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Mobility of Ni, Co, and Mn in ultramafic mining soils of New Caledonia, assessed by kinetic EDTA extractions

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Abstract The aim of this study was to determine the mobilization capability of Ni, Co, and Mn contained in New Caledonian ultramafic soils. Two series of soils were sampled: bare-surface mining soils in a Ni-mining context ($n = 10$), and forest soils, either in the vicinity of mine-working areas ($n = 3$) or far away from any known mining activity ($n = 2$). We focused on the < 100 μm soil fraction, because of its sensitivity to wind erosion, and its possible dissemination toward urbanized areas. In order to assess maximum potential metal mobility, EDTA kinetic extractions were performed over 24 h. Extraction curves were modeled as the sum of two first-order reactions. The first EDTA extracted pool corresponds to "quickly" released metals, while the second pool corresponds to "slowly" released metals. The remaining fraction is the EDTA non-extractable pool. Extractable Ni, Co, and Mn were always low in relation to total concentrations (< 5% for Ni, and 5–35% for Co and Mn). The extraction rate of the less labile pool was significantly higher for forest soils than for mining soils, whatever the metal. Despite the greater extractability potential in forest surface soils, mining soils represent a bigger environmental risk, because of their high metal content and, above all, because of their predisposition to surface runoff and eolian deflation.

Keywords Nickel mining · Metal · Environmental risk · Pollution

Introduction

A third of the main New Caledonian Island (South West Pacific Ocean) is covered by weathered ultramafic rocks, laterites, and saprolites with high concentrations of nickel (Ni), cobalt (Co), and manganese (Mn) (Trescases 1973). These superficial enriched alterites have been exploited since their discovery by Jules Garnier in 1864. New Caledonia accounts for approximately 10% of known nickel reserves worldwide (U.S.

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Geological Survey 2016). Around 30 opencast mining sites extend over almost the entire island (Bonvallot et al. 2013). Although of vital economic importance for the territory, such mining activity represents a threat for human health and the surrounding ecosystems, because of the deleterious effects for flora and fauna of Ni, Co, and Mn at high concentrations (Kabata-Pendias 2010; Kong et al. 2011; Prospero et al. 1983; Pumure et al. 2003).

Metal-rich particles are disseminated by wind or water runoff in the environment at all stages of mining activity (from ore extraction to its transportation for metallurgical treatment), thus contaminating soil and water (Gunkel-Grillon et al. 2014). This is especially true for reworked mining soils, much more subject to eolian erosion and mechanical erosion by runoff than unworked forest soils, naturally protected by vegetation. Although mining soils and the surrounding forest soils all developed on similar parent material, and therefore share comparable physicochemical properties, they have not undergone comparable environmental constraints over the past few decades, so that metal behavior within them may be quite different.

Analyzing total metal concentrations is the first step in environmental risk assessment. A second step, more informative for long-term management, is to understand how, and under which conditions, metal pollutants are transferred from the solid to the liquid phase. This is sometimes used as a rough evaluation of metal bioavailability. Sequential extractions involving several extracting agents with increasing strength have been developed since the 1970s to describe the chemical forms in which metals are associated with soil constituents, and hence to assess potential bioavailability (see Tessier et al. 1979, and studies adapting the procedure, such as Ure et al. 1993). These techniques, however, may suffer from the limited selectivity of extracting agents, and from readsorption of elements between extraction phases (Bermond et al. 1998; Gleyzes et al. 2002). These methods provide information about the mineralogical and organic phases hosting the metals, but not about the dynamics of metal release. Another more recent approach consists in examining the kinetic behavior of metals contained in soils. Kinetic extractions can be modeled by the sum of several first-order reactions, but two are generally sufficient (Gutzman and Langford 1993). These two reactions empirically define two different pools: the "labile" pool, attributed to readily extracted metals, and the "less labile" pool, composed of more slowly extracted metals, which corresponds to the "potentially mobile" metal fraction, more strongly bound (Fangueiro et al. 2005; Bermond et al. 2005). In other words, kinetic extractions discriminate metal pools by extraction speed (i.e., their mobilization rate), and not directly from the speciation of metals in soils, even if these questions are closely related. A third fraction, the non-extractable metal pool, is obtained by subtracting the first two fractions from the total metal concentration. Several extracting agents, such as ethylene diamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA), ammonium acetate, or ammonium citrate, can be used for such an experimental scheme. However, if the objective is to assess maximum potential metal mobility (relevant information to assess environmental risk), EDTA is a good choice. This strong chelate, complexes organically bound metals, together with metals associated with inorganic compounds, such as Fe, Al, and Mn oxides, as well as clay minerals (Gupta and Aten 1993; Sahuquillo et al. 2003). Moreover, EDTA is commonly used in kinetic extractions to evaluate total extractable metal pools (AFNOR 2004; Bermond et al. 2005; Camizuli et al. 2014; Chakraborty et al. 2014; Hamdoun et al. 2015; Labanowski et al. 2008), thus facilitating further comparison of metal behaviors in various environmental contexts.

Our objective here is to assess the kinetic behavior, and hence the potential bioavailability, of Ni, Co, and Mn in soil samples collected in mining areas, and in forests, either in the vicinity of mining areas, or far from any known mining activity. We focused on < 100 μm soil particles, since they are easily disseminated into the surface environment by runoff, and into the atmosphere by wind erosion. Metal behavior is estimated by means of kinetic parameters, obtained by fitting kinetic extraction curves to two first-order reaction models. The differences observed are discussed in terms of land use and related soil properties. To the best of our knowledge, no such experimental scheme, involving kinetic extraction, has previously been applied to soils in a Ni-mining context.

Materials and methods

Study area

The climate of New Caledonia is subtropical, with a warm rainy season, and a cooler season. On the main island, the mean annual temperature is 25 °C, with

1700 mm rainfall, but substantial differences exist between the west and east coasts. Three sites were selected for the present study (Fig. 1): two are mined, while the third is free of mining activity, and therefore considered as a reference area. The first mining site, located near Kone, started operating in 1880 (Fig. 1a). In 2009, after a long period of inactivity, mining recommenced with the implantation of the Koniamo Nickel SAS (KNS) industrial complex, developing both mining and metallurgical operations. The second mining area, located near Poro (Fig. 1b), includes two mines: (i) the Mine Française, in operation since 1874 and (ii) the Bonini mine, which reopened in 1999. The reference site is located on ultramafic alterites, close to the Blue River Provincial Park (Fig. 1c).

Sampling and sample preparation

A total of 15 georeferenced soils was collected from the three study sites (Table 1). Leaf and litter, if present, were carefully removed. Each soil was a composite sample obtained from nine subsamples, collected from the 0–10 cm horizon with a shovel, on a ca. 200 m^2 area. Five bare-surface soils were sampled at the mining sites of Poro (P-M1 to P-M5) and KNS (K-M1 to K-M5). They are representative of different mining workstations: exploration areas, active working faces, abandoned areas, mining tracks, and storage platforms. The soils were classified as truncated Ferric Technosoils, according to WRB (IUSS Working Group WRB 2014), and correspond to the former B horizons of humid weathering profiles.

Additional samples were collected in undisturbed forested areas, less than 1 km away from the Poro and KNS mining sites: two at Poro (P-F1 and P-F2) and one at KNS (K-F1). Finally, two samples were collected in a forest area, several km distant from any mining activity, close to the Blue River Park (BR-F1 and BR-F2). All forest soils were classified as Ferric Ferralsols. They correspond to the current A horizon of humid

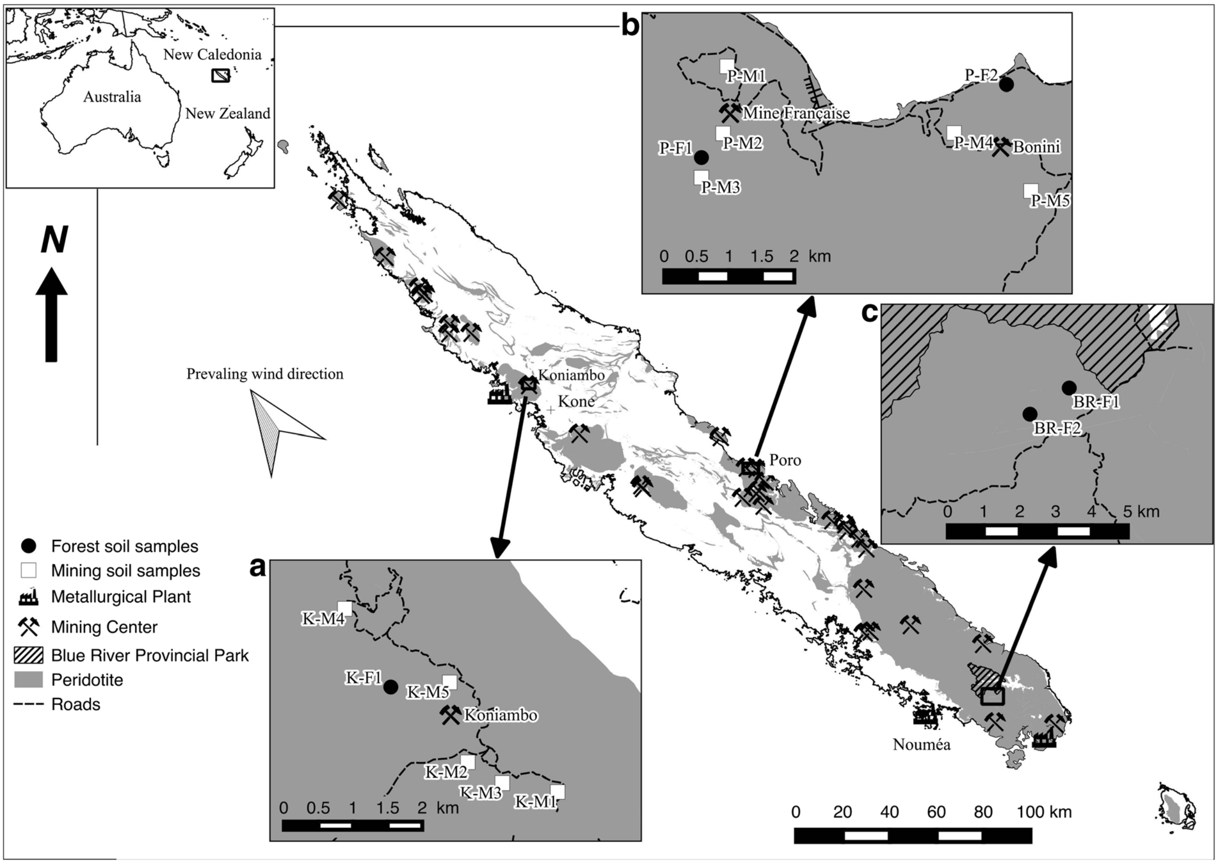

Fig. 1 Sampling sites in New Caledonia: close-up of Koniambo area (**a**), Poro (**b**), and Blue River Park reference site (**c**). See text for sample names

Table 1 Type, name, location, color, and context of the studied soils; latitude and longitude are provided in WGS84 system

Soils	Mining samples Ferric Technosols							
Site	KNS					Poro		
Name	K-M1	K-M2	K-M3	K-M4	K-M5	P-M1	P-M2	P-M3
Lon/Lat	164.819/− 20.991	164.807 /20.988	164.811/20.99	164.790/20.967	164.804/20.977	165.696/21.296	165.696/21.305	165.692 /21.311
Color	Reddish brown	Brownish yellow	Yellowish brown	Reddish yellow	Reddish yellow	Strong brown	Yellowish red	Strong brown
	5YR 4/4	10YR 6/6	10YR 5/6	7.5YR 6/6	7.5YR 6/6	7.5YR 4/6	5YR 4/6	7.5YR 4/6
Context	Exploration area	Mining roadway	Working face	Mining roadway	Storage platform	Storage platform	Storage platform	Abandoned working face

Soils	Mining samples Ferric Technosols		Forest samples Ferric Ferrasol				
Site	Poro		Blue River Park		Poro		KNS
Name	P-M4	P-M5	BR-F1	BR-F2	P-F1	P-F2	K-F1
Lon/Lat	165.73/21.305	165.741/21.313	166.721/22.178	166.710/22.185	165.690/21.310	165.739/21.298	164.796/20.977
Color	Dark-yellowish brown	Dark-reddish brown	Strong brown	Strong brown	Brown	Dark brown	Dark-yellowish brown
	10YR 4/4	5YR 3/4	7.5YR 4/6	7.5YR 5/6	7.5YR 4/3	7.5YR 3/3	10YR 3/6
Context	Abandoned working face						

weathering profiles. The composite soil samples were dried until constant mass at 35 °C in the laboratory, and sieved at 2 mm, and then at 100 µm.

Chemical and physical soil data

Soil color was determined using a Munsell color chart, and pH was measured in water medium with a 1:5, *v:v* ratio, on the < 2-mm soil fraction. The mineralogy of the < 100-µm fraction was determined by X-ray diffraction (INEL CPS 120° Curved Position Sensitive Detector, $K_{\alpha Co}$). Total concentrations of Ca, Na, K, Al, Mg, Fe, Co, Ni, and Mn in the < 100-µm soil fraction were measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), after total dissolution by suprapure grade HF, $HClO_4$, and HCl, at the INRA COFRAC-certified national soil analysis laboratory (Arras, France). Organic carbon content (via loss-on-ignition at 550 °C), C/N ratio (ISO 10694) using a Thermo NA 2000 CHN analyzer, cation-exchange capacity (CEC), and exchangeable cations using cobaltihexammine extraction (ISO 23470) were also analyzed at the same laboratory (AFNOR 2004). More details about analytical quality control can be found at https://www6.hautsdefrance.inra.fr/las.

Kinetic extraction

Kinetic extractions of Ni, Co, and Mn were carried out using a batch mode, with 3.0 g of the < 100-µm soil fraction, and 30 mL of extracting solution: 0.05 mol L^{-1} Na_2H_2-EDTA at pH = 6.5, similarly to other studies (Sahuquillo et al. 2003; Fangueiro et al. 2005; Bermond et al. 2005; Labanowski et al. 2008; Camizuli et al. 2014; Hamdoun et al. 2015). The solutions were agitated with a 3D Polymax 1040 Heidolph mechanical stirrer. Subsamples were collected at increasing time $t \in [5, 10, 15, 20, 30, 45, 60, 90, 120, 150, 200, 250, 300, 500, 1440]$ min, centrifuged at 6000 rpm, and filtered through a syringe equipped with a 0.45-µm-diameter membrane filter in cellulose acetate. The entire procedure was duplicated for each soil sample. Filtered supernatants were frozen prior to analysis using an ICP-AES, Spectro Arcos, installed in a clean room of the LISA laboratory (Paris Diderot University). Reproducibility between replicates was < ± 15%. Repeated measurement of SLR-5 river water, a certified reference material, was used to control stability and accuracy of ICP-AES measurements throughout the analytical session. Observed recovery ranged between 85 and 100% for all elements.

Data processing

Statistical treatment used the free R software (R Development Core Team 2012) with the nlme and nlstools packages (Baty et al. 2015; Pinheiro et al. 2018). Graphics were generated using the ggplot2 package (Wickham 2009). Mapping used the Quantum GIS free software (QGIS Development Team 2010).

Results and discussion

Physicochemical soil characteristics

Qualitatively, the mineralogy of the < 100 µm soil fraction is fairly homogeneous for all soils, dominated by goethite, hematite and quartz, with minor amounts of typical secondary mineral alteration phases, such as lizardite, antigorite, and talc/willemseite, mainly Mg-, Mg + Fe-, and Ni-bearing phyllosilicates, respectively (Supplementary material, SM1). These findings are consistent with previous works on New Caledonian ultramafic alterites (Becquer et al. 2001; Guillon 1975; Quantin et al. 1996). The Fe content was high, ranging from 10.3 to 55.9% (Table 2), explaining the range of color from orange to dark reddish brown (Table 1). Although Ni concentrations are higher in mining soils (1–2%) than in forest soils (0.4–1%) (Mann-Whitney *U* test, $p < 0.02$), no significant difference was observed for Co: 60–2500 mg kg^{-1}, and Mn: 503–11,000 mg kg^{-1} (Mann-Whitney *U* test, $p > 0.3$). Interestingly, Ni, Co, and Mn concentrations in the reference forest soils (BR-F1 and BR-F2) are lower than those from the other forested areas, close to mining sites. The undisturbed BR sites presented the lowest pH values (~4.7–4.8), contrasting with the rather neutral pH values (6.3–7.8) observed for the other forest samples. The CEC is quite low for all samples, between 1.02 and 10. $cmol^{+}$ kg^{-1}, with Ca and Mg compensating most of the negative charge. Low CEC values are typical of weathered soils developed from ultramafic rocks, due to high levels of oxides and 1:1 clays, with variable electric charges (Becquer et al. 2001). The cobaltihexammine extraction method does not substantially change soil pH, so that the CEC values represent the exchange capacity at the ZPC (zero point of charge). As expected, organic matter

Table 2 Main physicochemical characteristics of the < 100 μm soil fractions. -: not calculated; < for below the detection limit

Soils	Mining samples										Forest samples				
Site	KNS					Poro					Blue River Park		Poro		KNS
Name	K-M1	K-M2	K-M3	K-M4	K-M5	P-M1	P-M2	P-M3	P-M4	P-M5	BR-F1	BR-F2	P-F1	P-F2	K-F1
pH	6.15	7.3	6.85	6.3	6.85	6.49	6.24	7.36	7.8	6.95	4.72	4.75	6.29	6.35	6.48
C/N	32.4	-	26.7	34.7	36.1	45.1	-	32.8	26.5	19.5	23.5	20.8	19.9	22.8	19.8
OM (g kg^{-1})	11.1	1.51	5.65	6.45	2.42	2.41	1.63	2.83	1.73	4.21	56.7	39.3	52.9	22	42.3
Exchange capacity															
CEC (cmol kg^{-1})	1.02	10.8	4.49	2.19	1.58	1.89	1.62	5.75	9.61	4.35	2.15	1.21	5.63	4.46	7.53
$\mathrm{Ca_{exch}}$	0.13	0.40	0.18	0.19	0.08	0.11	0.56	0.21	0.63	0.17	0.42	0.13	1.58	1.94	1.23
$\mathrm{Mg_{exch}}$	1.11	10.8	4.61	4.14	2.00	3.97	6.31	5.83	8.78	3.94	0.39	0.28	2.82	2.43	5.74
$\mathrm{Na_{exch}}$	0.06	0.21	0.08	0.62	0.03	0.21	0.19	0.136	0.188	0.161	0.09	0.09	0.13	0.13	0.07
$\mathrm{K_{exch}}$	< 0.02	< 0.02	< 0.02	0.04	<0.02	< 0.02	< 0.02	< 0.02	0.02	< 0.02	0.06	0.04	0.08	0.09	0.11
$\mathrm{Fe_{exch}}$	0.17	0.04	0.10	0.16	0.191	0.09	0.10	0.07	0.02	0.08	0.07	0.06	0.07	0.08	0.06
$\mathrm{Mn_{exch}}$	0.082	< 0.005	< 0.005	0.005	0.011	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.218	0.019	0.217	0.027	0.08
$\mathrm{Al_{exch}}$	0.02	< 0.02	< 0.02	0.03	0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.12	0.55	< 0.02	< 0.02	< 0.02
Total metal (in % *w*/*w*, except Ni, Co, and Mn in mg kg^{-1})															
Ni	9690	19,400	22,300	14,200	14,400	15,200	15,800	23,600	17,900	19,300	4390	1190	10,400	11,800	9010
Co	583	582	661	1200	1390	539	838	1160	898	2540	357	59.3	1190	1560	884
Mn	8590	2440	3780	6510	5270	4330	6910	3530	2280	5330	1540	503	7570	11,400	7420
Fe	55.9	13.1	29.2	44.3	37.6	54.4	55.5	21.2	10.3	34.4	36.4	18.8	42.3	50.4	37.2
Mg	0.588	16	10.9	3.77	1.8	2.57	1.5	13.6	18.7	5.25	0.64	0.162	1.72	2.09	2.98
Al	2.2	0.37	1.15	2.62	1.2	1.49	1.47	0.53	0.24	0.83	5.25	8.78	1.36	1.86	2.53
Ca	< 0.02	0.12	0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.06	0.09	0.03	< 0.02	< 0.02	0.03	< 0.02	0.03

content in forest soils is much higher (ca. one order of magnitude) than in soils from mining areas (Mann-Whitney *U* test, $p < 10^{-3}$).

Modeling metal extraction kinetics

For all elements and all soils, the amount of metal extracted from the < 100 μm fraction initially exhibits a rapid release, and then a slower increase, tending toward a plateau value (see Fig. 2 for a typical example). This curve can be modeled by the sum of two first-order reactions:

$$Q_i(t) = Q_{1,\mathrm{i}}\left(1-e^{-\lambda_1 t}\right) + Q_{2,\mathrm{i}}\left(1-e^{-\lambda_2 t}\right) + \varepsilon_i, \qquad (1)$$

where $Q_i(t)$ corresponds to the amount of metal extracted per weight unit (in mg kg^{-1}) at a time *t* (in min), $Q_{1,i}$ corresponds to the rapidly released labile pool, and $Q_{2,i}$ to the less labile pool (in mg kg^{-1}). Both Q_1 and Q_2 are associated with kinetic constants, respectively λ_1 and λ_2 (expressed in min^{-1}); ε_i refers to the error term, and *i* to the duplicate sessions ($i = 1$ or 2). The parameters Q_1, Q_2, λ_1, and λ_2 were estimated using a nonlinear mixed model (Pinheiro et al. 2018); they are fixed effects, while $Q_{1,i}$ and $Q_{2,i}$ are random effects (Table 3). The R^2 values were > 0.97 and often better than 0.99 (Table 3). The regression estimates were always significantly non-null ($p < 0.05$). The amount of metal non-extractable by EDTA, Q_3 (in mg kg^{-1}), was obtained by subtracting the sum $(Q_1 + Q_2)$ from the total metal concentration, Q_tot, measured after total acid digestion:

$$Q_3 = Q_\mathrm{tot} - (Q_1 + Q_2) \qquad (2)$$

According to Fangueiro et al. (2005), the first pool, Q_1, comprises the water-soluble, exchangeable, weakly adsorbed metal fraction. The second pool, Q_2, includes more strongly bound metals. Experimental curves clearly indicate that after 1or 2 h, the conventional extraction time for single extractions (AFNOR 2004; Gupta and Sinha 2007; Ghanem 2008), the solid and liquid phases are not at equilibrium (Fig. 2).

Distribution of Ni, Co, and Mn in the three pools identified

In this study, Q_2 was always higher than Q_1: $Q_2/Q_1 =$ 1.0–5.7 for Ni, 1.1–40 for Co and 1.6–80 for Mn (Table 3), i.e., with a greater range of variation for Co and Mn than for Ni. The non-extractable pool, Q_3, always prevailed over the sum of the extractable pools: the $Q_3/(Q_1 + Q_2)$ ratios were in the range of 2–22 for Co, and 2–30 for Mn; the highest values were observed for Ni, with $Q_3/(Q_1 + Q_2) = 18$–525. Such results clearly highlight the relatively low capability of Ni to be transferred from the solid phase to the liquid, even in the presence of a strong chelate, such as EDTA ($Q_1 + Q_2$ represents less than 5% of total Ni in all cases). Nickel is predominantly located within the crystal structure of Ni-bearing silicates, such as willemseite, antigorite, and lizardite, and hence is not mobile. The extractability of Co and Mn was higher, and ranged from 3 to 35% of the total for both metals, with higher values generally observed in forest soils. Such higher values for Co and Mn could be related to the presence of Mn- and/or Co-oxides (asbolane), present in the ultrabasic alterites of New Caledonia (Dublet et al. 2012). Note that such mineral species were not detected by XRD, possibly due to fluorescence effects for Mn under Co kα radiation. After 1 h-EDTA extraction on ophiolitic soils, Angelone et al. (1991) obtained comparable results for Ni and Mn, but not for Co: less than 5–10% of total Ni was extracted, more than 20% of total Mn, but less than 1% of total Co was released.

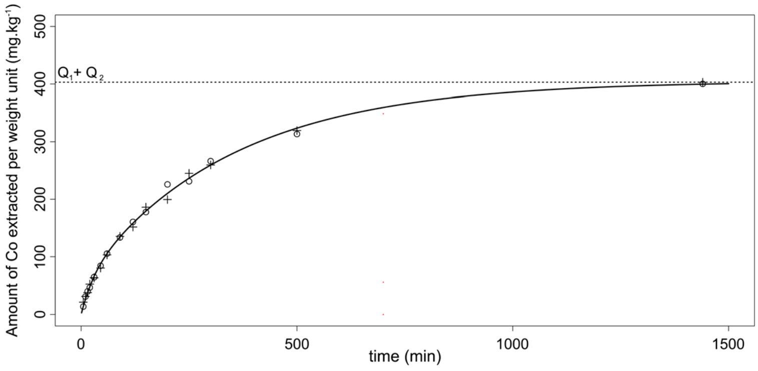

Fig. 2 Typical kinetic extraction curve. Here, the amount of Co extracted by EDTA (expressed in mg per kg of soil) as a function of time, for the P-F1 sample. Circles and crosses represent the two replicates, and the full line, the nonlinear regression

Table 3 Parameter values obtained by the two first-order reactions

	λ_1	sd	λ_2	sd	Q_1	sd	Q_2	sd	R^2	Q_3	Q_{tot}
Ni											
Mining											
K-M1	0.047	0.005	0.0015	0.0002	10	0.7	25	1.1	0.992	9655	9690
K-M2	0.074	0.009	0.0021	0.0002	220	11	600	16	0.993	18,580	19,400
K-M3	0.156	0.020	0.0021	0.0002	250	8.4	570	16	0.992	21,480	22,300
K-M4	0.076	0.015	0.0018	0.0002	50	4.8	160	8.8	0.984	13,990	14,200
K-M5	0.232	0.050	0.0016	0.0001	30	1.4	110	4.0	0.989	14,260	14,400
P-M1	0.062	0.009	0.0017	0.0002	60	4.1	150	8.0	0.985	14,990	15,200
P-M2	0.169	0.023	0.0018	0.0001	40	1.5	100	3.1	0.991	15,660	15,800
P-M3	0.073	0.009	0.0017	0.0001	110	8.0	510	11	0.994	22,980	23,600
P-M4	0.091	0.014	0.0017	0.0001	90	6.2	510	11	0.994	17,300	17,900
P-M5	0.111	0.011	0.0016	0.0001	130	6.5	400	14	0.992	18,770	19,300
Forest											
BR-F1	0.196	0.027	0.0046	0.0005	20	0.8	20	1.0	0.975	4350	4390
BR-F2	0.407	0.059	0.0041	0.0004	1	0.1	1	0.1	0.986	1188	1190
P-F1	0.182	0.028	0.0031	0.0001	140	5.8	390	9.3	0.992	9870	10,400
P-F2	0.144	0.022	0.0033	0.0002	70	3.7	230	4.5	0.993	11,500	11,800
K-F1	0.134	0.022	0.0044	0.0004	110	6.0	200	7.0	0.986	8700	9010
Co											
Mining											
K-M1	0.026	0.003	0.0029	0.0004	40	3.7	45	3.6	0.995	495	580
K-M2	0.041	0.009	0.0015	0.0001	5	0.4	30	1.0	0.995	545	580
K-M3	0.037	0.009	0.0020	0.0001	5	1.0	60	1.3	0.996	595	660
K-M4	0.014	0.004	0.0021	0.0003	25	7.8	100	6.5	0.997	1075	1200
K-M5	0.015	0.002	0.0016	0.0001	30	3.4	125	2.1	0.999	1235	1390
P-M1	0.020	0.004	0.0014	0.0002	5	0.7	20	0.7	0.996	515	540
P-M2	0.040	0.008	0.0017	0.0001	5	0.6	30	0.7	0.996	805	840
P-M3	0.046	0.015	0.0011	0.0001	2	0.8	80	1.5	0.996	1078	1160
P-M4	0.184	0.054	0.0009	0.0001	2	0.3	55	1.4	0.997	843	900
P-M5	0.190	0.086	0.0008	0.0001	5	0.5	210	6.1	0.999	2325	2540
Forest											
BR-F1	0.068	0.013	0.0077	0.0005	10	1.9	45	1.6	0.996	305	360
BR-F2	0.026	0.003	0.0031	0.0002	1	0.10	2	0.1	0.997	57	60
P-F1	0.034	0.006	0.0029	0.0001	55	7.8	350	7.0	0.997	780	1190
P-F2	0.029	0.005	0.0036	0.0002	70	11	270	9.6	0.996	1220	1560
K-F1	0.037	0.005	0.0038	0.0003	65	6.6	155	6.2	0.996	665	885
Mn											
Mining											
K-M1	0.027	0.003	0.0019	0.0003	55	42	830	38	0.994	7705	8590
K-M2	0.034	0.009	0.0014	0.0001	20	3.0	160	7.3	0.994	2260	2440
K-M3	0.025	0.006	0.0025	0.0002	50	9.7	255	15	0.993	3475	3780
K-M4	0.016	0.004	0.0018	0.0004	170	46	435	32	0.994	5905	6510
K-M5	0.021	0.003	0.0013	0.0001	140	13	540	14	0.998	4590	5270
P-M1	0.013	0.003	0.0011	0.0002	25	5.5	120	5.4	0.997	4185	4330

Table 3 (continued)

	λ_1	sd	λ_2	sd	Q_1	sd	Q_2	sd	R^2	Q_3	Q_{tot}
P-M2	0.041	0.008	0.0012	0.0001	25	3.0	230	7.0	0.996	6655	6910
P-M3	0.033	0.010	0.0014	0.0001	10	3.4	270	3.7	0.996	3250	3530
P-M4	0.130	0.070	0.0007	0.0001	3	1.1	265	9.4	0.997	2012	2280
P-M5	0.058	0.019	0.0012	0.0001	10	3.3	410	9.1	0.999	4910	5330
Forest											
BR-F1	0.119	0.020	0.0091	0.0006	120	11	300	9.9	0.994	1120	1540
BR-F2	0.141	0.031	0.0050	0.0003	5	0.4	20	0.4	0.992	475	500
P-F1	0.054	0.010	0.0047	0.0003	535	63	2090	58	0.996	4945	7570
P-F2	0.114	0.034	0.0067	0.0003	280	49	2270	39	0.996	8850	11,400
K-F1	0.058	0.008	0.0057	0.0005	670	67	1290	61	0.993	5460	7420

Q_1, Q_2, and λ_1, λ_2: amount of metal extracted with EDTA per kg of soil (in mg kg^{-1}), and associated kinetic constants (in min^{-1}), along with their respective standard deviation, sd; R^2 values. Q_{tot}: total metal concentration; Q_3: amount of non-extractable metals

Metal extraction rates

The λ_1 and λ_2 values of Ni, Co, and Mn varied within similar ranges: 0.013 to 0.4 min^{-1} for λ_1, and 7 10^{-4}–9 10^{-3} min^{-1} for λ_2 (i.e., with λ_2 one or two orders of magnitude slower than λ_1). Such ranges are consistent with other kinetic studies using EDTA extraction in other contexts: on sediments or on soils sampled in agricultural and mining areas (Camizuli et al. 2014; Chakraborty et al. 2014; Yu and Klarup 1994). Multiple comparisons of λ_1 and λ_2 values between mining and forest soils were undertaken to explore our dataset (using multiple Mann-Whiney *U* tests, with Bonferroni correction). Forest soils were always statistically discriminated from mining soils, either by a higher λ_2 value for Ni and Co, or by higher λ_1 and λ_2 values for Mn (Fig. 3). These result imply that, in forest soils, metals belonging to the second pool are released more rapidly.

Environmental implications

Our main objective was to examine metal extractability at the surface of two contrasting ecosystems: bare mining soils and tree-covered forest soils, whether impacted by mine dust or not. Mining surface soils mainly consist of truncated B-horizon material of former Ferralsols. This material was sometimes partially reworked, and its presence at the surface, i.e., subject to atmospheric agents, is recent. Although soils developed under humid subtropical conditions and have been deeply weathered for a very long period of time, metals are still predominantly included in mineral structures. By contrast, surface samples collected from forests correspond to A-horizons of ferric Ferralsols, including notable amounts of organic matter. In the absence of anthropogenic perturbation, the long period of alteration has led to soil acidification, and partial dissolution of silicate minerals, such as antigorite, detected in smaller amounts in the < 100 μm fraction of forest samples (Supplementary material, SM1). Consquently, the metals released may have entered the biogeochemical cycle, together with other leachable chemical elements. Their higher organic matter content may have led to enhanced microbial activity, and subsequent manganese oxide reduction, with increased Co mobility, because this element is often associated with manganese oxides in ultramafic soils. Quantin et al. (2001) reported that Fe and Mn oxides present in crystallized goethite were the source of mobile Mn, Co, and Ni, after bacterial reduction processes. Differences in the chemical speciation of Ni, Co, and Mn at the surface of forest and mining soils can explain the differences observed in the percentage of extractable metals and in the speed of extractability by EDTA.

Both λ_1 and λ_2 describe the intrinsic capacity of chemical elements to be extracted more or less rapidly (a surrogate for ease of extraction), constrained by extrinsic parameters, including physicochemical soil properties. In this study, higher λ_2 (and sometimes λ_1) values in forest soils do not necessarily imply more potentially harmful risks for the environment. First, the differences observed in terms of λ values mostly relate to the second pool, which is less likely to be released into the environment. Secondly, the risk of dispersion by soil erosion, whether

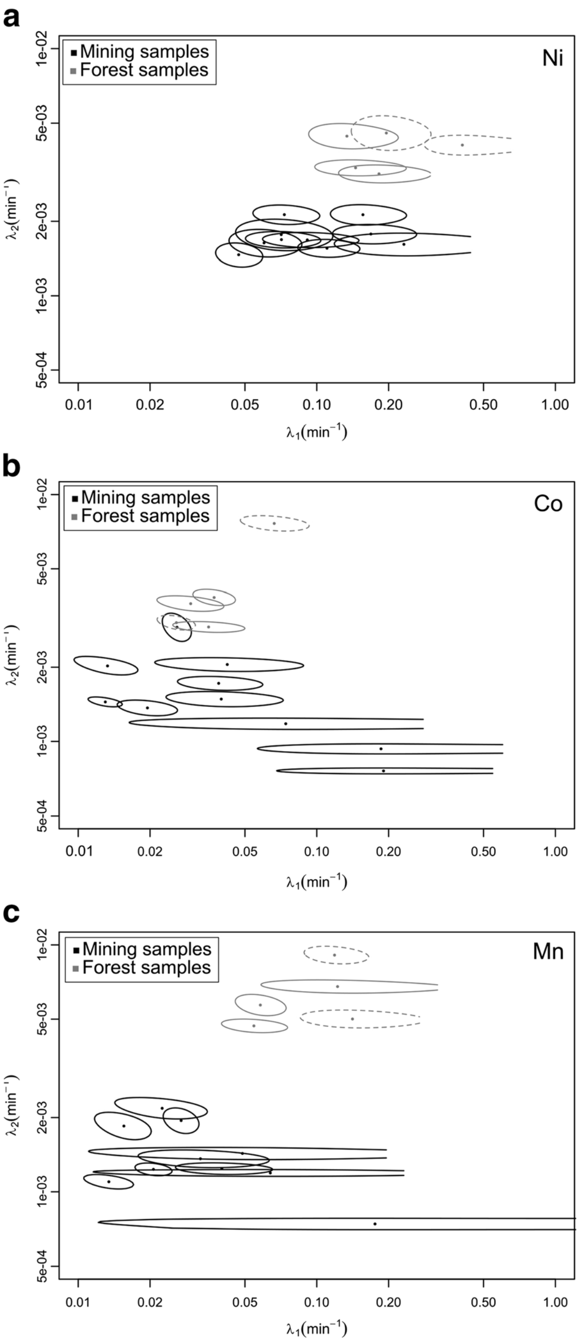

Fig. 3 λ_1 versus λ_2 for Ni (**a**), Co (**b**), and Mn (**c**), in mining (black) and forest (gray) samples; the 95% confidence region are also provided for each pair (λ_1, λ_2); the reference samples from the Blue River Park are plotted in forest soils with dotted lines

by surface runoff or eolian deflation, is undoubtedly higher for bare, mostly unconsolidated mining soils, due to their lack of protection by vegetation. Metal-rich particles may then be transferred downstream to the lagoon or by wind to urban areas. Here, the amount of easily and less easily extractable Ni, Co, and Mn (i.e., $Q_1 + Q_2$) in mining soils falls within the following ranges, respectively: 35–820 mg kg^{-1}, 25–215 mg kg^{-1}, and 145–885 mg kg^{-1}. By comparison, concentrations of Ni, Co, and Mn ranging respectively from 10 to 300 mg kg^{-1}, 25 to 100 mg kg^{-1}, and up to 400 mg kg^{-1} have been reported as toxic for most plants (Adriano 1986). Consequently, EDTA-extractable metals, a proxy for the maximum bioavailable pool, are present in non-negligible amounts in mining soils, and may thus represent a real threat for the surrounding environment.

Conclusion

A two first-order reactions model was used to model kinetic extraction of Ni, Co, and Mn in 15 surface samples originating from contrasting mining and forest environments. The total labile fractions were low in percentage for both systems, but non-negligible with respect to total metal contents. When focusing on the < 100 μm fractions, markedly higher λ_2 values were observed in forest soils for all metals. Despite these findings, mining soils represent a greater environmental risk, since these bare unconsolidated soils are highly sensitive to massive surface runoff erosion and eolian dust deflation.

Statistical inferences about metal behavior in soils based on a kinetic extraction approach are challenging. Here, for each of the 15 surface samples studied, one full extraction procedure generated 15 subsamples, and all operations were duplicated. Additionally, each sample was also analyzed for total element concentrations, CEC, pH, organic C, etc. Despite its demanding nature, such a scheme should nevertheless be recommended to statistically counterbalance the variable nature of soils. This approach would be useful for planning mining site establishment, working operations, and storage, as well as reclaiming mining sites, once mining activities have ceased.

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