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

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## ARTICLE INFO

## 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$_2$O$_4$, 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.

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## 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$_2$O$_4$, 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

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., µg $dm^{-3}$ 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 µg $dm^{-3}$ 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)/µg $dm^{-3}$ | Cr(III)/µg $dm^{-3}$ | 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.

polytetrafluoroethylene (PTFE) tube (1 mm i.d.) was connected to a silicone tube. Inside the end of the tube, a polypropylene (PP) filter tip was placed to block the ion-exchanger beads and to pack them into the light-path portion (Saputro et al., 2009).

The ion exchanger was measured with an ion-exchanger aliquoting device. A PTFE tube (1.0 mm i.d. and 7 cm long) was fitted on one side with a PP resin filter tip and connected to a 10 cm³ disposable syringe (Hase and Yoshimura, 1993).

### 2.3. Study areas

Different bed rock geologies in Fukuoka, Japan, were selected for investigating the chromium behaviour in natural waters. Natural water samples (from FEF-1, downstream, to FEF-7, upstream) were systematically collected from a surface stream in the Fukuoka Experimental Forest (FEF), Kyushu University, in a mountainous watershed of Japanese cypress near Hisayama, which is approximately 15 km east of Fukuoka City in western Japan (Fig. 1). The predominant forest soil is yellow-brown, and the underlying bedrock primarily consists of serpentinite, crystalline schist and ultrabasic rocks associated with chlorite and small amounts of chromite (Ide et al., 2007). Water samples FEF-8 and FEF-9 were collected from a surface stream near the Fukuoka Experimental Forest with different geologic features, such as Cretaceous granites and Tertiary coal-bearing sedimentary rocks. The MRY-1, MRY-2 and MRY-3 water samples were collected from Mt. Ryuo, and the CKH-1, CKH-2 and CKH-3 water samples were collected from Chikuho Town, Fukuoka, where the underlying bedrock consists of ultrabasic rocks with minable chromite deposits. Four water samples (i.e., KWC-1, KWC-2, KWC-3 and HSY) were collected from abandoned manganese mines in Kawachi and Hisayama, Fukuoka. The geology of the former is crystalline schist and granitic rocks whereas that of the latter is schist

and Tertiary sedimentary rocks. Samples SFR-1, SFR-2 and SFR-3 were collected in a granite region upstream from the Muromi River, on the mountainside of Mt. Sefuri, Fukuoka. The HR water samples were collected from two karst springs on the Hirao-dai Plateau, Kitakyushu, Fukuoka, whereas the AK samples were collected from five karst springs on the Akiyoshi-dai Plateau, Yamaguchi. Both karst regions are composed of Carboniferous to Permian rock rather than pure limestone, accretionary siliceous and/or clastic sedimentary rock and Mesozoic granitic rock. Deposits of copper, iron and tungsten are embedded around the contact between the limestone and intrusive rock.

Some regions located around the most active volcano in Indonesia, Mt. Merapi, on Java Island, were also selected for investigation of chromium behaviour in natural waters. Water samples were collected from the Central Java Province, Indonesia. Tlatar (Tl) and Ngabean (Ng) are natural groundwaters that continuously flow and are located approximately 7 and 10 km from Boyolali, Central Java (near the Mt. Merapi volcano), respectively. Tawangmangu (Tw) is a natural waterfall that is at 1100 m in altitude, covered with forest, and located 30 km from Surakarta, Central Java (Fig. 2). The underlying bedrock consists of volcanic rocks with lava and andesite breccias (Wati et al., 2010).

The water samples were filtered through a 0.20 μm membrane filter at the sampling site and stored without being acidified in a polyethylene (PE) bottle for Cr(VI) determination. For the total chromium determination, the sample was stored in a PTFE bottle, and 1 cm³ of highly purified nitric acid (Kishida, Osaka, Japan) was added to a 100 cm³ sample to avoid the adsorption of Cr(III) to the container wall. The pH and temperature of the water samples were measured using a pH meter (HM-14P, TOA DKK) at the sampling point, and the dissolved organic carbon (DOC) content was measured with a TOC apparatus (TOC-V$_E$, Shimadzu).

A sample containing antigorite, which is a serpentine mineral, was collected from the FEF to measure the leaching rate of Cr(VI) into water under various pH conditions. The mineral contained a small amount of chromite as one of the common sources of chromium in nature.

The river sediments (i.e., FEF-1 to FEF-7) were collected from the Fukuoka Experimental Forest (FEF), and samples Ng-2 (downstream of Ng-1) and Ng-3 (downstream of Ng-2) were collected from Ngabean-Pengging, Central Java.
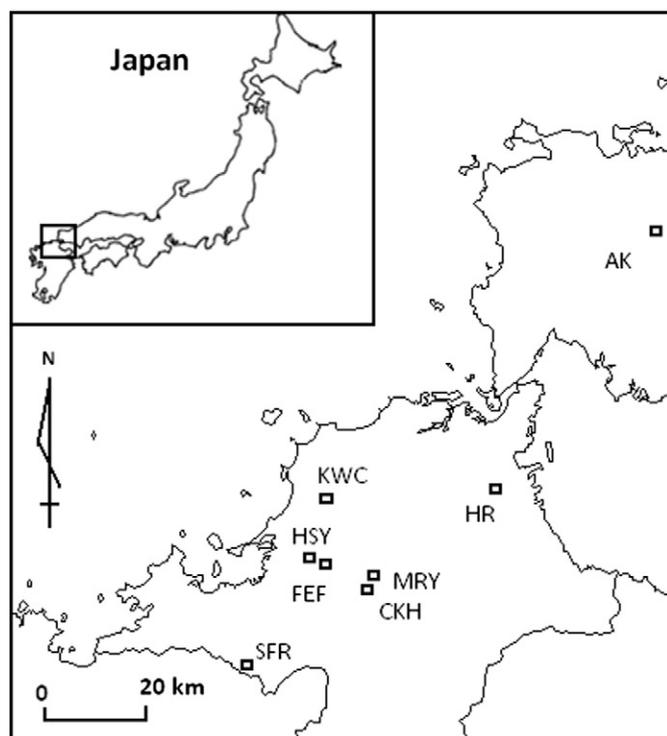


**Fig. 1.** Sampling sites of natural water, river sediments and rock in Fukuoka and Yamaguchi Prefectures, southwestern Japan. The latitude and longitude are 33.6°N and 130.5°E, respectively.
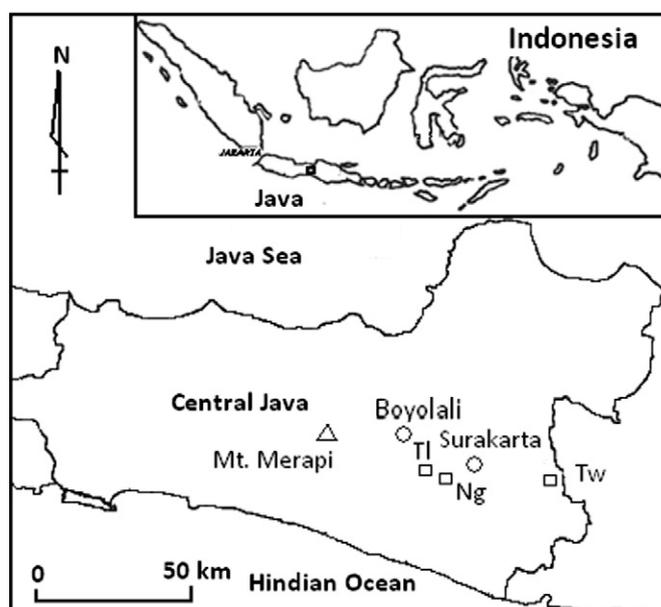


**Fig. 2.** Sampling sites of natural water and river sediments in Central Java, Indonesia. The latitude and longitude are 7.5°S and 110°E, respectively.

## 2.4. Determination of Cr(VI) using solid-phase spectrophotometry

A 20 $cm^3$ water sample was mixed with 1.0 $cm^3$ of the 2000 mg $dm^{-3}$ $Ca^{2+}$ solution, 1.0 $cm^3$ of the $H_2SO_4$ solution, 0.5 $cm^3$ of the colouring agent solution, and 0.06 $cm^3$ of the ion exchanger taken by the aliquoting device in a beaker. The mixture was stirred for 20 min at 20 °C. After allowing the ion exchanger to settle, the supernatant solution was removed, and approximately 1 $cm^3$ of the ion exchanger was transferred to a disposable PE syringe (SS-10S2, Terumo, Tokyo) that was connected to the flow cell. The absorbance was directly measured at 540 nm (absorption maximum wavelength) and 700 nm (non-absorption wavelength), and the difference between the two absorbances was used for Cr(VI) analyses. After the absorbance measurements, the ion-exchanger beads were removed from the cell prior to the subsequent measurement.

## 2.5. Analytical method for total chromium

The rock and sediment samples were decomposed using the method described below. A 0.10 g sediment sample was fused with 1 g of $Na_2CO_3$ in a platinum crucible by heating for 1 h to achieve a melted condition. After cooling, the sample was dissolved in 2 $cm^3$ of concentrated HCl and diluted to 100 $cm^3$ with water. The aliquots of the diluted solution were subjected to Cr determination by atomic absorption spectroscopy using a Shimadzu apparatus, Model AA-6300, in the presence of 1000 mg $dm^{-3}$ of La, 500 mg $dm^{-3}$ of Cs, and 0.1 mol $dm^{-3}$ of HCl.

For the total Cr determination in natural waters, an ICP-MS, Agilent Model 7500cx (Yokogawa, Japan), and an SPS using a double-beam UV–visible spectrophotometer (Model V-630, Jasco, Tokyo, Japan) after on-line electrochemical oxidation were used (Matsuoka et al., 1999). The Cr(VI) concentrations were analysed using the SPS method and the Cr(III) concentrations were determined from the difference between the values of total chromium analysed by ICP-MS and the Cr(VI) concentrations.

## 2.6. Leaching rate of Cr(VI) from serpentine to water

The serpentine samples (0.10 g), which were crushed into powders using an agate mortar, were added to 20 $cm^3$ of water and shaken for 6 h, 12 h, 1 day and 2 days. Prior to shaking, the pH values of the samples were adjusted to 8, 9 or 10 using an ammonia–ammonium chloride buffer solution (final concentration was 0.01 mol $dm^{-3}$) and to 4, 5 or 6 using an acetic acid-sodium acetate buffer solution for those containing $Na^+$ (5.7 mg $dm^{-3}$), $K^+$ (0.40 mg $dm^{-3}$), $Ca^{2+}$ (6 mg $dm^{-3}$) and $Mg^{2+}$ (53 mg $dm^{-3}$). After filtering the shaken solution through a 0.20 μm membrane filter, the Cr(VI) concentrations were determined using the improved SPS batch method (Saputro et al., 2009).

## 2.7. Cr(III) adsorption onto the sediments

The pH of the solution containing 5.0 μg $dm^{-3}$ Cr(III) and 0.01 mol $dm^{-3}$ ammonium acetate was adjusted to 5, 6, 8 or 9

**Table 2**
Analytical data for Cr(VI) obtained by SPS and Cr(III) obtained by ICP-MS in natural water samples.

| Sampling site | Date | pH | Water temp./°C | DOC/mg $dm^{-3}$ | Cr(VI)/μg $dm^{-3}$ | Cr(III)/μg $dm^{-3}$ |
|---|---|---|---|---|---|---|
| Metamorphic rock area | | | | | | |
| FEF-1 | Oct/10/08 | 8.04 | 19.6 | 1.58 | 0.61 ± 0.02[a] | 0.03[b] |
| FEF-2 | Oct/10/08 | 8.15 | 19.5 | 1.82 | 1.25 ± 0.03 | 0.04 |
| FEF-3 | Oct/10/08 | 8.24 | 19.4 | 1.67 | 1.98 ± 0.06 | 0.50 |
| FEF-4 | Oct/10/08 | 8.06 | 18.6 | 1.43 | 2.04 ± 0.02 | 0.53 |
| FEF-5 | Oct/10/08 | 8.22 | 18.8 | 1.52 | 3.60 ± 0.17 | 0.71 |
| FEF-6 | Oct/10/08 | 7.69 | 18.1 | 0.77 | 4.72 ± 0.18 | 1.19 |
| FEF-7 | Oct/10/08 | 7.86 | 18.6 | 1.12 | 3.19 ± 0.04 | 0.58 |
| FEF-8 | Oct/10/08 | 7.84 | 18.3 | 1.16 | 0.91 ± 0.01 | 0.05 |
| FEF-9 | Oct/18/08 | n.d. | n.d. | 1.87 | 0.20 ± 0.01 | 0.04 |
| MRY-1 | Jun/13/06 | 8.38 | 17.1 | 0.91 | 1.06 | 0.64 |
| MRY-2 | Jun/13/06 | 8.20 | 17.1 | 0.49 | 1.60 | 0.46 |
| MRY-3 | Jun/13/06 | 8.40 | 15.4 | 0.39 | 2.64 | 0.25 |
| CKH-1 | Mar/20/05 | 8.69 | 14.1 | 0.89 | 3.10 | 0.81 |
| CKH-2 | Mar/20/05 | 8.14 | 10.5 | 1.23 | 2.90 | 0.06 |
| CKH-3 | Mar/20/05 | 7.51 | 9.2 | 0.82 | 0.39 | 0.17 |
| KWC-1 | Mar/26/05 | 7.65 | 9.8 | 0.58 | 0.16 | 0.21 |
| KWC-2 | Mar/26/05 | 7.35 | 9.3 | 0.65 | 0.12 | 0.24 |
| KWC-3 | Mar/26/05 | 6.60 | 6.9 | 0.59 | 0.14 | 0.23 |
| HSY | Mar/26/05 | 6.77 | 13.1 | 0.39 | 0.41 | 0.46 |
| Andesite rock area | | | | | | |
| Tl | Aug/30/08 | 6.38 | 25.5 | 0.82 | 0.08 ± 0.00 | 0.00 |
| Ng-1 | Aug/30/08 | 6.35 | 28.0 | 0.78 | 0.09 ± 0.01 | 0.48 |
| Ng-2 | Aug/30/08 | 6.44 | 28.0 | 0.73 | 0.08 ± 0.01 | 0.18 |
| Tw | Aug/26/08 | 7.81 | 21.2 | 0.78 | 0.07 ± 0.01 | 0.00 |
| Granite area | | | | | | |
| SFR-1 | Jul/07/00 | 7.46 | 18.1 | n.d. | 0.02 | 0.02 |
| SFR-2 | Jul/07/00 | 7.33 | 17.3 | n.d. | 0.05 | 0.00 |
| SFR-3 | Jul/07/00 | 7.05 | 17.9 | n.d. | 0.00 | 0.02 |
| Karst area | | | | | | |
| HR-1 | Oct/18/08 | n.d. | n.d. | 0.67 | 0.34 ± 0.03 | 0.09 |
| HR-2 | Oct/18/08 | n.d. | n.d. | 0.55 | 2.51 ± 0.08 | 0.35 |
| AK-1 | May/30/98 | 7.92 | 15.1 | n.d. | 0.82 ± 0.02 | 0.00 |
| AK-2 | May/30/98 | 7.71 | 13.8 | n.d. | 0.95 ± 0.01 | 0.00 |
| AK-3 | May/30/98 | 7.48 | 14.5 | n.d. | 0.87 ± 0.02 | 0.05 |
| AK-4 | May/30/98 | 7.86 | 14.3 | n.d. | 0.83 ± 0.01 | 0.12 |

n.d. = no data.
[a] n = 3, 1σ.
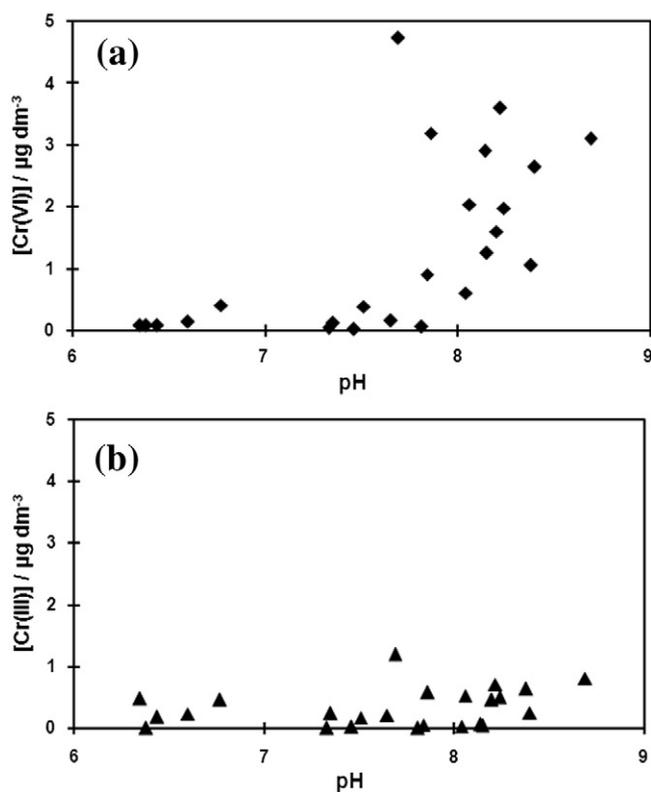[b] The difference between the values of total Cr and Cr(VI).

Fig. 3. pH dependence of dissolved chromium concentration in natural water samples obtained using the SPS method. (a) Cr(VI), (b) Cr(III).

immediately prior to the experiments using acetic acid or an ammonia solution. A 20 cm³ mixture of the solution containing either 0 or 0.040 g of the river sediment (FEF-3 or Ng-2) was shaken for 5, 10, 15, or 20 min. After filtering through a 0.20 μm membrane filter, 0.1 cm³ of high purity $HNO_3$ was added to 10 cm³ of the filtered solution. The concentration of Cr(III) was determined using an ICP-MS (Agilent Model 7500cx). The distribution ratio ($D$) of Cr(III) on the sediment was estimated using the following equation.

$$D = \left([Cr(III) \text{ in sediment}]/\text{mmol g}^{-1}\right) / \left([Cr(III) \text{ in solution}]/\text{mmol cm}^{-3}\right)$$
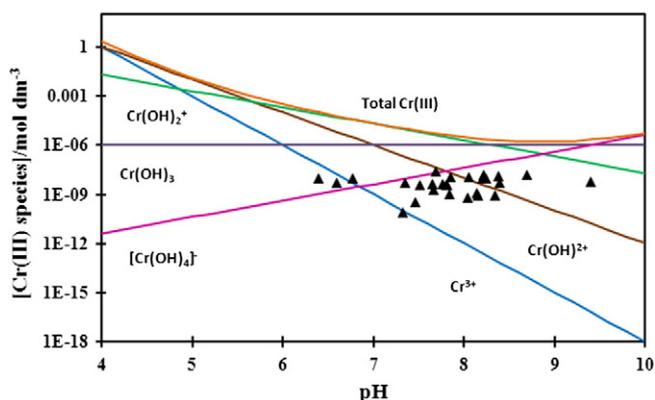(1)



Fig. 4. pH dependence of the solubility of amorphous $Cr(OH)_3$: concentration of Cr(III) obtained by the proposed method.

## 3. Results and discussion

### 3.1. Speciation of chromium dissolved in natural water at ultratrace level

The Cr concentrations are summarised in Table 2 along with the pH, the temperature of the water and the DOC. The reproducibility of the measurements was acceptable. For example, the concentrations of Cr(VI) were 0.04 ± 0.006 (n = 5) for sample Tw-2 and 0.34 ± 0.03 (n = 5) for sample HR-1, with a recovery of 96–101% and a low detection limit of 0.014 μg dm⁻³ (n = 5, 3σ) for the 20 cm³ samples. The SPS method enabled the determination of Cr in all of the water samples (Saputro et al., 2009).

The Cr concentrations are shown in Fig. 3 as a function of pH. Fig. 3a indicates that Cr(VI) was predominant in weakly alkaline water samples. In contrast to the report by Godgul and Sahu (1990), who reported that Cr(VI) is rarely found in nature, and Bartlett and James (1988), who stated that it was typically associated with industrial chemical releases when found in groundwater, our results, which are shown in Table 2 indicate that Cr(VI) can occur and be the predominant species in natural waters, especially in surface streams in/near chromite-bearing geologic formations, as observed in the samples collected from Mt. Ryuo, Fukuoka, Japan (MRY samples in Table 2, Tsuruhara et al., 2007), from the Fukuoka Experimental Forest in Hisayama, Fukuoka, Japan (FEF samples in Table 2, Saputro et al., 2009).

Fig. 3b indicates that the Cr(III) concentrations were less than 1 μg dm⁻³ in all of the natural water samples from the studied areas. Fig. 4 shows the $Cr(OH)_3$ solubility diagram that was calculated using the equilibrium constants reported by Stumm and Morgan (1996). Under neutral pH conditions, the calculated equilibrium concentration of the total dissolved Cr(III) species was approximately 10⁻⁵ mol dm⁻³. The analytical data for the current results are plotted in the diagram and indicate that the Cr(III) concentrations were lower than those calculated using the solubility of Cr$(OH)_3$(s). Therefore, the concentration of dissolved Cr(III) species observed in our water samples was not controlled by the dissolution equilibrium of amorphous $Cr(OH)_3$.

According to the results obtained thus far, the chromium speciation in uncontaminated natural water is controlled by the following elementary processes: the dissolution of Cr as Cr(VI) from Cr(III)-bearing minerals under oxic conditions; the reduction of Cr(VI) by organic compounds; and the removal of Cr(III) by the suspended matter and sediments as surface complexes. We examined these processes experimentally.

### 3.2. Dissolution process of Cr into natural water

As shown in Table 2, the Cr(III) concentrations were obviously lower than those calculated from the $Cr(OH)_3$ solubility, suggesting that the

Table 3
Analytical results for the total chromium content in sediment and rock samples.

| Sampling site | Date | Total Cr/g kg⁻¹ |
|---|---|---|
| River sediment | | |
| FEF-1 | Oct/10/08 | 0.51 ± 0.02[a] |
| FEF-2 | Oct/10/08 | 0.79 ± 0.03 |
| FEF-3 | Oct/10/08 | 1.32 ± 0.04 |
| FEF-4 | Oct/10/08 | 1.19 ± 0.03 |
| FEF-5 | Oct/10/08 | 1.29 ± 0.02 |
| FEF-6 | Oct/10/08 | 1.42 ± 0.03 |
| FEF-7 | Oct/10/08 | 1.21 ± 0.05 |
| Ng-2[b] | Aug/30/08 | 0.05 ± 0.004 |
| Ng-3[c] | Aug/30/08 | 0.09 ± 0.007 |
| Rock | | |
| FEF | Oct/10/08 | 1.76 ± 0.02 |

[a] n = 3, 1σ.
[b] Ngabean-Pengging, upstream of Ng-3, Boyolali, Central Java, Indonesia.
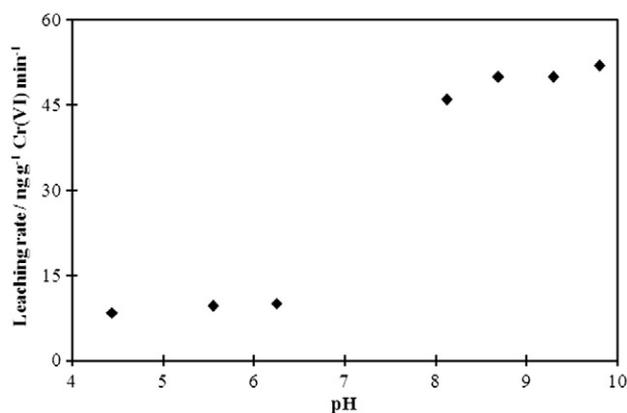[c] Ngabean-Pengging, downstream of Ng-2, Boyolali, Central Java, Indonesia.

Fig. 5. Leaching rate of Cr(VI) from Cr(III)-containing mineral under oxic conditions in natural waters at different pH values.

concentration may be regulated at a quasi-steady state during its supply and removal processes. In general, the source of chromium in natural water is considered to be from rocks. If the Cr(III) concentration is governed by the removal process, it is postulated that chromium is primarily supplied as $CrO_4^{2-}$ under oxic conditions. Therefore, the dissolution of Cr was examined using a Cr-bearing rock sample. Serpentinite, which was collected from the studied area, contained 1.76 g kg$^{-1}$ of chromium, as shown in Table 3.

The pathway of Cr(III) in primary minerals to Cr(VI) in water may result from the hydrolysis of Cr(III) to yield $Cr(OH)_2^+$ and/or $Cr(OH)_3$ in chromite during weathering, followed by oxidation of $Cr(OH)_3$ by the dissolved oxygen. The leached Cr(VI) was determined by SPS. At the beginning of the leaching experiments, no Cr(VI) was detected. The pH dependence of the initial leaching rate of Cr(VI) is shown in Fig. 5. The rate equation during the initial stage can be described by Eq. (2) as a pseudo zero-order reaction at a fixed pH.

$$d[Cr(VI)]/dt = k_{obs} \qquad (2)$$

where $k_{obs}$ is the observed oxidation rate constant. The Cr(VI) was well leached from serpentinite in a basic solution equilibrated with the atmosphere. Therefore, the reaction may obey the following reaction:

$$4Cr(OH)_3(s) + 8OH^- + 3O_2 = 4CrO_4^{2-} + 10H_2O \quad E^o = 0.511 \text{ V.} \qquad (3)$$

The results agreed with the fact that a higher concentration of Cr(VI) was observed in a weakly alkaline solution, as shown in Fig. 3a.

Some researchers have reported that Cr(III) could be oxidised by dissolved oxygen and manganese oxides. Rai et al. (1989) reported that manganese oxide was the only inorganic oxidant found in the environment that caused rapid oxidation of Cr(III) to Cr(VI). In addition, Johnson and Xyla (1991) studied the oxidation kinetics of Cr(III) to Cr(VI) on the surface of manganite (γ-MnOOH) and reported that the reaction was first order with respect to the manganite adsorption density and also to the Cr(III) concentration up to a critical adsorption density (0.2 μmol m$^{-2}$). Osaki et al. (1980) and Nakayama et al. (1981) reported that the oxidation of Cr(III) by only dissolved oxygen was very slow, and Schroeder and Lee (1975) observed that 2–3% of a $2.4 \times 10^{-6}$ mol dm$^{-3}$ Cr(III) solution was very slowly oxidised to Cr(VI) by dissolved oxygen over a 2-week period in buffer solutions at pH values ranging from 5.5 to 9.9 and in natural lake waters. The data from a deep well in the Mojave Desert, California, indicated that the Cr(VI) concentration decreased and the Cr(III) concentration increased as the concentration of dissolved oxygen decreased (Ball and Izbicki, 2004). The influences of depleted dissolved oxygen were present in the deep well due to the extremely long residence time. However, these conditions do not apply for surface streams. In this study, the Cr(VI) concentration was less than 1 μg dm$^{-3}$, even near abandoned
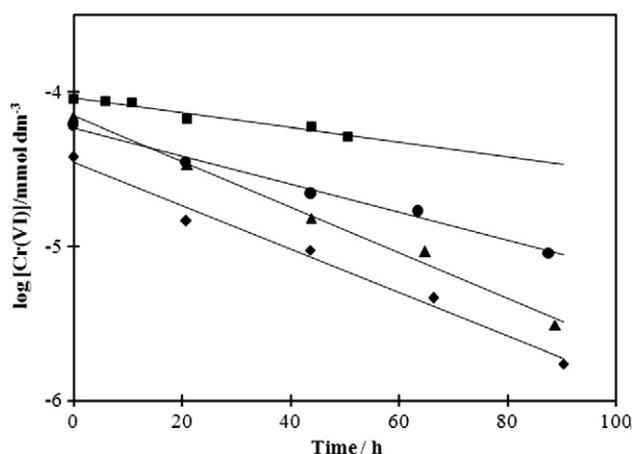


Fig. 6. Pseudo-first order reduction of Cr(VI) after the FEF natural water samples were acidified to pH 3.00. DOC 1.7 mg dm$^{-3}$; DOC 0.8 mg dm$^{-3}$; DOC 1.5 mg dm$^{-3}$; DOC 1.1 mg dm$^{-3}$.

manganese mines (KWC samples in Table 2). This result indicates that the residence time of the Cr(VI) in source water may be fairly short for the oxidation of Cr(III).

### 3.3. Cr removal process from natural water

The Cr(VI) species are reduced by dissolved organic matter, such as fulvic acid (Eckert et al., 1990; Wittbrodt and Palmer, 1995; Agrawal et al., 2009), Fe$^{2+}$ (Sedlak and Chan, 1997) and H$_2$S(g) (Smillie et al., 1981). The concentrations of the dissolved organic carbon in the water samples from the studied areas ranged from 0.39 to 1.82 mg C dm$^{-3}$, as listed in Table 2. However, the ratio of the Cr(III) and Cr(VI) concentrations did not exhibit any correlation to the concentration of dissolved organic carbon. Cr(VI) is reduced by dissolved organic matter at low pH values, such as pH values between 2 and 4 (Eckert et al., 1990), but the surface water in these areas was neutral to weakly basic (pH 6.35–8.24).

#### 3.3.1. Kinetics of Cr(VI) reduction

The time dependence of the Cr(VI) reduction at a constant pH is shown in Fig. 6. It is clear that the reaction order is 1 with respect to [Cr(VI)]. The reduction rate may be pseudo-first order with respect to [Cr(VI)] because the concentration of Cr(VI) is very low. The reduction rates of Cr(VI) were different for the samples collected at different
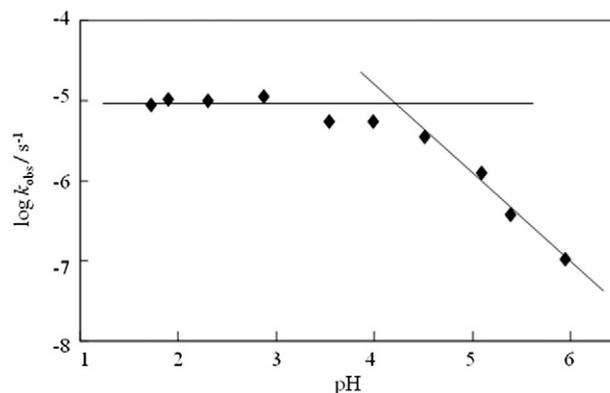


Fig. 7. pH dependence of the reduction rate constants in the presence of 0.91 mg C dm$^{-3}$ DOC.
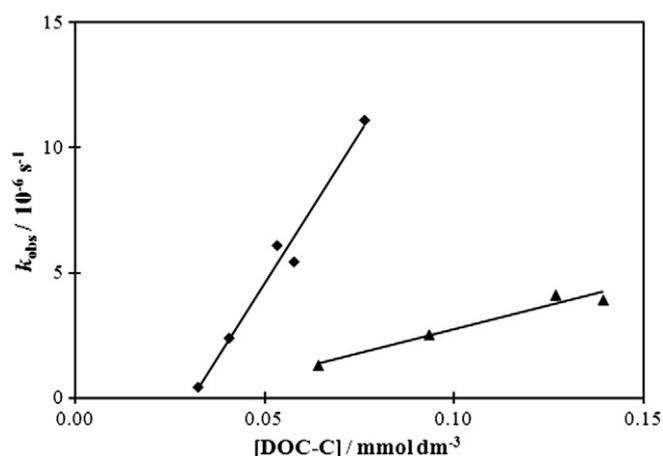
**Fig. 8.** Relationship between the reduction rate constant of Cr(VI) and the DOC for the water samples obtained from different sites. ◆, Mt. Ryuo, Fukuoka; ▲, FEF, Fukuoka.

sites, and depended on the DOM content. The rates are also expected to be a function of $[H^+]$. Therefore, the reduction rate of Cr(VI) can be expressed by Eq. (4).

$$-d[Cr(VI)]/dt = k_{obs}[Cr(VI)] = k[Cr(VI)]\left[H\right]^a[DOC]^b \qquad (4)$$

where $k_{obs}$ is the observed reduction rate constant, $k$ is the standard reduction rate constant, and $a$ and $b$ are the reaction order with respect to $H^+$ and DOC, respectively.

Fig. 7 shows the pH dependence of the reduction rate at a constant [DOC]. The reduction rates were constant at pH values less than 4, and they were proportional to $[H^+]$ at pH values higher than 4.5. The $a$ value was 0 at pH < 4 and −1 at pH > 4.5. A similar result was reported using tannic acid as a reductant, even though the pH range affecting the reduction rate was different (Osaki et al., 1980). For the acid dissociation constant of chromic acid ($pK_{a1} = -0.7$, $pK_{a2} = 5.81$), the results of the pH dependence suggest that the chemical species involved is the hydrogen chromate ion (Smith and Martell, 1976). However, the abundance of the $HCrO_4^-$ species calculated from the acid dissociation constants was not necessarily in agreement with the pH dependence of the reduction rate. This fact may indicate that the organic compounds with a $pK_a$ value near 4.0 participate in the reaction as reductants.

Fig. 8 shows the relationship between the concentration of DOC and $k_{obs}$ for the water from the Fukuoka Experimental Forest (FEF) and Mt. Ryuo (MRY) sites, with fixed pH values of 3.00 and 2.87, respectively. The reduction rates increased as a function of [DOC] on the order of 1. In the FEF studied area, nearly the same vegetation may supply dissolved organic matter (DOM) with similar compositions, and some fractions of the DOM do not participate in the redox reaction because the curve of $k_{obs}$ as a function of [DOC] did not pass through the origin. Similar results were obtained for water samples collected from Mt. Ryuo (MRY), Fukuoka. It is clear that some DOC fractions may be inactive toward redox reactions with Cr(VI). Natural water samples collected from the FEF exhibited lower $k_{obs}$ values, but higher DOC concentrations, and water samples from Mt. Ryuo exhibited higher $k_{obs}$ values and lower DOC concentrations. This result would result from the difference in the residence time of the dissolved organic matter in both water samples.

A half-life of Cr(VI) of approximately 400 days was estimated under the pH conditions of natural water (pH 7.0) in the presence of 0.91 mg C dm$^{-3}$ DOC by extrapolating the reduction rate shown in Fig. 7. This value supports the analytical results from a previous study on the natural waters of the Muromi River (Osaki et al., 1980). The authors reported that the Cr(VI) concentration downstream of the Minamihata Reservoir was lower than that of the upstream waters

and that Cr(III) was the predominant species. For the natural water sample, Ng, from Central Java, Indonesia, the Cr(III) concentration was 5.2 times higher than that of Cr(VI). This result is likely due to the water sample of Ng, which is located in a small lake with a long residence time, possessing a pH of 6.35 and containing a high level of dissolved organic matter.

It is believed that Cr(III) is predominant in natural water in the presence of organic matter because organic matter acts as a reductant toward Cr(VI). As mentioned above, this assumption is valid for acidic conditions. In addition, the acidic condition may affect the analytical results of the Cr speciation, especially in the preconcentration and/or separation steps. For example, Motomizu et al. (2003) reported the chromium speciation of fresh water by introducing a water sample solution to the flow system at pH 4.5 for the effective collection of both Cr(III) and Cr(VI). Similarly, Cespon-Romero et al. (1996) also reported that the predominant species of Cr in river, mineral and tap water was Cr(III). The authors used a flow injection system comprised of a chelating ion-exchange and flame AAS with a mini column (85 mm × 1.6 mm i.d.) filled with a poly(aminophosphonic acid) chelating resin (20–30 mesh) for the separation and preconcentration of Cr. The separation of the chemical species was performed using a small volume of 0.5 mol dm$^{-3}$ HCl. It might be possible for the Cr(VI) to be reduced under acidic conditions, resulting in Cr(III) as the predominant species.

### 3.3.2. Adsorption of Cr(III) species on river sediment and/or organic matters

The adsorption of Cr(III) species to river sediments of FEF-3 and Ng-2 at pH values between 5 and 9 was examined. Cr(III) can be adsorbed to some extent on the wall of a PTFE container under this pH condition, but no decrease in the Cr(III) concentration was observed within 20 min. The FEF-3 sample contained antigorite, quartz and chlorite, and the organic C content was 10.34 ± 0.40%. In the case of the Ng-2 sample, albite was the major sediment and hornblende and pyroxene were the minor sediments. The organic C content was 0.14 ± 0.01%. Except for the experiments at pH 5, over 90% of the added Cr(III) (i.e., 20 cm$^3$) was removed by 0.04 g of the sediments within 5 min, irrespective of the differences in the compositions of minerals and the organic matter content. By using the equilibrated Cr(III) concentration, the pH dependence of the distribution ratio is shown in Fig. 9, along with the mole fraction of $Cr(OH)_2^+ + Cr(OH)_3$ to the total Cr(III) concentration. The $D$ values for the two sediments were different, but the pH dependence behaviour was similar. The maximal adsorption was observed in the pH range of 6 to 9. In this pH range, $Cr(OH)_2^+$ and $Cr(OH)_3$ were predominant. It has been reported that the hydroxo complexes of Cr(III) were completely and irreversibly adsorbed onto the surface of silicates when the solution pH was 6.0 or higher (Bourette et al., 2009). Analogous to this report, Cr(III) species in natural water are also
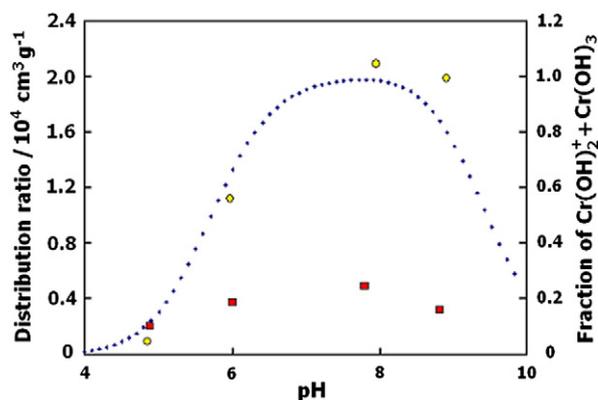


**Fig. 9.** Cr(III) adsorption onto river sediment ($I = 0.01$). ■, FEF-3 (Fukuoka Experimental Forest, Fukuoka); ○, Ng-2 (Ngabean Pengging, Central Java, Indonesia). Solution: 5 μg dm$^{-3}$ Cr(III) 20 cm$^3$; sediment: 0.04 g; stirring time: 20 min. ‥‥, mole fraction of $Cr(OH)_2^+ +$ $Cr(OH)_3$ to the total dissolved Cr(III).
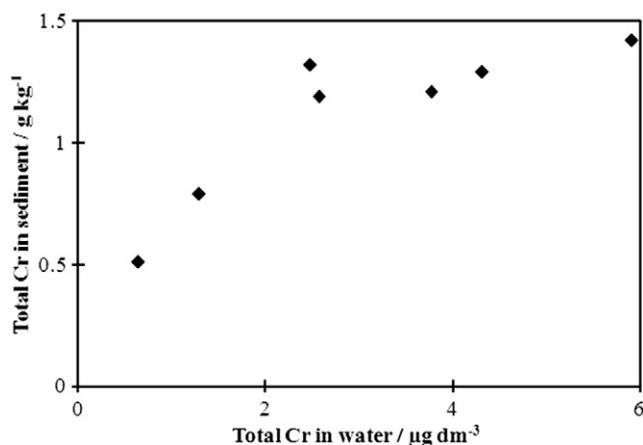
**Fig. 10.** Correlation between the total Cr concentration in water and sediment samples.

adsorbed on the sediments in the stream bed or suspended matter in the water. In addition, it is known that the adsorption rate of Cr(III) onto a solid in fresh water is somewhat faster than that of Cr(VI) reduction (half-life time of 8 days at pH 4.0) (Friedly et al., 1995), because the Cr(III) species formed by the reduction of Cr(VI) in water is immediately removed by the subsequent sorption to particles or sediments. Cr(III) is inert with respect to the substitution reaction, (i.e., the exchange between ligands is very slow). Therefore, the surface complex formation

due to a substitution reaction can be excluded, and the condensation between hydroxyl groups of Cr(III) and the surface, as well as cation exchange and/or hydrophobic interactions may be involved.

Fig. 10 shows the relationship between the total Cr content in the water and sediment samples. The chromium content in the river sediments from the FEF, Fukuoka, Japan (sample FEF-1 to FEF-7) was in the range of 0.51 to 1.42 g kg$^{-1}$ and that from Ngabean-Pengging, Central Java, Indonesia was 0.05 g kg$^{-1}$ to 0.09 g kg$^{-1}$, as listed in Table 3 (i.e., the sediments were rich in chromium). As shown in Fig. 10, a positive correlation was confirmed between the Cr content in the sediment and water, suggesting that Cr(III) was removed from the river water and adsorbed onto the river sediments in these areas.

It is clear that the adsorption of Cr(III) onto river sediments is a very important mechanism and determines the Cr content in the river water, thereby providing information about the hydrological circulation of chromium in natural waters.

### 3.4. Schematic models for chromium circulation

Based on the results mentioned above, we propose a schematic model for chromium circulation in Fig. 11. The amount of chromium in natural water would be controlled by the leaching of Cr(VI) from Cr(III)-bearing minerals such as chromite and the adsorption of Cr(III) onto river sediments. Chromium is first leached as Cr(VI) from Cr(III)-bearing minerals under neutral to alkaline conditions by oxidation with dissolved oxygen. The Cr(III) species leached as hydroxo complexes from a rock in an alkaline solution is readily adsorbed onto the river sediment or suspended matter. The hydroxo-complexes, such as
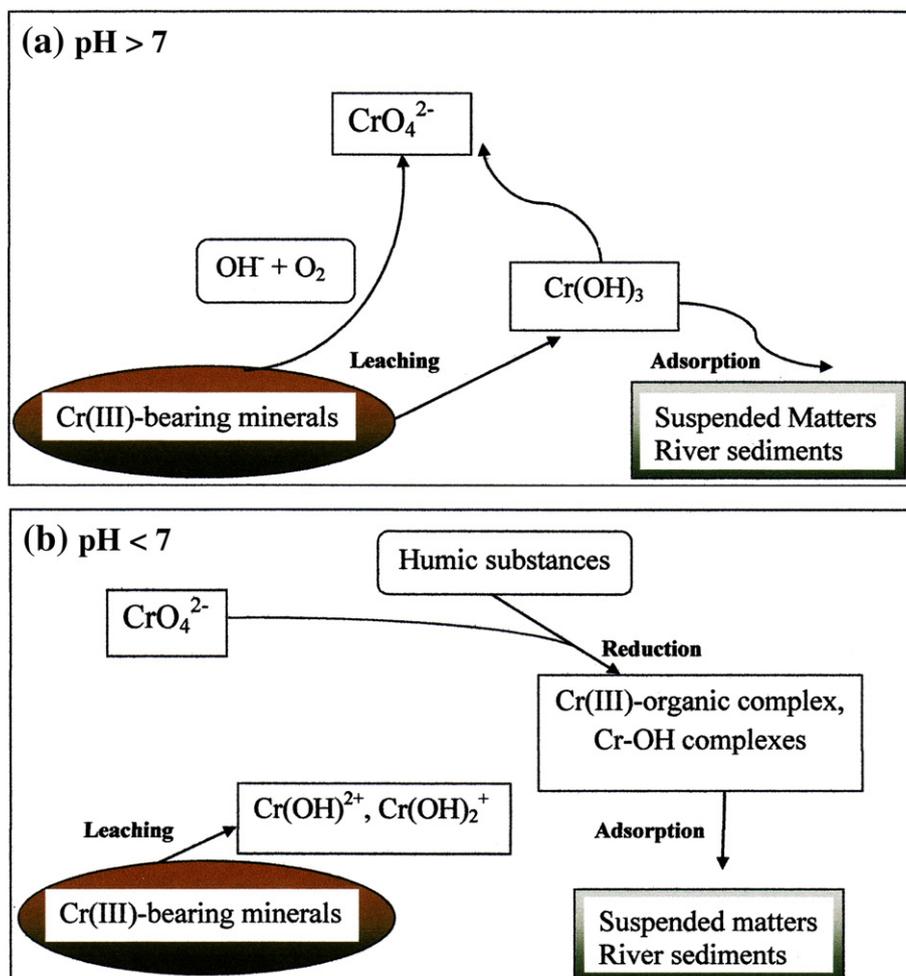


**Fig. 11.** Schematic model for chromium circulation in natural waters. (a) Under alkaline conditions, (b) under acidic conditions.

$CrOH^{2+}$ and $Cr(OH)_2^+$, leach out in an acidic solution and are adsorbed onto the solid, and Cr(III) is also adsorbed after Cr(VI) is reduced by organic matter. Under acidic conditions, Cr(III) exhibits a tendency to form many different complexes with naturally occurring organic matter, such as humic acid or fulvic acid (Nakayama et al., 1981). In the presence of humic substances, $CrO_4^{2-}$ can also be reduced thereby resulting in a Cr(III)-organic complex that is insoluble, immobile and unreactive.

## 4. Conclusions

The performance characteristics of the improved SPS method enabled the determination of Cr(VI) at sub-µg dm$^{-3}$ to µg dm$^{-3}$ levels, permitting the study of the concentration regulation mechanism and behaviour of Cr(III) and Cr(VI) dissolved in natural waters and to clarified its circulation. The results indicate that under oxic conditions, the leaching rate of Cr(III)-containing minerals of chromite is higher in an alkaline solution than that in an acidic solution. The reduction of Cr(VI) to Cr(III) by dissolved organic matter follows the equation, $-d[Cr(VI)]/dt = [H^+]^a[Cr(VI)][DOC]^b$, where $a = 0$ at pH < 4 and $a = -1$ at pH > 4.5. Cr(III) is readily adsorbed onto river sediments and/or suspended particulate matters, especially under weakly alkaline conditions. This study also indicates that the Cr(III) species in water samples are not present in the dissolved form, but are adsorbed onto river sediments in natural waters. The schematic models of the mechanism that control Cr concentrations and speciation in natural waters in two different pH regions were proposed. The elementary reactions are the same, but the predominant reactions are different in the two pH regions. In conclusion, a µg dm$^{-3}$ or sub-µg dm$^{-3}$ level chromium concentration and its circulation in natural waters may be primarily controlled by the dissolution of Cr(III)-containing minerals followed by redox and adsorption reactions.

## Acknowledgements

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