

Wildfires on Cr-rich Ferralsols can cause freshwater Cr(VI) pollution: A pilot study in New Caledonia

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ABSTRACT

In the context of global warming, environmental forcing of wildfires on continental ecosystems is on a growing trend. Among other environmental impacts, wildfires can enhance trace metals concentration in freshwater systems. In this regard, chromium is of particular environmental and health concern because the temperature-induced oxidation of the less mobile and toxic Cr(III) form to the most mobile and toxic Cr(VI) one might represent a risk of freshwater pollution. The aim of the present study was to make a first assessment of this risk in New Caledonia by quantifying the influence of soil heating on Cr(VI) mobility in Cr-rich Ferralsols that cover about 1/3 of this French overseas territory. The results obtained indicated an enhanced Cr(VI) mobility upon soil heating from 200 °C, with a marked turnaround from 400 °C. Based on these results, a solid/solution mass balance approach allowed to confirm the risk of freshwater Cr(VI) pollution as a function of suspended particulate matter (SPM) concentration issued from burned Cr-rich Ferralsols. In addition, the results obtained revealed an apparent control of the Fe-oxides/silicates ratio on Cr(VI) mobility upon soil heating. Since this ratio decreases from the top to the bottom of ultramafic catchments, this latter result suggests that the risk of freshwater Cr(VI) pollution could depend on the actual location of the wildfires at the top or slope/base of these catchments. Since freshwaters represent the major water resource for the inhabitants of New Caledonia, these results point to the need for a larger evaluation of the risk of wildfires-induced freshwater Cr(VI) pollution at other catchments composed of Cr-bearing soils like Cambisols and Vertisols. At the larger scale, they also point to the need to foster studies aimed at better evaluating the risk of wildfires-induced freshwater Cr(VI) pollution at Cr-bearing pedological settings worldwide.

1. Introduction

Every year, about 650 millions hectares (ha) of forests, savannas, scrublands and grasslands from boreal zones to the equator are burned by wildfires (Giglio et al., 2010; Bodi et al., 2014; Abraham et al., 2017a, 2017b; Alcañiz et al., 2018). In the context of global warming, wildfires are increasing both in frequency and intensity. During a wildfire, temperature depends on oxygen availability. When oxygen supply is limited, the temperature remains below 450 °C (Bertschi et al., 2003; DeBano et al., 1998; Ormeño et al., 2009). However, much higher temperatures

in the range of 700–800 °C, with local peaks above 1400 °C, can be reached when oxygen is highly available (Ormeño et al., 2009; Saura-Mas et al., 2010). Because of these high temperatures, heat can propagate towards several tens of centimeters in the soil, transforming/destructing organic matter and mineral components such as Fe-Mn-Al (hydr)oxides and phyllosilicates (Ulery et al., 1996; Ketterings et al., 2000; Grogan et al., 2003; Terefe et al., 2008; Reynard-Callanan et al., 2010; Trindade et al., 2010; Yusiharni and Gilkes, 2012). However, these soil components are known to be the major hosts for trace metals in soils (Alloway, 2013), and such thermal

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transformation/destruction can have a strong influence on their mobility (Wells, 2001). As a consequence, transformation/destruction of organic matter, Fe-Mn-Al (hydr)oxides and phyllosilicates upon soil heating favors trace metals release in the soil solution, and further dispersion towards freshwater (Terzano et al., 2021; Rascio et al., 2022). This is the reason why wildfires are considered to cause enhanced trace metals concentration in freshwater systems (Cerdeja and Lasanta, 2005; Shakesby and Doerr, 2006; Bogacz et al., 2011; Smith et al., 2011; Burton et al., 2016; Abraham et al., 2017a, 2017b).

Among trace metals, chromium is of particular environmental and health concern since recent studies reported oxidation of Cr(III) to Cr(VI) upon heating of synthetic Cr(III)-doped Fe-(hydr)oxides. In a first study focusing on synthetic Cr(III)-doped amorphous Fe-(hydr)oxides, about 40% of the Cr(III) initially incorporated in the starting solid was oxidized to Cr(VI) upon heating between 200 and 400 °C (Burton et al., 2019b). Moreover, between 17 and 70% of the Cr(VI) produced was extractable with a low-concentration phosphate solution considered to be representative of the exchangeable fraction of Cr(VI). The results of this study were confirmed by a second one focused on goethite, hematite and ferrihydrite, which showed that up to 50% of the Cr(III) initially incorporated in ferrihydrite and hematite could be oxidized to Cr(VI) between 200 and 400 °C (Burton et al., 2019a). For goethite, this percentage raised 100% at 800 °C. This second study also showed that 35% of the Cr(III) initially present in a Ferralsol was oxidized to Cr(VI) at 600 °C, about 40% of this hexavalent chromium being exchangeable (Burton et al., 2019a). These results were recently confirmed by a study focused on agricultural soils amended with compost derived from tannery sludges where Cr(III)-organic forms were expected to be particularly stable (Rascio et al., 2022). This study indicated that heating of such Cr-rich amended soils from 300 °C to 500 °C induced a significant oxidation of Cr(III) to Cr(VI), with 20%–90% in the exchangeable form. The changes observed on Cr speciation lead the authors to propose that Cr(III) oxidation to Cr(VI) resulted from the thermal destruction of organic matter, including Cr(III)-organic complexes (Rascio et al., 2022). However, in this latter study, no Cr(VI) was found in the control soil that has not been amended, which suggests that the fraction of Cr(III) oxidized to Cr(VI) upon heating might have come from the compost rather than from the soil. This latter hypothesis is supported by previous studies that demonstrated Cr(III) oxidation to Cr(VI) upon heating of tannery or artificial sludges (Mao et al., 2015; Zhou et al., 2021).

Whatever the origin of Cr(III), considering the known higher mobility and toxicity of Cr(VI) (Rai et al., 1989; Fendorf, 1995; Costa, 1997; Ball and Nordstrom, 1998; Sun et al., 2015), these studies emphasize the high potential of wildfires to disperse Cr(VI) from soils towards freshwater systems and thus to represent an health and/or ecological risk. This risk is especially important in New Caledonia where chromium occurs at very high concentrations (up to 30,000 g/kg) in Ferralsols developed on ultramafic rocks that cover 1/3 of the surface of the main island (Becquer et al., 2003, 2006, 2010; Massoura et al., 2006; Fandeur et al., 2009a,b; Fritsch, 2012; Isnard et al., 2016; Houles et al., 2018; Vincent et al., 2018) and wildfires have become an environmental issue during the last decade (Pellens and Grandcolas, 2009; Ibanez et al., 2013; Gomez et al., 2014; Curt et al., 2015; Mangeas et al., 2018; Toussaint, 2020). As an illustration, about 27,000 ha of vegetation (i.e. about 2% of the total surface of the main island) burned during the 2019–2020 hot season, whilst the surface of burned vegetation estimated during the period 1999–2010 is 25,000 ha (Curt et al., 2015). Vegetation in New Caledonia is composed of about 800,000 ha of savannas and thickets, 600,000 ha of maquis (i.e. the most common native vegetation type), 400,000 ha of rainforests and only 10,000 ha of dry forest (Jaffré et al., 1997). This latter ecosystem is the most exposed to wildfires because it is mainly used as private lands and the main cause of wildfires ignition in New Caledonia is land clearance for cultivation and hunting (Toussaint, 2020). As a consequence of these wildfires, the dry forest, which is usually associated with volcano-sedimentary and calcareous soils (Gomez et al., 2014), is considered to have been reduced

to a few fragments that represent only 1% of its original surface since the first human settlement in New Caledonia about 3,000 years ago (Bouchet et al., 1995; Jaffré et al., 1997; Gillepsie and Jaffre, 2003). Covering about 70% of the main island, savannas/thickets and maquis are also prone to wildfires. Although savannas/thickets are distributed across volcano-sedimentary and calcareous soils (Gomez et al., 2014), maquis is the most common native vegetation type on Ferralsols on ultramafic rocks (Jaffré et al., 1997). Considering these ecological and pedological characteristics, fire-promoted generation of Cr(VI) in Cr-rich Ferralsols from New Caledonia is likely to significantly impact the freshwater systems that represent the major water resource for the inhabitants of this French overseas territory.

The aim of the present study was to make a first assessment of the risk of freshwater Cr(VI) pollution after wildfires in New Caledonia by quantifying the influence of soil heating on chromium mobility in four Ferralsols representative of Cr-rich soils developed on ultramafic rocks. To reach this goal, X-ray diffraction analyses were combined with chemical extractions to follow the mineralogical evolution and Cr(VI) mobility in four selected Cr-rich Ferralsols after heating at 200 °C, 400 °C and 600 °C. Then, a mass balance calculation relying on Cr(VI) mobility in the four investigated Ferralsols allowed to compare the expected Cr(VI) concentration in freshwater as a function of the suspended particulate matter (SPM) concentration with the World Health Organization (WHO) guideline for drinking water quality (GDWQ) of 50 µg/L for chromium. The results obtained allowed confirming the risk of freshwater Cr(VI) pollution in burned ultramafic catchments composed of Cr-rich Ferralsols, but also proposing a possible modulation of this risk as a function of the actual location of the wildfires at the catchment scale (top vs. slope/base of the catchment).

2. Materials and methods

2.1. Study site and soils sampling

New-Caledonia is a French archipelago located in the South Pacific Ocean, approximately 3,200 km east of Australia and 2,400 km north of New Zealand. The archipelago is made up of a main island called “Grande Terre”, four Loyalty Islands (Lifou, Maré, Ouvéa, Tiga), the Belep archipelago, the Isle of Pines and uninhabited islets. For this study, the surface horizons (0–10 cm depth) of four Ferralsols from Grande Terre with differing chemistry and mineralogy (Houles et al., 2018; Vincent et al., 2018, Fig. 1; Tables 1 and S1) were considered. Soil TIE (S 20°28'19.20"; E 164°15'35.16") is a Geric Ferralsol (Munsell color as collected 10R3/3 for the 0–10 cm horizon; Fig. S1) sampled in the colluvium formed upon erosion at the bottom of the Tiebaghi regolith, one of the oldest lateritic Ni-ores mined in New Caledonia (Fig. 1). Soil PAND (S 21°01'35.84"; E 164°46' 58 68") is a Magnesic Ferralsol (Munsell color as collected 7.5YR3.5/4 for the 0–10 cm horizon; Fig. S1) sampled at the bottom of the Koniambo ultramafic regolith, one of the major lateritic Ni-ores from New Caledonia (Fig. 1). Soil PAND2 (S 21°01' 58.80"; S 164°46 40.77") is an Abruptic Ferralsol (Munsell color as collected 7.5YR3/2 for the 0–10 cm horizon; Fig. S1) sampled in the alluvial plain of the Pandanus river, whose catchment is part of the Koniambo ultramafic regolith (Fig. 1). Soil PIND (S 21°19'55.45"; E164°58'19'24") is an Haplic Ferralsol (Munsell color as collected 5YR3/3 for the 0–10 cm horizon; Fig. S1) sampled in the Pindai peninsula, close to the Kopeto ultramafic regolith another historic lateritic Ni-ore from New Caledonia (Fig. 1). According to the data clustered by the Environmental Observatory of New-Caledonia (<http://geoportail.oeil.nc/AlerteIncendies/>), the selected soils have not been affected by wildfires during the 5 years that preceded sampling in 2013.

2.2. Soil samples thermal treatment

Soil samples were sieved to 2 mm and ground mechanically in an

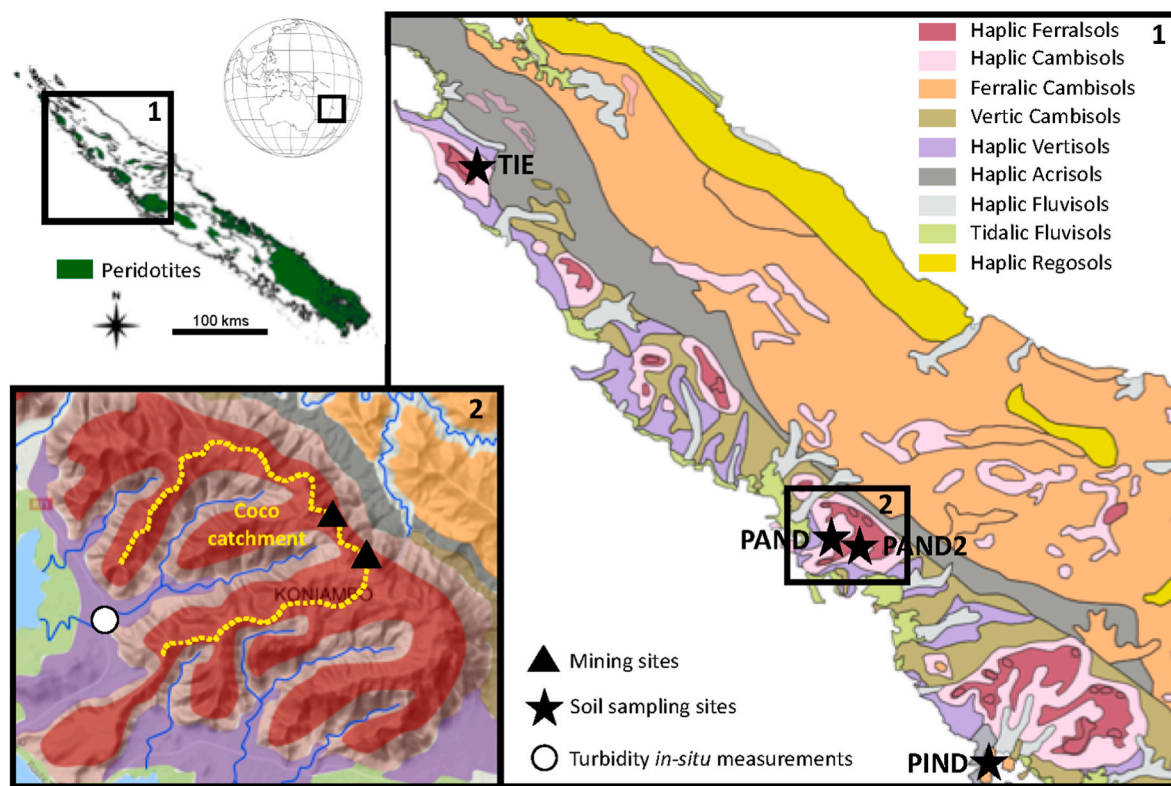


Fig. 1. Maps showing the location of New Caledonia at the world scale and the extent of the peridotites bedrock across Grande Terre, as well as the location of the four studied Ferralsols in the Northern Province (inset 1) and that of *in-situ* turbidity measurements at the outlet of the Coco catchment (Koniambo ultramafic regolith; inset 2).

agate mortar in order to maximize the effect of thermal treatment on Cr (III) to Cr(VI) oxidation. Then, a fraction of each of the four soil samples was heated in a ceramic crucible at 200 °C, 400 °C and 600 °C for 2 h in a pre-heated open-air furnace. This range of temperature is the one expected during wildfires, since the major type of vegetation at the sampled sites was scrubland with limited fuelling biomass (Neary et al., 1999; Gomez et al., 2014). The amount of sample heated for each soil ranged between 3 and 6 g, depending on the need for replicates. After 2 h heating, the samples were removed from the furnace without pre-cooling.

2.3. Chemical and mineralogical analyses

Concentration of major and trace elements (Si, Mg, Ca, K, Ti, Fe, Al, Mn, Ni, Cr, Co, Zn) in the studied samples was quantified by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) with a Varian 730-ES (PerkinElmer®) after alkaline fusion. Total organic carbon (C_{org}) concentration was quantified following the dry combustion method using a CHN SERCON® Integra 2 analyzer. All analyses were performed on the mechanically ground <2 mm fraction of the samples at the Laboratoire des Moyens Analytiques (LAMA-IMAGO) of Institut de Recherche pour le Développement (IRD) Noumea (New Caledonia). This ISO 9001 certified laboratory is member of the Global Soil Laboratory Network (GLOSOLAN; <http://www.fao.org/global-soil-partnership/glosolan/en/>) labelled by the Food and Agriculture Organization of the United Nations (UN-FAO). In addition to chemical analyses, the mineralogical composition of the mechanically ground <2 mm fraction of the non-heated and heated soil samples was assessed by X-ray diffraction (XRD). Non-heated soil samples were analysed at Institut de Mineralogy, de Physique des Matériaux et de Cosmochimie (IMPMC) of Sorbonne University (Paris, France) with an X'PERT PRO (Malvern Panalytical®) diffractometer configured in the Bragg-Brentano geometry and equipped with a Co anti-cathode and an X'celerator detector.

Each sample was analysed during 60 min on the 5–80 °2 θ range (0.017 °2 θ steps with a counting time of 200 s/step) in the spinner mode at a tension of 40 kV and intensity of 30 mA. Heated soil samples were analysed at Institut des Sciences Exactes et Appliquées (ISEA) of the University of New Caledonia (Noumea, New Caledonia) with an AERIS (Malvern Panalytical®) diffractometer configured in the Bragg-Brentano geometry and equipped with a Co anti-cathode and a PIXcel3D detector. Each sample was analysed during 25 min on the 5–80 °2 θ range (0.011 °2 θ steps with a counting time of 50 s/step) in the spinner mode at a tension of 40 kV and intensity of 15 mA. Quantitative analysis of the XRD powder patterns was performed according to the Rietveld method with the MAUD® version 2.7 software (Lutterotti et al., 1999). Despite different experimental conditions that are expected to have influenced the intensity of the XRD patterns between heated and non-heated samples, comparison of their quantitative mineralogy remained fully reliable because the Rietveld method normalizes the proportion of each of the mineral species quantified in a sample to their summed proportion.

2.4. Chromium mobility

Two sets of chemical extractions were performed to evaluate chromium behaviour upon soil heating. A first extraction with a 0.01 M $CaCl_2$ solution was used to mimic the ionic strength of the soil solution that could drive chromium mobility upon first rain after a wildfire (Houba et al., 1990, 2000). This extraction was done in a batch mode at a 1 g/10 mL solid/liquid ratio and with constant stirring during 2 h. After this reaction time, the pH was measured in the $CaCl_2$ -extracts. A second extraction with a 0.1 M KH_2PO_4 solution was done to remove all extractable Cr(VI) bound to soil organic and mineral surfaces. The protocol used slightly differed from that of (Bartlett, 1991), with a 1 g/30 mL solid/liquid ratio and constant stirring during 2 h. Despite its lowest solid/liquid ratio compared to $CaCl_2$ extraction, KH_2PO_4

extraction is designed to remove much larger amounts of Cr(VI) because of the higher concentration (i.e., 0.1M compared to 0.01M) and stronger efficiency of the reagent (i.e., $\text{PO}_4^{3-}/\text{HPO}_4^{2-}$ anions compared to Cl^- anions) that is expected to induce competitive exchange for sorption sites with $\text{CrO}_4^{2-}/\text{HCrO}_4^-$ anions. Both sets of extractions were performed in 15 mL Falcon® tubes. After each extraction, the tubes were centrifuged during 10 min at 3500 rpm and the supernatant was filtered through a 0.45 μm membrane. Filtered solutions were then stored at 4 °C to prevent any evaporation and to slow down any possible chemical and/or biological reactions before chemical analysis. Total chromium concentration in the filtered CaCl_2 extracts was quantified by ICP-OES at LAMA (Noumea, New Caledonia) within 96h after extractions. In addition, and within the same time, Cr(VI) concentration was quantified in these extracts, as well as in the filtered KH_2PO_4 extracts, according to the diphenyl carbazide (DPC) colorimetric method (Bartlett, 1991). These latter analyses were performed with a Lambda750 (PerkinElmer®) spectrophotometer at the Laboratoire de Spectroscopie de Noumea (IRD, Noumea, New Caledonia). Because of the detection limit of the method (i.e., 0.1 mg/L), only the samples heated at 400 °C and 600 °C were analysed for Cr(VI) concentration (Table 2).

2.5. Freshwater Cr(VI) pollution risk assessment

A first assessment of the potential risk of freshwater Cr(VI) pollution at burned ultramafic catchments was performed according to equations (1) and (2).

$$\text{Cr(VI)}_{\text{mg/L}}^{\text{freshwater}} = \left[\text{Cr(VI)}_{\text{mg/kg}}^{\text{CaCl}_2} / 10^6 \right] \cdot \text{SPM}_{\text{mg/L}}^{\text{freshwater}} \quad (1)$$

$$\text{Cr(VI)}_{\text{mg/kg}}^{\text{CaCl}_2} = \text{Cr(VI)}_{\text{mg/L}}^{\text{CaCl}_2} / R_{\text{solid-liquid}}^{\text{CaCl}_2} \quad (2)$$

In these equations, $\text{Cr(VI)}_{\text{mg/L}}^{\text{freshwater}}$ corresponds to the expected Cr(VI) concentration in freshwater (i.e., in mg/L), $\text{Cr(VI)}_{\text{mg/kg}}^{\text{CaCl}_2}$ and $\text{Cr(VI)}_{\text{mg/L}}^{\text{CaCl}_2}$ correspond to the amount of CaCl_2 -Cr(VI) in SPM that would originate from burned soils (i.e., respectively in mg/kg and mg/L), $\text{SPM}_{\text{mg/L}}^{\text{freshwater}}$ corresponds to the SPM concentration in freshwater (i.e., in mg/L) and $R_{\text{solid-liquid}}^{\text{CaCl}_2}$ corresponds to the solid/liquid ratio used in the CaCl_2 extractions (i.e., 1/10).

Application of Equations (1) and (2) for the four non-heated (i.e., 25 °C) and 200 °C, 400 °C and 600 °C-heated Ferralsols first allowed to depict the SPM concentration for which the expected Cr(VI) concentration in freshwater would exceed the WHO GDWQ for chromium (i.e. 50 $\mu\text{g/L}$). These threshold SPM concentrations were then compared with those measured during a 9 months survey (January 2014–September 2015) performed by the mining company Koniambo Nickel SAS (KNS) at the outlet of the Coco catchment in the Koniambo ultramafic regolith (Fig. 1). For this comparison, *in-situ* turbidity measurements (i.e., Nephelometric Turbidity Unit - NTU) performed automatically at a 10 min time-lapse with a PONSEL ODEON side-scatter turbidity sensor using infrared light at 880 nm were used to derive SPM concentrations (i.e., mg/L), thanks to the correlation between both parameters established on 30 measurements (slope = 0.56; $R^2 = 0.86$; Fig. S2).

3. Results and discussion

3.1. Chemical and mineralogical characteristics of the studied soils

In New Caledonia, most Ferralsols are particularly enriched in Cr, Mn, Ni and Co (Isnard et al., 2016; Houles et al., 2018; Vincent et al., 2018) because they have developed on ultramafic rocks (i.e. peridotites). This trend is illustrated by the concentrations of Cr, Mn, Ni and Co measured in the 0–10 cm samples collected in the four investigated soils that ranged from 16,082 to 40,286 mg/kg for Cr, from 4824 to 17,210 mg/kg for Mn, from 2623 to 6709 mg/kg for Ni and from 408 to 1201

mg/kg for Co (Table 1). After Fe that showed concentrations ranging from 250,300 to 505,300 mg/kg (i.e., from 25.03 to 50.53%; Table 1), Cr was thus the most enriched trace metal in the four investigated Ferralsols.

Quantitative analysis of X-Ray Diffraction (XRD) powder patterns (Figs. S3–S6) indicated that goethite ($\alpha\text{-FeOOH}$) was the major mineral species in soils PIND, PAND and PAND2 (Fig. S7; Table S1). These soils also contained significant amounts of quartz (SiO_2) and enstatite (MgSiO_3), as well as minor amounts of talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) and serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$). By comparison, hematite ($\alpha\text{-Fe}_2\text{O}_3$) was the major mineral species in soil TIE, where it occurred together with significant amounts of goethite and traces of quartz (Fig. S7; Table S1).

3.2. Thermal transformation of mineral species

Powder XRD analyses emphasized the thermal transformation or stability of the different mineral species identified in the investigated Ferralsols (Figs. S3–S7; Table S1). For all soils, the XRD powder patterns showed a progressive disappearance of the peaks related to goethite from 200 °C to 600 °C (Figs. S3–S6). At 600 °C, these XRD peaks have completely disappeared. Meanwhile, the intensity of the XRD peaks related to hematite tended to increase with increasing heating temperature. These changes are in agreement with the known thermal behaviour of goethite, which starts to transform into proto-hematite ($\text{Fe}_{5/3}\text{O}_2\text{OH}$) at 250 °C. This latter mineral species then transforms into hydro-hematite ($\text{Fe}_{11/6}\text{O}_{5/2}(\text{OH})_{1/2}$) at 400 °C. Finally, hydro-hematite is fully transformed into hematite Fe_2O_3 above 800 °C (Gualtieri and Venturelli, 1999; Landers and Gilkes, 2007; Perrier et al., 2006; Wells et al., 2006; Wolska and Schwertmann, 1989). This goethite-to-hematite thermal pathway corresponds to reactions under oxidising conditions. However, organic matter can favour reducing conditions during fire in soils. Under such conditions, goethite can partially or fully transform into maghemite (Fe_3O_4) rather than hematite (Eggleton and Taylor, 2008; Grogan et al., 2003; Ketterings et al., 2000; Perrier et al., 2006; Terefe et al., 2008). In our study, such a transformation of goethite to maghemite was limited due to the low amounts of organic matter measured in the investigated soils (i.e., total organic carbon ranging from 0.9 to 6.8 g/kg; Table 1).

Concerning phyllosilicates, the XRD patterns of heated soils showed the disappearance of the peaks related to serpentine from 400 °C (Figs. S3–S6). These changes are in agreement with the known thermal behaviour of this mineral species, which starts to dehydroxylate around 450 °C and is generally fully transformed to fosterite (Mg_2SiO_4) and enstatite (MgSiO_3) around 800 °C (Hang and Brindley, 1973; Cattaneo et al., 2003; Perrillat et al., 2005; Viti and Hirose, 2010; Gualtieri et al., 2012; Tritschack and Grobety, 2012; Tritschack et al., 2012). Although the formation of talc as an intermediate mineral species during this transformation is possible (McKenzie and Meinhold, 1994), XRD data did not allow to confirm such a thermal pathway in the investigated soils. Indeed, the peaks related to talc were already visible on the XRD powder patterns of all the initial soils, but TIE (Figs. S3–S6). Besides, the persistence of these XRD peaks in heated soils is in agreement with the known stability of this mineral species at temperature up to 800 °C (Ketterings et al., 2000). Finally, XRD data emphasized the disappearance of the XRD peak related to smectite upon soil heating (Figs. S3–S6), which is in agreement with the known collapsing behavior of this layered structure along the c axis (i.e., the crystallographic axis of sheets stacking) upon interlayer water removing (Brindley and Brown, 1980). Finally, when present in the non-heated soil, the persistence of the XRD peaks related to quartz and enstatite whatever the heating temperature (Figs. S3–S6) is in agreement with the P-T stability diagrams of these two mineral species (Swamy et al., 1994; Ulmer and Stadler, 2001; Gasparik, 2014).

Table 1

Chemical composition of the 0–10 cm samples collected in the four investigated Ferralsols.

Sample	Fe	Al	Si	Mg	Cr	Mn	Ni	Co	Zn	Ti	Ca	K	Corg
	(%)				(mg/kg)								(g/kg)
TIE	50.5	4.40	1.73	0.22	16,082	17,210	2622	714	248	1622	210	104	1.60
PAND	32.8	2.05	9.74	2.52	29,141	6709	6708	633	251	263	1070	81	3.50
PAND2	40.8	1.68	6.05	0.97	40,246	7054	4658	1201	319	480	130	91	0.90
PIND	25.0	5.03	14.3	1.05	20,641	4824	5107	408	93	4014	5770	1286	6.80

Table 2Total Cr (ICP-OES) and Cr(VI) (DPC colorimetric method) concentration in the CaCl₂ and KH₂PO₄ extracts for the four Ferralsols before (25 °C) and after heating at 200 °C, 400 °C and 600 °C. Concentration are expressed in g/kg in columns 2–4 and in % in column 5–7. Column 8 corresponds to the ratio between columns 6 and 7.

Sample	Total Cr CaCl ₂	Cr(VI) CaCl ₂	Cr(VI) KH ₂ PO ₄	Total Cr CaCl ₂	Cr(VI) CaCl ₂	Cr(VI) KH ₂ PO ₄	Cr(VI) CaCl ₂ /KH ₂ PO ₄
	(mg/kg)			(%)			(%)
TIE							
25	0.10	nd ^a	22.3	0.00	nd	0.14	nr ^b
200	0.60	nd	37.7	0.00	nd	0.23	nr
400	30.0	29.9	1772	0.19	0.20	11.0	1.82
600	65.0	52.9	635	0.40	0.30	3.95	7.59
PAND							
25	0.00	nd	<3.00 ^c	0.00	nd	<0.02 ^c	nr
200	0.29	nd	10.3	0.00	nd	0.04	nr
400	855	732	1034	2.94	2.51	5.01	50.1
600	751	644	863	2.58	2.22	4.18	53.1
PAND2							
25	0.00	nd	<3.00 ^c	0.00	nd	<0.02 ^c	nr
200	0.74	nd	108	0.00	nd	0.3	nr
400	701	583	1685	1.74	1.45	5.78	25.1
600	651	499	921	1.62	1.24	3.16	39.2
PIND							
25	0.00	nd	<3.00 ^b	0.0	nd	<0.02 ^c	nr
200	0.15	nd	3.38	0.0	nd	0.02	nr
400	793	560	2084	3.84	2.71	5.18	52.3
600	696	576	1373	3.37	2.79	3.41	81.8

^a Not determined due to concentration below the detection limit of the DPC colorimetric method (i.e., 0.1 mg/L; Bartlett, 1991).^b Not relevant.^c Calculated by considering the detection limit of the DPC colorimetric method as the Cr(VI) concentration in the KH₂PO₄ extract.

3.3. An enhanced chromium mobility after soil heating

Chemical extractions with a 0.01M CaCl₂ solution allowed to assess the effect of soil heating on chromium mobility at three levels. In a first step, total Cr concentration in the CaCl₂ extracts (i.e., total Cr-CaCl₂) allowed to assess the total amount of mobile chromium. The results showed an increase of this total amount of mobile chromium with temperature in all the soils investigated. However, although a similar

slight increase from less than 0.1 mg/kg at room temperature (i.e., 25 °C) to about 0.5 mg/kg at 200 °C was observed in all soils (Fig. 2; Table 2), a marked difference between soil TIE and the three other soils appeared from 200 °C. In soil TIE, the total amount of mobile chromium increased from 0.6 mg/kg at 200 °C to 30 mg/kg at 400 °C and then to 65 mg/kg at 600 °C (Fig. 2; Table 2). By contrast, the total amount of mobile chromium in soils PAND, PAND2 and PIND increased from about 0.5 mg/kg at 200 °C to more than 700 mg/kg at 400 °C (Fig. 2; Table 2).

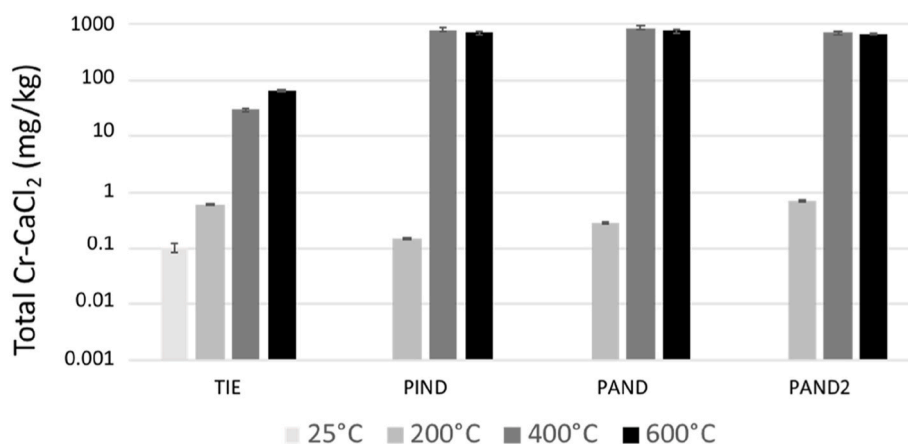


Fig. 2. Total amount of mobile chromium (expressed in mg/kg) in the four investigated Ferralsols as a function of heating temperature (non-heated, 200 °C, 400 °C and 600 °C). Each error bar represents the standard deviation on three replicates.

Then, the total amount of mobile chromium in these three soils did not increase significantly between 400 °C and 600 °C (Fig. 2; Table 2).

In a second step, the diphenyl carbazide (DPC) colorimetric method was used to quantify Cr(VI) in the CaCl₂ extracts and to compare this fraction of chromium with that of total CaCl₂-extracted Cr (Table 2). The results indicated a very good correlation between the fraction of Cr(VI) and that of total Cr in the CaCl₂ extracts (i.e. $R^2 = 0.97$; Fig. S8). Although this correlation supported the hypothesis that the major fraction of mobile chromium was Cr(VI), the slope of the regression (i.e. 0.80; Fig. S8) suggested that ca. 20% of mobile chromium might have occurred as Cr(III). Considering the reported capacity of natural organic matter to complex Cr(III) (Gustafsson et al., 2014; Löf et al., 2017), this fraction of mobile chromium could have resulted from the thermal destabilization/destruction of organic-Cr(III) complexes associated with soil organic matter.

In a third step, KH₂PO₄ extractions were used to assess total extractable Cr(VI) in the investigated soils. The results diverged from those of CaCl₂ extractions, since similar fractions of Cr(VI) were measured in the KH₂PO₄ extracts from soil TIE and the three other soils (Table 2). These extractions also showed larger fractions of Cr(VI)-KH₂PO₄ after heating at 400 °C compared to heating at 600 °C (Table 2). This latter result is in agreement with a recent study, which reported the formation of Cr(VI) upon heating of synthetic Cr(III)-doped Fe-oxides up to 800 °C, with the greatest extent of Cr(VI) formation found in the 200–400 °C range (Burton et al., 2019b). Finally, for both temperatures, the fraction of Cr(VI) in the KH₂PO₄ extracts was systematically larger than those of total chromium or Cr(VI) in the CaCl₂ extracts (Fig. S9; Table 2).

3.4. A chromium mobility likely driven by the hematite content and pH

Since KH₂PO₄ extraction is expected to release total extractable Cr(VI) in a given sample, comparison with CaCl₂ extraction allowed to calculate the percentage of mobile Cr(VI) in the four investigated soils after heating at 400 and 600 °C. These percentages indicated that, after heating at 400 °C, less than 2% of Cr(VI) was mobile in soil TIE compared to 25–50% in soils PAND, PAND2 and PIND (Table 2). After heating at 600 °C, the fraction of mobile Cr(VI) was below 8% in soil TIE compared to 39–82% in soils PAND, PAND2 and PIND (Table 2). These percentages emphasize the lower mobility of Cr(VI) in soil TIE compared to the three other investigated soils.

The mineralogical characteristics of the investigated soils might provide some clues on this difference. Although structural incorporation in oxides and phyllosilicates can be considered to have played a major control on Cr(III) mobility in the non-heated and heated Ferralsols (Schwertmann et al., 1989; Singh et al., 2002; Oze et al., 2004; Sileo et al., 2004; Garnier et al., 2006, 2008; Becquer et al., 2003, 2006; Wells et al., 2006; Fandeur et al., 2009a), sorption onto the surfaces of mineral species is expected to have been the major process controlling Cr(VI) mobility. In this regard, the Fe-oxides/silicates ratio seems especially important since several studies have emphasized the strong affinity of Cr(VI) for the surface of Fe-oxides (Singh et al., 1993; Fendorf, 1995; Fendorf et al., 1997; Ajouyed et al., 2010), whereas Cr(VI) sorption onto silicate minerals is rather limited (Bhattacharyya and Gupta, 2006; Guerra et al., 2010; Veselska et al., 2016). Our XRD analyses indicated an occurrence of almost 100% hematite after heating at 400 °C or 600 °C in soil TIE, compared to a mixture of 45–65% hematite and 35–55% silicate minerals (quartz, enstatite, serpentine, talc) in soils PAND, PAND2 and PIND (Fig. S7; Table S1). These results thus strongly suggest that the lower fraction of mobile Cr(VI) measured in soil TIE heated at 400 °C and 600 °C compared to the three other investigated soils might have been due to the larger fraction of hematite formed in this soil upon heating.

This assumption is well supported by the very good correlation obtained between the fraction of mobile Cr(VI) quantified in the four investigated soils heated at 400 and 600 °C and their hematite content

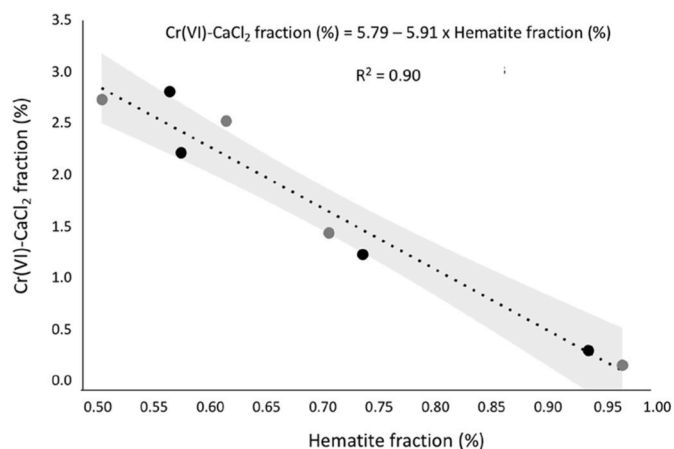


Fig. 3. Fraction of mobile Cr(VI) (i.e., Cr(VI)-CaCl₂ fraction) as a function of hematite fraction in the four investigated soils heated at 400 °C (gray dots) and 600 °C (black dots). Standard deviation within the dots size.

(Fig. 3). This latter result strongly suggests that the hematite content is a key parameter for Cr(VI) mobility in burned catchments composed of Cr-rich Ferralsols.

In addition, Cr(VI) sorption onto hematite depends on pH, with highest sorption below pH 7.0 and then a rapid decrease in the pH range 7.0–8.0 (Ajouyed et al., 2010). The pH of the soil solution is thus also expected to contribute to the fraction of mobile Cr(VI) in heated Ferralsols. In this regard, the pH around 5.0 measured in the CaCl₂ extracts of soils TIE heated at 400 °C and 600 °C (Table S1) is expected to have yielded optimal Cr(VI) sorption onto hematite in these two soil samples. In addition to the large amounts of hematite quantified in soil TIE heated at 400 °C and 600 °C (Fig. S7; Table S1), this pH effect can thus be considered to have also contributed to the low mobility of Cr(VI) measured in these two soils samples (Fig. 3; Table 2). In the same way sorption of Cr(VI) onto hematite should also have contributed to limit the fraction of mobile Cr(VI) in soils PAND and PAND2 heated at 400 °C and 600 °C since the CaCl₂ extracts of these soil samples showed pH values below 7.0 (Table S1). However, the significant mobility of Cr(VI) measured in these two soil samples (Fig. 3; Table 2) is likely explained by their lower hematite contents (Fig. S7; Table S1). Finally, the pH above 7.0 measured in the CaCl₂ extracts of soil PIND heated at 400 °C and 600 °C (Table S1) and the low amounts of hematite quantified in this soil whatever the temperature (Fig. S7; Table S1) likely explain the quite high mobility of Cr(VI) measured in these two soil samples (Fig. 3; Table 2).

3.5. A risk of Cr(VI) freshwater pollution in burned Cr-rich ultramafic catchments

All the above-mentioned results are in agreement with previous studies, which reported enhanced Cr(VI) release upon heating of synthetic Cr(III)-doped Fe-(hydr)oxides (Burton et al., 2019a, 2019b). They suggest that leaching of a burned Cr-rich Ferralsol during the first post-fire rain might release significant amounts of chromium (with up to 80% as the most hazardous Cr(VI) form) towards fresh- or groundwater systems. These results also suggest that SPM issued from burned Cr-rich Ferralsols from New Caledonia are expected to release significant amounts of Cr(VI) in receiving freshwater systems. A wildfire across an ultramafic catchment in New Caledonia could thus be a source of Cr(VI) pollution in the related waterways, depending on the concentration of SPM issued from burned Cr-rich Ferralsols.

A first assessment of this potential risk of freshwater Cr(VI) pollution in burned ultramafic catchments was performed according to Equation (1) that relates chromium concentration in solution to SPM concentration and mobile chromium (i.e., Cr-CaCl₂; Table 2). The results indicated

that the expected chromium concentration in solution would exceed the WHO GDWQ of 50 $\mu\text{g/L}$ in freshwater once the concentration of SPM issued from soils PIND, PAND and PAND2 heated at 400 $^{\circ}\text{C}$ or 600 $^{\circ}\text{C}$ would have reached 80 mg/L (Fig. 4). Regarding the much lower amount of mobile chromium (*i.e.*, Cr-CaCl₂) in soil TIE (Table 2), the WHO GDWQ for chromium would be exceeded for SPM concentration above 2400 mg/L or 1000 mg/L after soil heating at 400 $^{\circ}\text{C}$ or 600 $^{\circ}\text{C}$, respectively (Fig. 4).

Comparison of these threshold SPM concentrations with those actually measured during 9 months (January 2015–September 2015) at the outlet of an ultramafic catchment in New Caledonia (*i.e.*, Coco catchment in the Koniambo ultramafic regolith; Fig. 1) allowed to confirm the risk of fire-induced Cr(VI) pollution in Cr-rich ultramafic catchments from new Caledonia. Indeed, the time-dependent representation of the hourly-averaged SPM concentration at the outlet of the selected catchment showed some values that can reach up to 500 mg/L, especially in the wet season (*i.e.*, December–May; Fig. 5). More interestingly, comparison with the hourly-averaged waterflow that was also monitored during the same period indicated that for each rainy event the hourly-averaged SPM concentration almost systematically exceeded 80 mg/L, the threshold value above which chromium concentration would exceed the WHO GDWQ for soils PIND, PAND and PAND2 heated

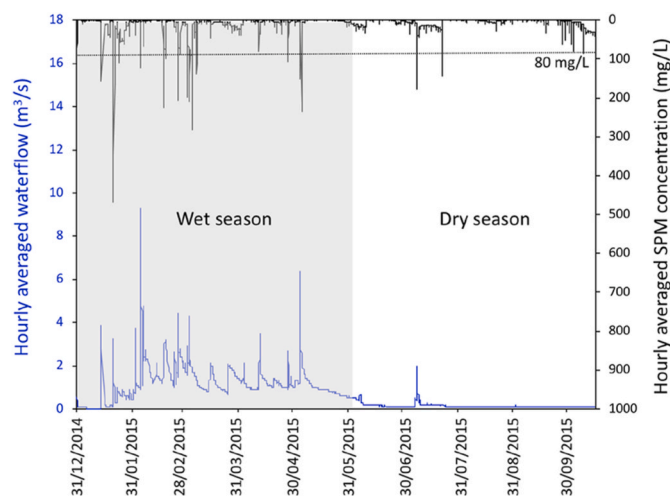


Fig. 5. Time-dependent evolution of the hourly-averaged waterflow (m^3/s) and SPM concentration (mg/L) measured over a 9 months period (January 2015–September 2015) at the outlet of the Coco catchment in the Koniambo ultramafic regolith (New Caledonia; Fig. 1).

at 400 $^{\circ}\text{C}$ or 600 $^{\circ}\text{C}$ (Fig. 5).

Considering that the selected creek is representative of freshwater systems related to ultramafic catchments composed of Cr-rich Ferralsols in New Caledonia and taking into account that 80% of mobile chromium in the heated Ferralsols was found as the most hazardous Cr(VI), these results confirm the risk of Cr(VI) pollution in such freshwater systems during the first rains after wildfires. In addition, this risk of Cr(VI) freshwater pollution after wildfires on Cr-rich Ferralsols due to enhanced chromium mobility at the SPM/water interface could be decoupled by enhanced erosion after vegetation burning. Indeed, the first consequence of wildfires is vegetation loss (Neary et al., 1999; Certini, 2005; Alcañiz et al., 2018) and several studies have related higher SPM loadings in freshwater systems of burned catchments through subsequent enhanced erosion after such a vegetation loss (Shakesby and Doerr, 2006; Moody et al., 2013; Smith et al., 2011; Bladon et al., 2013).

3.6. A risk of Cr(VI) freshwater pollution that could depend on the geomorphology of the burned Cr-rich ultramafic catchments

Considering the soils investigated in this study, the risk of Cr(VI) freshwater pollution is expected to occur after wildfires on Cr-rich Ferralsols with characteristics similar to those of soils PIND, PAND and PAND2. As indicated by our mineralogical data, these Ferralsols contain significant amounts of residual silicate and/or clay minerals after heating, whereas soil TIE is free of these mineral species (Fig. S7; Table S1). Moreover, the negative correlation found between the hematite content and the fraction of mobile Cr(VI) in the investigated Ferralsols (Fig. 3) suggests a control of the Fe-oxides/silicates ratio on the enhanced Cr(VI) mobility upon heating of these soils where Fe-oxides are expected to transform to hematite. In New Caledonia, Ferralsols with significant amounts of silicate and/or clay minerals are found along the slopes or at the bottom of lateritic regoliths, whereas deeply weathered Ferralsols depleted in silicate and/or clay minerals are found on the top of ultramafic regoliths (Becquer et al., 2006; Chevillote et al., 2006; Dublet et al., 2012, 2015; De Boissieu et al., 2018; Ulrich et al., 2019). As a consequence, the risk of Cr(VI) freshwater pollution related to wildfires on Cr-rich Ferralsols in New Caledonia is expected to be the highest on the slopes or at the bottom of lateritic ultramafic catchments, whereas it might be considered substantially lower on the top of these catchments.

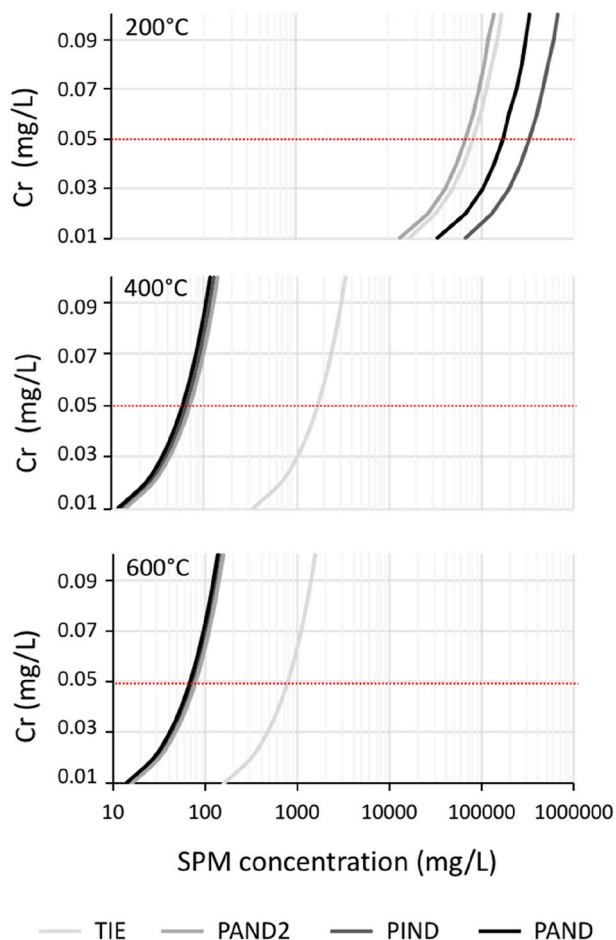


Fig. 4. Chromium concentration (mg/L) as a function of the suspended particulate matter (SPM) concentration (mg/L) in freshwater systems calculated according to Equation (1) by considering total Cr-CaCl₂ (mg/kg) measured on the studied Ferralsols heated at 200 $^{\circ}\text{C}$, 400 $^{\circ}\text{C}$ and 600 $^{\circ}\text{C}$ (Table 2). The horizontal red line on each panel corresponds to the WHO GDWQ of 50 $\mu\text{g/L}$ for chromium. The lower the SPM concentration needed to reach this guideline value, the higher the risk of potential freshwater Cr(VI) pollution in the related freshwater system. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

4. Conclusions

The results of this study indicate that heating Cr-rich Ferralsols from New Caledonia at medium temperatures (*i.e.* 400 °C or 600 °C) can result in a significant increase of mobile chromium from less than 0.2% to about 2.5% of total chromium. These temperatures are relevant to wildfires in New Caledonia since the major biomass fuel on Ferralsols is scrubland. Moreover, about 80% of mobile chromium after Ferralsols heating occurs as Cr(VI), the most mobile and hazardous form of chromium. A burned Cr-rich Ferralsol from New Caledonia might thus be a direct source of aqueous Cr(VI) towards fresh- or groundwater systems upon leaching during the first rains after wildfires. More importantly, SPM dispersed from a burned Cr-rich Ferralsol from New Caledonia might also release significant amounts of Cr(VI) in freshwater systems. A first assessment of this risk of freshwater Cr(VI) pollution indicates that the WHO GDWQ of 50 µg/L might be frequently exceeded after wildfires on the slopes or at the bottom of lateritic ultramafic catchments from New Caledonia. Beyond this first study on Ferralsols, further investigations are needed to evaluate the risk of freshwater Cr(VI) pollution after wildfires on other Cr-rich soils from New Caledonia. Indeed, previous studies have shown that Cambisols or Vertisols can contain significant amounts of chromium (*i.e.* up to 5,000 mg/kg; Houles et al., 2018; Vincent et al., 2018), which raises the question of the potential release of this trace metal after heating of those soil types upon wildfires. Beyond the single case of New Caledonia, the large occurrence of Ferralsols in Brazil, Australia or Central Africa that are increasingly exposed to large wildfires (https://earthobservatory.nasa.gov/global-maps/MOD14A1_M_FIRE) raises the question of the potential consequences of this environmental disturbance on the quality of freshwater systems at a larger scale. This latter point emphasizes the urgent need for fostering studies aimed at better assessing the potential environmental and health impacts of wildfires on freshwater systems worldwide.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2022.105513>.

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