, along with the input of volcanic acids from hydrothermal sources (Rad et al., 2011) may explain why volcanic areas have the highest area normalized weathering rates recorded (Gaillardet et al., 2011). Temperature is an important influence on reaction kinetics (Eiriksdottir et al., 2013), but we cannot evaluate the extent to which it influences the variations we observe in global rivers due to the large variations in runoff.

When comparing ultramafic regions in the Philippines with the ultramafic Hunting Creek watershed in California, mean $\text{Ca}^* + \text{Mg}^*$ and bicarbonate fluxes are higher in the Philippines, due to more runoff in the tropical climate. However, for a given

runoff value (**Fig. 13 a, b**), fluxes from Hunting Creek are also higher than Philippine ultramafic regions and global rivers. Although we do not know the extent to which physical erosion differs between the two sites, the differences in concentration suggests a chemical as opposed to physical control. The amphibolite and greenschist facies minerals present in Philippine ultramafic regions examined by Schopka et al. (2011) have different reactivity than serpentinite bedrock in the Hunting Creek watershed. The different mineral assemblages and their weathering products could explain the higher $\text{Ca}^* + \text{Mg}^*$ concentrations in rivers draining our study compared to Philippine ultramafic regions, that, in turn, result in the higher area-normalized $\text{Ca}^* + \text{Mg}^*$ fluxes for a given runoff.

Our results confirm that ultramafic rocks have some of the highest weathering rates of any rock type, consistent with the findings of Schopka et al. (2011). Therefore, we investigated their role in the long-term carbon cycle. For ultramafic watersheds (this study and Schopka et al. (2011)) the mean area-normalized bicarbonate flux is $1 \times 10^6 \text{ mol/km}^2/\text{yr}$, more than three times higher than the global mean CO_2 consumption of $2.5 \times 10^5 \text{ mol/km}^2/\text{yr}$ (Gaillardet et al., 1999). Assuming the global area of plutonic mafic and ultramafic rocks at the surface is $2.66 \times 10^5 \text{ km}^2$ (Durr et al., 2005), and that 60% of this area drains into oceans (Dai and Trenberth, 2003), we estimate that the bicarbonate flux from weathering of plutonic mafic and ultramafic rocks is $1.6 \times 10^{11} \text{ mol/yr}$. This represents approximately 0.7% of the modern day weathering fluxes reported by Gaillardet et al. (1999), although these rocks constitute approximately 0.2% of the Earth surface area. This estimate exceeds, by three-fold, the expected amount based on the areal extent alone. For comparison, Hartmann et al. (2009) also reported a disproportional contribution, estimating that plutonic mafic and ultramafic rocks contribute 0.4% to global bicarbonate fluxes by using fluxes from another lithologic class: mafic volcanics. Similarly, continental volcanics may account for up to 30% of weathering fluxes, although they only make up 5% of the Earth surface (Dupré et al., 2003), and volcanic arcs may account for 10% of weathering fluxes although they only make up ~1% of Earth surface (Schopka et al., 2011). Therefore, not only the weathering of volcanics, but also the weathering of ultramafics may have a disproportionate impact on the long-term carbon cycle and Earth's climate.

4.2.5. Chemical weathering rates as a proxy for Cr and trace element fluxes

To evaluate whether major elements can be used as a proxy for Cr, we compare major element fluxes and Cr fluxes in global rivers (**Fig. 13 c, d**). Area-normalized Cr fluxes in global rivers and the ultramafic watersheds of this study do increase with increasing area-normalized $\text{Ca}^* + \text{Mg}^*$ and bicarbonate fluxes. This relationship suggests that weathering results in relatively constant ratios of $\text{Cr(TOT)}/\text{Ca}^* + \text{Mg}^*$ and $\text{Cr(TOT)}/\text{HCO}_3^*$, although the ratio may vary some with lithology. These results, although reflective of a relatively small set of rivers, suggest that $\text{Ca}^* + \text{Mg}^*$ or bicarbonate fluxes may be useful as a proxy for Cr fluxes. Over geologic timescales, changes in climate and atmospheric CO_2 levels, among other factors, may have increased Cr and major element chemical weathering rates. Because riverine Cr fluxes are thought to be a major control on oceanic Cr concentrations, it may therefore be possible to predict past oceanic Cr concentrations from records of changing major element fluxes.

Building on the Cr flux investigation, dissolved trace metal fluxes are important to quantify as they moderate redox conditions, reflect human influence on environment,

and may influence global biogeochemical cycling (*e.g.* toxic, bioavailable). We have shown that ultramafic rocks are efficient Cr exporters to the environment during weathering. Although these rocks also have elevated concentrations of other trace metals such as Mn and Fe, Cr constitutes a large portion (> 50%) of dissolved reactive metal flux, primarily due to the mobility of Cr(VI) under oxidizing conditions (**Table 3**). Because of the oxic nature of most global rivers, we would expect the majority of dissolved reactive metal fluxes to be made up of elements that are more mobile in their oxidized form (*e.g.* U, Mo, Se, V). Trace metal mobility at the watershed scale (Herndon and Brantley, 2011; Nordstrom, 2011; 2009; Yesavage et al., 2012) and soil profile scale (Navarre-Sitchler and Brantley, 2007; Navarre-Sitchler et al., 2009) as well as studies of metal release over geologic time (Hausrath et al., 2009; Neaman et al., 2005a; 2005b) have revealed the complexity of bridging spatial and temporal scales as well as the importance of trace metals in weathering. However, there are few rivers where the whole suite of trace elements have been measured (Gaillardet and Dupré, 2003), thus making it difficult to determine if there are any patterns in the fluxes of trace elements globally.

Global trace element fluxes and the factors that control them would be useful to quantify. Trace element inventories in seawater through time are governed by changes in the relative rates of supply or removal, for example changing riverine fluxes (*e.g.* Cr) or authigenic enrichment (*e.g.* Mo, U). Past ocean redox conditions or paleo-productivity can be inferred if the concentrations of biologically important trace elements (*e.g.* P, Ni, Mo, Cu, Zn, V) in marine sedimentary rocks reflect these changes in ocean chemistry (Algeo et al., 2012; Tribovillard et al., 2006) and references within). In the absence of modern, let alone ancient, riverine trace element fluxes, it is difficult to evaluate the magnitude over which the delivery of trace elements to seawater and biologic responses may have varied (Konhauser et al., 2009; Little et al., 2015; Meyer and Kump, 2008; Meyer et al., 2011; Vance et al., 2008; 2009). Our results support a weathering flux control on oceanic Cr concentrations, and suggest caution in interpreting temporal variations in other trace element levels without careful normalization to account for potential changes in weathering rates, which may also influence oceanic concentrations and residence time and ultimately what is recorded in the rock record.

5. Conclusion

To quantify Cr fluxes and speciation in rivers, we compiled a comprehensive dataset of Cr concentrations and discharge from 73 rivers globally, accounting for ~35% of the global river discharge to the ocean, and also studied a small ultramafic watershed in the central California Coast Range Mountains that is naturally enriched in Cr and drains to the Pacific Ocean. Specifically, we evaluated how lithology, hydrology and geochemistry affect Cr sources, Cr aqueous speciation, and modern riverine Cr fluxes.

Riverine Cr concentration and speciation in ultramafic catchments is governed by rock weathering and elemental cycling along hydrologic flow paths. Weathering of ultramafic rocks, which have elevated concentrations of Cr, Mn and Fe, creates a rare combination of ideal circumstances for enhanced Cr release and redox cycling controlled by the availability of electron donors and acceptors (*e.g.* Mn(III/IV)-oxides, oxygen, Fe(II), organics). Dissolved Cr in alkaline river water draining ultramafic catchments is exported not only as soluble hexavalent Cr(VI) species (CrO_4^{2-} , MgCrO_4), but also as trivalent Cr(III) species ($\text{Cr}(\text{OH})_3$, $\text{CrOH}(\text{CO}_3)_2^{2-}$); the latter were previously thought to

have low solubility. Riverine dissolved Cr concentrations and speciation are further modified by geochemical reactions in the San Francisco Bay Estuary (Abu-Saba and Flegal, 1997; 1995), decreasing riverine Cr flux to the Pacific ocean.

Compared to large rivers globally, ultramafic catchments are efficient exporters of both Cr as well as Mg + Ca and alkalinity, as they have higher area normalized fluxes for a given runoff. Therefore, ultramafic catchments may have a disproportionately large impact on global Cr-budgets, the long-term carbon cycle, and Earth's climate. The linear relationship between Cr fluxes and major element fluxes in both ultramafic catchments and global rivers suggests that weathering is a key control on riverine Cr fluxes. Thus, major ion chemical weathering fluxes may be useful as a proxy to estimate Cr and other trace element fluxes.

Globally, the contemporary flux of dissolved Cr from rivers to the ocean is spatially variable and estimated to be 1.7×10^9 mol/yr, which is over three times higher than previous estimates (Bonnand et al., 2013; Gaillardet and Dupré, 2003). Throughout Earth history, Cr weathering fluxes may have varied with climactic factors (*e.g.* fCO_2 or runoff), Cr concentration in rocks, and the distribution of ultramafic rocks. Therefore it may not be appropriate to extrapolate modern riverine Cr fluxes to geologic timescales. This work highlights the importance of evaluating bedrock weathering and geochemical reactions from headwater streams through estuaries to oceans to identify the factors controlling variability in Cr concentration and isotope composition in rivers and seawater.

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Appendix A. Supplementary Information

Fig. A.1. Cr(VI) as a function of Cr(TOT) for 11 global rivers. 1:1 dashed line shown. Some measurements were taken at different times or locations along rivers.

Table A.1. Putah Creek watershed water sample discharge (m^3/hr), pH, concentrations ($\mu mol/L$), and molar Φ ratio. Seawater concentrations for calculating atmospheric solute sources are from MBARI Chemical Sensor Program (2014).

Table A.2. Average bedrock chemical composition for major rocks types in Putah Creek watershed. Molar Φ ratio ($Ca+K+Mg+Na / Si$).

Table A.3. Pearson's correlation coefficients for surface water samples from the Putah Creek watershed.

Table A.4. Pearson's correlation coefficients for spring water samples from the Putah Creek watershed.

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Fig. 1. (a) Map of ultramafic bedrock and study location in the Coast Range Mountains, California, USA **(b)** Putah Creek watershed map showing ultramafic bedrock and surface water (squares) and spring (circles) sampling locations **(c)** Hunting Creek and neighboring watersheds, showing ultramafic bedrock, spring water (triangles), surface water (filled circles) and water discharge (open circles) sampling locations (CIWMC, 2010; Ludington et al., 2007).

Fig. 2. Piper diagram showing major cation and anion composition of surface water (circle) and spring water (triangle) samples from the Putah Creek watershed. Waters are all Mg-HCO₃⁻.

Fig. 3. Saturation index (SI = log(Q/K)) of Putah Creek watershed surface water samples (circles) and spring samples (triangles) as a function pH with respect to the following minerals: **(a)** hydromagnesite, **(b)** brucite, **(c)** calcite and **(d)** amorphous SiO₂. SI > 0 indicates oversaturation, SI < 0 indicates undersaturation, SI = 0 indicates saturation. Calculations were performed using The Geochemist's Workbench 2010.

Fig. 4. Na/Mg and Ca/Mg molar ratios for Putah Creek watershed surface water samples (circles), spring samples (triangles), serpentinite bedrock (large square) and regional great valley formation bedrock (large diamond).

Fig. 5. (a) Cr(VI) concentration as a function of Cr(TOT) and **(b)** Cr(III) concentration as a function of Cr(TOT) concentrations in surface waters (circles) and springs (triangles) from the Putah Creek watershed. 1:1 dashed line and Cr(VI) drinking water limit (MCL: 10 µg/L, 192 nmol/L) is shown for reference.

Fig. 6. Chromium concentration as a function of carbonate alkalinity for (a) Cr(VI), (b) Cr(III) for surface water (circles) and spring water (triangles) samples from the Putah Creek watershed. Cr(VI) drinking water limit (MCL: 10 µg/L, 192 nmol/L) shown.

Fig. 7. Box plot of Cr(VI) concentration in surface water of the Putah Creek watershed binned by stream bed type (sediment or bedrock), showing median (filled circles), first and third quartiles (solid lines), 1.5*interquartile distance (dotted lines), and outliers (open circles). Cr(VI) drinking water limit (MCL: 10 µg/L, 192 nmol/L) shown.

Fig. 8. Cr speciation shown for a range of Eh and pH conditions at 25 °Celsius, 1.013 bars and average concentrations for surface and spring waters in the Putah Creek watershed. The Eh/pH range of surface and spring water samples are shown in dark gray. The Mn ($\text{MnCO}_{3(\text{aq})}$ /Birnessite) and Fe ($\text{FeCO}_{3(\text{aq})}$ / $\text{Fe}(\text{OH})_{3(\text{aq})}$) redox couples for site conditions in the pH range 8 to 10 are also shown as dotted lines in red and blue respectively. Average activities used are as follows: Cr ($10^{-7.14}$), Mg ($10^{-2.599}$), HCO_3 ($10^{-2.117}$), Mn ($10^{-6.622}$), Fe ($10^{-6.77}$). The following minerals and aqueous species were suppressed: eskolite, Magnesiochromite, CrO_2 , CrO_4^{3-} , goethite, hematite, magnetite, Mg-ferrite, Fe-organic aqueous species, bixbyite, hausmannite, pyrolusite, manganite, gamma MnO_2 , todorokite and Mn-organic species because they are unlikely to be the solubility controlling phases under site conditions. The Geochemist's Workbench version 10 with the LLNL database (including additions of Cr species, see text) was used for these calculations.

Fig. 9. Chromium(VI) speciation for surface and spring water samples from the Putah Creek watershed: (a) fraction of different Cr(VI) species as a function of pH (vertically stacked symbols are from the same sampling location), (b) Cr(VI) concentration (nmol/L) as a function of pH, with drinking water limit (MCL: 10 µg/L, 192 nmol/L) and 95th percentile for surface waters (270 nmol/L) shown as dotted and dashed lines, respectively. The Geochemist's Workbench version 10 with the LLNL database (including our additions) was used for speciation calculations.

Fig. 10. Chromium(III) speciation for surface and spring water samples from the Putah Creek watershed: (a) fraction of different Cr(III) species as a function of pH (vertically stacked symbols are from the same sampling location), (b) Cr(III) concentration (nmol/L) as a function of pH, with dashed lines showing equilibrium solubility between $\text{Cr}(\text{OH})_{3(\text{am})}$ and $\text{Cr}(\text{OH})_{3(\text{aq})}$ and $\text{Cr}_{0.49}\text{Fe}_{0.51}(\text{OH})_{3(\text{am})}$. The Geochemist's Workbench version 10 with the LLNL database (including our additions) was used for speciation calculations.

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normalized flux as a function of runoff. Dotted lines show drinking water limits (MCL's: Cr(TOT)- 50 µg/L, 692 nmol/L, Cr(VI)- 10 µg/L, 192 nmol/L). Dashed lines on Cr(TOT) figures show equilibrium with Cr(OH)₃, while dashed lines on Cr(VI) figures show 330 nmol/L, the 95th percentile.

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Figure A1

Table 1. Surface water sampling locations where volumetric water discharge was measured, showing sub-basin characteristics in the upper Hunting Creek watershed, CA.

Sample ID	Latitude	Longitude	Elevation min (m)	Elevation max (m)	Relief (m)	Area (km ²)	Discharge (m ³ /hr)	Runoff (mm/yr)
MC11-53	38.8031	-122.3877	295.7	916.6	620.9	40.8	887.1	190
HC-05	38.8289	-122.3785	401.5	916.6	515.1	23.1	726.8	275
MC11-89	38.8062	-122.3583	374.6	601.0	226.4	4.2	17.0	35
MC11-90	38.8065	-122.3581	375.5	601.0	225.5	2.0	11.6	51
MC11-91	38.8075	-122.3580	377.9	589.3	211.4	1.2	8.6	64
MC11-87	38.8052	-122.3523	390.3	600.3	210.0	2.0	12.3	54
MC11-86	38.8035	-122.3490	406.5	600.3	193.8	1.8	7.3	36

Table 2. Dissolved weathering fluxes for seven sub-basins in the upper Hunting Creek watershed, California Coast Range.

Sample ID	Φ^a	Cation weathering flux ^b 10^6 mol/yr	Ca*+Mg* flux 10^6 mol/yr	Total weathering flux ^c 10^6 mol/yr	Bicarbonate flux 10^6 mol/yr
<i>Total fluxes</i>					
MC11-53	5.3	56.73	52.39	61.22	38.23
HC-05		31.44	28.34		
MC11-89	2.9	0.91	0.89	1.05	0.93
MC11-90	2.2	0.60	0.59	0.71	0.57
MC11-91	1.9	0.43	0.42	0.53	0.43
MC11-87	5.1	0.76	0.71	0.82	0.72
MC11-86	4.4	0.44	0.41	0.48	0.42
		10^6 mol/km ² /yr	10^6 mol/km ² /yr	10^6 mol/km ² /yr	10^6 mol/km ² /yr
<i>Area-normalized fluxes</i>					
MC11-53	5.3	1.39	1.28	1.50	0.94
HC-05		1.36	1.23		
MC11-89	2.9	0.22	0.21	0.25	0.22
MC11-90	2.2	0.30	0.30	0.36	0.29
MC11-91	1.9	0.36	0.36	0.44	0.36
MC11-87	5.1	0.38	0.36	0.41	0.36
MC11-86	4.4	0.25	0.23	0.27	0.23

^a Φ = (Ca+Mg+K+Na)/SiO₂ computed in units of mg/L

^bCation weathering flux = Ca*+Mg*+K*+Na*

^cTotal weathering flux = Ca*+Mg*+K*+Na*+SiO₂*

Table 3. Dissolved metal fluxes for seven sub-basins in the upper Hunting Creek watershed, California Coast Range.

Sample ID	Metal flux mol/yr	Cr(TOT)* flux mol/yr	Cr(VI) flux mol/yr	Cr(III) flux mol/yr	Cr(TOT)* /Metal flux %
<i>Total Fluxes</i>					
MC11-53	2696.75	1893.53	1146.66	746.88	70%
HC-05		367.31			
MC11-89		52.17	39.97	12.20	
MC11-90		33.04	17.36	15.68	
MC11-91	38.92	20.91	10.11	10.80	54%
MC11-87	44.06	41.34	23.56	17.78	94%
MC11-86	22.85	18.94	10.85	8.10	83%
	mol/km ² /yr	mol/km ² /yr	mol/km ² /yr	mol/km ² /yr	%
<i>Area normalized fluxes</i>					
MC11-53	66.04	46.37	28.08	18.29	70%
HC-05		15.89			
MC11-89		12.38	9.49	2.90	
MC11-90		16.67	8.76	7.91	
MC11-91	32.79	17.61	8.52	9.10	54%
MC11-87	22.17	20.80	11.85	8.94	94%
MC11-86	12.88	10.68	6.11	4.56	83%

^aMetal flux = Fe*+Mn*+Cr*

Table 4. List of 73 global rivers.

River	Country	Region	Area (10 ³ km ²)	Discharge (km ³ /yr)	Runoff (mm/yr)	Min Year	Max Year	n ^a	Citation for Area & Discharge
Acheloos	Greece	Europe	6.8	5.7	838.2	1998	1999	80	Milliman, 2011
Aliakmonas	Greece	Europe	9.5	3.1	326.3	1998	1999	80	Milliman, 2011
Alphios	Greece	Europe	3.7	1.7	459.5	1998	1999	40	Milliman, 2011
Amazon	Brazil	South America	6100	6469.2	1060.5	N.D.	N.D.	N.D.	Gaillardet, 2003
Apalachicola	USA	North America	44.289	20.1	454.6	1979	1991	50	GEMS
Arno	Italy	Europe	8.228	0.9	108.0	1997	1997	1	Cortecchi, 2009
Asopos	Greece	Europe	0.718	0.1	97.6	1998	1999	80	Vasilatos, 2008
Avon	England	Europe	1.65	0.6	344.3	1991	1996	79	GEMS
Axios	Greece	Europe	24	4.9	204.2	1998	1999	80	Milliman, 2011
Barito	Indonesia	Oceania	57	28.4	498.3	1979	1981	21	GEMS
Chao Phrya	Thailand	Asia	110.569	27.8	251.2	1978	1981	23	GEMS
Cimanuk	Indonesia	Asia	1.931	3.6	1846.7	1979	1981	41	GEMS
Citarum ^b	Indonesia	Oceania	1.718	1.9	1083.7	1979	1994	84	GEMS
Colorado	USA	North America	434.602	11.9	27.3	1979	1996	70	GEMS
Columbia ^b	USA	North America	622.636	168.8	271.2	1977	1997	59	GEMS
Congo	Congo, DR	Africa	3500	1233.9	352.5	N.D.	N.D.	N.D.	Gaillardet, 2003
Dee	England	Europe	1.75	0.9	541.0	1980	1996	71	GEMS
Deleware	USA	North America	17.56	10.6	603.8	1979	1991	51	GEMS
Doce	Brazil	South America	58.9	9.8	166.6	2000	2005	12	GEMS
Evros	Greece	Europe	55	6.8	123.6	1998	1999	80	Milliman, 2011
Evrotas	Greece	Europe	2.4	0.8	333.3	1998	1999	40	Milliman, 2011
Exe	England	Europe	0.601	0.5	840.1	1992	1996	79	GEMS
Hai He	China	Asia	263.631	14.5	55.2	1988	1997	93	GEMS
Han	Korea	Asia	23.166	9.2	396.4	1985	1992	154	GEMS
Hudson	USA	North America	20.953	12.4	590.4	1979	1991	43	GEMS

Ishikari	Japan	Asia	12.697	12.2	964.3	2009	2011	11	GEMS
Jequitinhonha	Brazil	South America	44	8.4	191.5	1997	2002	22	GEMS
Kelani	Sri Lanka	Asia	2.3	2.5	1097.6	2008	2008	96	GEMS
Keritis	Greece	Europe	0.16036	0.0	138.8	2004	2005	56	Papafilippaki, 2008
Kiso	Japan	Asia	4.956	11.9	2406.9	1979	2012	303	GEMS
Koksoak	Canada	North America	130	54.0	415.4	2009	2011	11	Milliman, 2011
Liao He	China	Asia	228.96	3.4	14.7	1988	1997	103	GEMS
Maas	Netherlands	Europe	29	7.9	272.0	1979	1995	395	GEMS
Mackenzie	Canada	North America	1680	284.0	169.1	N.D.	N.D.	N.D.	Gaillardet, 2003
Mersey	England	Europe	1.2	0.7	552.2	1990	1996	56	GEMS
Min Jiang	China	Asia	60.992	48.9	802.0	1988	1996	106	GEMS
Mississippi	USA	North America	2953.9	511.9	173.3	1979	1991	46	GEMS
Musi ^b	Indonesia	Oceania	46.1	50.5	1095.3	1979	1993	21	GEMS
Negro	Brazil	South America	279.95	507.1	1811.5	2003	2005	19	GEMS
Nestos	Greece	Europe	6.2	3.1	500.0	1998	1999	80	Milliman, 2011
Niger	Nigeria	Africa	141	28.6	203.0	N.D.	N.D.	N.D.	Gaillardet, 2003
Orinoco	Venezuela	South America	1100	1100.0	1000.0	2004	2006	84	Milliman, 2011
Ouse	England	Europe	8.9	2.0	224.7	2002	2002	2	Milliman, 2011
Oyapock	French Guiana	South America	25.52	26.5	1038.7	2004	2005	22	GEMS
Panuco	Mexico	North America	61.063	129.4	2118.9	1985	1985	3	GEMS
Parana	Argentina	South America	2275.126	469.6	206.4	2012	2012	3	GEMS
Pardo	Brazil	South America	6.1	0.3	51.7	1997	2002	20	GEMS
Pearl	China	Asia	350	212.9	608.1	1985	1992	95	GEMS
Pinios	Greece	Europe	11	3.2	290.9	1998	1999	80	Milliman, 2011
Po	Italy	Europe	74	46.0	621.6	1988	1990	70	Milliman, 2011
Potomac	USA	North America	29.97	9.7	322.2	1979	1994	56	GEMS
Qiantang	China	Asia	42.156	38.7	917.0	1988	1996	102	GEMS
Rhine	Germany	Europe	210	69.4	330.6	1979	1995	373	GEMS

Rio Grande	USA	North America	456.702	1.1	2.4	1979	1997	62	GEMS
Sacramento	USA	North America	60.87	21.2	348.9	1979	1996	56	GEMS
Sao Francisco	Brazil	South America	195	64.5	330.6	1997	2004	41	GEMS
Sarno	Italy	Europe	0.44	0.0	0.9	1997	1998	12	Arienzo, 2000
Scheldt	Belgium	Europe	4.85	1.2	242.3	2012	2012	11	GEMS
Seine	France	Europe	44	8.2	186.5	N.D.	N.D.	N.D.	Gaillardet, 2003
Shinano ^b	Japan	Asia	11.67	8.9	762.6	1979	2007	254	GEMS
St. Lawrence	USA	North America	773.89	216.4	279.6	1979	1991	51	GEMS
Strymonas	Greece	Europe	17	4.1	241.2	1998	1999	80	Milliman, 2011
Susquehanna	USA	North America	62.419	30.8	493.9	1979	1991	49	GEMS
Thames	England	Europe	9.95	2.5	247.4	1991	1996	66	GEMS
Tone	Japan	Asia	6.01	4.5	756.1	1979	2003	79	GEMS
Trent	England	Europe	7.49	2.6	345.5	1980	1996	356	GEMS
Tweed	Scotland	Europe	1.5	1.0	694.3	1990	1996	320	GEMS
Uruguay	Argentina	South America	62.058	48.6	782.6	1997	2013	141	GEMS
Yangtze	China	Asia	1488.036	710.0	477.2	1985	1992	96	GEMS
Yellow	China	Asia	751.494	46.5	61.9	1985	1991	77	GEMS
Yodo	Japan	Asia	7.28	9.3	1278.7	1979	1985	77	GEMS
Yoshino	Japan	Asia	3.215	1.7	539.9	1995	2012	128	GEMS
Yukon	Canada	North America	831.39	181.1	217.8	1979	1991	51	GEMS
<i>World Total</i>			79500	37288				5653	Dai and Ternberth 2003

N.D. indicates no data.

^aTotal number of samples

^bSee Table 6 for area, discharge and runoff for Cr(VI) measurements

Table 5. List of 60 global rivers with average values for dissolved Cr(TOT) concentration and Cr(TOT) flux.

River	Area ^a (10 ³ km ²)	Discharge ^a (km ³ /yr)	Runoff (mm/yr)	Cr(TOT) (nmol/L)	Cr(TOT) flux (10 ⁶ mol/yr)	Cr(TOT) flux (mol/km ² /yr)	Citation for concentration
Acheloos	6.8	5.7	838.2	22.20	0.127	18.61	Lekkas, 2004
Aliakmonas	9.5	3.1	326.3	231.49	0.718	75.54	Lekkas, 2004
Alphios	3.7	1.7	459.5	564.45	0.960	259.34	Lekkas, 2004
Amazon	6100.0	6469.2	1060.5	13.79	89.200	14.62	Gaillardet, 2003
Apalachicola	44.3	20.1	454.6	81.54	1.642	37.07	GEMS
Arno	8.2	0.9	108.0	167.31	0.149	18.08	Cortecchi, 2009
Asopos	0.7	0.1	97.6	110.99	0.008	10.84	Lekkas, 2004
Avon	1.7	0.6	344.3	36.51	0.021	12.57	GEMS
Axios	24.0	4.9	204.2	161.73	0.792	33.02	Lekkas, 2004
Citarum	1.7	1.9	1083.7	321.25	0.598	348.15	GEMS
Colorado	434.6	11.9	27.3	43.41	0.515	1.19	GEMS
Columbia	622.6	168.8	271.2	48.42	8.175	13.13	GEMS
Congo	3500.0	1233.9	352.5	9.63	11.888	3.40	Gaillardet, 2003
Dee	1.8	0.9	541.0	93.72	0.089	50.70	GEMS
Deleware	17.6	10.6	603.8	82.20	0.872	49.64	GEMS
Evros	55.0	6.8	123.6	214.05	1.456	26.46	Lekkas, 2004
Evrotas	2.4	0.8	333.3	72.93	0.058	24.31	Lekkas, 2004
Exe	0.6	0.5	840.1	20.69	0.010	17.38	GEMS
Han	23.2	9.2	396.4	204.58	1.879	81.10	GEMS
Hudson	21.0	12.4	590.4	92.13	1.140	54.39	GEMS
Ishikari	12.7	12.2	964.3	96.15	1.177	92.72	GEMS
Kelani	2.3	2.5	1097.6	742.99	1.876	815.53	GEMS
Keritis	0.2	0.0	138.8	44.25	0.001	6.14	Papafilippaki, 2008
Kiso	5.0	11.9	2406.9	19.23	0.229	46.29	GEMS
Koksoak	130.0	54.0	415.4	4.95	0.267	2.06	Environment Canada

Maas	29.0	7.9	272.0	30.37	0.240	8.26	GEMS
Mackenzie	1680.0	284.0	169.1	7.21	2.048	1.22	Gaillardet, 2003
Mersey	1.2	0.7	552.2	98.90	0.066	54.62	GEMS
Mississippi	2953.9	511.9	173.3	81.10	41.513	14.05	GEMS
Musi	46.1	50.5	1095.3	434.62	21.944	476.01	GEMS
Negro	280.0	507.1	1811.5	8.81	4.466	15.95	GEMS
Nestos	6.2	3.1	500.0	30.13	0.093	15.06	Lekkas, 2004
Niger	141.0	28.6	203.0	8.65	0.248	1.76	Gaillardet, 2003
Orinoco	1100.0	1100.0	1000.0	4.81	5.288	4.81	Mora, 2009
Ouse	8.9	2.0	224.7	7.82	0.016	1.76	Comber, 2003
Oyapock	25.5	26.5	1038.7	9.97	0.264	10.35	GEMS
Panuco	61.1	129.4	2118.9	1923.08	248.814	4074.71	GEMS
Parana	2275.1	469.6	206.4	50.00	23.482	10.32	Frei, 2014
Pearl	350.0	212.9	608.1	64.60	13.750	39.29	GEMS
Pinios	11.0	3.2	290.9	762.64	2.440	221.86	Lekkas, 2004
Po	74.0	46.0	621.6	21.15	0.973	13.15	Pettine 1994
Potomac	30.0	9.7	322.2	92.03	0.889	29.65	GEMS
Rhine	210.0	69.4	330.6	35.30	2.451	11.67	GEMS
Rio Grande	456.7	1.1	2.4	44.04	0.049	0.11	GEMS
Sacramento	60.9	21.2	348.9	30.91	0.656	10.78	GEMS
Sarno	0.4	0.0	0.9	576.92	0.000	0.51	Arienzo, 2000
Scheldt	4.9	1.2	242.3	19.23	0.023	4.66	GEMS
Seine	44.0	8.2	186.5	220.38	1.808	41.10	Gaillardet, 2003
Shinano	11.7	8.9	762.6	38.46	0.342	29.33	GEMS
St. Lawrence	773.9	216.4	279.6	73.53	15.908	20.56	GEMS
Strymonas	17.0	4.1	241.2	63.42	0.260	15.30	Lekkas, 2004
Susquehanna	62.4	30.8	493.9	90.27	2.783	44.59	GEMS
Thames	10.0	2.5	247.4	100.82	0.248	24.94	GEMS

Tone	6.0	4.5	756.1	96.15	0.437	72.70	GEMS
Trent	7.5	2.6	345.5	141.31	0.366	48.82	GEMS
Tweed	1.5	1.0	694.3	19.41	0.020	13.48	GEMS
Yangtze	1488.0	710.0	477.2	76.92	54.618	36.70	GEMS
Yellow	751.5	46.5	61.9	76.92	3.578	4.76	GEMS
Yoshino	3.2	1.7	539.9	96.15	0.167	51.91	GEMS
Yukon	831.4	181.1	217.8	52.04	9.422	11.33	GEMS
<i>World</i>	<i>79500^b</i>	<i>37288^b</i>		<i>149.8^c</i>	<i>1716^d</i>	<i>21.59^e</i>	<i>This study</i>

^aSee Table 4 for citations for area and discharge

^bWorld area and discharge from Dai and Ternberth (2003)

^cWorld average Cr(TOT) concentration from this study

^dGlobal Cr(TOT) flux = sum of Cr(TOT) flux / fraction of world discharge

^eGlobal area normalized Cr(TOT) flux = Global Cr(TOT) flux / world area

Table 6. List of 24 global rivers with average values for dissolved Cr(VI) concentration and Cr(VI) flux.

River	Area ^a (10 ³ km ²)	Discharge ^a (km ³ /yr)	Runoff (mm/yr)	Cr(VI) (nmol/L)	Cr(VI) flux (10 ⁶ mol/yr)	Cr(VI) flux (mol/km ² /yr)	Citation for concentration
Barito	57.0	28.4	498.3	326.92	9.285	162.90	GEMS
Chao Phrya	110.6	27.8	251.2	199.00	5.526	49.98	GEMS
Cimanuk	1.9	3.6	1846.7	326.92	1.166	603.72	GEMS
Citarum	6.0	13.8	2304.7	326.92	4.498	753.45	GEMS
Columbia	670.0	240.0	358.2	3.07	0.738	1.10	Cranston, 1980
Doce	58.9	9.8	166.6	192.31	1.887	32.04	GEMS
Hai He	263.6	14.5	55.2	222.75	3.240	12.29	GEMS
Jequitinhonha	44.0	8.4	191.5	244.76	2.062	46.87	GEMS
Kiso	5.0	11.9	2406.9	384.62	4.588	925.72	GEMS
Liao He	229.0	3.4	14.7	263.26	0.889	3.88	GEMS
Min Jiang	61.0	48.9	802.0	76.74	3.754	61.54	GEMS
Musi	46.1	15.8	342.3	326.92	5.158	111.89	GEMS
Ouse	8.9	2.0	224.7	3.53	0.007	0.79	Comber, 2003
Pardo	6.1	0.3	51.7	269.23	0.085	13.93	GEMS
Pearl	350.0	212.9	608.1	76.92	16.373	46.78	GEMS
Po	74.0	46.0	621.6	18.27	0.840	11.36	Pettine, 1994
Qiantang	42.2	38.7	917.0	76.92	2.974	70.54	GEMS
Sao Francisco	195.0	64.5	330.6	201.69	13.003	66.68	GEMS
Shinano	11.2	6.1	545.9	195.73	1.192	106.86	GEMS
Tone	6.0	4.5	756.1	65.38	0.297	49.44	GEMS
Uruguay	62.1	48.6	782.6	52.92	2.570	41.41	GEMS
Yangtze	1488.0	710.0	477.2	76.92	54.618	36.70	GEMS
Yellow	751.5	46.5	61.9	79.73	3.709	4.93	GEMS
Yodo	7.3	9.3	1278.7	192.31	1.790	245.91	GEMS

<i>World</i>	<i>79500^b</i>	<i>37288^b</i>	<i>175.16^c</i>	<i>3506^d</i>	<i>44.10^e</i>	<i>This study</i>
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^aSee Table 4 for citations for area and discharge

^bWorld area and discharge from Dai and Ternberth (2003)

^cWorld average Cr(VI) concentration from this study

^dGlobal Cr(VI) flux = sum of Cr(VI) flux / fraction of world discharge

^eGlobal area normalized Cr(VI) flux = Global Cr(VI) flux / world area

Table A.2. Average bedrock chemical composition for major rocks types in Putah Creek watershed.

Rock Type	n ^a	Al %	Ba mg/kg	Ca %	Cr mg/kg	Fe mg/kg	K %	Mg %	Mn mg/kg	Na %	Ni mg/kg	Rb mg/kg	Si %	Sr mg/kg	Ti mg/kg	Φ ^b	Citation
Serpentine	7	2.66	6.83	0.93	1924	5.8	0.01	24.68	675	0.56	1899	0.5	20.23	15.97	405	1.476	this study
Great Valley	36	8.11	570	1.29	170.3	5.05	1.22	1.87	331	1.85	73	37	29.7	200	4100	0.198	Goldhaber, 2009

^aNumber of samples^bΦ = molar phi ratio = (Ca+K+Mg+Na / Si).

Table A.3. Pearson's correlation coefficients for surface water samples.

	pH	alk	Cr(VI)	Cr(III)	Cl	NO ₃	SO ₄	PO ₄	Ba	Ca	Fe	K	Mg	Mn	Na	Rb	Si	Sr	Al	Cr(TOT)	Co	Ni	Cu	Pb	U
pH	1.00																								
alkalinity	0.14	1																							
Cr(VI)	0.18	0.80	1																						
Cr(III)	0.06	0.73	0.71	1																					
Cl	0.52	0.58	0.46	0.22	1																				
NO ₃	0.20	0.62	0.70	0.52	0.25	1																			
SO ₄	0.17	-0.09	-0.31	-0.40	0.44	-0.46	1																		
PO ₄	0.10	0.65	0.66	0.55	0.19	0.91	-0.51	1																	
Ba	-0.07	-0.67	-0.68	-0.64	-0.28	-0.29	0.24	-0.40	1																
Ca	-0.07	-0.57	-0.77	-0.60	-0.24	-0.57	0.47	-0.64	0.77	1															
Fe	-0.66	-0.19	-0.21	-0.20	-0.15	-0.11	0.13	-0.14	0.19	0.07	1														
K	0.20	-0.65	-0.53	-0.73	0.10	-0.59	0.49	-0.68	0.49	0.48	0.05	1													
Mg	0.16	0.97	0.76	0.75	0.58	0.48	-0.04	0.51	-0.71	-0.55	-0.20	-0.61	1												
Mn	-0.65	-0.22	-0.27	-0.28	-0.14	-0.21	0.17	-0.23	0.22	0.15	0.98	0.14	-0.20	1											
Na	0.33	-0.24	-0.41	-0.48	0.51	-0.45	0.67	-0.54	0.46	0.59	0.04	0.74	-0.19	0.15	1										
Rb	-0.08	0.74	0.50	0.32	0.45	0.63	-0.12	0.68	-0.32	-0.37	0.11	-0.38	0.64	0.12	-0.07	1									
Si	-0.33	0.31	0.07	0.18	-0.30	0.23	-0.23	0.42	-0.40	-0.40	0.07	-0.61	0.27	0.03	-0.64	0.32	1								
Sr	-0.18	-0.46	-0.74	-0.53	-0.28	-0.56	0.47	-0.58	0.63	0.96	0.07	0.35	-0.45	0.15	0.49	-0.27	-0.20	1							
Al	0.24	-0.70	-0.61	-0.74	-0.07	-0.40	0.34	-0.47	0.48	0.50	0.03	0.77	-0.74	0.06	0.53	-0.46	-0.43	0.40	1						
Cr(TOT)	0.14	0.83	0.95	0.89	0.39	0.68	-0.38	0.67	-0.72	-0.75	-0.22	-0.66	0.82	-0.30	-0.48	0.46	0.12	-0.71	-0.71	1					
Co	-0.45	-0.01	-0.01	-0.13	0.16	0.14	0.03	0.08	0.15	-0.06	0.87	-0.01	-0.05	0.86	0.14	0.34	-0.04	-0.11	-0.03	-0.06	1				
Ni	-0.70	-0.34	-0.37	-0.27	-0.25	-0.36	0.16	-0.30	0.22	0.25	0.86	0.08	-0.31	0.88	0.06	-0.06	0.03	0.26	0.02	-0.35	0.74	1			
Cu	0.00	-0.56	-0.58	-0.37	-0.31	-0.43	0.28	-0.44	0.52	0.68	-0.09	0.22	-0.55	-0.10	0.14	-0.58	-0.27	0.59	0.36	-0.53	-0.20	0.20	1		
Pb	-0.17	0.28	0.12	0.26	-0.08	0.16	-0.19	0.51	-0.45	-0.38	-0.03	-0.46	0.23	-0.08	-0.42	0.33	0.63	-0.22	-0.31	0.19	-0.07	0.06	-0.20	1	
U	-0.28	-0.67	-0.67	-0.56	-0.28	-0.61	0.37	-0.66	0.59	0.76	0.45	0.45	-0.62	0.52	0.42	-0.45	-0.42	0.69	0.43	-0.67	0.33	0.71	0.65	-0.35	1

Table A.4. Pearson's correlation coefficients for spring water samples.

	pH	alk	Cr(VI)	Cr(III)	Cl	NO ₃	SO ₄	PO ₄	Ba	Ca	Fe	K	Mg	Mn	Na	Rb	Sr	Al	Cr(TOT)	Ni	Cu	Pb
pH	1																					
alkalinity	0.18	1																				
Cr(VI)	0.93	0.37	1																			
Cr(III)	-0.08	0.88	0.18	1																		
Cl	0.49	-0.13	0.46	-0.25	1																	
NO ₃	-0.42	0.43	-0.46	0.51	-0.32	1																
SO ₄	0.79	-0.24	0.77	-0.25	0.34	-0.67	1															
PO ₄	-0.53	-0.15	-0.70	-0.27	0.07	0.52	-0.79	1														
Ba	0.17	-0.11	-0.14	-0.23	0.15	0.57	-0.09	0.50	1													
Ca	-0.45	-0.18	-0.62	0.00	-0.08	0.78	-0.46	0.60	0.74	1												
Fe	-0.92	-0.26	-0.89	-0.10	-0.63	0.21	-0.72	0.47	-0.27	0.21	1											
K	0.56	-0.38	0.62	-0.31	0.51	-0.83	0.88	-0.70	-0.36	-0.51	-0.54	1										
Mg	0.61	0.41	0.76	0.13	0.26	-0.61	0.40	-0.50	-0.55	-0.93	-0.43	0.40	1									
Mn	-0.48	-0.26	-0.55	-0.43	-0.42	-0.13	-0.51	0.49	-0.20	-0.17	0.75	-0.43	0.03	1								
Na	0.29	-0.38	0.16	-0.44	0.92	-0.14	0.21	0.31	0.42	0.26	-0.47	0.37	-0.12	-0.34	1							
Rb	-0.14	-0.56	-0.37	-0.76	0.44	-0.10	-0.27	0.76	0.38	0.24	0.19	-0.12	-0.20	0.49	0.63	1						
Sr	-0.02	0.29	-0.15	0.18	0.37	0.73	-0.44	0.66	0.76	0.69	-0.23	-0.52	-0.39	-0.27	0.51	0.35	1					
Al	-0.53	-0.66	-0.67	-0.45	-0.65	0.01	-0.11	0.11	0.07	0.32	0.66	-0.14	-0.61	0.44	-0.36	0.09	-0.40	1				
Cr(TOT)	0.74	0.68	0.91	0.57	0.28	-0.17	0.53	-0.69	-0.21	-0.52	-0.78	0.39	0.69	-0.64	-0.06	-0.63	-0.05	-0.75	1			
Ni	-0.42	-0.30	-0.60	-0.50	-0.41	0.07	-0.54	0.64	0.14	0.07	0.67	-0.56	-0.15	0.94	-0.24	0.59	-0.04	0.50	-0.71	1		
Cu	-0.26	0.09	-0.24	0.45	-0.10	0.66	-0.11	0.00	0.39	0.75	-0.06	-0.16	-0.71	-0.66	0.08	-0.38	0.43	0.12	-0.01	-0.52	1	
Pb	-0.24	-0.56	-0.45	-0.76	0.31	-0.10	-0.35	0.78	0.30	0.20	0.33	-0.20	-0.19	0.63	0.50	0.99	0.26	0.18	-0.70	0.71	-0.44	1