Toxic chromium release from nickel mining sediments in surface waters, New Caledonia

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Toxic chromium release from nickel mining sediments in surface waters, New Caledonia

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Abstract Mining sediments are excavated from nickel ore exploitation in New Caledonia. In those sediments, chromium (Cr) occurs as Cr(III), but Cr(III) can be oxidized to the toxic Cr(VI) under oxic conditions, for instance in overlying water. Here, we aimed to determine whether mining sediments could release available Cr(VI) in surface waters. Water samples were collected in a mine and in the village downstream, and then were analysed for Cr. Batch leaching experiments were performed on mining sediments in order to determine their exchangeable and their water-soluble Cr content as a function of pH. Results show that mine waters contain high concentrations of total dissolved Cr, of up to 0.73 mg/L. Moreover, Cr(VI) concentration in village waters increases with the rainfall rate upto 0.34 mg/L. Cr is released from sediments solely as Cr(VI). Desorption of chromate complexes is the main process involved in Cr release. We conclude that drainage of sediments mobilized by opencast Ni mines is a source of toxic Cr(VI) for surface waters.

Keywords Ni mines · Mining sediments · Chromium · Surface water · Ophiolitic substrate

Introduction

New Caledonia is a south-west pacific territory composed by one main island, in a middle of a large lagoon, and three smaller islands, "Loyalty Islands". The surrounding barrier

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reef was listed by UNESCO on the World Heritage List under the name "The Lagoons of New Caledonia: Reef Diversity and Associated Ecosystems" on 7 July 2008. Another important characteristic of New Caledonia is that ophiolitic complexes cover 2/3 of the main island, including alterites with Ni concentrations of economic interest. This Ni enrichment (laterite and saprolite) results from tropical miocene to present weathering of peridotites and pyroxenites. Since nickel ore is located at 10–30 m depth under lateritic levels, extraction technique adopted is strip mining, resulting in large opencast areas. After rainfalls, mining sediments are therefore conveyed along mining catchments, which are a significant water resource for domestic and agricultural use. Moreover, suspended particulate matter can reach quickly rivers and mouths of rivers because Ni mines are located close to the coast. It may result in a diffusive pollution of the lagoon. It is then crucial to understand the reactivity of the suspended particulate matter generated by mining activities. Among the elements present in mining sediments, the trivalent Cr form (Cr(III)) widely occurs in chromite $[(Mg,Fe)(Al,Cr,Fe)_2O_4]$. Cr(III) leaching rate from chromite minerals depends on pH, but the process is negligible since hexavalent chromium (Cr(VI)) is much more soluble than Cr(III) (Saputro et al. 2014). Cr(VI) is generated due to natural oxidation of Cr(III)-bearing minerals. The occurrence of hexavalent chromium (Cr(VI)) in laterite is related to the oxidative reaction of Cr(III) with Mn oxides (Fandeur et al. 2009). In mining sediments, the predominant mineral phase is goethite FeO(OH). Pure goethite is known to adsorb Cr(VI), and the reaction is reversible (Deng et al. 1996). But besides readsorption of Cr(VI) onto Fe oxyhydroxides, several reactions with or without the support of dissolved species may occur at the interface of these natural mineral mixtures. Reactions may be Cr(VI) reduction and

precipitation or Cr(VI) reduction and readsorption (Saputro et al. 2014). Mining sediments may then become a source of chromium for aqueous media by Cr(VI) or Cr(III) desorption, or dissolution of Cr(III) precipitates formed at the interface. In opencast Ni mining systems, generated sediments contain Cr(III)-bearing phases, Mn oxides and Fe oxyhydroxides, suggesting that after excavation, they should become a reservoir of Cr(III) and Cr(VI); since under oxic conditions, the transformation of Cr(III) to Cr(VI) should be facilitated and the secondary sorption reaction onto Fe oxides should significantly occur. The aim of the present study was to determine under realistic environmental conditions which oxidative state Cr(III) or Cr(VI) is significantly leached from Cr(III)-bearing minerals and then which oxidative state is involved in chromium circulation in surface waters influenced by Ni mining activities. Cr(VI) is considered as the most toxic form for living organisms. It can affect vital organs of freshwater fish (Mishra and Mohanty 2008), cause toxic and tissue-specific genotoxic effects to freshwater stinging catfish (Ahmed et al. 2013), and affect testicular function of adult male rats (Marouani et al. 2012) or photosynthesis in plants (Rodriguez et al. 2012). It is also carcinogenic for the human body (International Agency for Research on Cancer 1990). Cr(III) is an essential nutrient for animal metabolism (Anderson 1981), but accumulated at high levels, it can anyway generate serious troubles and diseases (Meibian et al. 2008).

The objectives of the present study were to analyse chromium content in mining-influenced surface waters and to evaluate the potential of Cr release from mining sediments. The exchangeable Cr(VI) content was determined with $NH_4H_2PO_4$ or KH_2PO_4 0.1 M solution designed to remove sorbed chromate. The water-soluble Cr content as a function of pH is also determined. pH is one of the key parameters for heavy metals mobility in sediments (Gäbler 1997), and thus, the water-soluble Cr content is determined for a wide range of pH encountered in natural waters. This is the first time that Cr concentration and speciation are determined in waters influenced by Ni mining activities in New Caledonia and the results of the present study may then have implications for management of mining catchments.

Experimental

Site description

New Caledonia is located in the south-west Pacific Ocean (20–23°S). Its subtropical climate varies from a hot and humid period with high rainfalls (November to March) to a dry period (June to August). The studied site is the mining centre of Poro, the oldest mining centre (exploitation from 1874), located on the east coast of New Caledonia. The mining site includes ultramafics (harzburgite, websterite) and their derived weathered rocks (saprolite, laterite). The Poro catchment surface is 33.3 ha, and the annual rainfall average is 2,801.5 mm/year (average of 2013, 2012, 2011 and 2010 for Poindimié; www.meteo.nc). Infrastructures exist to ensure the waters retention using bridging methods of the bench walls to sustain the residues and attenuate the erosive capacity of the waters' flow and also using rainwater channelling, drainage and sedimentation.

Sampling

Five sampling sites were selected from the top of the mining catchment to the mouth of the river (Fig. 1). A, B and D are sites located within the mine boundaries, while E and F are located downstream in the village of Poro.

Water samples were collected at the top of the mine at a resurgence just below carries (A), at the bottom of the mine outlet the latest settling tank of the mine (D), in the river going through Poro village (E) and at the mouth of the river (F). Samples were collected within the humid period from 14 March 2011 to 29 April 2011 after two high rainfall rates (100 mm/24 h and 132.5 mm/24 h), a medium and a low rainfall rate (50 mm/24 h and 3.5 mm/24 h) and without rainfall (0 mm/24 h). Water samples, collected in HDPE bottles, were kept at 6 °C prior to analysis.

Two sediment samples were collected: one at the top of the mine in a settling tank located at the upstream part of the first outlet (B) and another one at the bottom of the mine in the latest settling tank of the mine (D). About 2 kg was collected from the top layer (0–30 cm), dried at 45 °C until constant weight, sieved at 2 mm and manually mixed to obtain a homogenous material.

Extraction procedures and analytical techniques

Exchangeable anionic chromium (exchangeable Cr(VI)) was extracted by shaking 1 g of sediment with 34 mL of KH_2PO_4 0.1 M (1 h, 20 °C).

Water-soluble Cr was extracted as a function of pH by shaking 6 g of sediments in 30 ml of deionized water with pH acidified or alkalinized with HNO_3 or NaOH or buffered with MES (2-(*N*-morpholino)ethanesulfonic acid) or HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) or MOPS (3-(N-morpholino)propanesulfonic acid) 0.1 M around neutral pH because of the buffer capacity of sediments.

Water samples and leachates were filtered at 0.22 μm before analysis. Cr(VI) concentration was measured using spectrocolorimetric determination of a complex formed with diphenylcarbazide (absorption at 540 nm), and total

Fig. 1 The mining centre, the village of Poro and location of the five sampling sites at the *top* of the mining catchment (*A, B*), at the *bottom* of the mine (*D*), in the river (*E*) and at its mouth (*F*). Pictures of the river before and after a rainfall show particulate matter run-off

River(E) before rainfall

River (E) after rainfall

Cr (Cr(III) + Cr(VI)) was measured by atomic absorption spectrometry according to the AFNOR French procedure (NF EN 1233, AFNOR 1996). All reagents were of analytical grade.

Particle size analysis (volume-based measurement) was performed using a Malvern Mastersizer 2000 Particle Size Analyser. Mineral phases were identified from powder by X-ray diffraction of sediments with Inel CPS 120 instrument.

Results

Dissolved chromium content in surface waters

Total dissolved Cr content in surface waters is high and ranges from 0.05 to 2.41 mg/L (Fig. 2a). Cr contents are higher in mine waters than in village waters. At the top of the mine (A), total Cr decreases as the rainfall rate increases, while in the village, at the mouth of the river (F) it increases as the rainfall rate increases.

Dissolved Cr(VI) content in mine waters (A, D) is very high ranging from 0.18 to 1.62 mg/L (Fig. 2b). The dissolved Cr(VI) content in village waters (E, F) is lower than in mine water ranging from 0.02 to 0.34 mg/L (Fig. 2c). Cr(VI) content at the top of the mine (A) decreases as the rainfall rate increases (Fig. 2 b) such as previously observed for the total Cr content. Cr(VI) content reduces significantly with rainfall rate at the top of the mine (A) due to dilution even if the concentrations remain very high. At the bottom of the mine (D), it is quite constant (Fig. 2c). In village waters (E, F), Cr(VI) content increases significantly with the rainfall rate (Fig. 2c). After rainfalls, there is a sediment load in the river (Fig. 1) and Cr(VI) dilution is then probably counterbalanced by Cr
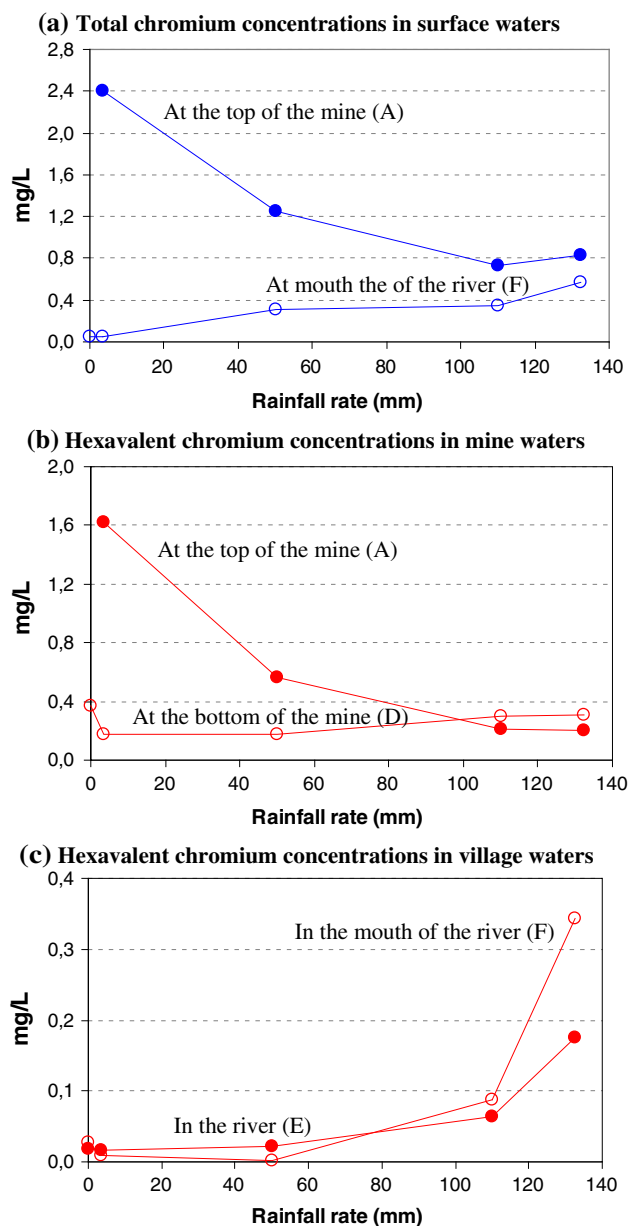
remobilization from suspended materials provided by mining sediments. As demonstrated for Pb and Zn (Superville et al. 2014), metal desorption from disturbed sediments is the most relevant process responsible for the Cr content increase in surface waters.

Chromium leaching behaviour in mining sediments

In mining sediments, chromium is one of the major components after iron and magnesium since chromium oxide content is, respectively, 1.6 and 3.1 % in sediments collected at the top (B) and the bottom (D) of the mine (Table 1). The main mineral phases identified for both sediments on the X-ray diffractograms are goethite, talc and serpentine; goethite is dominant.

Exchangeable hexavalent chromium as a function of particle size

Exchangeable Cr(VI) content is very high for sediments collected at the top of the mine (B) with 577 mg/kg, while it is 9 times lower for those collected at the bottom (D) with 64 mg/kg (Table 1). These concentrations are in good agreement with contents of exchangeable Cr(VI) found for ultramafic soils with contents sometimes upper than 1000 mg/kg (Becquer et al. 2003, Garnier et al. 2006, Raous et al. 2013). With the hypothesis of desorption reaction, anionic hexavalent chromium content should be related to sediments texture. Sediment B is fractionated in three granulometric fractions by sieving in order to get five samples with different texture: crude sediment B with Dv90 = 76 μm, crude sediment D with Dv90 = 502 μm, the granulometric fraction of B >2000 μm (no size analysis possible for such large particles) and two granulometric fractions of B with Dv90 = 44 and Dv90 = 154 μm.

(a) Total chromium concentrations in surface waters

(b) Hexavalent chromium concentrations in mine waters

(c) Hexavalent chromium concentrations in village waters

Fig. 2 Total chromium and hexavalent chromium concentrations as a function of the rainfall rate. They both decrease at the *top* of the mine, while they both increase at the mouth of the river

Results show that exchangeable Cr(VI) content decreases when particle size increases (Fig. 3a). Cr(VI) occurs then as sorption complexes. Mining sediments are then an important reservoir of exchangeable Cr(VI), especially the thinnest fractions.

Water-soluble chromium as a function of time and pH

Batch leaching experiments on the crude sediment B (fraction Dv90 = 76 μm) were performed at various pH and demonstrate that no significant amount of water-
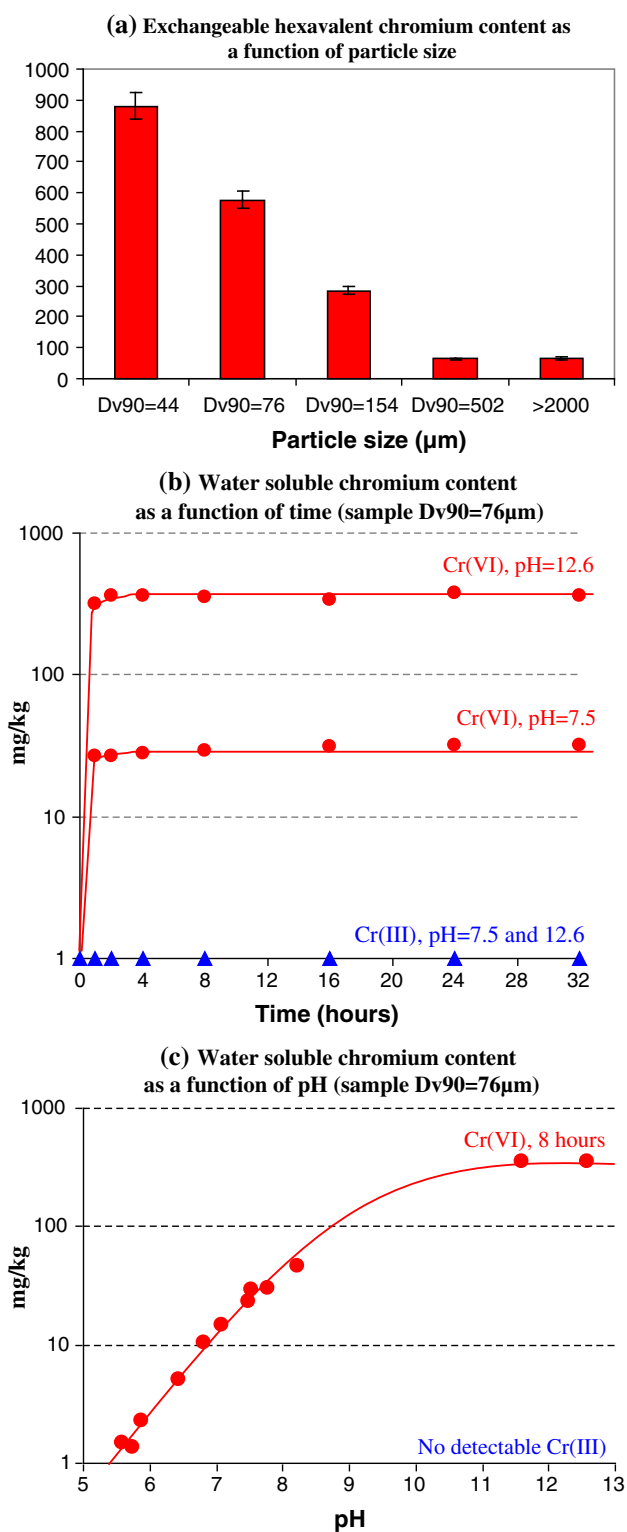
Table 1 Physico-chemical properties of mining sediments: mean values ($n = 3$) for elemental composition (percentage weight), for exchangeable anionic chromium content and for Dv 90 (maximum particle diameter below which 90 % of the sample volume exists)

(wt%)	Physico-chemical properties of mining sediments collected	
	At the top of the mine (B)	At the bottom of the mine (D)
Fe_2O_3	44.5	44.6
SiO_2	20.3	23.2
MgO	11.8	11.0
Cr_2O_3	1.6	3.1
NiO	2.4	1.5
Al_2O_3	1.6	2.0
MnO	0.7	0.6
CaO	0.05	0.05
TiO_2	0.05	0.10
CoO	0.09	0.07
Exch. Cr(VI) (mg/kg)	577 ± 9	64 ± 5
Dv 90 (μm)	76 ± 5	502 ± 11

soluble Cr(III) is detected (Fig. 3b). It indicates that Cr is only released as Cr(VI) and that no significant Cr(III) desorption or dissolution of Cr(III) precipitates occurs. Cr(VI) release is fast (high concentrations measured as soon as 1 h), and the rate of dissolved Cr reaches a maximum value of 358 ± 16 mg/kg after 8 h for pH 12.6 and 31 ± 1 mg/kg for pH 7.5 (Fig. 3b). Over the entire pH range tested (5.9–12.6), the water-soluble Cr(VI) fraction increases with the pH of the solution (Fig. 3c) and no significant amount of Cr(III) was measured. It is known that chromate ions adsorption by Mn, Fe and Al oxides decreases as pH increases (Richard and Bourg 1991). The process involved with mining sediments, which main mineral phase is goethite, is then the opposite process, *i.e.* increasing Cr(VI) desorption with pH. Here, we then demonstrate that mining sediments are a reservoir of easily leachable Cr(VI), especially when alkaline media are of concern. Afterwards, dissolved Cr(VI) can be reduced to Cr(III) in the aqueous media by organic matter such as humic substances (Saputro et al. 2014).

Conclusion

Mine waters and village waters contain high Cr contents as Cr(VI) but also as Cr(III). Batch experiments demonstrated that mining sediments are an important reservoir of easily leachable Cr(VI), and Cr(VI) leaching depends on pH and on sediments texture. Cr(III) leaching is negligible, and no significant Cr(III) desorption or Cr(III) precipitates

(a) Exchangeable hexavalent chromium content as a function of particle size

(b) Water soluble chromium content as a function of time (sample Dv90=76μm)

(c) Water soluble chromium content as a function of pH (sample Dv90=76μm)

Fig. 3 Chromium leaching behaviour in mining sediments. Mining sediments release chromium only as its hexavalent form

dissolution occurs. Cr circulation in water is then here related to Cr(VI) desorption. Thus, run-off from the mines carries along suspended particulate matters able to easily and quickly release Cr(VI) when the medium is disturbed and/or when the pH of the media increases such as in the mouth of the river or in the sea water. Afterwards, Cr(VI) can be reduced to Cr(III) in the aqueous media depending on local chemical composition. This study demonstrates, through the example of Poro, that drainage of ultramafic material mobilized from Ni mines is a source of Cr as Cr(VI) for local surface waters. For a sustainable exploitation of mining resource compatible with the conservation of the natural environment of New Caledonia, the authors greatly encourage mining industries to prevent transport of solid matter in mining catchment including the thinnest solid matter.

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