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Heavy metals partioning in three French forest soils by sequential extraction procedure

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Abstract. To know the concentration of heavy metal associated to chemical compounds is important to evaluate the environmental risks on soils, particularly regarding ion bioavailability. The relative mobility and strength of binding of heavy metals to the soil components can be studied using a sequential extraction procedure which provides a meaningful comparison between different soil profiles. The heavy metals partitioning has been identified in three different french forest soils: one cambic podzol, one calcaric cambisol and one mollic andosol, using a new sequential extraction method. Results show that metal fractionation is metal and site specific. The water leaching phase does not contain any metals. The proportion of heavy metal leached in the exchangeable and the acid-soluble phase is significant for Cd. The residual phase is important for Cr, Pb, and to a lesser extend for Ni. The organic matter fraction is dominant for Zn and Cu. Thus, the considered heavy metals are mainly bounded to iron oxides, to the organic matter and to the mineral residue. The order of heavy metals availability in the three soils would be: Zn>Cd>Cu>Pb>Ni>Cr. Lead isotopes in some extracts of the extraction procedure corroborate the anthropogenic inputs for two soils. These both infomations allow to trace the origin, the mobility and the distribution of Pb in the soil.

1. INTRODUCTION

Today every one agrees that to prevent and to evaluate the heavy metal contamination in soils, it is not sufficient to know the total content but to determine the distribution and the position of heavy metal on reactive phases.

The sequential extraction procedures have been developed to study the metal partitioning among soils [9]. The procedure is based on the principle that bound heavy metals can be displaced from the geochemical phases by the use of appropriate chemical reagent of extraction [15]. Many sequential extraction procedures are described in the literature; nevertheless, the method developed by Tessier *et al.* [21] is the most widely used and the best known; it was originally developed for sediment analysis [7, 12]. After what, it has been modified to be applied to soil analysis [6, 20, 19, 9, 3].

The sequential extractions provide useful information on metal partitioning, and by this way on trace element mobility and availability in the environment; this information is highly worthy for the evaluation of potential risk of migration by metal contamination [16], and the feasibility of remediation. However, the sequential approach has been often criticized mainly because of the nonselectivity of the reagents and the possible redistribution on extracted metals during the multistage process [18, 2]. Raksasataya *et al.* [18] observed a redistribution of Pb at contaminated sites and Calmano *et al.* [2] point out the risk of misinterpretation due to redistribution of the analyte during the extraction phases. However, this risk is higher when procedures initially developed for samples weakly contaminated are used on highly contaminated soil samples.

To prevent these inconvinients, a selective sequential extraction developed by Leleyter and Probst [11] was used to study the metal partitioning on non-heavily contaminated forest soils. To our knowledge this method is the only one where the accuracy, the efficiency and the reproductibility were widely tested and verify. This method was originally developed and validated for sediment samples.

The objective of this study is to quantify and to characterize trace metal contamination in three selected soil profiles : one calcaric cambisol (SP 05), one cambic podzol (EPC 08) and one mollic andosol (EPC 63) and to evaluate the anthropogenic *versus* lithogenic contribution in some extraction phases of the clayed fraction (<2µm) of SP 05 and EPC 08.

2. MATERIELS AND METHODS

The sites were selected based on the soil type and the heavy metal concent [5]. The soil samples concern three forest sites from the French RENECOFOR network (National Network for the long term Monitoring of Forest Ecosystem), managed by the ONF (National Forest Board).

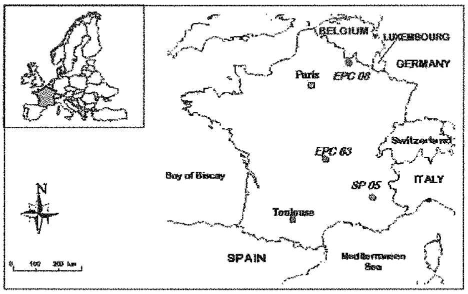

Figure 1. Location of the three selected sites

2.1 Analytical Methods

The heavy metal content of the filtered solution and the isotope ratios [1] have been determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Perkin Elmer ELAN 6000). The residue of each sample was dissolved after the sequential extraction by acid digestion on hot plates at atmospheric pressure with a mixture of $HF/HNO_3/HClO_4/H_2O_2$. For calibration and mass fractionation, corrections were based on repeated measurements of Pb standard NIST-SRM 981. The precision of isotopic ratio was 0.3%.

2.2 Extraction Procedure

Table 1. Protocol of sequential extraction (Leleyter and Probst, [11])

Phase	Reagent *(ultrapur quality or analytical grade)*	Reaction time	Temp
Water	Water (pH 5,7)	30 min	20 °C
Exchangeable	$Mg(NO_3)_2$ 1M, (pH 5,0)	2 hours	20 °C
Acid-Soluble	NaOAc 1M, (pH4,5)	5 hours	20 °C
MnO	NH_2OH HCl 0,1M, (pH 3,5)	30 min	20 °C
FeO amorphous	{0,2M $(NH_4)_2C_2O_4$- 0,2M$H_2C_2O_4$} in darkness, (pH 3,0)	4 hours	20 °C
FeO crystalline	0,2M $(NH_4)_2C_2O_4$- 0,2M$H_2C_2O_4$ - 0,1M $C_6H_8O_6$} (pH 2,3)	30 min	85 °C
Oxidizable (organic matter)	1) HNO_3 and H_2O_2 35% (pH 2,0) 2) NH_4OAc, (pH 2,0)	1) 5 h 2) 30 min	1) 85 °C 2) 20 °C

The samples were leached by a sequential extraction protocol (table 1). Almost all the reagents are ultrapur quality or analytical grade. The method performs seven extraction phases with a decreasing gradient of pH. One gram of soil (<2 mm) was used and extractions were carried out in a teflon container closed to prevent evaporation with continuous agitation; when the reaction is finished the residue is filtered through a 0,45 µm pore size Millipore filter (HVLP type), and washed with 20 ml of Milli-Q water. The leachate is stored in polypropylene tubes to 4°C and the residue is dried to 40°C before to continue with the next extraction step.

3. RESULTS

The figure 1 presents the percentage of Cr and Pb extracted in each one of the extraction phases. Almost no metal is leached in the water soluble fraction. The proportion of Zn, Cd and Cu in the exchangeable phase is <10% [20, 9, 4]. Cu and Pb extracted by the acid-soluble phase is also weak (<10%, <5% respectively) whereas it represents more than 10% for Cd in EPC 63 and SP 05. According to Flores-

Velez [4], higher percentages of Cu can be extracted if one increases the time of agitation (6-16 hours). Only Zn and Cd are associated to manganese oxides. The proportion of Cr, Zn and Ni linked to the iron oxydes is weak whereas it is between 20 to 45% for Pb; this affinity has been reported by [19, 13, 10]. 20 to 70% of Cu was associated to crystalline iron oxides. For most heavy metals, the proportions linked to crystalline iron oxides are higher than to amorphous iron oxides [22]. Cu (20-45%) and Pb (10-30%) are better extracted with the oxidizable phase. As reported by [20, 19, 8], when soils have higher organic matter content, the binding of Cu with this fraction is preponderant. Zn is well-distributed among all fractions however, 20-70% of Zn is linked to organic matter [17]. Cr is the less leached element. The extraction of Ni and Cd depends on the soil type; Ni and Cd are strongly associated to organic matter in calcaric podzol but weakly in the cambic podzol. Our results show that the organic matter content and the origin of the soils are very important parameters in heavy metal distribution.

Cr is mostly in the residual part (40-90%) of the three soils; similar results have been founded by [13, 17, 8]. Ni is mainly in the residual part of the cambic podzol and the calcaric cambisol (>30-70%), and to a lesser extend of the mollic andosol (20-30%). Cu proportion in the residue was more important for the mollic andosol.

The partitioning of heavy metals in non residual fractions thus differs for each type of soil (Table 2); nevertheless, organic matter and iron oxides are prevailing bearing phases for the three soils; only the order of metal differs according to the extraction percentage.

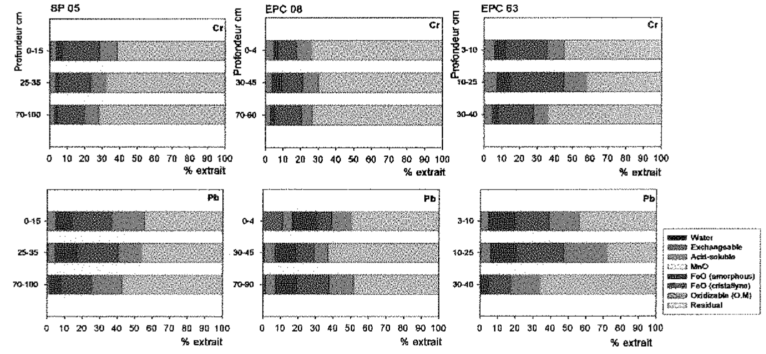

Figure 1. Pourcentage of Cu and Pb extracted in SP 05, EPC 08 and EPC 63 profiles

3.1 The Pb isotopes in the extraction phases

One can observe on fig 2 that the isotopic ratio $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ of the filtered extracted solution of the iron oxyde phase from the clayed fraction (<2 µm) were found closer to the mixing line for the two soils than the organic matter phase. This results confirms the anthropogenic origin of Pb in surface and middle horizons from SP 05 and EPC 08 [5] and identify the phases incorporationg the anthropogenic Pb.

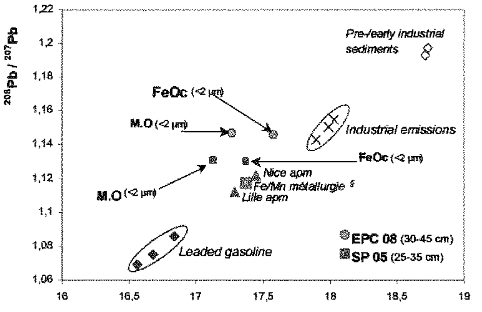

Figure 2. Pb isotopic composition diagram ($^{206}Pb/^{207}Pb$ vs. $^{206}Pb/^{204}Pb$) for the clayed fraction (< 2µm) of the middle horizons of EPC 08 and SP 05

Table 2. Summary of heavy metals relationships in nonresidual fractions

Phase	**EPC 08**	**EPC 63**	**SP 05**
Water	-	-	-
Exchangeable	*Zn* > **Cd**	*Cd > Zn*	Cd
Acid-Soluble	*Cu > Zn >* ***Cd*** *>* Cr, Pb > **Ni**	*Cu > Pb > Zn > Ni > Cd >* Cr	*Zn > Cu > Pb > Cr >* Cd
MnO	*Zn*	*Cd >Zn*	Cd
FeO (a)	Cr > *Zn* > **Cu** > **Cd** > **Pb**	*Ni* > Cr > Zn > Cu > Pb > **Cd**	*Cr* > Zn, Cu > Ni > Pb > Cd
FeO (c)	**Pb > Cd > Zn > Cr > Ni > Cu**	Cd > **Zn** > **Ni** > **Pb > Cu > Cr**	*Zn > Cd* > Ni > **Pb > Cr > Cu**
Oxidizable (O.M)	**Ni > Cd > Cu > Pb > Cr > Zn**	**Cr > Cd > Pb, Zn > Cu > Ni**	Cu > **Cr > Pb > Cd > Zn > Ni**

< 2% non reported ; < 10 % italics ; > 20 % indicated by boldface

4. CONCLUSION

The partitioning of trace elements on some french forest soils inferred from the sequential extraction method was successfully performed. It shows a variability due to the composition of soils and the considered metals. But the risk of misinterpretation due to the redistribution of the metal during the extraction phases was found to be weak compared to highly contaminated samples. Even if the non uniformity of the different extraction protocols can not allow the comparison of the results, the affinity of heavy metals for some extraction phases has been confirmed. Whatever the soils, the cadmium and zinc were found to be the most available elements. Pb is associated to iron oxides and residual phases on three soil samples; it does mean that we can expect a rather low mobility of this element. Ni and Cr are the lowest mobile elements; they are mainly included into the mineral structures. A potential order of availability is proposed: Zn> Cd> Cu> Pb> Ni> Cr. Among the non-residual fractions, the iron oxides and the organic matter were the most dominant bearing metal compounds in the three soil samples. The anthropogenic lead found in the fine earth of some soils (cf. Hernandez *et al.*, same volume) was detected in the phases bounded to iron oxides and organic matter of the clay fractions from the mid soil horizon of the calcaric cambisol (SP 05) and the cambic podzol (EPC 08).

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