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Chemico-mineralogical changes of ultramafic topsoil during stockpiling: implications for post-mining restoration

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Abstract Lateritic topsoils, which are usually removed and stored apart before mining operations take place, play an essential role in the success of post-mining restoration. They contain elements to recover chemical (organic matter, nutrients) and biological (seed and bud banks, microorganisms) fertility of the soil. Conserving topsoil fertility during storage time is essential for a successful use of topsoil during restoration. In this study, different chemico-mineralogical properties of a lateritic topsoil from the Goro nickel mine (New Caledonia) were monitored from its original in situ emplacement on the soil profile, immediately after its stockpiling and after 24 months of storage. Our analyses show that topsoil experienced noticeable changes immediately after storage, mostly produced by mixing of different soil profiles. Cation Exchange Capacities and concentrations of most elements did not vary even after 24 months of storage. However, a slight reduction of Ni, Cr, K, Na and of the C:N ratio, and an increase of Ca have been observed. Stockpiling has not affected negatively the chemical fertility of the topsoil, although biological parameters should be considered to have a complete view of stockpiling sustainability.

Keywords Cation exchange capacity · Laterites · New Caledonia · Organic matter · Topsoil stockpiling

Introduction

Nickel is a widely used metal in many applications including the production of stainless steel. Its demand has been growing constantly in the last decades (Adriano 2001; Mudd 2010; Mudd and Jowitt 2014). Historically, nickel sulphide ores have been the main source of Ni, being Canada and Russia the first two world producers. However, during the second half of the 20th century occurred a shift of Ni mining activities from high grade ore Ni sulphides to low grade ore Ni laterites, which currently represent around 50% of mined Ni ores (Mudd 2010; Mudd and Jowitt 2014).

Nickel laterites are formed by an intense weathering of olivine-rich ultramafic rocks (and their metamorphosed derivatives) under warm and humid climate conditions (Brand et al. 1998; Butt and Cluzel 2013). They are mainly distributed on tropical wet savanna (New Caledonia, Cuba, certain areas in Brazil) and tropical rainforest areas (Indonesia, Colombia, New Caledonia) although some laterites are found on areas with temperate or Mediterranean climate (such as Australia, Greece, USA or Russia). However, latter areas are considered to be under humid warm and humid climate when lateritisation occurred (Butt and Cluzel 2013). Lateritisation involves dissolution of the primary minerals of the ultramafic bedrock, which leads to leaching of soluble elements (Si, Mg) and in situ neoformation of mineral phases (mainly oxy-hydroxides) that host the insoluble elements (Fe, Al, and Cr) (Quesnel et al. 2017). Nickel has an intermediate behavior and is accumulated at the bottom of the profile. Depending on the Ni-bearing ore, three types of laterites are defined: oxides, hydrous Mg silicates and clay silicates (Brand et al. 1998; Freyssinet et al. 2005; Butt and Cluzel 2013). Lithology partially determines the type of laterite, with oxides prevailing in dunite

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whereas peridotite can evolve to any of the three types and serpentinised peridotites produce mainly silicates (Butt and Cluzel 2013; Echevarria 2018).

New Caledonian nickel laterites host 11% of world nickel reserves (Quesnel et al. 2017). They are the result of the weathering of a peridotite nappe that covers around 40% of surface of the main island (Grande Terre) (Becquer et al. 2001; Quesnel et al. 2017). This peridotitic ophiolite was obducted on the Norfolk ridge during late Eocene and then exposed to recurrent periods of erosion and lateritisation that shaped major landforms in the landscape (Dublet et al. 2015). Most of the nappe is composed by harzburgite, which is concentrated in a main ultramafic area in southeast of the island (Massif du Sud), whereas lherzolite dominates in three smaller ultramafic bodies placed in the Centre and North of the island (Ulrich et al. 2010). Ni-lateritic profile in New Caledonian belongs to hydrous Mg silicates type (Cluzel and Vigier 2008). High pluviometry and drainage lead to the leaching of mobile elements such as K, Na, Mg, Ca or Si and the development of a goethite-dominant limonite horizon that may reach tens of meters thickness (Losfeld et al. 2015; Echevarria 2018). Nickel is leached along the profile and it concentrates in the saprolite zone which comprises secondary serpentine, and neofomed goethite, smectite clays and garnierite (Cluzel and Vigier 2008). A ferricrete (iron pan) may develop on top of the soil profile due to the dehydration and crystallization of iron oxides. Due to the nature of bedrock material and the intense leaching during pedogenesis, nickel laterites are extremely nutrient-poor. Moreover, iron pan formation seals soil surface, leading to the formation of Hyper-skeletal Leptosols, often a few decimetres deep, sustaining a low vegetation (Echevarria 2018). Dominant plant species in these areas usually depend on root symbiosis for the provisioning of basic nutrients (such as N, P or K). For instance, a stunted secondary forest dominated by *Nothofagus* spp., *Arillastrum gummiferum* (associated with ectomycorrhiza), and *Gymnostoma* spp. (associated with N-fixing actinobacteria) develops on ferricretes in New Caledonia (Isnard et al. 2016). In those sites, nutrient state of plants is kept by an intense recycling of decayed organic matter (Echevarria 2018).

Due to its low ore grade, Ni-mining on laterites is highly destructive: strip-mining is developed on wide areas and involves the excavation of the complete soil profile (O'Dell and Claassen 2009). Moreover, it generates huge quantities of spoils and tailings: e.g. in New Caledonia current trends indicate that 3.5 t of lateritic spoils are moved to access 1 t ore (Losfeld et al. 2015). Restoration of those degraded lands is a complicated task that must face the extremely low concentrations of essential nutrients, the presence of potentially toxic concentrations of metals (mainly Ni and Cr) as well as reduced chemical properties related to soil fertility such as cation exchange capacity (CEC) or water holding capacity (WHC) (O'Dell and Claassen 2009).

Lateritic topsoils, which are usually removed and stored apart before mining, play an essential role in restoration (Bradshaw 1997; O'Dell and Claassen 2009; Losfeld et al. 2015). They contain elements to improve the chemical (organic matter, nutrients) as well as the biological (microorganisms, plant propagules) fertility of the soil (Bradshaw 1997; Echevarria and Morel 2015). Therefore, keeping topsoil fertility during storage time is essential in order to use topsoil for the restoration of post-mining landscapes.

Modification of topsoil properties during storage has been observed by different authors, either by degradation of organic matter (Hunter and Currie 1956), modification of microbial communities that lead to a loss of nitrogen (Davies et al. 1995) or loss of organic carbon due to lack of organic inputs from vegetation (Schwenke et al. 2000). These modifications can be partially controlled by the development of adequate management practices (Sheoran et al. 2010). However, most of this information comes from coal or bauxite mines, and scarce information about the specific case of laterite topsoils is available (Echevarria and Morel 2015).

Here we present a study aimed at the assessment of the evolution of chemico-mineralogical properties of Ni-laterites topsoil during storage in a mine area. More precisely, we want to answer the following questions: (i) does storage affect the chemical fertility of topsoils?, and (ii) do changes in topsoil properties involve changes in mobility and availability of potentially toxic trace elements? For that, we have quantified and followed up the evolution of different chemico-mineralogical properties of ultramafic topsoil in the Goro nickel mine (New Caledonia), from its natural emplacement on the soil profile through its excavation to its storage during a 24 months period.

Materials and methods

Study area and soil sampling

This study was developed in the area of the Goro nickel mine in New Caledonia, which is placed inside the main ultramafic area in the south of the island (Massif du Sud). Inside the mine concession area, a 100 m² plot was marked before its excavation. Surface soil in this plot is a Leptosol (International Union of Soil Sciences Working Group World Reference Base for Soil Resources (IUSS Working Group WRB 2015) developed on top of an iron pan. From this plot, two composite samples of topsoil (made up of 5 different sampling points each) were collected at layers A1 (0–20 cm, coded as TOP A soil) and A1/C (20–30 cm, coded as TOP B soil).

After sampling, all the topsoil in the plot was excavated on 0–30 cm thick and stockpiled over 2 m thick in the mine area. Soil samples were collected from this pile at two storage times: 0 months (T0, the day the pile was

built) and 24 months (T24). Soils at T0 (five samples) were collected on surface. However, soils at T24 were sampled at four different depths (three samples per depth level) in the soil pile: 0, 50, 100 and 150 cm depth (Table 1).

Additional soil sample, representing the main type of lateritic soils in Goro area (Geric Ferralsols, IUSS Working Group WRB 2015), was collected at different depths in a point (Plaine des Lacs) outside the mine concession and used as geochemical reference (Table 1). These soil samples were coded as SFFC (abbreviation for “Sol Ferralitique Ferritique Colluvial”, the equivalent to Geric Ferralsol (IUSS Working Group WRB 2015) in the French soil classification; Commission de pédologie et de cartographie des sols (C.P.C.S. 1967).

Soil analyses

Sampled soils were air-dried and sieved at 2 mm. Cation exchange capacity (CEC) was determined after treatment of the soil with a solution of cobaltihexamine trichloride 0.05 N, following the standard method AF-NOR NF-X 31–130. All the samples were analysed as duplicates. The residual concentration of cobaltihexamine ions left in solution after the exchange reaction was measured using UV spectrometry. The difference between initial and residual concentrations of cobaltihexamine was used to calculate CEC. The concentrations of exchangeable elements were determined on the filtered soil:cobaltihexamine extracts by means of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Liberty II, Varian Inc, Australia).

The main crystalline mineral phases in TOP A, TOP B, TOP T0 and SFFC soils were identified by X-ray diffraction (XRD) in ground samples sieved at 150 μm , and using a D8 Advance Bruker diffractometer with a Co $K_{\alpha 1}$ radiation source, operated at 35 kV and 45 mA ($\lambda = 1.7902 \text{ \AA}$). XRD patterns were collected on the angular range (2θ) of 3° – 64° , with a 0.034° step size and a 3 s collecting time. The measurements were performed at LIEC (Vandoeuvre les Nancy, France).

Soil samples (< 2 mm fraction) were extracted with CaCl_2 , EDTA and DTPA using standard protocols. Extractable concentrations of Co, Cr and Ni were quantified in the solutions by ICP-AES.

Finely ground soil samples (< 100 μm) were mixed with LiBO_2 and acid-digested with HNO_3 . Total concentrations of major elements were quantified by ICP-AES, whereas trace elements were quantified by ICP-Mass Spectrometry (ICP-MS). Total soil C and N was estimated by combustion in a CHNS analyser (Vario Micro Cube, Elementar, Germany).

The composition of organic matter in topsoil samples before excavation (TOP A, B) and in excavated topsoils at $t = 0$ and at $t = 24$ months (TOP T0, TOP T24) was further explored by means of fourier transformed infrared spectroscopy (FTIR). This technique has been successfully applied to the analysis of organic matter from bulk soil samples (Haberhauer and Gerzabek 1999; Haberhauer et al. 2000; Chapman et al. 2001; Artz et al. 2008). Finely ground soil samples were thoroughly mixed with KBr (FTIR grade) and pelletized at 6 bars using a press. Mid-infrared transmission spectra were recorded from pellets by using the Equinox 55 spectrometer (Bruker, Wissemburg, France) from Georesources Laboratory (CNRS-Universite de Lorraine, France). Spectra were recorded from 400 to 4000 cm^{-1} . Identity of FTIR bands were interpreted in accordance to several sources (Haberhauer and Gerzabek 1999; Ruan et al. 2001; Fu and Quan 2006; Liu et al. 2013).

Data analyses

Soil chemical dataset including total concentrations of major elements, total and extractable concentrations of Co, Cr and Ni, CEC and exchangeable cations, and C and N concentrations was used to compute a principal component analysis (PCA).

A mineral species abundance matrix (classes 1—low—3—high—) was constructed from XRD results from t0 soils. SFFC, TOP A/B and TOP T0 samples were grouped on the basis of their mineralogical composition

Table 1 List of soils sampled for our study

Soil	Layer or depth	Time (months)	Code	No. of samples
Leptosol above iron crust (Goro mine area)	A1 (0–20 cm)	–	TOP A	1 (composite)
	A1/C (20–30 cm)	–	TOP B	1 (composite)
Excavated topsoil	–	0	TOP T0	5
Stockpiled topsoil	0 cm	24	TOP T24 (0 cm)	3
	50 cm	24	TOP T24 (50 cm)	3
	100 cm	24	TOP T24 (100 cm)	3
	150 cm	24	TOP T24 (150 cm)	3
Geric Ferralsol (colluvial) (Plaine des lacs)	A1 (0–10 cm)	–	SFFC 1	1 (composite)
	B (120 cm)	–	SFFC 2	1 (composite)
	B/C (350 cm)	–	SFFC 3	1 (composite)

For each soil is indicated the sampling depth (or the layer), the number (N) of collected samples and, for topsoils, the time (months) between excavation and stockpiling

SFFC Sol Ferralitique Ferritique Colluvial

by means a non metric multidimensional scaling (NMDS) analysis.

Differences in CEC, major and trace element concentrations between TOPT0 and TOPT24 samples (at four different depths) were explored by means of one way ANOVA analysis. Separate analyses were used to compare T0 and T24 soils at surface (effect of time) and to compare T24 soils at different depths. Significant differences were further explored by post hoc analysis applying a Bonferroni correction for multiple comparisons. Variables whose distribution did not meet ANOVA requirements were analysed by the non-parametrical Kruskal–Wallis test, followed by a Bonferroni–Dunn post hoc test.

PCAs and ANOVAs were computed using SPSS (v. 15, SPSS Inc., Chicago, IL, USA). NMDS were computed using “metaMDS” instruction from R package “vegan v. 2.4–4” (Oksanen et al. 2017). Kruskal–Wallis and Bonferroni–Dunn post hoc tests were performed in R software (version 3.3.1, R Foundation for Statistical Computing, Vienna, Austria) using library “stats” (R Core Team, 2013) and package “PMCMR” (Pohlert 2014).

Results

Mineralogical analysis showed that iron (hydro)oxides (goethite and hematite) were the most abundant mineral species in all the samples. In contrast, chromites had medium abundance in TOPA and TOP T0 samples and in SFFC3 sample (at the bottom of the lateritic profile). Talc was present only in SFFC3, whereas quartz was present (with low abundance) only in TOPB and TOP T0 samples (table S1, supplementary material). NMDS analysis grouped T0 samples in function of their mineralogical composition (Fig. 1). Iron minerals (goethite and hematite, placed around 0 values for the two dimensions) had no effect in the distinction of different samples; quartz and chromite had negative weights on first dimension, whereas manganese and magnesium minerals (galaxite and talc) had more weight on second dimension. TOP B sample (number 2 in Fig. 1) was placed close to SFFC (Plain des Lacs) samples. Stockpiled soil at $t = 0$ (TOP T0) resulted from the mixing of TOP A and TOP B have an intermediate position between them (numbered as 1 and 2 in Fig. 1).

According to chemical analyses, Fe was the predominating element in soil, with Fe contents from 33 to 50%. Surface layer of Leptosol (TOP A sample) had much lower Fe concentration (16%). Regarding total concentrations of other major elements (Ca, Mg, K, Na, and P), all of them are below 1% in all soil samples. In some cases (such as Ca and Na in Ferralsol and TOP B samples, or Na and K in TOP T24 samples) the concentrations of these elements were below the detection limits. Cr was the predominating trace element, with concentrations that overpassed $40,000 \text{ mg kg}^{-1}$ in TOP

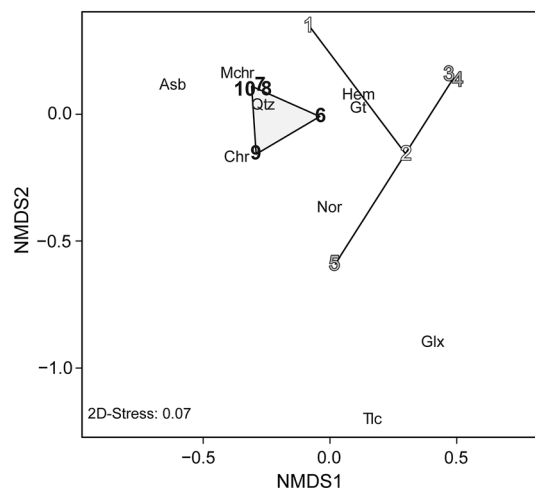


Fig. 1 Two dimensional non-metric multidimensional scaling (NMDS) of soil samples at time = 0. White numbers indicate Leptosol samples. Grey numbers indicate Geric Ferralsol (Sol Ferralitique Ferritique Colluvial) samples. Black numbers indicate stockpiled topsoil samples at $t = 0$. Grey areas and lines are convex hulls grouping all the sites from same type. Letter codes indicate mineral species: *Asb* asbolane, *Chr* chromite, *Glx* galaxite, *Hem* hematite, *Gt* goethite, *Mchr* magnesiochromite, *Qtz* quartz, *Tlc* talc. Chemical formulae for minerals are presented in supplementary material (Table S1)

T0 samples. Ferralsols (SFFC samples) had CEC values around 0, whereas this parameter had the maximum value in TOP A sample ($20.1 \text{ cmol}_c \text{ kg}^{-1}$) where the organic matter content was the highest. TOP A had the highest concentrations of chemically-available Ni (e.g. DTPA-extractable) of all samples (Table 2 and supplementary material, table S2) reaching 65.9 mg kg^{-1} , which were much higher than the available Ni in the different horizons of the Ferralsol (maximum value: 0.31 mg kg^{-1}). PCA on chemical variables including all soil samples retrieved five Principal Components (PCs) explaining around 90% of total variance. First PC (explaining 32% of variance) is related to fertility: variables with positive loadings on PC1 were CEC, several exchangeable cations, organic C and also Ni-DTPA concentrations; whereas iron and aluminium oxides have negative loadings. Second PC (explaining 24% of variance) is related to the depth in the laterite profile: total concentrations of Si, Mn, Co and Ni, as well as CaCl_2 -extractable Cr had positive loadings on PC2, whereas negative contributions were total and exchangeable Ca concentrations and total P concentration (Fig. 2a). A scatterplot of soil samples onto the first two PCs showed clear differences between soils of different origin (Fig. 2b): samples from the Plaine des Lacs (SFFC1–3) have values around 0 on PC1 (low fertility parameters), but they are plotted along PC2 following a depth gradient (deepest horizon, with highest total Ni concentration (around 8000 mg kg^{-1}) had the most positive extreme values on PC2). In the case of samples from Goro mine area, they are spread along PC1. TOP A composite sample has an extreme positive position on

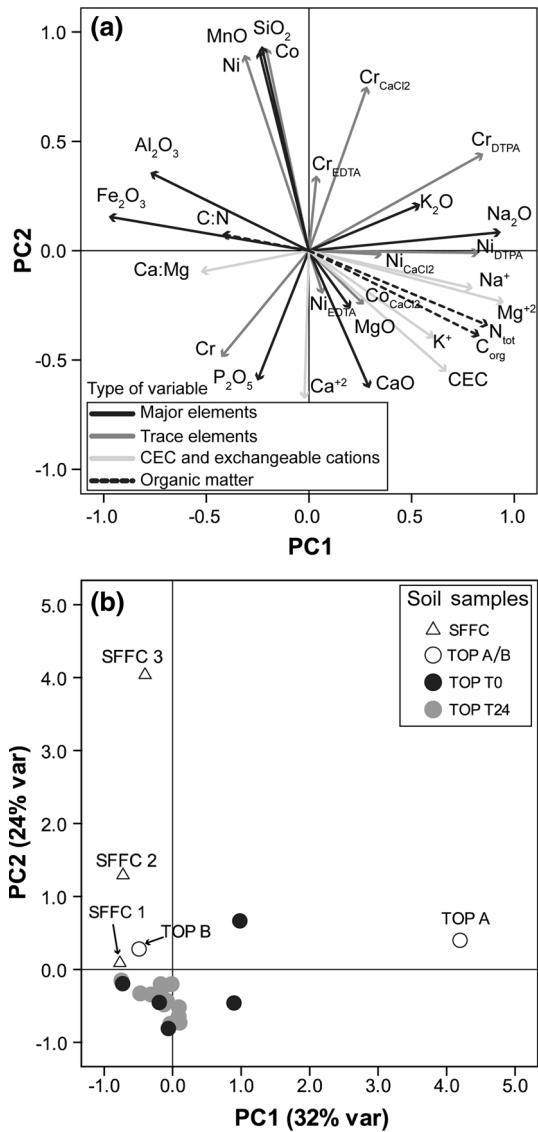


Fig. 2 Principal Component Analysis (PCA) of soil data. **a** Loadings of soil variables on first two principal components (PCs). Black arrows, total concentrations of macroelements; dark grey arrows, total and calcium chloride (CaCl₂), Ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA) extractable concentrations of Trace Elements; light grey arrows, Cation Exchange Capacity (CEC) and exchangeable base cations; dashed black arrows, organic C (C_{org}) and total N (N_{tot}). **b** Scatterplot of soil samples (one point equals one soil sample) on two first PCs. Triangles, Geric Ferralsol (Sol Ferralitique Ferritique Colluvial) samples; empty circles, leptosol (TOP A-B) samples; black filled circles, stockpiled topsoil samples at t = 0 (TOP T0); grey filled circles, stockpiled topsoil samples at t = 24 (TOP T24).

PC1, which involves a relative high CEC, high organic C, and high exchangeable concentrations of several macronutrients. In contrast, TOP B composite sample is plotted on negative values for PC1 (close to SFFC1 sample) which corresponds to lower CEC and nutrient concentrations. Samples from stockpiled topsoil (TOP T0 and TOP T24), which can be considered a mixture of

sample types TOP A and TOP B, are placed in intermediate positions between TOP A and TOP B. They mainly show negative values on both PCs, indicating lower nutrient concentrations (compared to TOP A sample) and lower total trace element concentrations (compared to SFFC3 sample). PCA also shows a certain difference between T0 and T24 samples: T24 are in a dense swarm in negative quadrant, whereas T0 are less grouped, two of them having positive values on at least one of the PCs.

Stored topsoil showed high stability during stockpiling, and for most of the 29 analysed chemical parameters no significant differences were found. Considering the effect of time (T0 vs T24 samples at 0 cm depth), an increase in total Co as well as total and exchangeable Ca was observed. In contrast, CaCl₂-extractable concentrations of Cr and Ni, and exchangeable Na and K decreased (Table 2). Considering T24 samples only, we observed an increase of exchangeable Na and K with depth (Table 2).

FTIR spectra were, in general, very similar for all samples, showing the same set of vibration bands (Fig. 3). Main differences occurred between Leptosol TOP A, and the other samples (Fig. 3) and involved a reduction in intensity of several bands related to organic matter, and even more markedly the bands of vibration of water molecules (wavenumbers 3402 and 1629 cm⁻¹). Two bands (at 3365 and 3157 cm⁻¹) related to OH from goethite and three main bands at 906, 809 and 480 cm⁻¹, which correspond with iron oxides and hydroxides (mainly goethite) were increased in Leptosol TOP B and stocked topsoil samples (TOP T0 and TOP T24), due to a relative loss of organic matter. However, a band at 560 cm⁻¹, which corresponds with hematite (iron oxide), is more expressed in TOP A than in the other soil samples. Stocked topsoil samples (TOP T0 and TOP T24) mimicked the profile of Leptosol TOP B sample. No apparent difference was observed between stocked topsoil at T0 and at T24. However, peak at 3365 cm⁻¹ was slightly reduced in TOP T24—1.5 m, compared to TOP T24—0 m, which may involve an increased loss of -OH groups with depth.

Discussion

Topsoil is an invaluable resource for the restoration of post-mining areas, since it stores essential nutrients and other fertility factors (such as CEC or water holding capacity) as well as the needed biota (seed and bud bank, microorganisms, soil fauna) to recover a functional ecosystem (Bradshaw 1997, 2000). In this paper we have dealt with the evolution of chemico-mineralogical properties of ultramafic topsoil, since its original place as a Leptosol over an iron crust (ferricrete), to its removal and stockpiling and 2 years after stockpiling.

Mineralogical analyses of soil samples showed the dominant presence of iron oxides and hydroxides, and

Table 2 Evolution of topsoil during stockpiling

	TOP T0		TOP T24							
			0 cm		50 cm		100 cm		150 cm	
	Mean (<i>n</i> = 5)	SD	Mean (<i>n</i> = 3)	SD	Mean (<i>n</i> = 3)	SD	Mean (<i>n</i> = 3)	SD	Mean (<i>n</i> = 3)	SD
Total concentration of major elements (%)										
SiO ₂	0.54	0.10	0.43	0.03	0.44	0.02	0.45	0.06	0.41	0.05
Al ₂ O ₃	4.89	0.52	4.76	0.12	4.78	0.06	4.81	0.04	4.79	0.20
Fe ₂ O ₃	57.06	5.18	59.33	1.25	59.97	1.22	62.17	1.21	61.87	2.66
MnO	0.14	0.03	0.13	0.01	0.14	0.01	0.13	0.03	0.11	0.00
MgO	0.62	0.08	0.52	0.02	0.52	0.01	0.50	0.02	0.52	0.02
CaO	0.12*	0.03	0.22	0.01	0.22	0.03	0.19	0.01	0.17	0.04
Na ₂ O	0.00	0.01	< d.l.		< d.l.		< d.l.		< d.l.	
K ₂ O	0.03	0.01	< d.l.		< d.l.		< d.l.		< d.l.	
P ₂ O ₅	0.06	0.01	0.06	0.00	0.06	0.00	0.07	0.01	0.06	0.01
LOI	30.11	5.22	29.03	1.46	28.67	1.38	26.20	0.92	26.23	2.85
Total concentration of TE (mg kg ⁻¹)										
Co	184.4*	31.8	270.3	68.5	262.0	22.9	368.3	92.1	297.7	62.4
Cr	43,504.0	5850.2	35,323.3	763.6	34,850.0	357.6	34,130.0	1375.0	35,010.0	645.8
Ni	1556.6	256.6	1247.3	40.0	1311.3	37.2	1300.0	170.9	1128.3	36.3
CaCl ₂ -extractable TE (µg kg ⁻¹)										
Co	1121.4	642.7	488.7	107.8	503.0	52.9	695.0	440.9	396.7	45.1
Cr	194.8*	49.8	100.6	11.7	84.0	2.6	85.1	13.8	96.0	2.4
Ni	2484.0*	1222.6	1160.0	81.9	1176.7	55.1	1420.0	356.8	1223.3	205.3
DTPA-extractable TE (mg kg ⁻¹)										
Cr	0.60	0.17	0.55	0.03	0.58	0.23	0.46	0.23	0.80	0.19
Ni	11.78	8.95	8.33	0.29	8.30	0.49	8.37	2.73	6.66	0.43
EDTA-extractable TE (mg kg ⁻¹)										
Cr	25.32*	10.28	14.70	0.35	18.47	2.45	21.43	5.44	17.47	1.76
Ni	18.04	11.88	11.60	1.06	12.67	1.18	13.48	4.18	9.78	0.85
CEC and exchangeable cations (cmol kg ⁻¹)										
CEC	10.00	2.08	12.21	1.46	12.29	0.95	9.98	1.44	10.28	0.84
%Saturation	73.68	6.32	76.97	10.37	78.33	9.21	76.60	13.70	75.10	14.08
Na	0.52*	0.11	0.20 ^{ab}	0.01	0.16 ^{ab}	0.03	0.13 ^b	0.02	0.24 ^a	0.05
K	0.36*	0.07	0.16 ^b	0.01	0.17 ^b	0.04	0.16 ^b	0.02	0.27 ^a	0.03
Ca	3.01*	0.53	5.06	0.89	5.24	0.87	3.92	0.27	3.78	1.01
Mg	3.25	1.30	3.59	0.75	3.61	0.26	2.93	0.27	3.08	0.71
Ca:Mg mol ratio	0.88*	0.11	1.41	0.05	1.44	0.15	1.34	0.08	1.22	0.08
C and N (%)										
C _{org}	12.21	2.54	11.41	2.12	10.17	1.45	8.49	0.86	8.99	1.81
N _{tot}	0.41	0.13	0.42	0.08	0.38	0.05	0.32	0.03	0.35	0.07
C:N _{ratio}	30.36	2.73	26.98	1.57	26.36	0.75	26.15	0.10	25.44	1.04

Mean values for topsoil at *t* = 0 (TOP T0) and after 24 months of stockpiling (TOP T24, at 4 different depths) are presented. Asterisks indicate significant differences (ANOVA, *P* < 0.05) between T0 and T24 soils at 0 cm depth, whereas different letters indicate significant differences (ANOVA or Kruskal–Wallis test followed by Bonferroni–Dunn post hoc test, *P* < 0.05) between different depths of T24 soils < *d.l.* below detection limit, *TE* trace elements, *LOI* loss on ignition, *CEC* cation exchange capacity, *%Saturation* percent of cation saturation, *C_{org}* organic carbon, *N_{tot}* total nitrogen

the absence of clay minerals as it would be expected from limonitic and ferricrete layers of lateritic soils and a leptosol developed above ferricrete. Thus, in this case, CEC (a basic parameter for soil fertility) relies entirely on organic matter. The organic matter is very abundant in the surface of this laterite, which is quite unusual. This is due to the specific physical properties of sealed ferricrete that isolates the topsoil and plant roots from the rest of the laterite. The accumulation of organic matter in the surface and the limited development of the soil profile lead to a Leptosol (IUSS Working Group WRB 2015).

Different analytical approaches (XRD mineralogical analysis, chemical analyses, FTIR) have indicated that, in the sequence from Leptosol to topsoil at *t* = 0 and to

topsoil at *t* = 24, most important changes in soil properties (mineral composition, CEC, nutrient concentrations...) have occurred during the excavation of Leptosol and immediately after its placement in a mound. Samples from two Leptosol soil layers (TOP A and TOP B) showed much contrasted properties (CEC, organic matter content, major elements concentrations...) in only ten to fifteen cm of depth. When these two layers were excavated, mixed and stored, the properties of the resultant topsoil (TOP T0) were closer to the lower layer of the Leptosol (TOP B) than to upper layer. We think that these changes are mainly due to a “dilution effect” of mollic organic-rich TOP A soil layer with more mineral TOP B layer. This effect has been reported for physico-chemical parameters in different kinds of

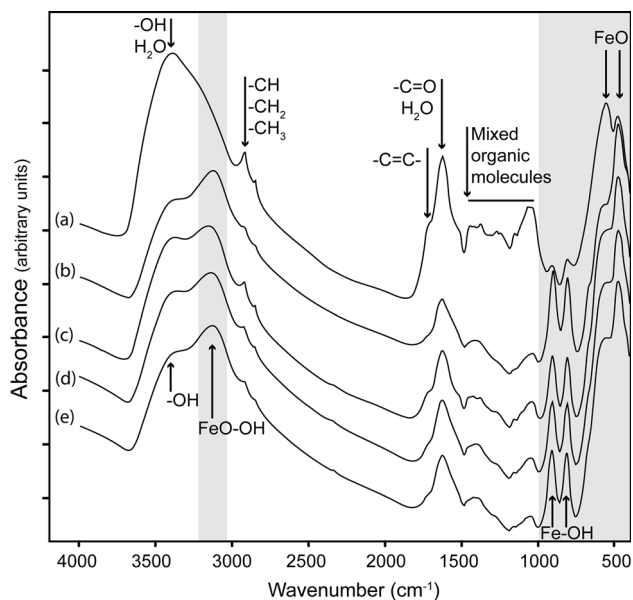


Fig. 3 Fourier transform infrared spectroscopy (FTIR) analysis of soil samples. FTIR spectra are presented (from top to bottom) for: **a** Leptosol TOP A, **b** Leptosol TOP B, **c** topsoil TOP T0, **d** topsoil TOP T24 at 0 cm depth, and **e** topsoil TOP T24 at 150 cm depth. Arrows indicate those bands that correspond with known organic functional groups and molecular bonds. Shaded areas indicate those bands that correspond with mineral compounds (mainly Fe–OH and Fe–O vibration bands)

topsoil by several researchers (Hunter and Currie 1956; Tomlinson 1980; Visser et al. 1984; Schwenke et al. 2000), but also for the dilution of seedbank by mixing topsoils from different depths (Rokich et al. 2000). The losses during this specific stage were unnoticeable for total major elements, including nutrients Ca and K. However, they are quite pronounced for exchangeable Mg. This cation, which is the majoritarian in the exchange complex seems to be the most affected by the observed reduction in CEC from TOP A ($20.08 \text{ cmol}_c \text{ kg}^{-1}$) + TOP B ($5.96 \text{ cmol}_c \text{ kg}^{-1}$) excavation and mixing to TOP T0 ($10.00 \text{ cmol}_c \text{ kg}^{-1}$). As a consequence, the chemical fertility of the topsoil might increase because the exchangeable Ca:Mg quotient reaches a value of 1.

Due to abovementioned mineralogical properties of topsoil, main fertility risks during stockpiling are related to the degradation of organic matter and increased leaching of nutrients and trace elements due to the exposure to intense rain regimes. The CEC of these soils completely relies on the stock of organic matter, so any qualitative and quantitative change in organic matter of soils will affect the behaviour towards cations: major (Ca, Mg, K) and metals (Ni, Co, Mn). Surprisingly, our results have shown that stockpiled topsoil is quite stable over the medium term and have suffered only slight changes after 24 months of storage. These changes have affected total and extractable concentrations of trace elements (Co, Cr, Ni), as well as macronutrients (Ca, K, Na). Observed effects are different depending on

the element concerned. Regarding trace elements, CaCl_2 -extractable Cr and Ni and EDTA-extractable Cr were slightly reduced during stocking, whereas total Co increased. These variations were independent of the depth of the sample. Previous works have shown that although Ni and Cr are mostly trapped into crystalline structures (e.g. goethite and hematite) in lateritic soils, a small amount of Ni and Cr is released from limonitic spoils (with a mineral composition similar to the stored topsoil in our work) (Raous et al. 2010; Echevarria and Morel 2015). Also, the topsoils of Goro are extremely rich in organic matter (around 12% of organic C), which is rather rare in lateritic contexts, and there are significant effects of biogeochemical cycling on the build-up of a stock of available nutrients and metals (mostly on the organic-matter dependent CEC) as clearly seen for Ni. These piled topsoils probably release more nutrients and metals than pure limonitic materials when experimented by Raous et al. (2010, 2013).

After 24 months, surface exchangeable concentrations of K and Na have decreased and exchangeable Ca has increased. Moreover, comparisons along the profile of the topsoil mound showed an increase of exchangeable K and Na in depth. These differences could be attributed to the leaching (during humid periods) of more mobile monovalent cations (Na^+ and K^+) with respect to divalent cations (Ca^{2+} , Mg^{2+}). Regarding organic matter, we observe a reduction of aliphatic groups that is congruent with a decreasing trend of the C:N ratio. However, the degradation of the quality of organic matter during storage seems to be quite limited.

Aluminium is an important element in lateritic bauxites (Freysinet et al. 2005). However, in our analyses Ni-laterites, it is present in low percentage and in the topsoil samples it did not vary along time or depth. Little differences were found between samples SFFC1 to SFFC3 (taken from 3 depths of a Ferralsol; i.e. lateritic profile), and TOP A and TOP B samples (taken from a Leptosol developed on ironcrust). In this case, variation in Al is not due to leaching, but to dilution of mineral fraction in Leptosol due to high concentration of organic matter (especially in sample TOP A, see Loss on Ignition (LOI) values). The resulting mixture of TOP A and TOP B (TOP T0) has an Al concentration that is slightly lower than TOP B and it is quite consistent with the evolution of the LOI during the formation of TOP T0.

Several studies have reported that anaerobic conditions are built up inside stockpiles at 1 m below the surface (Visser et al. 1984; Harris et al. 1989; Williamson and Johnson 1990), although the depth may vary in function of soil permeability and porosity (Abdul-Kareem and McRae 1984). Anaerobic conditions promote the mineralisation of organic matter by anaerobic bacteria, the increase of dissolved organic carbon and the accumulation of mineral nitrogen in the form of $\text{NH}_4\text{-N}$. Change to aerobic conditions during topsoil application for restoration provokes rapid transformation of $\text{NH}_4\text{-N}$ to nitrate and its loss due to leaching (Wil-

liamson and Johnson 1990). No significant changes in C or N, or in the degradation of organic functional groups, have been observed in topsoil in depth. However, there is a steady decrease of C:N ratio with depth that is not significant. Low height of stockpile (around 2 m) together with high porosity and extremely low water retention (porous cups had been introduced at different depths in the stockpile to sample soil pore water and, in spite of enough pumping pressure, no water was recovered over the duration of storage, G. Echevarria personal observation) in the mound may have reduced the intensity of anaerobic conditions, so the differences in C:N along the profile may be the result of aerobic mineralisation of organic matter and leaching of mineral N forms produced inside the profile.

In summary, our results indicate that stockpiling during 2 years did not provoke a reduction in chemical fertility of the lateritic topsoil, nor significant release in metals, allowing its use for ecological restoration. However, other parameters linked to the biological fertility of topsoil (e.g. seed bank status, microbial biomass and activities) should be combined to obtain a complete view of the sustainability of stockpiling.

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