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Speciation of dissolved chromium and the mechanisms controlling its concentration in natural water

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ABSTRACT

The circulation of chromium at naturally occurring concentration levels (i.e., 1 μg dm^{-3} or lower) was examined using solid-phase spectrophotometry and inductively coupled plasma-mass spectrophotometry (ICP-MS) to determine the Cr(VI) and Cr(Total) concentrations, respectively. Natural water and stream sediments were collected from areas with various types of geologic features, such as metamorphic rocks, volcanic rocks and limestone in Japan and Indonesia. Cr(VI) was predominant in weakly alkaline natural waters, and the Cr(III) concentration was less than 1 μg dm^{-3}, which was considerably lower than that expected based on the solubility of $Cr(OH)_3$. The dissolution of chromium in natural water was described by the leaching of Cr(VI) from Cr(III)-containing minerals under oxic conditions. The Cr(VI) concentration in a solution that was in contact with chromite, $FeCr_2O_4$, linearly increased with the reaction time. The results indicated that under oxic conditions at $P_{O2} = 0.21$ atm, the leaching rate of Cr(VI) was pseudo zero-order at a fixed pH and was higher in alkaline than in acidic solutions. The removal of Cr from natural waters was due to the reduction of Cr(VI) to Cr(III) by organic matter, such as humic substances, as well as to the adsorption of Cr(III) onto suspended matter and river sediments. The reduction of Cr(VI) to Cr(III) followed the equation $-d[Cr(VI)]/dt = [H^+]^a[Cr(VI)][DOC]$ with $a = 0$ at pH < 4 and $a = -1$ at pH > 4.5. The removal of Cr(III) by river sediments and/or suspended particulate matter was rapid and the adsorbability of Cr(III) was dependent on pH, which suggests that the active species were $Cr(OH)_2^+$ and $Cr(OH)_3$. Schematic models of the circulation of dissolved chromium in natural water were proposed under acidic and alkaline conditions.

1. Introduction

Among the trace chemical components present in natural water, chromium is one of the most important heavy metal ions and has attracted considerable attention because hydrological circulation processes strongly depend on its physicochemical forms. Chromium enters the environment from both natural and anthropogenic sources. Chromium dissolved in natural waters is primarily present in two oxidation states, (i.e., Cr(III) and Cr(VI)). Both species possess significantly different physicochemical properties as well as chemical and biochemical reactivities. Cr(III) is well known to be an essential trace element for humans for the maintenance of normal glucose, cholesterol and fatty acid metabolism. However, water-soluble Cr(VI) is highly toxic to both humans and animals (Kota's and Stasicka, 2000) and other studies have indicated that it is an extremely toxic carcinogen (Zayed and Terry, 2003).

Among the dominant species of chromium, the trivalent form widely occurs in nature in chromite ore or silicate minerals and is extremely immobile. The most common chromic ore is ferrous chromite, $FeCr_2O_4$, which is one of the natural sources. The higher oxidation state, Cr(VI), is rarely found in primary minerals (Godgul and Sahu, 1990). The rock–water interaction and hydrochemical conditions allow the release of chromium into the aqueous systems. The rate of oxidation at room temperature is very low, which enables Cr(III) to be involved in faster concurrent reactions (sorption or precipitation). The oxidation of Cr(III) by oxygen is unlikely in soils (Richard and Bourg, 1991).

Although it has been proposed that Cr(VI) is thermodynamically stable in well-oxygenated water, the interconversion between Cr(III) and Cr(VI) typically occurs in natural water (Rai et al., 1989). These processes depend on the pH, oxygen concentration, presence of appropriate reductants and mediators functioning as ligands or catalysts. It has been

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reported that Cr(VI) in fresh water may be reduced at a considerable rate by organic matter, such as tannic acids, some humic substances (even in the neutral pH region) (Osaki et al., 1980), fulvic acid (Eckert et al., 1990; Wittbrodt and Palmer, 1995; Agrawal et al., 2009), Fe^{2+} (Sedlak and Chan, 1997) and sulphide species (Smillie et al., 1981; Naghmush et al., 1994). Based on the capabilities of Fe(II) to readily reduce Cr(VI) to Cr(III) in groundwater systems (Sedlak and Chan, 1997), the dissolved concentrations of Fe(II) and Cr(VI) should be correlated.

Cr(III) is rapidly oxidised by a large excess of MnO_2 and slowly oxidised by dissolved oxygen under natural water conditions (Osaki et al., 1980). In general, anionic Cr(VI) species are the most mobile form of dissolved chromium in groundwater at a neutral to basic pH and in oxygen-rich environments (Johnson, 1990; Ball and Izbicki, 2004). Cr(VI) is the predominant species in groundwater from the area near chromite mines located in the state of Orissa, India (Krisna et al., 2004) as well as in local ophiolite and ultramafite areas from the La Spezia Province in Italy (Fantoni et al., 2002). Cr(VI) was also predominant in the surface waters collected from the volcanic sedimentary basin in Sao Paulo, Brazil (Bourette et al., 2009). Naturally occurring Cr(VI) has also been detected in the Aromas Red Sands aquifer, California, USA, with little or no dissolved iron (Gonzalez et al., 2005), as well as in the Columbia River under oxic conditions (Cranston and Murray, 1978). The chromium concentration is sensitive to the aquifer pH and oxygen conditions (Richard and Bourg, 1991), and natural waters predominantly containing Cr(VI) in all of the studied areas are neutral or weakly alkaline under oxic conditions.

As shown in Table 1, the speciation of dissolved Cr, especially at contaminated levels, is complex and depends on various chemical conditions as well as the geology of the aquifer. While the general perception is that Cr(VI) is more likely to be present under near natural pH conditions, there is still disagreement. One of the reasons for this discrepancy may be due to the low quality of the speciation methods used. For example, the detection limits are not low enough to cover the naturally occurring levels of chromium in natural water (i.e., $\mu g\ dm^{-3}$ or lower). The solid-phase spectrophotometry (SPS) method, with its simplicity of operation, high sensitivity, and low detection limit, is based on the direct measurement of the degree of light absorption by a cation-exchange resin that has sorbed a reaction product of Cr(VI) and diphenylcarbazide and would be an effective tool for the speciation analysis of Cr dissolved in natural waters (Yoshimura et al., 1976; Yoshimura and Ohashi, 1978). In contrast to other previous methods, the SPS method allows for the determination of trace components in natural water samples without preconcentration steps that may result in Cr oxidation state transformations (Yoshimura et al., 1976; Yoshimura and Waki, 1985).

The aim of this study was to elucidate the concentration regulation mechanism of Cr(III) and Cr(VI) dissolved in uncontaminated natural waters and to clarify the circulation of chromium at naturally occurring concentration levels, (i.e., 1 $\mu g\ dm^{-3}$ or lower), using an improved SPS method (Saputro et al., 2009). The addition mechanism of chromium into natural water was investigated from the dissolution of Cr(III)-bearing minerals, such as chromite in serpentinite, under oxic conditions. The removal of Cr from natural water was described using the reduction reaction data of Cr(VI) to Cr(III) and the adsorption of Cr(III) onto river sediments and/or organic matter.

2. Materials and methods

2.1. Reagents

All of the reagents used were of analytical grade. Highly purified water prepared by a Milli-Q SP system (Millipore, Milford, MA, USA) was used throughout the study. A standard Cr(VI) solution (1000 $mg\ dm^{-3}$) for atomic absorption spectrometry (Kishida, Osaka, Japan) was used. A standard Cr(III) solution (100 $mg\ dm^{-3}$) was prepared by dissolving $KCr(SO_4)_2 \cdot 12H_2O$ in solution, and the concentration was determined by atomic absorption spectrometry. A sulphuric acid solution (approximately 0.5 $mol\ dm^{-3}$) was prepared by diluting 6.8 cm^3 of concentrated sulphuric acid with water to 250 cm^3. A colouring reagent solution was prepared by dissolving 0.25 g of DPC (diphenylcarbazide, Wako, Osaka, Japan) and diluting to 100 cm^3 with acetone. A Muromac 50 W-X2 cation exchanger (100–200 mesh, Muromachi, Tokyo, Japan) was used. The pH of the solution was adjusted to 4, 5 or 6 with an acetate buffer and to 8, 9 or 10 with an ammonia buffer until the final concentration was 0.01 $mol\ dm^{-3}$.

2.2. Apparatus

Absorbance measurements for Cr(VI) were performed using a double-beam UV–visible spectrophotometer (Model V-630, Jasco, Tokyo, Japan). A flow cell (FLM 220B-B-1.5) was supplied from GL Science (Tokyo, Japan). The flow cell was black-sided, 10 mm in length and 1.5 mm in diameter. At the outlet of the cell, a

Table 1
Summarised data for chromium speciation from some different geological sites.

Sample	Geologic or other conditions	Cr(VI)/$\mu g\ dm^{-3}$	Cr(III)/$\mu g\ dm^{-3}$	Method	Ref
Groundwater	Ophiolite	5–73	<1	ICP-OES[a]	[1]
Groundwater (pH 8.4)	Chromite	184 ± 9	12 ± 3	ICP-MS[b]	[2]
Groundwater	Sandstone	15	4	GF-AAS[c]	[3]
		5.7	0.2		
		29	3		
Shallow well (pH 5.8)	Volcanic rock	2 ± 3	4 ± 3	AAS[d]	[4]
Intermediate well (pH 6.6)	Volcanic rock	13 ± 8	0	AAS[d]	[4]
Deep well (pH 7.4)	Volcanic rock	44 ± 42	70 ± 45	AAS[d]	[4]
River water	Oxic	0.17 ± 0.03	0.01 ± 0.01	AAS[e]	[5]
Estuarine water	Oxic	0.12 ± 0.04	0.02 ± 0.02	AAS[e]	[5]
Estuarine water	Anoxic	0.01 ± 0.01	0.04 ± 0.01	GF-AAS[e]	[5]
Lake water	–	0.14	<0.02	GF-AAS[f]	[6]
Natural water	–	0.50 ± 0.23	1.36 ± 0.16	FL-AAS[g]	[7]

[1] Fantoni et al. (2002); [2] Krisna et al. (2004); [3] Gonzalez et al. (2005); [4] Bourette et al. (2009); [5] Cranston and Murray (1978); [6] Johnson (1990); [7] Naghmush et al. (1994).

[a] Cr(III) by ICP-OES after preconcentration with cation-exchange resin. Cr(VI) analysed using the DPC method.

[b] Total Cr by ICP MS, Cr(VI) by the DPC method.

[c] Cr(VI) was separated from Cr(III) using a liquid membrane extraction.

[d] Total Cr by AAS, Cr(VI) by the DPC method.

[e] Both Cr(III) and Cr(VI) are quantitatively co-precipitated by adjusting the Fe(II) ammonium sulphate to pH 8.

[f] Cr(III) was separated and concentrated using a cation exchanger column at pH 2.0–2.5, Cr(VI) was separated and concentrated with an anion exchanger at pH 3.5–4.5.

[g] Cr(VI) was concentrated using a cellulose sorbent with quaternary amine groups, and Cr(III) was separated using phosphonic acid exchange groups.