



**HAL**  
open science

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

Gaël Thery, Farid Juillot, Michaël Meyer, Thomas Quiniou, Magali David, Philippe Jourand, Marc Ducouso, Emmanuel Fritsch

### ► To cite this version:

Gaël Thery, Farid Juillot, Michaël Meyer, Thomas Quiniou, Magali David, et al.. Wildfires on Cr-rich Ferralsols can cause freshwater Cr(VI) pollution: A pilot study in New Caledonia. *Applied Geochemistry*, 2023, 148, pp.105513. 10.1016/j.apgeochem.2022.105513 . hal-04490307

HAL Id: hal-04490307

<https://hal.science/hal-04490307v1>

Submitted on 8 Jan 2025

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1

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

4

5 Gaël Thery<sup>1,2,3</sup>, Farid Juillot<sup>1,2\*</sup>, Michael Meyer<sup>4</sup>, Thomas Quiniou<sup>4</sup>, Magali David<sup>1,2</sup>,  
6 Philippe Jourand<sup>5</sup>, Marc Ducouso<sup>5</sup> and Emmanuel Fritsch<sup>1,2</sup>

7

8

9 <sup>1</sup> *Institut de Mineralogie, de Physique des Materiaux et de Cosmochimie (IMPMC), Sorbonne*  
10 *Universite, UMR CNRS 7590, MNHN, ERL IRD 206, Paris, France*

11 <sup>2</sup> *Institut de Recherche pour le Developpement (IRD), ERL 206 IMPMC, Noumea, New Caledonia*

12 <sup>3</sup> *Geosciences Paris Saclay (GEOPS), Universite Paris Saclay, UMR CNRS 8148, Orsay, France*

13 <sup>4</sup> *Institut des Sciences Exactes et Appliquees (ISEA), Universite de la Nouvelle-Caledonie, Noumea,*  
14 *New Caledonia*

15 <sup>5</sup> *Laboratoire des Symbioses Tropicales et Mediterraneennes (LSTM), Universite Montpellier, UMR*  
16 *IRD 040, UMR CIRAD 082, Campus International de Baillarguet, Montpellier, France*

17

18

19

20

21

22

23

24

25 \* Corresponding author : [farid.juillot@ird.fr](mailto:farid.juillot@ird.fr)

26

27

28

29 **Keywords:** Wildfire, Ferralsols, Chromium, Freshwater, SPM, Pollution

30 **Abstract**

31

32 In the context of global warming, environmental forcing of wildfires on continental  
33 ecosystems is on a growing trend. Among other environmental impacts, wildfires can enhance  
34 trace metals concentration in freshwater systems. In this regard, chromium is of particular  
35 environmental and health concern because the temperature-induced oxidation of the less mobile  
36 and toxic Cr(III) form to the most mobile and toxic Cr(VI) one might represent a risk of  
37 freshwater pollution. The aim of the present study was to make a first assessment of this risk in  
38 New Caledonia by quantifying the influence of soil heating on Cr(VI) mobility in Cr-rich  
39 Ferralsols that cover about 1/3 of this French overseas territory. The results obtained indicated  
40 an enhanced Cr(VI) mobility upon soil heating from 200°C, with a marked turnaround from  
41 400°C. Based on these results, a solid/solution mass balance approach allowed to confirm the  
42 risk of freshwater Cr(VI) pollution as a function of suspended particulate matter (SPM)  
43 concentration issued from burned Cr-rich Ferralsols. In addition, the results obtained revealed  
44 an apparent control of the Fe-oxides/silicates ratio on Cr(VI) mobility upon soil heating. Since  
45 this ratio decreases from the top to the bottom of ultramafic catchments, this latter result  
46 suggests that the risk of freshwater Cr(VI) pollution could depend on the actual location of the  
47 wildfires at the top or slope/base of these catchments. Since freshwaters represent the major  
48 water resource for the inhabitants of New Caledonia, these results point to the need for a larger  
49 evaluation of the risk of wildfires-induced freshwater Cr(VI) pollution at other catchments  
50 composed of Cr-bearing soils like Cambisols and Vertisols. At the larger scale, they also point  
51 to the need to foster studies aimed at better evaluating the risk of wildfires-induced freshwater  
52 Cr(VI) pollution at Cr-bearing pedological settings worldwide.

53

54

55

56

57

58

## 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; Alcaniz 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/destroying 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 & Gilkes, 2012). However, these soil components are known to be the major hosts for trace metals in soils (Alloway et al., 2013), and such thermal transformation/destruction can have a strong influence on their mobility (Wells et al., 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 (Cerda & Lacenta, 2005 ; Shakesby & 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-

85 (hydr)oxides, about 40% of the Cr(III) initially incorporated in the starting solid was oxidized  
86 to Cr(VI) upon heating between 200 and 400°C (Burton et al., 2019b). Moreover, between 17  
87 and 70% of the Cr(VI) produced was extractable with a low-concentration phosphate solution  
88 considered to be representative of the exchangeable fraction of Cr(VI). The results of this study  
89 were confirmed by a second one focused on goethite, hematite and ferrihydrite, which showed  
90 that up to 50% of the Cr(III) initially incorporated in ferrihydrite and hematite could be oxidized  
91 to Cr(VI) between 200 and 400°C (Burton et al., 2019a). For goethite, this percentage raised  
92 100% at 800°C. This second study also showed that 35% of the Cr(III) initially present in a  
93 Ferralsol was oxidized to Cr(VI) at 600°C, about 40% of this hexavalent chromium being  
94 exchangeable (Burton et al., 2019a). These results were recently confirmed by a study focused  
95 on agricultural soils amended with compost derived from tannery sludges where Cr(III)-organic  
96 forms were expected to be particularly stable (Rascio et al., 2022). This study indicated that  
97 heating of such C-rich amended soils from 300°C to 500°C induced a significant oxidation of  
98 Cr(III) to Cr(VI), with 20% to 90% in the exchangeable form. The changes observed on Cr  
99 speciation lead the authors to propose that Cr(III) oxidation to Cr(VI) resulted from the thermal  
100 destruction of organic matter, including Cr(III)-organic complexes (Rascio et al., 2022).  
101 However, in this latter study, no Cr(VI) was found in the control soil that has not been amended,  
102 which suggests that the fraction of Cr(III) oxidized to Cr(VI) upon heating might have come  
103 from the compost rather than from the soil. This latter hypothesis is supported by previous  
104 studies that demonstrated Cr(III) oxidation to Cr(VI) upon heating of tannery or artificial  
105 sludges (Mao et al., 2015; Zhou et al., 2021).

106 Whatever the origin of Cr(III), considering the known higher mobility and toxicity of Cr(VI)  
107 (Rai et al., 1989; Fendorf et al., 1995 ; Costa, 1997; Ball & Nordstrom, 1998; Sun et al., 2015),  
108 these studies emphasize the high potential of wildfires to disperse Cr(VI) from soils towards  
109 freshwater systems and thus to represent an health and/or ecological risk. This risk is especially

110 important in New Caledonia where chromium occurs at very high concentrations (up to 30,000  
111 g/kg) in Ferralsols developed on ultramafic rocks that cover 1/3 of the surface of the main island  
112 (Becquer et al., 2003; 2006 ; 2010 ; Massoura et al., 2006 ; Fandeur et al., 2009a; 2009b ;  
113 Fritsch, 2012; Isnard et al., 2016; Houles et al., 2018; Vincent et al., 2018) and wildfires have  
114 become an environmental issue during the last decade (Pellens & Grandcolas, 2009; Ibanez et  
115 al. 2013; Pascal et al., 2013; Gomez et al., 2014; Curt et al., 2015; Mangeas et al., 2019;  
116 Toussaint, 2019). As an illustration, about 27,000 ha of vegetation (*i.e.* about 2% of the total  
117 surface of the main island) burned during the 2019-2020 hot season, whilst the surface of burned  
118 vegetation estimated during the period 1999-2010 is 25,000 ha (Curt et al., 2015). Vegetation  
119 in New Caledonia is composed of about 800,000 ha of savannas and thickets, 600,000 ha of  
120 maquis (*i.e.* the most common native vegetation type), 400,000 ha of rainforests and only  
121 10,000 ha of dry forest (Jaffré et al., 1997). This latter ecosystem is the most exposed to  
122 wildfires because it is mainly used as private lands and the main cause of wildfires ignition in  
123 New Caledonia is land clearance for cultivation and hunting (Toussaint, 2019). As a  
124 consequence of these wildfires, the dry forest, which is usually associated with volcano-  
125 sedimentary and calcareous soils (Gomez et al., 2014), is considered to have been reduced to a  
126 few fragments that represent only 1% of its original surface since the first human settlement in  
127 New Caledonia about 3,000 years ago (Bouchet et al., 1995; Jaffre et al., 1997; Gillespie &  
128 Jaffre, 2003). Covering about 70% of the main island, savannas/thickets and maquis are also  
129 prone to wildfires. Although savannas/thickets are distributed across volcano-sedimentary and  
130 calcareous soils (Gomez et al., 2014), maquis is the most common native vegetation type on  
131 Ferralsols on ultramafic rocks (Jaffré et al., 1997). Considering these ecological and pedological  
132 characteristics, fire-promoted generation of Cr(VI) in Cr-rich Ferralsols from New Caledonia  
133 is likely to significantly impact the freshwater systems that represent the major water resource  
134 for the inhabitants of this French overseas territory.

135 The aim of the present study was to make a first assessment of the risk of freshwater Cr(VI)  
136 pollution after wildfires in New Caledonia by quantifying the influence of soil heating on  
137 chromium mobility in four Ferralsols representative of Cr-rich soils developed on ultramafic  
138 rocks. To reach this goal, X-ray diffraction analyses were combined with chemical extractions  
139 to follow the mineralogical evolution and Cr(VI) mobility in four selected Cr-rich Ferralsols  
140 after heating at 200°C, 400°C and 600°C. Then, a mass balance calculation relying on Cr(VI)  
141 mobility in the four investigated Ferralsols allowed to compare the expected Cr(VI)  
142 concentration in freshwater as a function of the suspended particulate matter (SPM)  
143 concentration with the World Health Organization (WHO) guideline for drinking water quality  
144 (GDWQ) of 50 µg/L for chromium (WHO, 2020). The results obtained allowed confirming the  
145 risk of freshwater Cr(VI) pollution in burned ultramafic catchments composed of Cr-rich  
146 Ferralsols, but also proposing a possible modulation of this risk as a function of the actual  
147 location of the wildfires at the catchment scale (top vs. slope/base of the catchment).

148

## 149 **2. MATERIALS AND METHODS**

150

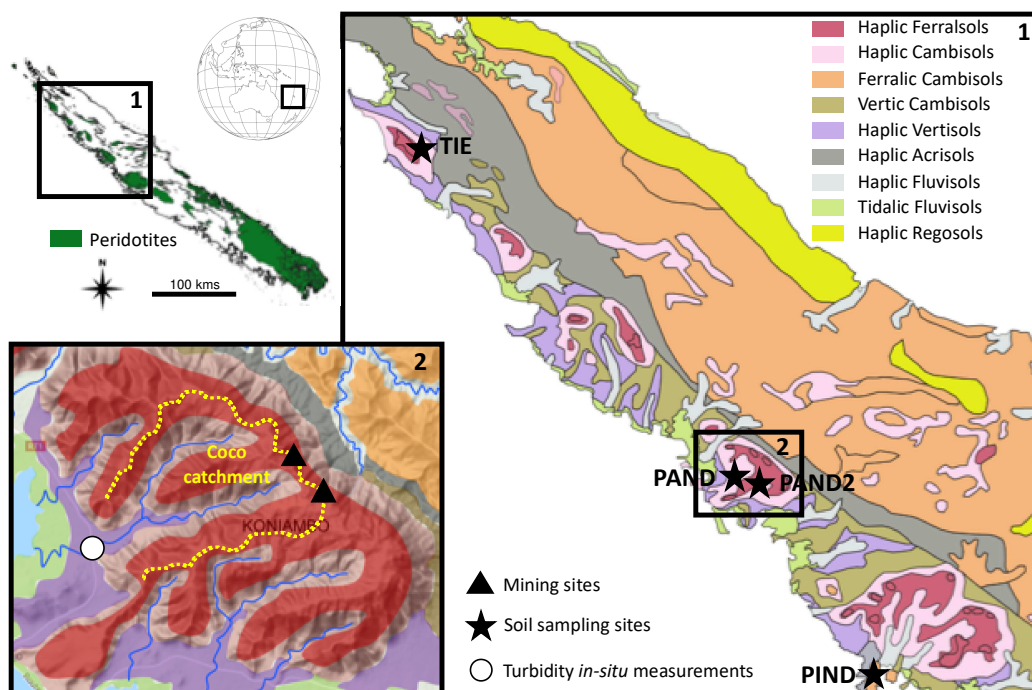
### 151 *2.1 Study site and soils sampling*

152

153 New-Caledonia is a French archipelago located in the South Pacific Ocean, approximately  
154 3,200 km east of Australia and 2,400 km north of New Zealand. The archipelago is made up of  
155 a main island called "Grande Terre", four Loyalty Islands (Lifou, Maré, Ouvéa, Tiga), the Belep  
156 archipelago, the Isle of Pines and uninhabited islets. For this study, the surface horizons (0-10  
157 cm depth) of four Ferralsols from Grande Terre with differing chemistry and mineralogy  
158 (Houles et al., 2018; Vincent et al., 2018; Figure 1; Tables 1 and S1) were considered. Soil TIE  
159 (S 20°28'19.20"; E 164°15'35.16) is a Geric Ferralsol (Munsel color as collected 10R3/3 for  
160 the 0-10 cm horizon; Figure S1) sampled in the colluvium formed upon erosion at the bottom

161 of the Tiebaghi regolith, one of the oldest lateritic Ni-ores mined in New Caledonia (Figure 1).  
 162 Soil PAND (S 21°01'35.84"; E 164°46' 58 68") is a Magnesian Ferralsol (Munsell color as  
 163 collected 7.5YR3.5/4 for the 0-10 cm horizon; Figure S1) sampled at the bottom of the  
 164 Koniambo ultramafic regolith, one of the major lateritic Ni-ores from New Caledonia (Figure  
 165 1). Soil PAND2 (S 21° 01' 58.80"; S 164°46 40.77") is an Abruptic Ferralsol (Munsell color as  
 166 collected 7.5YR3/2 for the 0-10 cm horizon; Figure S1) sampled in the alluvial plain of the  
 167 Pandanus river, whose catchment is part of the Koniambo ultramafic regolith (Figure 1). Soil  
 168 PIND (S 21°19'55.45"; E164°58'19'24") is an Haplic Ferralsol (Munsell color as collected  
 169 5YR3/3 for the 0-10 cm horizon; Figure S1) sampled in the Pindaï peninsula, close to the  
 170 Kopeto ultramafic regolith another historic lateritic Ni-ore from New Caledonia (Figure 1).  
 171 According to the data clustered by the Environmental Observatory of New-Caledonia  
 172 (<https://geoportail.oeil.nc/AlerteIncendies/>), the selected soils have not been affected by  
 173 wildfires during the 5 years that preceded sampling in 2013.

174



175

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



180        *2.2 Soil samples thermal treatment*

181

182        Soil samples were sieved to 2mm and ground mechanically in an agate mortar in order to  
183 maximize the effect of thermal treatment on Cr(III) to Cr(VI) oxidation. Then, a fraction of  
184 each of the four soil samples was heated in a ceramic crucible at 200°C, 400°C and 600°C for  
185 2 hours in a pre-heated open-air furnace. This range of temperature is the one expected during  
186 wildfires, since the major type of vegetation at the sampled sites was scrubland with limited  
187 fuelling biomass (Neary et al., 1999; Gomez et al., 2014). The amount of sample heated for  
188 each soil ranged between 3 and 6 g, depending on the need for replicates. After 2 hours heating,  
189 the samples were removed from the furnace without pre-cooling.

190

191        *2.3 Chemical and mineralogical analyses*

192

193        Concentration of major and trace elements (Si, Mg, Ca, K, Ti, Fe, Al, Mn, Ni, Cr, Co, Zn)  
194 in the studied samples was quantified by Inductively Coupled Plasma Optical Emission  
195 Spectroscopy (ICP-OES) with a Varian 730-ES (PerkinElmer®) after alkaline fusion. Total  
196 organic carbon ( $C_{org}$ ) concentration was quantified following the dry combustion method using  
197 a CHN SERCON® Integra 2 analyzer. All analyses were performed on the mechanically ground  
198 < 2 mm fraction of the samples at the Laboratoire des Moyens Analytiques (LAMA-IMAGO)  
199 of Institut de Recherche pour le Developpement (IRD) Noumea (New Caledonia). This ISO  
200 9001 certified laboratory is member of the Global Soil Laboratory Network (GLOSOLAN;  
201 <http://www.fao.org/global-soil-partnership/glosolan/en/>) labelled by the Food and Agriculture  
202 Organization of the United Nations (UN-FAO). In addition to chemical analyses, pH was  
203 measured in the non-heated and heated soil samples after agitation in doubly-distilled water at  
204 a 1/5 solid/liquid ratio during 1h according to the NF ISO 10390 procedure. These analyses

205 were performed on the < 2 mm fraction of the samples without pre-grinding. Finally, the  
206 mineralogical composition of the mechanically ground < 2 mm fraction of the non-heated and  
207 heated soil samples was assessed by X-ray diffraction (XRD). Non-heated soil samples were  
208 analysed at Institut de Mineralogy, de Physique des Materiaux et de Cosmochimie (IMPMC)  
209 of Sorbonne University (Paris, France) with an X'PERT PRO (Malvern Panalytical®)  
210 diffractometer configured in the Bragg-Brentano geometry and equipped with a Co anti-cathode  
211 and an X'celerator detector. Each sample was analysed during 60 min on the 5-80 °2 $\Theta$  range  
212 (0.017 °2 $\Theta$  steps with a counting time of 200 seconds/step) in the spinner mode at a tension of  
213 40 kV and intensity of 30 mA. Heated soil samples were analysed at Institut des Sciences  
214 Exactes et Appliquees (ISEA) of the University of New Caledonia (Noumea, New Caledonia)  
215 with an AERIS (Malvern Panalytical®) diffractometer configured in the Bragg-Brentano  
216 geometry and equipped with a Co anti-cathode and a PIXcel3D detector. Each sample was  
217 analysed during 25 min on the 5-80 °2 $\Theta$  range (0.011 °2 $\Theta$  steps with a counting time of 50  
218 seconds/step) in the spinner mode at a tension of 40 kV and intensity of 15 mA. Quantitative  
219 analysis of the XRD powder patterns was performed according to the Rietveld method with the  
220 MAUD® version 2.7 software (Lutterotti et al., 1999). Despite different experimental  
221 conditions that are expected to have influenced the intensity of the XRD patterns between  
222 heated and non-heated samples, comparison of their quantitative mineralogy remained fully  
223 reliable because the Rietveld method normalizes the proportion of each of the mineral species  
224 quantified in a sample to their summed proportion.

225

#### 226 *2.4 Chromium mobility*

227

228 Two sets of chemical extractions were performed to evaluate chromium behaviour upon soil  
229 heating. A first extraction with a 0.01 M CaCl<sub>2</sub> solution was used to mimic the ionic strength

230 of the soil solution that could drive chromium mobility upon first rain after a wildfire (Houba  
231 et al., 1990; 2000). This extraction was done in a batch mode at a 1g/10mL solid/liquid ratio  
232 and with constant stirring during 2 hours. A second extraction with a 0.1 M  $\text{KH}_2\text{PO}_4$  solution  
233 was done to remove all extractable Cr(VI) bound to soil organic and mineral surfaces. The  
234 protocol used slightly differed from that of (Bartlett, 1991), with a 1g/30mL solid/liquid ratio  
235 and constant stirring during 2 hours. Despite its lowest solid/liquid ratio compared to  $\text{CaCl}_2$   
236 extraction,  $\text{KH}_2\text{PO}_4$  extraction is designed to remove much larger amounts of Cr(VI) because  
237 of the higher concentration (*i.e.*, 0.1M compared to 0.01M) and stronger efficiency of the  
238 reagent (*i.e.*,  $\text{PO}_4^{3-}/\text{HPO}_4^-$  anions compared to  $\text{Cl}^-$  anions) that is expected to induce competitive  
239 exchange for sorption sites with  $\text{CrO}_4^{2-}/\text{HCrO}_4^-$  anions. Both sets of extractions were performed  
240 in 15mL Falcon<sup>®</sup> tubes. After each extraction, the tubes were centrifuged during 10 minutes at  
241 3500 rpm and the supernatant was filtered through a 0.45  $\mu\text{m}$  membrane. Filtered solutions  
242 were then stored at 4°C to prevent any evaporation and to slow down any possible chemical  
243 and/or biological reactions before chemical analysis. Total chromium concentration in the  
244 filtered  $\text{CaCl}_2$  extracts was quantified by ICP-OES at LAMA (Noumea, New Caledonia) within  
245 96h after extractions. In addition, and within the same time, Cr(VI) concentration was  
246 quantified in these extracts, as well as in the filtered  $\text{KH}_2\text{PO}_4$  extracts, according to the diphenyl  
247 carbazide (DPC) colorimetric method (Bartlett, 1991). These latter analyses were performed  
248 with a Lambda750 (PerkinElmer<sup>®</sup>) spectrophotometer at the Laboratoire de Spectroscopie de  
249 Noumea (IRD, Noumea, New Caledonia). Because of the detection limit of the method (*i.e.*,  
250 0.1 mg/L), only the samples heated at 400°C and 600°C were analysed for Cr(VI) concentration  
251 (Table 2).

252

253

254

255 2.5 Freshwater Cr(VI) pollution risk assessment

256  
257 A first assessment of the potential risk of freshwater Cr(VI) pollution at burned ultramafic  
258 catchments was performed according to equation (1).

259  
260 
$$Cr(VI)_{freshwater} = [Cr(VI)_{CaCl_2} \cdot SPM_{freshwater}] / R_{solid-liquid}^{CaCl_2} \quad (1)$$

261  
262 In this equation,  $Cr(VI)_{freshwater}$  corresponds to the expected Cr(VI) concentration in  
263 freshwater (*i.e.*, mg/L),  $Cr(VI)_{CaCl_2}$  corresponds to the amount of CaCl<sub>2</sub>-Cr(VI) in SPM that  
264 would originate from burned soils (*i.e.*, mg/L),  $SPM_{freshwater}$  corresponds to the SPM  
265 concentration in freshwater (*i.e.*, mg/L) and  $R_{solid-liquid}^{CaCl_2}$  corresponds to the solid/liquid ratio  
266 used in the CaCl<sub>2</sub> extractions (*i.e.*, 1/10).

267 Application of Equation (1) for the four non-heated (*i.e.*, 25°C) and 200°C, 400°C and  
268 600°C-heated Ferralsols first allowed to depict the SPM concentration for which the expected  
269 Cr(VI) concentration in freshwater would exceed the WHO GDWQ for chromium (*i.e.* 50 µg/L;  
270 WHO, 2020). These threshold SPM concentrations were then compared with those measured  
271 during a 9 months survey (January 2014 – September 2015) performed by the mining company  
272 Koniambo Nickel SAS (KNS) at the outlet of the Coco catchment in the Koniambo ultramafic  
273 regolith (Figure 1). For this comparison, *in-situ* turbidity measurements (*i.e.*, Nephelometric  
274 Turbidity Unit - NTU) performed automatically at a 10 minutes time-lapse with a PONSEL  
275 ODEON side-scatter turbidity sensor using infrared light at 880 nm were used to derive SPM  
276 concentrations (*i.e.*, mg/L), thanks to the correlation between both parameters established on  
277 30 measurements (slope = 0.56; R<sup>2</sup> = 0.86; Figure S2).

278

279

280

### 281 3. RESULTS AND DISCUSSION

282

#### 283 3.1 Chemical and mineralogical characteristics of the studied soils

284

285 In New Caledonia, most Ferralsols are particularly enriched in Cr, Mn, Ni and Co (Isnard  
286 et al., 2016; Houles et al., 2018; Vincent et al., 2018) because they have developed on ultramafic  
287 rocks (*i.e.* peridotites). This trend is illustrated by the concentrations of Cr, Mn, Ni and Co  
288 measured in the 0-10 cm samples collected in the four investigated soils that ranged from 16,082  
289 to 40,286 mg/kg for Cr, from 4824 to 17,210 mg/kg for Mn, from 2623 to 6709 mg/kg for Ni  
290 and from 408 to 1201 mg/kg for Co (Table 1). After Fe that showed concentrations ranging  
291 from 250,300 to 505,300 mg/kg (*i.e.*, from 25.03 to 50.53 %; Table 1), Cr was thus the most  
292 enriched trace metal in the four investigated Ferralsols.

293

294 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	C <sub>org</sub>
	(%)				(mg/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

295

296 Quantitative analysis of X-Ray Diffraction (XRD) powder patterns (Figures S3-S6)  
297 indicated that goethite ( $\alpha$ -FeOOH) was the major mineral species in soils PIND, PAND and  
298 PAND2 (Figure S7; Table S1). These soils also contained significant amounts of quartz (SiO<sub>2</sub>)  
299 and enstatite (MgSiO<sub>3</sub>), as well as minor amounts of talc (Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>) and serpentine  
300 (Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>). By comparison, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) was the major mineral species in soil  
301 TIE, where it occurred together with significant amounts of goethite and traces of quartz (Figure  
302 S7; Table S1).

### 3.2 Thermal transformation of mineral species

304

305 Powder XRD analyses emphasized the thermal transformation or stability of the different  
306 mineral species identified in the investigated Ferralsols (Figures S3-S7; Table S1). For all soils,  
307 the XRD powder patterns showed a progressive disappearance of the peaks related to goethite  
308 from 200°C to 600°C (Figures S3-S6). At 600°C, these XRD peaks have completely  
309 disappeared. Meanwhile, the intensity of the XRD peaks related to hematite tended to increase  
310 with increasing heating temperature. These changes are in agreement with the known thermal  
311 behaviour of goethite, which starts to transform into proto-hematite ( $\text{Fe}_{5/3}\text{O}_2\text{OH}$ ) at 250°C. This  
312 latter mineral species then transforms into hydro-hematite ( $\text{Fe}_{11/6}\text{O}_{5/2}(\text{OH})_{1/2}$ ) at 400°C. Finally,  
313 hydro-hematite is fully transformed into hematite  $\text{Fe}_2\text{O}_3$  above 800°C (Gualtieri & Venturelli,  
314 1999; Schwertmann & Taylor, 2003 ; Landers and Gilkes, 2007; Perrier et al., 2006; Wells et  
315 al., 2006; Wolska & Schwertmann, 1989). This goethite-to-hematite thermal pathway  
316 corresponds to reactions under oxidising conditions. However, organic matter can favour  
317 reducing conditions during fire in soils. Under such conditions, goethite can partially or fully  
318 transform into maghemite ( $\text{Fe}_3\text{O}_4$ ) rather than hematite (Eggleton & Taylor, 2008; Grogan et  
319 al., 2003; Ketterings et al., 2000; Perrier et al., 2006; Terefe et al., 2008). In our study, such a  
320 transformation of goethite to maghemite was limited due to the low amounts of organic matter  
321 measured in the investigated soils (*i.e.*, total organic carbon ranging from 0.9 to 6.8 g/kg; Table  
322 1).

323 Concerning phyllosilicates, the XRD patterns of heated soils showed the disappearance of  
324 the peaks related to serpentine from 400°C (Figures S3-S6). These changes are in agreement  
325 with the known thermal behaviour of this mineral species, which starts to dehydroxylate around  
326 450°C and is generally fully transformed to fosterite ( $\text{Mg}_2\text{SiO}_4$ ) and enstatite ( $\text{MgSiO}_3$ ) around  
327 800°C (Hang & Brindley, 1973; Cattaneo et al., 2003 ; Perrillat et al., 2005 ; Viti & Hirose,

2010 ; Viti, 2010 ; Gualtieri et al., 2012 ; Trittschack et al., 2012a ; 2012b ; 2013). Although the formation of talc as an intermediate mineral species during this transformation is possible (McKenzie & 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 (Figures 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 (Figures 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 & 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 (Figures S3-S6) is in agreement with the P-T stability diagrams of these two mineral species (Swamy et al., 1994; Ulmer & Stalder, 2001; Gasparik, 2014).

342

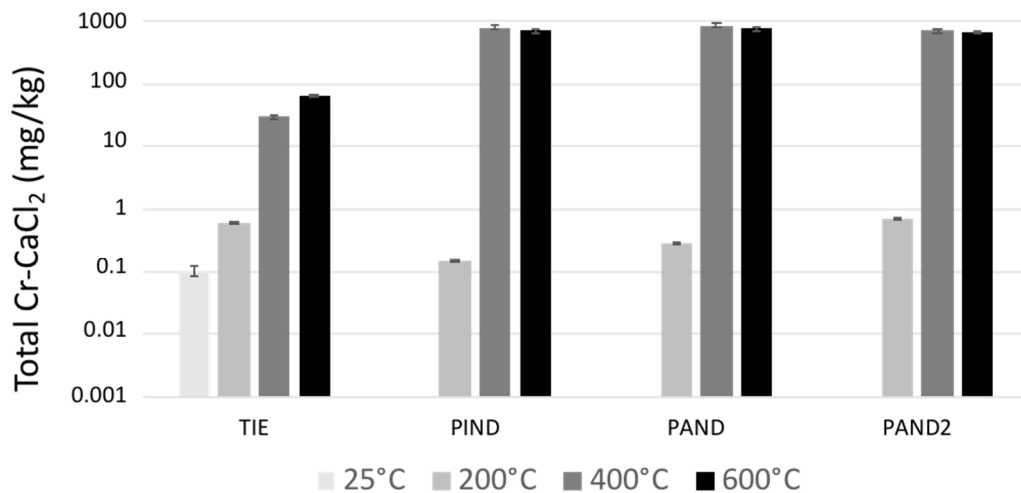
### 343 *3.3 An enhanced chromium mobility after soil heating*

344

Chemical extractions with a 0.01M CaCl<sub>2</sub> solution allowed to assess the effect of soil heating on chromium mobility at three levels. In a first step, total Cr concentration in the CaCl<sub>2</sub> extracts (*i.e.*, total Cr-CaCl<sub>2</sub>) 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 (Figure 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

353 400°C and then to 65 mg/kg at 600°C (Figure 2; Table 2). By contrast, the total amount of  
 354 mobile chromium in soils PAND, PAND2 and PIND increased from about 0.5 mg/kg at 200°C  
 355 to more than 700 mg/kg at 400°C (Figure 2; Table 2). Then, the total amount of mobile  
 356 chromium in these three soils did not increase significantly between 400°C and 600°C (Figure  
 357 2; Table 2).

358



359

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

363

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



374  
375  
376  
377  
378

Table 2. Total Cr (ICP-OES) and Cr(VI) (DPC colorimetric method) concentration in the CaCl<sub>2</sub> and KH<sub>2</sub>PO<sub>4</sub> 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 <sub>2</sub>	Cr(VI) CaCl <sub>2</sub> (mg/kg)	Cr(VI) KH <sub>2</sub> PO <sub>4</sub>	Total Cr CaCl <sub>2</sub>	Cr(VI) CaCl <sub>2</sub> (%)	Cr(VI) KH <sub>2</sub> PO <sub>4</sub>	Cr(VI) CaCl <sub>2</sub> / KH <sub>2</sub> PO <sub>4</sub> (%)
<b>TIE</b>							
25	0.10	nd <sup>(1)</sup>	22.3	0.00	nd	0.14	nr <sup>(2)</sup>
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
<b>PAND</b>							
25	0.00	nd	<3.00 <sup>(3)</sup>	0.00	nd	<0.02 <sup>(3)</sup>	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
<b>PAND2</b>							
25	0.00	nd	<3.00 <sup>(3)</sup>	0.00	nd	<0.02 <sup>(3)</sup>	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
<b>PIND</b>							
25	0.00	nd	<3.00 <sup>(2)</sup>	0.0	nd	<0.02 <sup>(3)</sup>	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

379  
380  
381  
382  
383

<sup>(1)</sup> : not determined due to concentration below the detection limit of the DPC colorimetric method (*i.e.*, 0.1 mg/L; Bartlett, 1991); <sup>(2)</sup> : not relevant; <sup>(3)</sup> : Calculated by considering the detection limit of the DPC colorimetric method as the Cr(VI) concentration in the KH<sub>2</sub>PO<sub>4</sub> extract.

384 In a third step, KH<sub>2</sub>PO<sub>4</sub> extractions were used to assess total extractable Cr(VI) in the  
385 investigated soils. The results diverged from those of CaCl<sub>2</sub> extractions, since similar fractions  
386 of Cr(VI) were measured in the KH<sub>2</sub>PO<sub>4</sub> extracts from soil TIE and the three other soils (Table  
387 2). These extractions also showed larger fractions of Cr(VI)-KH<sub>2</sub>PO<sub>4</sub> after heating at 400°C  
388 compared to heating at 600°C (Table 2). This latter result is in agreement with a recent study,  
389 which reported the formation of Cr(VI) upon heating of synthetic Cr(III)-doped Fe-oxides up  
390 to 800°C, with the greatest extent of Cr(VI) formation found in the 200-400 °C range (Burton  
391 et al., 2019b). Finally, for both temperatures, the fraction of Cr(VI) in the KH<sub>2</sub>PO<sub>4</sub> extracts was

392 systematically larger than those of total chromium or Cr(VI) in the CaCl<sub>2</sub> extracts (Figure S9;  
393 Table 2).

394

### 395 *3.4 A chromium mobility likely driven by the hematite content and pH*

396

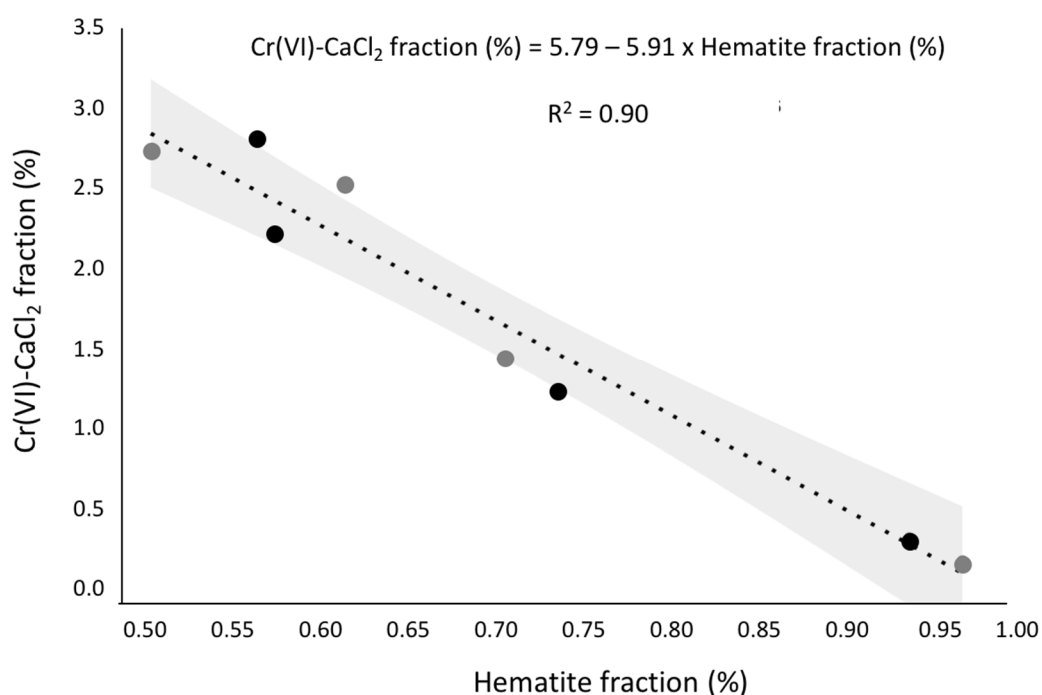
397 Since KH<sub>2</sub>PO<sub>4</sub> extraction is expected to release total extractable Cr(VI) in a given sample,  
398 comparison with CaCl<sub>2</sub> extraction allowed to calculate the percentage of mobile Cr(VI) in the  
399 four investigated soils after heating at 400 and 600°C. These percentages indicated that, after  
400 heating at 400°C, less than 2% of Cr(VI) was mobile in soil TIE compared to 25-50% in soils  
401 PAND, PAND2 and PIND (Table 2). After heating at 600°C, the fraction of mobile Cr(VI) was  
402 below 8% in soil TIE compared to 39-82% in soils PAND, PAND2 and PIND (Table 2). These  
403 percentages emphasize the lower mobility of Cr(VI) in soil TIE compared to the three other  
404 investigated soils.

405 The mineralogical characteristics of the investigated soils might provide some clues on this  
406 difference. Although structural incorporation in oxides and phyllosilicates can be considered to  
407 have played a major control on Cr(III) mobility in the non-heated and heated Ferralsols  
408 (Schwertmann et al., 1989; Singh et al., 2002; Oze et al., 2004; Sileo et al., 2004; Garnier et  
409 al., 2006; 2007; Becquer et al., 2006; Wells et al., 2006; Fandeur et al., 2009a), sorption onto  
410 the surfaces of mineral species is expected to have been the major process controlling Cr(VI)  
411 mobility. In this regard, the Fe-oxides/silicates ratio seems especially important since several  
412 studies have emphasized the strong affinity of Cr(VI) for the surface of Fe-oxides (Zachara et  
413 al., 1987; Singh et al., 1993; Fendorf, 1995; 1997; Wu et al., 2007; Ajouyed et al., 2010),  
414 whereas Cr(VI) sorption onto silicate minerals is rather limited (Bhattacharyya & Gupta, 2006;  
415 Guerra et al., 2010; Veselska et al., 2016). Our XRD analyses indicated an occurrence of almost  
416 100% hematite after heating at 400°C or 600°C in soil TIE, compared to a mixture of 45-65%

417 hematite and 35-55% silicate minerals (quartz, enstatite, serpentine, talc) in soils PAND,  
418 PAND2 and PIND (Figures S7; Table S1). These results thus strongly suggest that the lower  
419 fraction of mobile Cr(VI) measured in soil TIE heated at 400°C and 600°C compared to the  
420 three other investigated soils might have been due to the larger fraction of hematite formed in  
421 this soil upon heating.

422 This assumption is well supported by the very good correlation obtained between the  
423 fraction of mobile Cr(VI) quantified in the four investigated soils heated at 400 and 600°C and  
424 their hematite content (Figure 3). This latter result strongly suggests that the hematite content  
425 is a key parameter for Cr(VI) mobility in burned catchments composed of Cr-rich Ferralsols.

426



427

428 Figure 3. Fraction of mobile Cr(VI) (*i.e.*, Cr(VI)-CaCl<sub>2</sub> fraction) as a function of hematite fraction in the four  
429 investigated soils heated at 400°C (gray dots) and 600°C (black dots). Standard deviation within the dots size.

430

431 In addition, Cr(VI) sorption onto hematite depends on pH, with highest sorption below pH  
432 7.0 and then a rapid decrease in the pH range 7.0-8.0 (Zachara et al., 1987; Ajouyed et al.,  
433 2010). The pH of the soil solution is thus also expected to contribute to the fraction of mobile

434 Cr(VI) in heated Ferralsols. In this regard, the pH around 5.0 measured in the CaCl<sub>2</sub> extracts of  
435 soils TIE heated at 400°C and 600°C (Table S1) is expected to have yielded optimal Cr(VI)  
436 sorption onto hematite in these two soil samples. In addition to the large amounts of hematite  
437 quantified in soil TIE heated at 400°C and 600°C (Figure S7; Table S1), this pH effect can thus  
438 be considered to have also contributed to the low mobility of Cr(VI) measured in these two  
439 soils samples (Figure 3; Table 2). In the same way sorption of Cr(VI) onto hematite should also  
440 have contributed to limit the fraction of mobile Cr(VI) in soils PAND and PAND2 heated at  
441 400°C and 600°C since the CaCl<sub>2</sub> extracts of these soil samples showed pH values below 7.0  
442 (Table S1). However, the significant mobility of Cr(VI) measured in these two soil samples  
443 (Figure 3; Table 2) is likely explained by their lower hematite contents (Figure S7; Table S1).  
444 Finally, the pH above 7.0 measured in the CaCl<sub>2</sub> extracts of soil PIND heated at 400°C and  
445 600°C (Table S1) and the low amounts of hematite quantified in this soil whatever the  
446 temperature (Figure S7; Table S1) likely explain the quite high mobility of Cr(VI) measured in  
447 these two soil samples (Figure 3; Table 2).

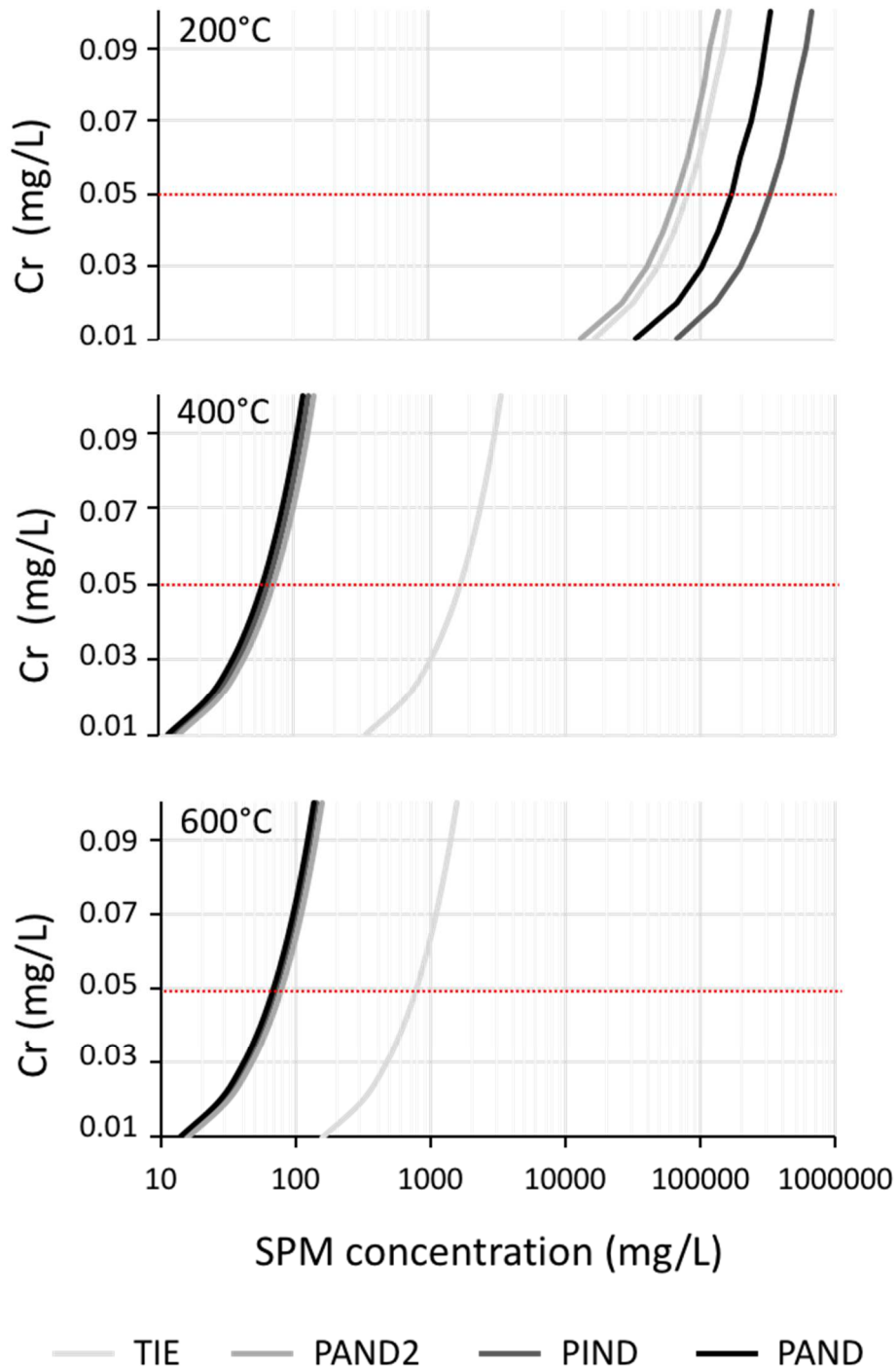
448

### 449 *3.5 A risk of Cr(VI) freshwater pollution in burned Cr-rich ultramafic catchments*

450

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

458 catchment in New Caledonia could thus be a source of Cr(VI) pollution in the related  
 459 waterways, depending on the concentration of SPM issued from the burned Cr-rich Ferralsols.  
 460



461  
 462

463 Figure 4. Chromium concentration (mg/L) as a function of the suspended particulate matter (SPM) concentration  
 464 (mg/L) in freshwater systems calculated according to Equation (1) by considering total Cr-CaCl<sub>2</sub> (mg/kg) measured  
 465 on the studied Ferralsols heated at 200°C, 400°C and 600°C (Table 2). The horizontal red line on each panel  
 466 corresponds to the WHO GDWQ of 50 µg/L for chromium. The lower the SPM concentration needed to reach  
 467 this guideline value, the higher the risk of potential freshwater Cr(VI) pollution in the related freshwater system.

468

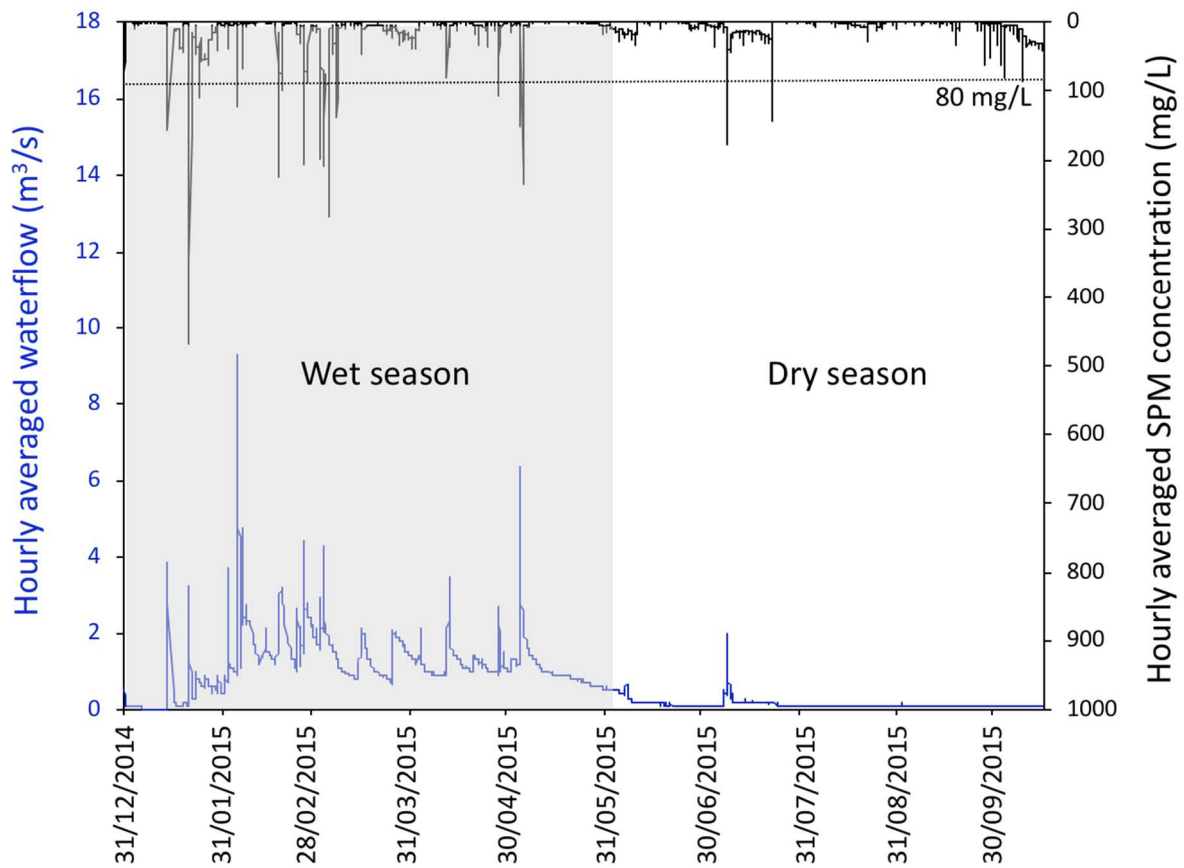
469 A first assessment of this potential risk of freshwater Cr(VI) pollution in burned ultramafic  
470 catchments was performed according to Equation (1) that relates chromium concentration in  
471 solution to SPM concentration and mobile chromium (*i.e.*, Cr-CaCl<sub>2</sub>; Table 2). The results  
472 indicated that the expected chromium concentration in solution would exceed the WHO GDWQ  
473 of 50 µg/L in freshwater once the concentration of SPM issued from soils PIND, PAND and  
474 PAND2 heated at 400°C or 600°C would have reached 80 mg/L (Figure 4). Regarding the much  
475 lower amount of mobile chromium (*i.e.*, Cr-CaCl<sub>2</sub>) in soil TIE (Table 2), the WHO GDWQ for  
476 chromium would be exceeded for SPM concentration above 2400 mg/L or 1000 mg/L after soil  
477 heating at 400°C or 600°C, respectively (Figure 4).

478 Comparison of these threshold SPM concentrations with those actually measured during 9  
479 months (January 2015 – September 2015) at the outlet of an ultramafic catchment in New  
480 Caledonia (*i.e.*, Coco catchment in the Koniambo ultramafic regolith; Figure 1) allowed to  
481 confirm the risk of fire-induced Cr(VI) pollution in Cr-rich ultramafic catchments from new  
482 Caledonia. Indeed, the time-dependent representation of the hourly-averaged SPM  
483 concentration at the outlet of the selected catchment showed some values that can reach up to  
484 500 mg/L, especially in the wet season (*i.e.*, December-May; Figure 5). More interestingly,  
485 comparison with the hourly-averaged waterflow that was also monitored during the same period  
486 indicated that for each rainy event the hourly-averaged SPM concentration almost  
487 systematically exceeded 80 mg/L, the threshold value above which chromium concentration  
488 would exceed the WHO GDWQ for soils PIND, PAND and PAND2 heated at 400°C or 600°C  
489 (Figure 5).

490 Considering that the selected creek is representative of freshwater systems related to  
491 ultramafic catchments composed of Cr-rich Ferralsols in New Caledonia and taking into  
492 account that 80% of mobile chromium in the heated Ferralsols was found as the most hazardous

493 Cr(VI), these results confirm the risk of Cr(VI) pollution in such freshwater systems during the  
494 first rains after wildfires. In addition, this risk of Cr(VI) freshwater pollution after wildfires on  
495 Cr-rich Ferralsols due to enhanced chromium mobility at the SPM/water interface could be  
496 decoupled by enhanced erosion after vegetation burning. Indeed, the first consequence of  
497 wildfires is vegetation loss (Neary et al., 1999; Certini, 2005; Alcaniz et al., 2018) and several  
498 studies have related higher SPM loadings in freshwater systems of burned catchments through  
499 subsequent enhanced erosion after such a vegetation loss (Shakesby & Doerr, 2006; Moody et  
500 al., 2013; Smith et al., 2011; Bladon et al., 2013).

501



502

503 Figure 5. Time-dependent evolution of the hourly-averaged waterflow (m³/s) and SPM concentration (mg/L)  
504 measured over a 9 months period (January 2015 – September 2015) at the outlet of the Coco catchment in the  
505 Koniambo ultramafic regolith (New Caledonia; Figure 1).

506

507

508

509        *3.6 A risk of Cr(VI) freshwater pollution that could depend on the geomorphology of the*  
510                *burned Cr-rich ultramafic catchments*

511  
512        Considering the soils investigated in this study, the risk of Cr(VI) freshwater pollution is  
513 expected to occur after wildfires on Cr-rich Ferralsols with characteristics similar to those of  
514 soils PIND, PAND and PAND2. As indicated by our mineralogical data, these Ferralsols  
515 contain significant amounts of residual silicate and/or clay minerals after heating, whereas soil  
516 TIE is free of these mineral species (Figure S7; Table S1). Moreover, the negative correlation  
517 found between the hematite content and the fraction of mobile Cr(VI) in the investigated  
518 Ferralsols (Figure 3) suggests a control of the Fe-oxides/silicates ratio on the enhanced Cr(VI)  
519 mobility upon heating of these soils where Fe-oxides are expected to transform to hematite. In  
520 New Caledonia, Ferralsols with significant amounts of silicate and/or clay minerals are found  
521 along the slopes or at the bottom of lateritic regoliths, whereas deeply weathered Ferralsols  
522 depleted in silicate and/or clay minerals are found on the top of ultramafic regoliths (Becker et  
523 al., 2001; 2006; Chevillote et al., 2006; Dublet et al., 2012; 2015; De Boissieu et al., 2018;  
524 Ulrich et al., 2019). As a consequence, the risk of Cr(VI) freshwater pollution related to  
525 wildfires on Cr-rich Ferralsols in New Caledonia is expected to be the highest on the slopes or  
526 at the bottom of lateritic ultramafic catchments, whereas it might be considered substantially  
527 lower on the top of these catchments.

528  
529        **4. CONCLUSIONS**

530  
531        The results of this study indicate that heating Cr-rich Ferralsols from New Caledonia at  
532 medium temperatures (*i.e.* 400°C or 600°C) can result in a significant increase of mobile  
533 chromium from less than 0.2% to about 2.5% of total chromium. These temperatures are



534 relevant to wildfires in New Caledonia since the major biomass fuel on Ferralsols is scrubland.  
535 Moreover, about 80% of mobile chromium after Ferralsols heating occurs as Cr(VI), the most  
536 mobile and hazardous form of chromium. A burned Cr-rich Ferralsol from New Caledonia  
537 might thus be a direct source of aqueous Cr(VI) towards fresh- or groundwater systems upon  
538 leaching during the first rains after wildfires. More importantly, SPM dispersed from a burned  
539 Cr-rich Ferralsol from New Caledonia might also release significant amounts of Cr(VI) in  
540 freshwater systems. A first assessment of this risk of freshwater Cr(VI) pollution indicates that  
541 the WHO GDWQ of 50 µg/L might be frequently exceeded after wildfires on the slopes or at  
542 the bottom of lateritic ultramafic catchments from New Caledonia. Beyond this first study on  
543 Ferralsols, further investigations are needed to evaluate the risk of freshwater Cr(VI) pollution  
544 after wildfires on other Cr-rich soils from New Caledonia. Indeed, previous studies have shown  
545 that Cambisols or Vertisols can contain significant amounts of chromium (*i.e.* up to 5,000  
546 mg/kg; Houles et al., 2018; Vincent et al., 2018), which raises the question of the potential  
547 release of this trace metal after heating of those soil types upon wildfires. Beyond the single  
548 case of New Caledonia, the large occurrence of Ferralsols in Brazil, Australia or Central Africa  
549 that are increasingly exposed to large wildfires ([https://earthobservatory.nasa.gov/global-](https://earthobservatory.nasa.gov/global-maps/MOD14A1_M_FIRE)  
550 [maps/MOD14A1\\_M\\_FIRE](https://earthobservatory.nasa.gov/global-maps/MOD14A1_M_FIRE)) raises the question of the potential consequences of this  
551 environmental disturbance on the quality of freshwater systems at a larger scale. This latter  
552 point emphasizes the urgent need for fostering studies aimed at better assessing the potential  
553 environmental and health impacts of wildfires on freshwater systems worldwide.

554  
555  
556  
557  
558  
559  
560  
561  
562  
563

564 **ACKNOWLEDGMENTS**

565

566 This work was supported by funding from the Centre National de Recherche  
567 Technologique sur le nickel et son environnement under the *CHRONICK* project (grant CNRT  
568 CSF 7PS2017). Soil samples collection was done under the *ADASPIR* project funded by the  
569 Agence Nationale de la Recherche (grant ANR-12-ADAP-0017-01-03). The authors are  
570 indebted to Leocadie Jamet, Anne Desnues, Stephanie Berne and Felise Liufau for ICP-OES  
571 measurements at the Laboratoire des Moyens Analytiques (LAMA-IMAGO) of Institut de  
572 Recherche pour le Developpement (IRD) Noumea (New Caledonia). Koniambo Nickel Society  
573 (KNS) is acknowledged for providing the results of *in-situ* turbidity and suspended particulate  
574 matter measurements performed at the outlet of the Coco catchment.

575

576 **REFERENCES**

577

578 Abraham, J., Dowling, K., Florentine, S., 2017a. The unquantified risk of post-fire metal  
579 concentration in soil : A review. *Water, Air Soil Poll.* 228, 175-208. [https://doi.org/](https://doi.org/10.1007/s11270-017-3338-0)  
580 10.1007/s11270-017-3338-0

581 Abraham, J., Dowling, K., Florentine, S., 2017b. Risk of post-fire metal mobilization into  
582 surface water resources : A review. *Sci. Tot. Environ.* 599-600, 1740-1755. [https://doi.org/](https://doi.org/10.1016/j.scitotenv.2017.05.096)  
583 10.1016/j.scitotenv.2017.05.096

584 Alcañiz, M., Outeiro, L., Francos, M., Úbeda, X., 2018. Effects of prescribed fires on soil  
585 properties: A review. *Sci. Total Environ.* 613–614, 944–957.  
586 <https://doi.org/10.1016/j.scitotenv.2017.09.144>

587 Bartlett, R.J., 1991. Chromium cycling in soils and water: links, gaps, and methods. *Environ.*  
588 *Health Perspect.* 92, 17–24. <https://doi.org/10.1289/ehp.919217>

589 Becquer, T., Quantin, C., Sicot, M., Boudot, J.P., 2003. Chromium availability in ultramafic  
590 soils from New Caledonia. *Sci. Total Environ.* 301, 251–261. [https://doi.org/10.1016/S0048-](https://doi.org/10.1016/S0048-9697(02)00298-X)  
591 9697(02)00298-X

592 Bertschi, I., Yokelson, R.J., Ward, D.E., Babbitt, R.E., Susott, R.A., Goode, J.G., Hao, W.M.,  
593 2003. Trace gas and particle emissions from fires in large diameter and belowground biomass  
594 fuels: Emissions from smoldering biomass. *J. Geophys. Res. Atmospheres* 108, n/a-n/a.  
595 <https://doi.org/10.1029/2002JD002100>

596 Bodi, M.E., Martin, D.A., Balfour, V.N., Santin, C., Doerr, S.H., Pereira, P., Cerda, A., Mataix-  
597 Solera, J., 2014. Wildland fire ash : Production, composition and eco-hydro-geomorphic  
598 effects. *Earth Sci. Rev.* 130, 103-127. [https://doi.org/10.1116/ j.earscrev.2013.12.007](https://doi.org/10.1116/j.earscrev.2013.12.007)

599 Brindley, G.W., Ali, S.C., 1950. X-ray study of thermal transformations in some magnesian  
600 chlorite minerals. *Acta Crystallogr.* 3, 25–30. <https://doi.org/10.1107/S0365110X50000069>

601 Burton, E.D., Choppala, G., Karimian, N., Johnston, S.G., 2019a. A new pathway for  
602 hexavalent chromium formation in soil: Fire-induced alteration of iron oxides. *Environ. Pollut.*  
603 247, 618–625. <https://doi.org/10.1016/j.envpol.2019.01.094>

604 Burton, E.D., Choppala, G., Vithana, C.L., Karimian, N., Hockmann, K., Johnston, S.G.,  
605 2019b. Chromium(VI) formation via heating of Cr(III)-Fe(III)-(oxy)hydroxides: A pathway for  
606 fire-induced soil pollution. *Chemosphere* 222, 440–444.  
607 <https://doi.org/10.1016/j.chemosphere.2019.01.172>

608 Chevillote, V., Chardon, D., Beauvais, A., Maurizot, P., Colin, F. 2006. Long-term tropical  
609 morphogenesis of New Caledonia (Southwest Pacific): Importance of positive epeirogeny and  
610 climate change. *Geomorphology* 81, 361-375. [https://doi.org/](https://doi.org/10.1016/j.geomorph.2006.04.020)  
611 10.1016/j.geomorph.2006.04.020

612 DeBano, L.F., Neary, D.G., Ffolliott, P.F., 1998. Fire's effects on ecosystems. J. Wiley, New  
613 York.

614 De Boissieu, F., Sevin, B., Cudahy, T., Mangeas, M., Chevrel, S., Ong, C., Rodger, A.,  
615 Maurizot, P., Laukamp, C., Lau, I., Touraivane, T., Cluzel, D., Despinoy, M. 2018. Regolith-

- 616 geology mapping with support vector machine: A case study over weathered Ni-bearing  
617 peridotites, New Caledonia. *Int. J. Appl. Geoinformation* 64, 377-385. [https://doi.org/](https://doi.org/10.1016/j.jag.2017.05.012)  
618 10.1016/j.jag.2017.05.012
- 619 Dumas, P., Toussaint, M., Herrenschmidt, J.-B., Conte, A., Mangeas, M., 2013. Le risque de  
620 feux de brousse sur la Grande Terre de Nouvelle-Calédonie : l'Homme responsable, mais pas  
621 coupable. *Rev. Géographique Est* 53. <https://doi.org/10.4000/rge.4598>
- 622 Eggleton, R.A., Taylor, G., 2008. Impact of fire on the Weipa Bauxite, northern Australia. *Aust.*  
623 *J. Earth Sci.* 55, S83–S86. <https://doi.org/10.1080/08120090802438266>
- 624 Fandeur, D., Juillot, F., Morin, G., Olivi, L., Cognigni, A., Ambrosi, J.-P., Guyot, F., Fritsch,  
625 E., 2009. Synchrotron-based speciation of chromium in an Oxisol from New Caledonia:  
626 Importance of secondary Fe-oxyhydroxides. *Am. Mineral.* 94, 710–719.  
627 <https://doi.org/10.2138/am.2009.3073>
- 628 Fendorf, S.E., 1995. Surface reactions of chromium in soils and waters. *Geoderma* 67, 55–71.  
629 [https://doi.org/10.1016/0016-7061\(94\)00062-F](https://doi.org/10.1016/0016-7061(94)00062-F)
- 630 Giglio, L., Randerson, J.T., van der Werf, G.R., Kasibhatla, P.S., Collatz, G.J., Morton, D.C.,  
631 DeFries, R.S., 2010. Assessing variability and long-term trends in burned area by merging  
632 multiple satellite fire products. *Biogeosciences* 7, 1171–1186. [https://doi.org/10.5194/bg-7-](https://doi.org/10.5194/bg-7-1171-2010)  
633 1171-2010
- 634 Golubev, S.V., Bauer, A., Pokrovsky, O.S., 2006. Effect of pH and organic ligands on the  
635 kinetics of smectite dissolution at 25°C. *Geochim. Cosmochim. Acta* 70, 4436–4451.  
636 <https://doi.org/10.1016/j.gca.2006.06.1557>
- 637 Grogan, K.L., Gilkes, R.J., Lottermoser, B.G., 2003. Maghemite Formation in Burnt Plant  
638 Litter at East Trinity, North Queensland, Australia. *Clays Clay Miner.* 51, 390–396.  
639 <https://doi.org/10.1346/CCMN.2003.0510404>
- 640 Gualtieri, A.F., Venturelli, P., 1999. In situ study of the goethite-hematite phase transformation  
641 by real time synchrotron powder diffraction. *Am. Mineral.* 84, 895–904.  
642 <https://doi.org/10.2138/am-1999-5-624>
- 643 Guerra, D.L., Oliveira, H.C.P., da Costa, P.C.C., Viana, R.R., Airoldi, C., 2010. Adsorption of  
644 chromium(VI) ions on Brazilian smectite: Effect of contact time, pH, concentration, and  
645 calorimetric investigation. *Catena* 82, 35–44. <https://doi.org/10.1016/j.catena.2010.04.008>
- 646 Hang, P.T., 1973. The Nature of Garnierites—III Thermal Transformations. *Clays Clay Miner.*  
647 21, 51–57. <https://doi.org/10.1346/CCMN.1973.0210108>
- 648• Houba, VJG., Novozamsky, I., Lexmond T.M., van der Lee, J.J., 1990. Applicability of 0.01M  
649 CaCl<sub>2</sub> as a single extraction solution for the assessment of the nutrient status of soils and other  
650 diagnostic purposes. *Comm. Soil Sci., Plant Anal.* 21, 2281-2290.  
651 <https://doi.org/10.1080/00103629009368380>
- 652• Houba, VJG., Temminghoff, E.J.M., Gaikhorst, G.A., van Vark, W., 2000. Soil analysis  
653 procedure using 0.01M calcium chloride extraction reagent. *Comm. Soil Sci., Plant Anal.* 31,  
654 1299-1396. <https://doi.org/10.1080/00103620009370514>

655 Houles, A., Vincent, B., David, M., Ducouso, M., Galiana, A., Juillot, F., Hannibal, L.,  
656 Carriconde, F., Fritsch, E., Jourand, P., 2018. Ectomycorrhizal Communities Associated with  
657 the Legume *Acacia spirorbis* Growing on Contrasted Edaphic Constraints in New Caledonia.  
658 *Microb. Ecol.* 76, 964–975. <https://doi.org/10.1007/s00248-018-1193-1>

659 Jaffré, T., Veillon, J.-M., Rigault, F., Dagostini, G., 1997. Impact des feux de brousse sur le  
660 milieu naturel en Nouvelle-Calédonie.

661 Jouany, J.M., Vasseur, P., Ferard, J.F., 1982. Ecotoxicité directe et intégrée du chrome  
662 hexavalent sur deux niveaux trophiques associés: *Chlorella vulgaris* et *Daphnia magna*.  
663 *Environ. Pollut. Ser. Ecol. Biol.* 27, 207–221. [https://doi.org/10.1016/0143-1471\(82\)90026-5](https://doi.org/10.1016/0143-1471(82)90026-5)

664 Ketterings, Q.M., Bigham, J.M., Laperche, V., 2000. Changes in Soil Mineralogy and Texture  
665 Caused by Slash-and-Burn Fires in Sumatra, Indonesia. *Soil Sci. Soc. Am. J.* 64, 1108–1117.  
666 <https://doi.org/10.2136/sssaj2000.6431108x>

667 Kühn, R., Pattard, M., 1990. Results of the harmful effects of water pollutants to green algae  
668 (*Scenedesmus subspicatus*) in the cell multiplication inhibition test. *Water Res.* 24, 31–38.  
669 [https://doi.org/10.1016/0043-1354\(90\)90061-A](https://doi.org/10.1016/0043-1354(90)90061-A)

670 Landers, M., Gilkes, R., 2007. Dehydroxylation and dissolution of nickeliferous goethite in  
671 New Caledonian lateritic Ni ore. *Appl. Clay Sci.* 35, 162–172.  
672 <https://doi.org/10.1016/j.clay.2006.08.012>

673 Löv, A., Sjöstedt, C., Larsbo, M., Persson, I., Gustafsson J.P., Cornelis, G., Kleja, D.B. 2017.  
674 DSolubility and transport of Cr(III) in ahistorically contaminated soil - Evidence of a rapidly  
675 reacting dimeric Cr(III) organic matter complex. *Chemosphere* 189, 709-716.  
676 <https://doi.org/10.1016/j.chemosphere.2017.09.088>

677 Mao, L., Gao, B., Deng, N., Zhai, J., Zhao, Y., Li, Q., Cui, H. 2015. The role of temperature on  
678 Cr(VI) formation and reduction during heating of chromium-containing sludge in the presence  
679 of CaO. *Chemosphere* 138, 197-204. <https://doi.org/10.1016/j.chemosphere.2015.05.097>

680 Ormeño, E., Céspedes, B., Sánchez, I.A., Velasco-García, A., Moreno, J.M., Fernandez, C.,  
681 Baldy, V., 2009. The relationship between terpenes and flammability of leaf litter. *For. Ecol.*  
682 *Manag.* 257, 471–482. <https://doi.org/10.1016/j.foreco.2008.09.019>

683 Perrier, N., Gilkes, R.J., Colin, F., 2006. Heating Fe oxide-rich soils increases the dissolution  
684 rate of metals. *Clays Clay Miner.* 54, 165–175. <https://doi.org/10.1346/CCMN.2006.0540203>

685 Rai, D., Eary, L.E., Zachara, J.M., 1989. Environmental chemistry of chromium. *Sci. Total*  
686 *Environ.* 86, 15–23. [https://doi.org/10.1016/0048-9697\(89\)90189-7](https://doi.org/10.1016/0048-9697(89)90189-7)

687 Rascio, I., Allegretta, I., Gattullo, C.E., Porfido, C., Suranna, G?P., Grisorio, R., Spiers, K.M.,  
688 Falkenberg, G., Terzano, R., 2022. FEvidence of hexavalent chromium formation and changes  
689 of Cr speciation after laboratory-simulated fires of composted tannery sludges long-term  
690 amended agricultural soils. *J. Hazard. Mat.* 436, 129117.  
691 <https://doi.org/10.1016/j.jhazmat.2022.129117>

692 Saura-Mas, S., Paula, S., Pausas, J.G., Lloret, F., 2010. Fuel loading and flammability in the  
693 Mediterranean Basin woody species with different post-fire regenerative strategies. *Int. J.*  
694 *Wildland Fire* 19, 783. <https://doi.org/10.1071/WF09066>

695 Schwertmann, U., 1991. Solubility and dissolution of iron oxides. *Plant Soil* 130, 1–25.  
696 <https://doi.org/10.1007/BF00011851>

697 Schwertmann, U., Gasser, U., Sticher, H., 1989. Chromium-for-iron substitution in synthetic  
698 goethites. *Geochim. Cosmochim. Acta* 53, 1293–1297. [https://doi.org/10.1016/0016-](https://doi.org/10.1016/0016-7037(89)90063-X)  
699 [7037\(89\)90063-X](https://doi.org/10.1016/0016-7037(89)90063-X)

700 Singh, B., Sherman, D.M., Gilkes, R.J., Wells, M.A., Mosselmans, J. F.W., 2002.  
701 Incorporation of Cr, Mn and Ni into goethite ( $\alpha$ -FeOOH): mechanism from extended X-ray  
702 absorption fine structure spectroscopy. *Clay Miner.* 37, 639–649.  
703 <https://doi.org/10.1180/000985502374066>

704 Singh, D.B., Gupta, G.S., Prasad, G., Rupainwar, D.C., 1993. The Use of Hematite for  
705 Chromium(VI) Removal. *J. Environ. Sci. Health Part Environ. Sci. Eng. Toxicol.* 28, 1813–  
706 1826. <https://doi.org/10.1080/10934529309375979>

707 Terefe, T., Mariscal-Sancho, I., Peregrina, F., Espejo, R., 2008. Influence of heating on various  
708 properties of six Mediterranean soils. A laboratory study. *Geoderma* 143, 273–280.  
709 <https://doi.org/10.1016/j.geoderma.2007.11.018>

710 Terzano, R., Rascio, I., Allegretta, I., Porfido, C., Spagnuolo, M., Khanghahi, M.Y., Crecchio,  
711 C., Sakellariadou, F., Gattullo, C.E., 2021. Fire effects on the distribution and bioavailability  
712 of potentially toxic elements (PTEs) in agricultural soils. *Chemosphere* 281, 130752.  
713 <https://doi.org/10.1016/j.chemosphere.2021.130752>

714 Vincent, B., Jourand, P., Juillot, F., Ducouso, M., Galiana, A., 2018. Biological in situ nitrogen  
715 fixation by an Acacia species reaches optimal rates on extremely contrasted soils. *Eur. J. Soil*  
716 *Biol.* 86, 52–62. <https://doi.org/10.1016/j.ejsobi.2018.03.003>

717 Wells, M.A., 2001. Properties and Acid Dissolution of Metal-Substituted Hematites. *Clays Clay*  
718 *Miner.* 49, 60–72. <https://doi.org/10.1346/CCMN.2001.0490105>

719 Wells, M.A., Fitzpatrick, R.W., Gilkes, R.J., 2006. Thermal and mineral properties of Al-, Cr,  
720 Mn-, Ni- and Ti-substituted goethite. *Clays Clay Miner.* 54, 176–194.  
721 <https://doi.org/10.1346/CCMN.2006.0540204>

722 Wolska, E., Schwertmann, U., 1989. Nonstoichiometric structures during dehydroxylation of  
723 goethite. *Z. Für Krist. - Cryst. Mater.* 189. <https://doi.org/10.1524/zkri.1989.189.3-4.223>

724 Yusiharni, E., Gilkes, R.J., 2012. Changes in the mineralogy and chemistry of a lateritic soil  
725 due to a bushfire at Wundowie, Darling Range, Western Australia. *Geoderma* 191, 140–150.  
726 <https://doi.org/10.1016/j.geoderma.2012.01.030>

727 Zhou, Y., Chen, Z., Gong, H., Yang, Z., 2021. Chromium speciation in tannery sludge residues  
728 after different thermal decomposition processes. *J. Clean. Prod.* 314, 128071.  
729 <https://doi.org/10.1016/j.jclepro.2021.128071>

730

731