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Eprints ID: 3646

To link to this article: DOI:10.1111/j.1365-2389.2009.01215.x
URL: <http://dx.doi.org/10.1111/j.1365-2389.2009.01215.x>

To cite this version: Gandois, Laure and Probst, Anne and Dumat, Camille (2010) *Modelling trace metal extractability and solubility in French forest soils by using soil properties*. European Journal of Soil Science, vol. 61 (n° 2). pp. 271-286. ISSN 1351-0754

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Modelling trace metal extractability and solubility in French forest soils by using soil properties

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Summary

Soil/solution partitioning of trace metals (TM: Cd, Co, Cr, Cu, Ni, Sb, Pb and Zn) has been investigated in six French forest sites that have been subjected to TM atmospheric inputs. Soil profiles have been sampled and analysed for major soil properties, and CaCl₂-extractable and total metal content. Metal concentrations (expressed on a molar basis) in soil (total), in CaCl₂ extracts and soil solution collected monthly from fresh soil by centrifugation, were in the order: Cr > Zn > Ni > Cu > Pb > Co > Sb > Cd, Zn > Cu > Pb = Ni > Co > Cd > Cr and Zn > Ni > Cu > Pb > Co > Cr > Cd > Sb, respectively. Metal extractability and solubility were predicted by using soil properties. Soil pH was the most significant property in predicting metal partitioning, but TM behaviour differed between acid and non-acid soils. TM extractability was predicted significantly by soil pH for pH < 6, and by soil pH and Fe content for all soil conditions. Total metal concentration in soil solution was predicted well by soil pH and organic carbon content for Cd, Co, Cr, Ni and Zn, by Fe content for Cu, Cr, Ni, Pb and Sb and total soil metal content for Cu, Cr, Ni, Pb and Sb, with a better prediction for acidic conditions (pH < 6). At more alkaline pH conditions, solute concentrations of Cu, Cr, Sb and Pb were larger than predicted by the pH relationship, as a consequence of association with Fe colloids and complexing with dissolved organic carbon. Metal speciation in soil solutions determined by WHAM-VI indicated that free metal ion (FMI) concentration was significantly related to soil pH for all pH conditions. The FMI concentrations of Cu and Zn were well predicted by pH alone, Pb by pH and Fe content and Cd, Co and Ni by soil pH and organic carbon content. Differences between soluble total metal and FMI concentrations were particularly large for pH < 6. This should be taken into account for risk and critical load assessment in the case of terrestrial ecosystems.

Modélisation de l'extractabilité et de la solubilité des métaux traces dans les sols forestiers français en utilisant les propriétés du sol.

Résumé

La partition entre phases solide et solution des Eléments Traces Métalliques (ETM : Cd, Co, Cr, Cu, Ni, Sb, Pb and Zn) a été étudiée dans six sols forestiers français impactés par des apports atmosphériques. Les profils de sol ont été échantillonnés et les principaux paramètres des sols, ainsi que les concentrations en ETM totales et extractibles au CaCl₂ ont été déterminés. Les concentrations des éléments (en moles) totales, extractibles et dissoutes dans les solutions de sol extraites par centrifugation se classent respectivement ainsi : Cr > Zn > Ni > Cu > Pb > Co > Sb > Cd, Zn > Cu > Pb = Ni > Co > Cd > Cr et Zn > Ni > Cu > Pb > Co > Cr > Cd > Sb. L'extractabilité et la solubilité des ETM dans les sols ont été prédites à partir des paramètres du sol. Le pH du sol est le paramètre le plus significatif pour la prédiction de la partition des ETM. Cependant, il a été mis en évidence une dynamique différente pour des pH inférieurs et supérieurs à 6. L'extractabilité des ETM peut être correctement prédite par le pH du sol en conditions acides et par le pH du sol et la teneur en Fer pour toute la gamme de pH considérée. Les

concentrations totales dans la solution de sol sont prédites de manière significative par le pH du sol, couplé à la teneur en carbone organique (pour Cd, Co, Cr, Ni et Zn), en fer (pour Cu, Cr, Ni, Pb et Sb), et à la teneur totale en métal (Cu, Cr, Ni, Pb, Sb). La prédiction est améliorée pour les valeurs de pH les plus basses (pH < 6). En effet, pour les valeurs de pH les plus élevées, la complexation des ETM par le carbone organique dissous et l'association avec des colloïdes inorganiques (hydroxydes de fer) entraîne une augmentation des concentrations totales en solution. La spéciation des ETM en solution a été déterminée grâce au logiciel WHAM-VI. Les concentrations en ion libre en solution sont significativement corrélées au pH du sol. Ainsi, les concentrations en ion libres de la plupart des métaux peuvent être efficacement prédites à partir du pH du sol du pH et de la teneur en Fer pour Pb, et du pH et de la teneur en CO dans le cas de Cd, Co et Ni. Les différences de concentrations observées entre le métal total et l'ion libre sont plus importantes pour les pH élevés. Ceci devrait être pris en compte dans le cadre de l'évaluation des risques et des charges critiques pour les écosystèmes terrestres.

Introduction

Natural processes as well as anthropogenic activities lead to trace metal (TM) (cadmium, Cd; cobalt, Co; chromium, Cr; copper, Cu; nickel, Ni; antimony, Sb; lead, Pb; and zinc, Zn) dispersion in the atmosphere (Nriagu & Pacyna, 1988; Nriagu, 1989; Pacyna *et al.*, 2007). TMs can reach remote areas (Steinnes & Friedland, 2006). Surface soils in the northern hemisphere undergo, to a large extent, atmospheric contamination by TMs (Steinnes & Friedland, 2006) and French forest soils were shown to be contaminated by atmospheric inputs of some TMs by Hernandez *et al.* (2003). Forest ecosystems are particularly sensitive to atmospheric contamination because the canopy interacts with atmospheric metallic pollutants and may concentrate them (Lovett & Lindberg, 1984). Therefore, metal behaviour and potential impact of TM in forest soils has to be evaluated.

TM availability and potential toxicity to sensitive organisms are governed by their concentration in soil solution, because soil solution is a vector of available metal to plant, microorganism and soil invertebrates. Soil extraction by dilute salts allows the evaluation of the exchangeable and easily mobilized fraction of TM (Aten & Gupta, 1996) in soil samples. Total metal concentration in soil solution is used to assess metal leaching from soils to surface water. TM speciation plays an important role in metal availability and toxicity, since free metal ion content (FMI) is often recognized as the most toxic form (Florence, 1982). Critical loads assessment is based on the determination of a critical limit, which is the maximum tolerable FMI concentration in soil solution for soil organisms (Lofts *et al.*, 2004; de Vries *et al.*, 2007). Protection of terrestrial ecosystems from atmospheric pollution at the European scale is based on the calculation of critical loads (defined as 'a quantitative estimate of an exposure to one or more pollutants below which important harmful effects on specified sensitive elements of the environment do not occur according to present knowledge': Nilsson & Grennfelt, 1988). In order to protect forest ecosystems, knowledge on TM availability

and concentration in soil solution is thus needed for a large variety of ecosystems.

Total metal content and some other soil properties are frequently measured and available in data bases for numerous terrestrial ecosystems at national scales. However, data on TM concentration in soil solution are scarce on a large scale. Soil solution compositions are thus predicted with transfer functions (de Vries *et al.*, 2007), linking soil solution and soil properties to TM concentration in soil solutions. Numerous studies discuss TM (mostly Pb, Cd, Cu, Zn and more rarely Ni) partitioning in soils between solid and dissolved phases (Jopony & Young, 1994; McBride *et al.*, 1997; Römkens & Salomons, 1998; Sauvé *et al.*, 2000; Krisnamurti *et al.*, 2002; Tipping *et al.*, 2003), but mostly for contaminated soils, whereas only a few (Sauvé *et al.*, 2003; Watmough *et al.*, 2005) examine weakly contaminated forest soils. Consequently, forest soils are under-represented in data sets (Pampura *et al.*, 2007). These studies show that soil (or soil solution) pH is always an important property for predicting TM partitioning. Other soil properties, such as organic carbon content or soil metal content were also found to be important. The difficulty of taking into account the influence of soil solution composition, particularly dissolved organic carbon (DOC), on TM partitioning has been highlighted (Tipping *et al.*, 2003, Sauvé *et al.*, 2003).

Most of the existing studies are based on estimates of TMs in soil solution (water or dilute salt extraction). An accurate assessment of the properties that significantly predict TM extractability and solubility in forest ecosystems is needed. For that purpose, we investigated several French forest soils, which were very diverse in terms of vegetation cover and soil types. This study is aimed at (i) determining concentrations for eight TMs (Cd, Co, Cu, Cr, Ni, Sb, Pb and Zn) in different soil pools (total, extractable and soil solution) for French forest soils, covering a wide range of soil properties, (ii) evaluating TM extractability and availability by investigating the partition between soil phases and solution speciation, (iii) defining transfer functions between solid phase and soil solution based on appropriate soil properties,

to predict soil solution composition for critical load modelling, and (iv) evaluating the processes that control TM solubility and speciation.

Materials and methods

Study sites

Six sites were selected for the study which belonged to the French network RENECOFOR (Réseau National de suivi à long terme des Ecosystèmes Forestiers, i.e. National Network for the long-term Monitoring of Forest Ecosystem; Ulrich, 1995), managed by the ONF (Office National de Forêts: the National Forest Board). These sites are integrated into the ICP (International Co-operative Programme) forest European network (Level II sites) and are located all over France (Figure 1).

The selected sites are representative of various chemical and physical properties of French forest soils. Forests of three main tree species were considered (spruce, *Picea abies* L.; beech, *Fagus sylvatica* L. Karst; and silver fir, *Abies Alba* Mill.) and four main types of soils (podzol, andosol, cambisol and luvisol (IUSS, 2006)), covering a wide range of pH values (3.9–8.5), organic carbon (9–126 g kg⁻¹) and iron (0.4–8%) contents. The main characteristics of the study sites are summarized in Table 1.

Sampling procedure and soil pre-treatment

All soil layers were sampled in two pits from each forest site. Twelve profiles, with a total of 58 samples, were thus collected down to the deepest soil layer. Soil pits (described by Brêthes & Ulrich, 1997) were cleaned with clean plastic tools before sampling. In the laboratory, soil samples were dried at

room temperature, sieved with a 2-mm nylon mesh and kept in polypropylene bags before analysis of total metal content, extractable pool and main soil properties. In addition, fresh soils were sampled monthly over 1 year (August 2007 to July 2008) in order to take into account spatial and temporal variability of soil solution chemical composition. For that purpose, soil samples ($n = 310$) were collected after removal of the humus layer, using an auger in four locations around the pits previously sampled. Potential contamination of soil solution by using an auger was checked and was found to be negligible. Soil samples were collected according to soil layers down to 60 cm. Finally, a composite sample was made by pooling the four sub-samples corresponding to each soil layer. The samples were kept in plastic bags, brought back to the laboratory and treated within 48 hours.

Sample treatment

Dilute salt extraction. TM availability in soils was investigated by using 0.01 M CaCl₂ extraction (Houba *et al.*, 1996; Menzies *et al.*, 2007) according to the protocol described by Houba *et al.* (2000). Three grams of dried soil (<2 mm fraction) were shaken for 2 hours with 30 ml of 0.01 M CaCl₂ in polypropylene tubes (previously rinsed with 0.1 M HCl and extra pure water). Each tube was centrifuged for 20 minutes at 3000 g. The supernatant was removed. An aliquot was used for pH measurement. The supernatant was then filtered (SFAC filters, 0.2 µm) and acidified (2% ultrapure HNO₃) for analytical work. This procedure was applied to all samples ($n = 58$).

Soil solution extraction. Fresh soil samples collected each month from each soil layer were centrifuged by using Teflon double bottomed centrifugation devices (adapted from Giesler & Lundström, 1993) on a Beckman Coulter Aventi J26 XPI centrifuge (Beckman Coulter France S.A.S., Paris, France), equipped with four 1-litre swinging buckets. Centrifuge speed was 3400 g, in order to extract soil solution at a pF around 4 (Ranger *et al.*, 2001). Each month, 38 fresh samples were centrifuged. Depending on the sample moisture content, soil solution extraction was not always possible (for approximately 20% of the samples): a total of 310 soil solution samples were extracted.

Analytical procedure

Soil analysis. The main soil properties of texture, pH (measured in water and 0.1 M KCl), organic carbon (OC) content, nitrogen content, cation exchange capacity (CEC), exchangeable cations, carbonate (when appropriate), total iron and aluminium, total soil metal content of trace (Cd, Cr, Co, Cu, Ni, Pb, Sb, Zn) and major (calcium, Ca; sodium, Na; potassium, K; magnesium, Mg; aluminium, Al; iron, Fe) elements after HF/HClO₄ dissolution, and silicon (Si) content after alkaline fusion, were analysed at the INRA Laboratory of Soil Science (Arras, France) following standard methods (<http://www.arras.inra.fr/>).

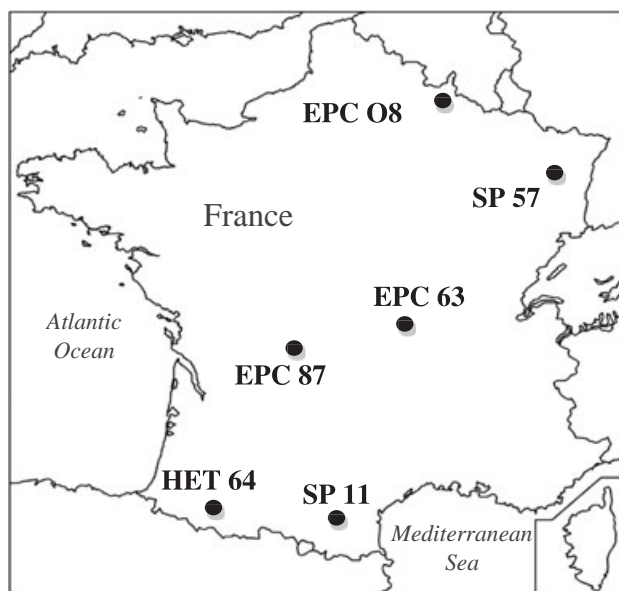


Figure 1 Location of the study sites.

Table 1 Main soil characteristics of the study sites. Mean and range (minimum and maximum) values are shown

Site	Vegetation cover	Soil type ^a	Texture	OC / g kg ⁻¹			Total metal content / $\mu\text{mol kg}^{-1}$							
				0–30 cm	pH ^b	Iron content / %	Cd	Co	Cu	Cr	Ni	Pb	Sb	Zn
EPC 08	<i>Picea abies</i> (L.) Karst	Cambic podzol	Silty clay loam	53	4.18	2.66	1.57	48.4	363.8	1341	145	245	18	613
					3.8/4.8	1.4/3.6	0.35/4.86	25.8/80.1	181.1/577.9	783/2115	66/262	98/753	11.1/42	399/1038
EPC 63	<i>Picea abies</i> (L.) Karst	Mollic andosol	Silt loam	126	4.9	5.93	3.19	362.27	303.4	1286	464	171	9.5	1854
					4.6/6.5	3.9/8.3	1.40/4.99	229.2/543.3	192.1/535.4	798/2000	279/780	37/389	3.6/20.3	1590/2064
EPC 87	<i>Picea abies</i> (L.) Karst	Cambic podzol	Sandy loam	48	4.6	1.22	0.65	42.4	87.3	260	101	137	2.7	895
					4.4/4.9	0.9/1.9	0.18/0.93	18.7/73.0	50.7/171.7	115/365	63/181	120/198	1.9/4.7	556.6/1177
HET 64	<i>Fagus</i> <i>sylvatica</i> L.	Eutric cambisol	Silty clay	24	5.2	3.35	1.62	199.5	370.7	1597	558	116	7.5	1276
					4.9/5.3	2.4/5.0	0.50/4.57	169.8/237.2	250.4/533.9	1208/2019	397/874	98/140	6.1/8.8	898/1789
SP 11	<i>Albies Alba</i> M.	Stagnic luvisol	Silty clay	49	7.2	3.21	2.43	186.0	156.2	1628	593	99	5.5	1311
					6.6/8.5	2.3/3.8	1.87/3.09	84.9/234.3	91.6/209.5	1010/2000	404/736	52/123	4.1/6.1	818/1528
SP 57	<i>Albies Alba</i> M.	Dystric cambisol	Sand	9	4.5	0.57	0.17	30.8	42.8	214	82	71	5.9	237
					3.9/5	0.4/0.7	<0.18/0.22	<0.18/40.4	23.6/72.9	144/285	36/128	47/127	4.7/7.7	143/361

^aIUSS (2006).^bpH water.

Soil solution analysis. After extraction, an aliquot of soil solution was reserved for pH measurement. DOC was analysed on filtered solution after HCl acidification using a Shimadzu TOC 5000 (Shimadzu, Paris, France) and major anions were analysed by HPLC (Dionex Co., Sunnyvale, CA, USA). For both soil and soil solution samples, major elements (Ca, Mg, Na, K) were analysed by ICP-OES (Thermo IRIS INTREPID II XDL, Waltham, MA, USA) and trace elements by ICP-MS (7500 ce, Agilent Technologies Santa Clara, CA, USA). Analyses were performed after HNO₃ acidification to 2%. For ICP-MS analysis, indium/renium was added as an internal standard. Detection limits were below 100 µg l⁻¹ for ICP-OES analysis, below 10 ng l⁻¹ for Al, Cd, Co, Cu, Cr, Ni, Sb, Pb and Zn, and below 100 ng l⁻¹ for Fe for ICP-MS analysis. The analytical error was less than 5%.

Soil solution speciation

Soil solution speciation was estimated with WHAM-VI software (Tipping, 1998). According to previous studies (Tipping *et al.*, 2003; Pampura *et al.*, 2007; Buekers *et al.*, 2008), dissolved organic matter was assumed to contain 50% carbon comprising 65% of active fulvic acids (FA). Equilibrium with atmospheric CO₂ was assumed. Input data included soil solution pH, FA content, and major cation and anion (Ca²⁺, K⁺, Na⁺, Mg²⁺, Cl⁻, NO₃⁻, SO₄²⁻) and trace element (Cd, Co, Cu, Ni, Pb and Zn) concentrations. Total concentrations of Fe were measured but Fe³⁺ activity was assessed by considering equilibrium with Fe hydroxides. A value of $K_{so} = 2.7$ was selected (Tipping *et al.*, 2003). Fe³⁺ values predicted by WHAM-VI using total Fe inputs were always larger than theoretical Fe³⁺ in equilibrium with hydroxides, indicating that soil solution was over-saturated with regard to Fe hydroxides. The predicted Fe³⁺ activities, derived from hydroxides equilibrium, were used as input data. For Al, the expected values of Al³⁺ in equilibrium with Al hydroxides were calculated with a value for K_{so} of 8.5 (Tipping *et al.*, 2003). The measured dissolved Al concentrations were usually below the calculated values in equilibrium with Al hydroxides, indicating that Al solubility in soil solution was not controlled by Al hydroxides. Consequently, total Al measured concentrations were used as input data. Sometimes, predicted Al³⁺ values with WHAM-VI exceeded Al³⁺ calculated values (for alkaline pH solutions). In that case, calculated Al³⁺ activities based on hydroxides equilibrium were used as input data. Because of the small amount of extracted water, the data set was not complete and only 224 samples could be used for speciation analysis.

Statistical analysis

All statistical analyses were performed with STATISTICA software (Statsoft, Tulsa, OK, USA). Because of the sampling procedure, temporal trends for TM concentrations could not reasonably be investigated. Sampling was considered as independent repetition. For each layer considered, a mean value (calculated from

$n = 4$ to $n = 12$, depending on the success of soil solution extraction) was calculated from samples taken at different periods. The typical relative standard deviation for a single layer was 15–70%.

Results

Total metal content in soils

Trace metal concentrations were very variable (Table 1) in the studied soils. They can be considered as either not, or slightly, contaminated because values fall within background values (Kabata-Pendias & Pendias, 1992), except for Pb and Co. The order of metal abundance (µmol kg⁻¹) in mineral layers was Cr > Zn > Ni > Cu > Pb > Co > Sb > Cd. Pb, Zn and Cr concentrations were very variable, depending on soil type (Table 1). Lead, Sb and Cd had larger concentrations in organic layers, which might indicate the influence of atmospheric inputs in some soils (Hernandez *et al.*, 2003). The enrichment factor (EF), calculated by using cesium (Roussiez *et al.*, 2005) and deeper soil layers as references, exceeded 2.0 in upper soil layers of sites EPC 08 (Cd, Co, Pb, Sb and Zn), EPC 63 (Cd, Pb and Sb), EPC 87 (Sb) and SP 57 (Pb). EPC 08, located in the northern part of France, is the site most affected by anthropogenic inputs and with larger total metal content and EF, as already reported by Hernandez *et al.* (2003).

Correlations between soil properties and total metal contents in soils were performed to determine the main solid phases containing TMs (Table 2). Some TMs are more likely to be associated with soil fine fractions (clays and silts) and Cr and Ni were positively correlated with clay and silt contents and negatively with sand. TM affinity for fine fractions is related to their larger sorption surfaces (Hernandez *et al.*, 2003). Cobalt, Cr, Zn and especially Ni total concentrations were positively correlated with soil pH, and negatively with Sb. These patterns are probably linked to processes such as weathering or leaching of soil minerals (Aubert *et al.*, 2004; Watmough *et al.*, 2005). Lead, Sb and Cd were positively correlated with OC content. Lead and Cd can be absorbed by soil OC (Basta *et al.*, 1993; McBride *et al.*, 1997) and they were enriched in surface layers, which had the largest OC content. Moreover, Pb and Sb had a specific behaviour because they were strongly correlated with each other but not with Fe, in contrast to Cr, Cu, Ni, Zn and Co, which were strongly correlated with each other and with Fe (and to a lesser extent with Al and Mn). This is consistent with the well-known association of this group of TMs with secondary minerals or hydroxides, according to soil type (Hernandez *et al.*, 2003).

Extractable trace metals in soils

Extractable TM concentrations. The concentrations of extractable TM in studied soils are given in Table 3. On the basis of extracted amounts (nmol kg⁻¹), extractable TM can be classified as follows: Zn > Cu > Pb = Ni > Co > Cd > Cr. Extractable Sb concentrations were below detection limits and thus not considered in this part of the study. Extractable amounts

Table 2 Correlation matrix (Pearson correlation coefficients) between total metal concentrations in soils and soil properties ($n = 58$; bold numbers are for $P < 0.001$, underlined numbers for $P < 0.01$ and those in italics for $P > 0.01$)

	Clay	Silt	Sand	OC	pH _{water}	Cr	Cu	Ni	Zn	Co	Pb	Cd	Sb	Al	Fe	Mn
Clay	1	0.08	-0.80	-0.04	<u>0.40</u>	0.58	0.32	0.54	0.21	0.04	0.10	0.28	0.11	0.00	-0.01	-0.18
Silt		1	<u>-0.40</u>	0.20	-0.01	0.27	0.13	0.03	0.23	0.13	0.18	0.34	0.26	0.27	0.22	0.20
Sand			1	-0.11	-0.21	-0.58	-0.35	-0.27	-0.11	0.04	-0.29	<u>-0.39</u>	<u>-0.39</u>	-0.12	-0.02	0.16
OC				1	-0.36	-0.31	-0.03	-0.27	0.20	0.01	0.85	0.59	0.68	-0.09	-0.01	0.16
pH _{water}					1	0.52	-0.03	0.76	<u>0.46</u>	<u>0.43</u>	-0.42	0.27	<u>-0.44</u>	0.15	0.34	0.13
Cr						1	0.71	0.81	0.50	0.58	-0.20	0.27	0.01	0.59	0.67	0.26
Cu							1	0.49	0.35	<u>0.41</u>	0.14	0.24	0.36	0.56	0.58	0.27
Ni								1	0.73	0.75	-0.30	0.34	-0.26	<u>0.44</u>	0.69	<u>0.43</u>
Zn									1	0.84	-0.05	0.60	-0.12	0.65	0.81	0.77
Co										1	-0.21	0.37	-0.21	0.59	0.92	0.85
Pb											1	<u>0.48</u>	0.89	-0.20	-0.18	-0.12
Cd												1	<u>0.42</u>	0.19	0.41	<u>0.39</u>
Sb													1	-0.12	-0.10	-0.14
Al														1	0.77	<u>0.48</u>
Fe															1	0.79
Mn																1

With: clay, silt and sand in %, OC = organic carbon (g kg^{-1}), total metal content in $\mu\text{g g}^{-1}$.

varied over several orders of magnitude, as indicated by the range (minimum–maximum values). The mean percentage of extractable metal depends also on the element (Table 3a) and ranged from 0.015 to 25.5% for Cr and Cd, respectively. When expressed on a percentage basis for extractable TMs in soils, TM can be ordered as follows: $\text{Cd} > \text{Cu} > \text{Zn} > \text{Co} > \text{Ni} > \text{Pb} > \text{Cr}$.

Modelling metal extractability using soil properties. The partition coefficient between the extractable (M_{CaCl_2}) and total trace metal (M_{tot}) pool in soils is a useful tool to evaluate TM behaviour, particularly for case studies with small TM contents, where sorption sites are unlikely to be saturated. Extractability of TMs can be defined as follows (Rieuwerts *et al.*, 2006):

$$\text{Extractability} = \text{Log}(M_{\text{CaCl}_2}/M_{\text{tot}}), \quad (1)$$

where M_{CaCl_2} and M_{tot} are expressed in $\mu\text{mol g}_{\text{soil}}^{-1}$. The influence of soil properties on TM extractability was investigated through correlation analysis, using log (TM extractability) as a

Table 3 (a) Extractable concentrations (nmol kg^{-1}) and percentage of metal extracted by CaCl_2 (% total metal content). Mean and range (minimum and maximum) values are shown

(a)	n	Extractable amount / nmol kg^{-1}	Extractable proportion / %
Cd	36	2.17 (2.3×10^{-4} –14.73)	25.5 (0.92–84.5)
Co	38	3.20 (2.5×10^{-4} –22.44)	1.32 (0.04–8.79)
Cu	46	59.47 (4.1×10^{-4} –192.66)	8.3 (0.03–58.7)
Cr	58	0.53 (6.97×10^{-5} –2.27)	0.015 (0–0.13)
Ni	48	10.38 (3.010^{-3} –61.68)	1.2 (0.01–6.18)
Pb	53	10.12 (4.2×10^{-4} – ³ –124.57)	0.5 (0.006–4.56)
Zn	54	288.29 (2.7×10^{-3} –1489.2)	6.3 (0.02–40.7)

Table 3 (b) Pearson coefficient between trace metal extractability and soil properties (bold numbers are for $P < 0.001$, underlined numbers for $P < 0.01$ and those in italics for $P > 0.01$)

(b)	Organic carbon	pH	Fe
Cd	-0.028	-0.876	-0.526
Co	0.042	-0.770	-0.647
Cu	0.234	0.241	-0.078
Cr	0.113	-0.683	-0.824
Ni	0.049	-0.740	-0.539
Pb	0.149	-0.718	-0.480
Zn	0.120	-0.927	-0.414

variable because extractability values ranged by several orders of magnitude for a given element. The log-transformed data had a normal distribution (Shapiro-Wilk Test) and thus the Pearson correlation coefficient was used. Organic carbon was never significantly correlated with TM extractability (Table 3b). Soil Fe content was significantly negatively correlated with Cr ($P < 0.001$) and Co ($P < 0.01$) extractabilities. All TM extractabilities, except Cu, were significantly negatively correlated with soil pH. However, the influence of pH on TM extractability was stronger in acid conditions ($\text{pH} < 6$, see Figure 2), especially for Pb. Above pH 6 (open symbols in Figure 2), extractability did not depend on pH. As seen in Table 4, significant linear regressions between TM extractability and soil pH were found for $\text{pH} < 6$ for Cd, Co, Ni, Pb and Zn. In order to predict TM extractability for the whole pH range, other soil properties were included in a multi-regression. Only soil Fe concentration was a significant factor for Cd, Co, Cr and Zn: soil Fe content predicted 80% of variance in Cr extractability.

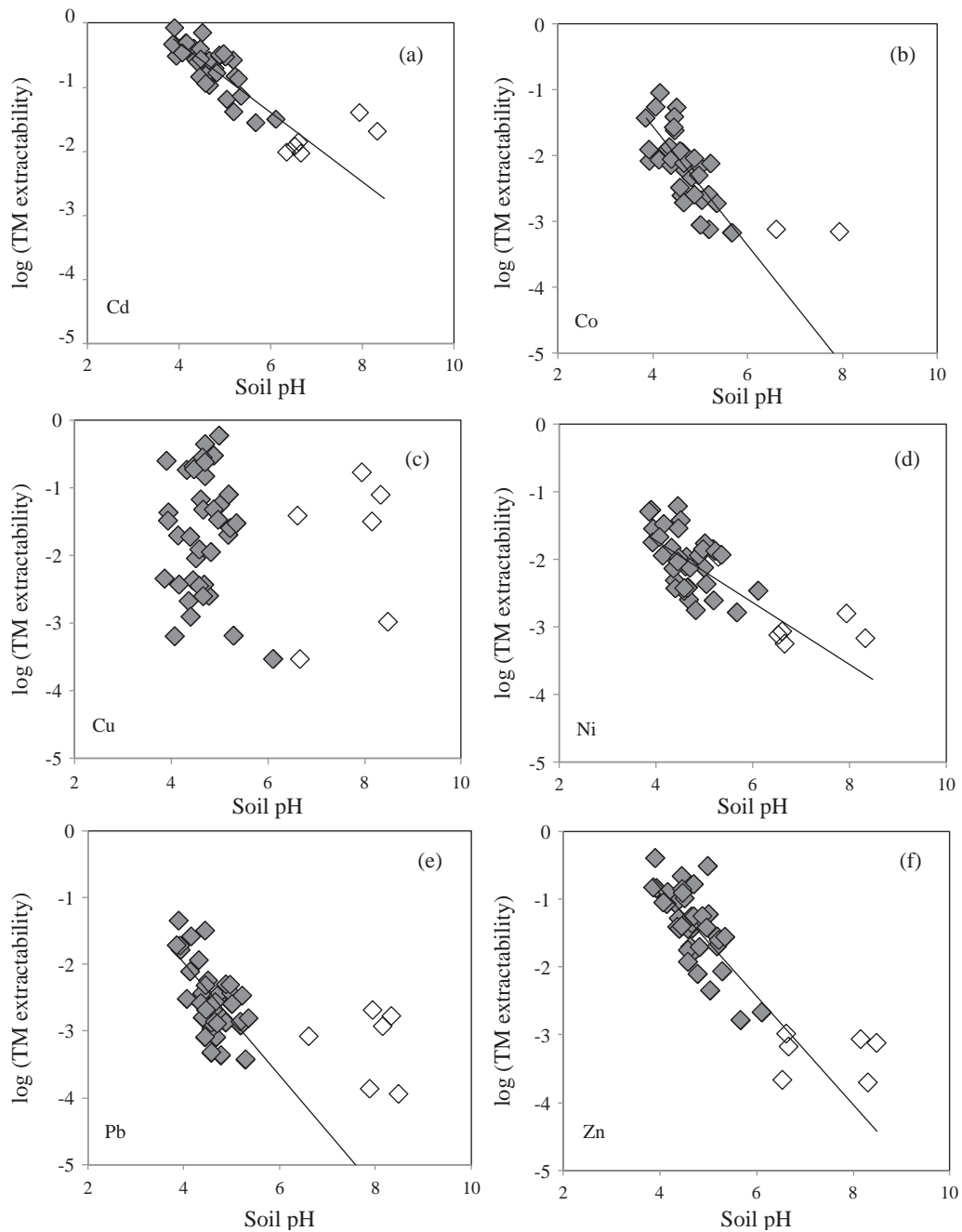


Figure 2 Relationships between metal extractability ($\log(M_{CaCl_2}/M_{tot})$) and soil pH for all the studied soils. (a) Cd; (b) Co; (c) Cu; (d) Ni; (e) Pb; (f) Zn. The lines represent the relationship between TM extractability and soil pH for pH < 6, and open symbols are for pH > 6.

Trace metals in soil solution: prediction and speciation

TM concentrations in soil solution. Trace metal concentrations in soil solutions vary over several orders of magnitude (Table 5). Important variations were observed within soil profiles and between the sites. Zinc had the largest concentration in soil solution, with the smallest deviation. As a whole, TM concentrations can be ordered as follows: Zn > Ni > Cu = Pb > Co > Cr > Cd > Sb.

Correlations were made between TM concentrations in soil solutions and soil solution properties (Table 6). Zinc, Cd and Mn concentrations were significantly correlated with each other and with Al concentration. These elements are negatively correlated with pH and positively with Ca concentration. Another group of elements composed of Pb, Sb, Cu and Cr were significantly and positively correlated with Fe and DOC concentrations in soil solution.

Table 4 Coefficients of multiple regressions between log (TM extractability) and soil properties. The first group corresponds to correlation with pH only, for pH < 6. The second group corresponds to multi-regression for the whole pH range

pH			Constant	pH	Log Fe	r ²	n	P
<6	Cd	Log (Cd _{Extract.})	1.83 ± 0.36	-0.54 ± 0.08	-	0.60	36	****
	Co	Log (Co _{Extract.})	2.04 ± 0.71	-0.91 ± 0.15	-	0.53	34	****
	Ni	Log (Ni _{Extract.})	0.11 ± 0.57	-0.46 ± 0.12	-	0.30	37	***
	Pb	Log (Pb _{Extract.})	1.67 ± 0.36	-0.91 ± 0.14	-	0.38	40	****
	Zn	Log (Zn _{Extract.})	2.38 ± 0.57	-0.80 ± 0.12	-	0.52	43	****
All	Cd	Log (Cd _{Extract.})	1.20 ± 0.22	-0.38 ± 0.05	-0.39 ± 0.15	0.73	42	****
	Co	Log (Co _{Extract.})	0.09 ± 0.37	-0.42 ± 0.08	-0.79 ± 0.19	0.66	36	****
	Cr	Log (Cr _{Extract.})	-3.76 ± 0.06	-	-1.31 ± 0.13	0.78	56	****
	Ni	Log (Ni _{Extract.})	-0.32 ± 0.28	-0.34 ± 0.06	-0.30 ± 0.17	0.56	43	****
	Zn	Log (Zn _{Extract.})	1.50 ± 0.27	-0.59 ± 0.06	-0.52 ± 0.17	0.79	49	****

r² = Pearson correlation coefficient; n = number of samples; P = level of significance: ****P < 0.0001, ***P < 0.001.

Table 5 Concentrations of DOC (mg l⁻¹) and TMs (nmol l⁻¹) in soil solutions. Mean, minimum, maximum and standard deviation are shown: n = 37

	Mean	Standard deviation	Minimum	Maximum
DOC	25	18	3	78
Cd	7.91	7.62	0.67	33.6
Co	28.2	22.6	2.57	87.1
Cu	37.1	25.8	2.46	90.6
Cr	21.2	18.2	0.20	67.1
Ni	76.9	63.2	9.13	330
Pb	37.3	56	0.18	168
Sb	1.84	1.83	0.01	6.12
Zn	943	624	137	2340

Relationships between TM in soil solution and soil properties

Influence of pH. Inverse relationships between TM concentration in soil solution and soil pH were seen for all elements (Figure 3). For pH values <6, a significant negative linear relationship was observed. For pH values above 6 (open symbols, Figure 3), there was no relationship and concentrations were greater than expected from the relationship established for values <6. The difference between measured and expected concentrations depends on the element considered. This difference is in the order: Pb > Cr > Sb > Cu > Cd > Co > Ni > Zn. Ni dependence on pH for acid conditions is very weak.

Multiple regression between TM concentration in soil solution and soil properties. The influence of soil properties on TM concentrations in soil solution was assessed by correlation and multi-regression analysis. As for extractable TMs, we used logarithms of the values for concentrations. Correlation analysis indicated that soil pH, OC content, soil Fe content and, for some elements, total metal content were significantly correlated with TMs in soil solution. Multiple regressions were performed (Table 7) between log (TM concentration in soil solution) and soil pH, OC content,

Fe content and total metal content. Regression analysis was made with all samples and also with a subset of samples with pH < 6.

Equation (2) is derived from the competitive sorption model (McBride *et al.*, 1997; Sauvé *et al.*, 2000), which states that metallic cations compete with protons for sorption on soil exchange sites (here OC and Fe). The relationship for TMs in all soil solutions was:

$$\log(\text{TM})_{\text{sol.}} = a + b \text{pH} + c \log \text{OC} + d \log \text{Fe} + e \log(\text{M})_{\text{tot}}, \quad (2)$$

where (TM)_{sol} is the concentration of the element in soil solution (mol l⁻¹), OC is soil organic carbon content (in g kg⁻¹), Fe is soil iron content (%) and (M)_{tot} is soil total metal content (in mol kg⁻¹). For Cu, Cr, Sb and Pb, DOC was a significant variable and was then included in the regression and the equation became:

$$\log(\text{TM})_{\text{sol}} = a + b \log \text{OC} + c \text{pH} + d \log \text{Fe} + e \log(\text{M})_{\text{tot}} + \log(\text{DOC}). \quad (3)$$

Non-significant variables (P > 0.05) were excluded from the regressions. Prediction of TM concentration in soil solution was improved when soils of pH < 6 only were considered (Table 7). Organic C content was negatively correlated with Cd, Zn and Co concentrations in soil solutions and positively correlated with Cr and Ni concentrations. Soil Fe content was negatively correlated with Cu, Cr, Pb Ni and Sb. Total metal content was significant in predicting Cu, Cr, Ni, Pb and Sb concentrations in soil solution. As a whole, multiple regressions using only soil properties were able to predict total metal concentrations in soil solutions. Including DOC concentrations (positive correlation) slightly improved Cu, Cr, Sb and Pb total concentration prediction over the whole pH range compared with using soil properties only.

TM speciation in soil solution

The concentration of free metal ions (FMI) in soil solution has been suggested to be a useful measure of toxicity to organisms

Table 6 Correlation matrix between total soluble TM and major component in soil solutions ($n = 37$; bold numbers are for $P < 0.001$, underlined numbers for $P < 0.01$ and those in italics for $P > 0.01$)

	pH	DOC	Fe	Al	Ca	Mn	Cd	Cr	Co	Cu	Ni	Sb	Pb	Zn
pH	1	0.05	-0.02	-0.69	0.79	-0.56	-0.46	-0.12	-0.27	-0.19	-0.12	-0.38	-0.37	-0.68
DOC		1	0.78	0.30	0.14	-0.07	0.12	0.70	0.07	0.62	0.17	<u>0.53</u>	0.66	-0.01
Fe			1	0.14	0.06	-0.01	0.32	0.88	0.10	0.79	0.37	0.63	0.84	0.00
Al				1	-0.75	0.57	0.58	0.40	0.55	0.42	0.17	0.62	<u>0.53</u>	0.75
Ca					1	-0.39	<u>-0.47</u>	-0.19	-0.37	-0.11	0.01	-0.41	-0.31	-0.70
Mn						1	0.68	0.22	0.74	0.38	0.56	0.29	0.37	0.57
Cd							1	0.54	0.72	0.68	0.68	<u>0.53</u>	0.62	0.76
Cr								1	0.42	0.83	<u>0.51</u>	0.67	0.88	0.20
Co									1	0.44	<u>0.62</u>	0.31	0.37	0.58
Cu										1	0.60	0.71	0.87	0.39
Ni											1	0.09	0.47	0.33
Sb												1	0.80	<u>0.48</u>
Pb													1	0.43
Zn														1

(Florence, 1982; Lofts *et al.*, 2004). WHAM-VI software was used to predict FMI concentration in soil solution for six of the studied elements: Cd, Cu, Co, Ni, Pb and Zn. As done previously for total metal concentration, correlations were performed on log-transformed data of all sets of samples in order to determine which soil properties predicted effectively FMI concentration in soil solution. Multiple regressions indicated (Table 8) that pH was significant (negative correlation) for each TM. Organic C content also made a significant contribution to the prediction of Cd, Co and Ni FMI concentrations.

Contrary to what was observed for total concentration in soil solution, the relationships between free TM concentration and pH were significant for the whole range of soil pH, except for Co and Ni (Figure 4). For more alkaline pH values, these two elements had larger FMI concentrations than predicted by the linear relationship with pH. This might indicate that their complexation with DOC at alkaline pH is underestimated by WHAM-VI, as already noted for Ni by Van Laer *et al.* (2006).

Prediction of FMI concentration in soil solution can thus be efficiently achieved by using simple soil properties, such as pH and OC content, depending on the metal. The percentage of variance explained ranged from 57% (Co) to 87% (Cu). As previously observed for total metal concentration in soil solutions, pH, OC (Cd, Co, Ni) and soil Fe content (Pb) alone can efficiently predict FMI concentration in soil solutions. For these weakly contaminated forest soils, total soil metal content is thus a less important characteristic.

Discussion

Extractable vs soluble pool of metal in soils

Both extractable and soluble TM pools have been investigated in weakly contaminated French forest soils. The order of concentration of TMs in CaCl₂-extracted solution and soil solution

was almost similar. Zinc was the most concentrated element in all pools. Cd was the most extractable element, in line with its labile characteristics (Maiz *et al.*, 1997; Hernandez *et al.*, 2003) and probable enhanced extraction because of complex formation with chloride (Lebourg *et al.*, 1998; Degryse *et al.*, 2003). Metals in both extractable fraction and soil solution were significantly negatively correlated with soil pH (except extractable Cr and Cu), for pH values < 6. Extracted TMs correspond to extractable and potentially available pools (Houba *et al.*, 1996; Menzies *et al.*, 2007). However, CaCl₂ extracts and soil solution concentrations were very different. Chromium concentrations were larger by a factor of two to three in the soil solution compared with the extract. For all the other elements, concentrations in CaCl₂ extracts were greater (by 2-fold for Ni, 5-fold for Zn, Cd and Pb, and 20-fold for Co and Cu). Exchange with Ca, as well as complexation with Cl⁻ (especially for Cd) may have induced a greater release of TM in the CaCl₂ extracts. No significant relationship was observed between the two sets of concentrations. The exception was for Cr ($r = 0.67$, $P < 0.001$) and Pb ($r = 0.61$, $P < 0.001$), but with a very large distribution of the data. Moreover, for more alkaline soil pH, the results showed that metal extractability did not increase, contrary to concentration trends of some elements (especially Cu, Cr, Pb and Sb) in soil solutions.

It has been previously suggested that differences in soil solution and CaCl₂ extracts were partly due to differences in DOC concentrations (Degryse *et al.*, 2009). In our study, DOC concentrations in CaCl₂ extracts were, on average, five times smaller than in soil solutions. Several processes might explain the lower DOC concentration in the extract, including an increase of concentration from re-wetting dry soils, DOC coagulation because of large Ca concentrations and dilution as the soil/solution ratio was larger than in soil solution (Borken *et al.*, 1999; Amery *et al.*, 2007; Fest *et al.*, 2008). Therefore, DOC measured in CaCl₂ extracts does not mimic soil solution DOC under field conditions, whereas DOC partly controls metal speciation in solutions (Pedrot

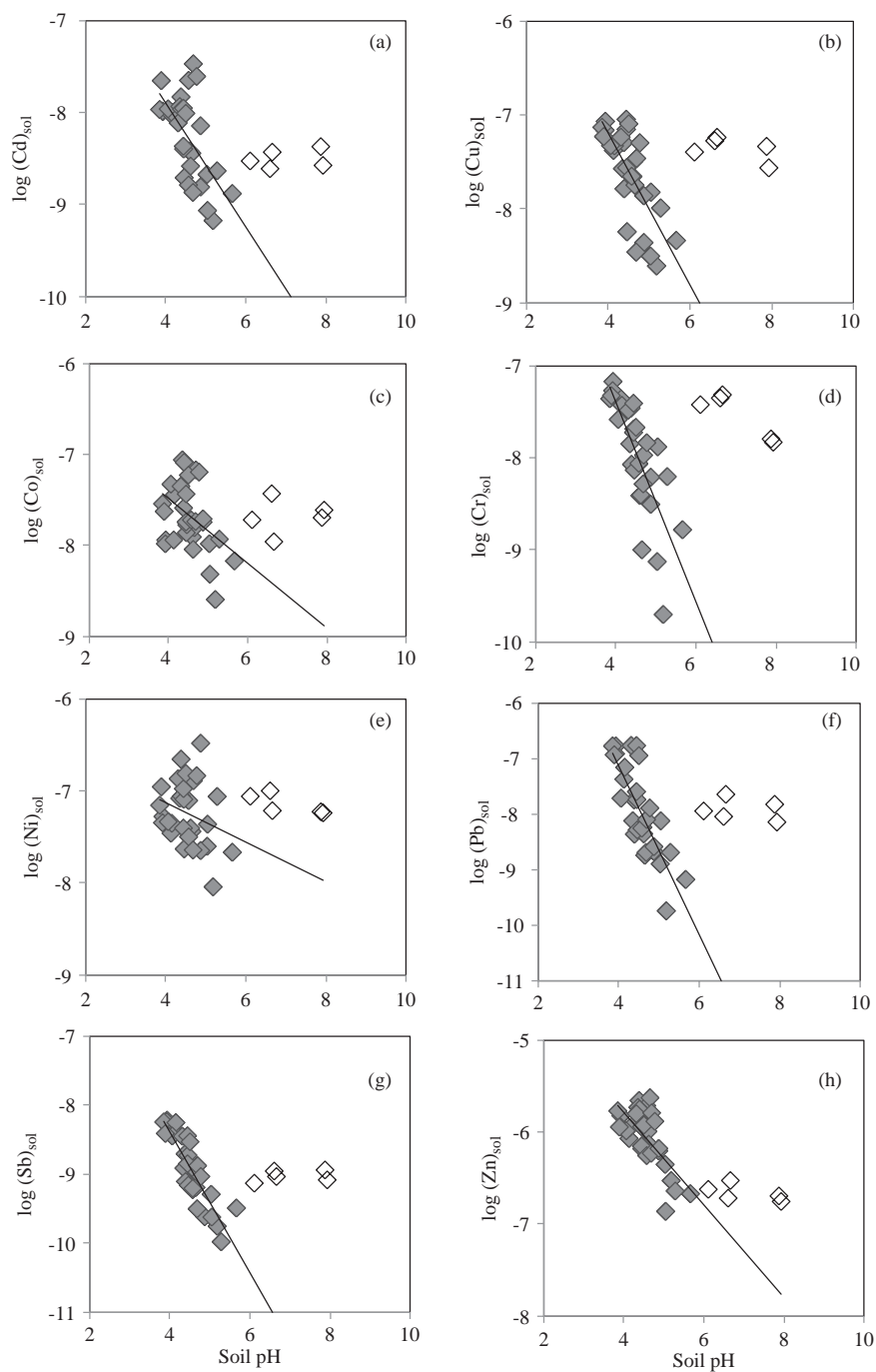


Figure 3 Relationships between total metal concentrations in soil solution ($\log(TM)_{sol}$) and soil pH: (a) Cd; (b) Co; (c) Cr; (d) Cu; (e) Ni; (f) Pb; (g) Sb; (h) Zn. Each data-point is a mean value of four to twelve measurements. The lines represent the relationship between $\log(TM)_{sol}$ and soil pH for soil pH < 6 and open symbols are for pH > 6.

et al., 2008). Thus, $CaCl_2$ extraction should not be considered as a proxy for soil solution composition in the case of weakly contaminated forest soils.

On the other hand, $CaCl_2$ extracts provide useful information about the TM pool that can be easily leached (and hence accessible to other pathways), rather than TM bioavailability, although good correlations with biological response have been observed (Owojori *et al.*, 2009). However, because extractability increases when pH becomes more acidic, the link between TM extractability and

soil pH must be taken into account when considering the soil acidification process.

Influence of pH, organic matter and Fe oxides on TM solubility

Our study showed that, in weakly contaminated soils, TM partitioning between soil and soil solution was strongly related to soil pH. A negative significant correlation was observed between soil pH, TM extractability and total metal concentration in soil

Table 7 Multiple regressions between log (TM) concentration in soil solution and soil properties

	Constant	pH	log OC	log Fe	Log (M) _{tot}	log (DOC)	pH	n	r ²	P
Cd	-6.72 ± 0.38	-0.21 ± 0.06	-0.40 ± 0.13	-	-	-	All	36	0.36	***
	-4.2 ± 0.62	-0.74 ± 0.13	-0.45 ± 0.11	-	-	-	<6	31	0.64	****
Co	-7 ± 0.16	-	-0.47 ± 0.10	-	-	-	All	36	0.38	****
	-4.88 ± 0.49	-0.44 ± 0.10	-0.54 ± 0.09	-	-	-	<6	31	0.65	****
Cu	-3.22 ± 1.1	+0.18 ± 0.07	-	-1.78 ± 0.34	+1.24 ± 0.32	-	All	36	0.47	***
	-2.96 ± 1.01	-0.45 ± 0.20	-	-0.99 ± 0.37	+0.62 ± 0.32	-	<6	31	0.65	****
Cr	-0.02 ± 1.13	-	+0.47 ± 0.14	-3.42 ± 0.41	+2.40 ± 0.35	-	All	36	0.70	****
	-1.04 ± 1.07	-0.69 ± 0.15	-	-1.65 ± 0.38	+1.05 ± 0.33	-	<6	31	0.77	****
Ni	-6.73 ± 0.32	-	+0.29 ± 0.11	-0.26 ± 0.16	-	-	All	36	0.33	***
	-1.77 ± 1.72	-0.46 ± 0.16	+0.37 ± 0.11	-0.58 ± 0.25	+0.69 ± 0.29	-	<6	31	0.53	****
Pb	-2.43 ± 1.39	-	-	-1.60 ± 0.26	+1.32 ± 0.35	-	All	36	0.57	****
	-2.11 ± 0.80	-1.24 ± 0.18	-	-0.86 ± 0.21	-	-	<6	31	0.78	****
Sb	-3.54 ± 0.97	-	-	-0.86 ± 0.16	+1.00 ± 0.18	-	All	35	0.57	****
	-3.31 ± 0.75	-0.76 ± 0.15	-	-0.38 ± 0.17	+0.41 ± 0.19	-	<6	30	0.80	****
Zn	-4.83 ± 0.20	-0.27 ± 0.04	-	-	-	-	All	36	0.56	****
	-3.44 ± 0.46	-0.53 ± 0.09	-0.16 ± 0.08	-	-	-	<6	31	0.54	****
Cu	-5.41 ± 1.06	-	-	-0.91 ± 0.27	+0.72 ± 0.25	+0.63 ± 0.18	All	36	0.55	****
Cr	-3.02 ± 0.86	-	-	-2.18 ± 0.27	+1.74 ± 0.24	+0.94 ± 0.14	All	36	0.83	****
Pb	-1.94 ± 2.13	-	-0.57 ± 0.26	-1.02 ± 0.28	+1.58 ± 0.46	+0.91 ± 0.28	All	36	0.69	****
Sb	-4.45 ± 0.83	-	-	-0.62 ± 0.15	+0.98 ± 0.15	+0.58 ± 0.15	All	35	0.69	****

**** $P < 0.0001$, *** $P < 0.001$, ** $P < 0.01$ – $P > 0.05$.

n = number of samples; r^2 = Pearson correlation coefficient; P = level of significance.

For each element, the first line for each metal corresponds to the regression for all samples. The second line corresponds to the regression analysis for samples with pH < 6. All variables are significant ($P < 0.05$). For Cu, Cr, Sb and Pb, a second group of regression analyses is shown, which includes DOC for the whole pH range. (TM)_{sol} is concentration of the element in soil solution (mol l⁻¹); OC is soil organic carbon content (g kg⁻¹); Fe is soil iron content (%); M_{tot} is soil total metal content (mol kg⁻¹) and DOC is dissolved organic carbon in soil solution (mg l⁻¹).

solution for pHs below 6 and free metal ion concentrations for all elements studied. This suggests a competition between protons and TMs for sorption or complexation sites on soil components (Sauvé *et al.*, 2000). For extractable and total trace metal in soil solution, this process occurred under acidic conditions. For more alkaline pH conditions, the weak effect of pH on total metal concentrations was the result of increased complexation. In the case of FMI concentrations, a negative correlation between concentration and soil pH was observed for all pH values.

In the context of this study, two main soil components could be identified for TM sorption on solid phases: soil organic matter and iron oxides. According to McBride *et al.* (1997), Sauvé *et al.* (2000) or Tipping *et al.* (2003), soil organic matter exhibits a strong affinity for TMs. In our study, this was confirmed for Cd, Co and Zn as a negative correlation was observed between the concentration of these elements in soil solution and soil organic matter content. However, the lack of a significant correlation between some elements (Cu, Pb, Sb) and OC, as previously reported (McBride *et al.*, 1997; Sauvé *et al.*, 2000), does not mean that sorption to this phase did not occur. In fact, interaction with DOC can lead to inconsistent relationship to OC. For Ni and Cr, a positive relationship was observed. Larger OC content in the solid phase can induce greater DOC release and consequent increase of TMs in soil solution by the formation of DOC-TM complexes (Sauvé *et al.*, 2003; Rieuwerts

et al., 2006). The negative correlation observed between soil iron content and extractable (Cr, Cd and Co) and dissolved (Cu, Cr, Ni, Sb and Pb) TMs, indicated that TMs were strongly associated with iron oxides in forest soils (Hernandez *et al.*, 2003; Probst *et al.*, 2003a).

Specific interaction between TM, DOC and Fe

For soil pH above 6, measured concentrations of TMs in soil solution did not depend on soil pH. In these conditions, greater TM concentrations were measured compared with values obtained at pH close to 6. This increase depended on the element concerned; thus while Cd, Co, Ni and Zn concentrations only increased a little, Cu, Cr, Sb and Pb concentrations increased with increasing pH by several orders of magnitude. This could be partly related to the influence of soil pH on soil organic matter partitioning. From pH 5 to 8, large DOC concentrations were observed (Figure 5a), as previously shown by Yin *et al.* (2001) and Lofts *et al.* (2001). Moreover, more alkaline pH enhanced complexing between TMs and dissolved organic matter (Figure 5b, see Pb as an example) because in these conditions proton competition is weaker and cation hydrolysis facilitated. The influence of DOC on TM speciation was thus predominant.

In the soil solutions, significant ($P < 0.001$) correlations between TMs (Cr, Cu, Sb and Pb), DOC and Fe concentration

Table 8 Multiple regressions between log FMI and soil properties: $(M^{2+})_{sol}$ is FMI concentration in soil solution (mol l^{-1}), OC is soil organic carbon content (g kg^{-1}) and Fe is soil iron content (%)

		Constant	Log OC	pH	Log Fe	<i>n</i>	r^2	<i>P</i>
Cd	$\log (Cd^{2+})_{sol}$	-5.07 ± 0.36	-0.36 ± 0.12	-0.58 ± 0.06	–	37	0.74	****
Co	$\log (Co^{2+})_{sol}$	-5.85 ± 0.27	-0.40 ± 0.09	-0.27 ± 0.05	–	37	0.58	****
Cu	$\log (Cu^{2+})_{sol}$	-1.70 ± 0.47	–	-1.40 ± 0.09	–	37	0.87	****
Ni	$\log (Ni^{2+})_{sol}$	-5.72 ± 0.28	-0.34 ± 0.09	-0.23 ± 0.05	–	37	0.49	****
Pb	$\log (Pb^{2+})_{sol}$	-1.68 ± 0.48	–	-1.36 ± 0.10	-0.76 ± 0.30	37	0.85	****
Zn	$\log (Zn^{2+})_{sol}$	-3.47 ± 0.21	–	-0.57 ± 0.04	–	37	0.84	****

**** $P < 0.0001$, *** $P < 0.001$ – $P < 0.05$.

n = number of samples; r^2 = Pearson correlation coefficient; *P* = level of significance.

were found (Table 6). Including DOC concentration in multiple regressions improved Cr, Cu, Sb and Pb total concentration in soil solution prediction. In soil solution, TMs are associated with iron oxides, DOC and/or organo-mineral colloids (Pokrovsky *et al.*, 2005; Grybos *et al.*, 2007; Lofts *et al.*, 2008), because dissolved organic matter stabilizes ferric-TM colloids (Pedrot *et al.*, 2008). The order of the increase of concentration measured for $\text{pH} > 6$, compared with concentrations that would be expected from the linear relationship with pH, was $\text{Pb} > \text{Cr} > \text{Sb} > \text{Cu} > \text{Cd} >$

$\text{Co} > \text{Ni} > \text{Zn}$. This order was in accordance with the order of strength of complexes formed by TMs with soil humic material (Pandey *et al.*, 2000). Zinc, Cd (and Co and Ni) concentrations did not increase to a large extent for $\text{pH} > 6$. These elements have a smaller affinity for DOC in soil solution (Römken & Salomons, 1998; Weng *et al.*, 2002; Citeau *et al.*, 2003). Chromium, Cu, Sb and Pb concentrations increased at $\text{pH} > 6$. The large affinity of Fe, Cu, Cr and Pb for organic colloids has been described previously (Sauvé *et al.*, 1997; Kalbitz & Wennrich, 1998; Sauvé

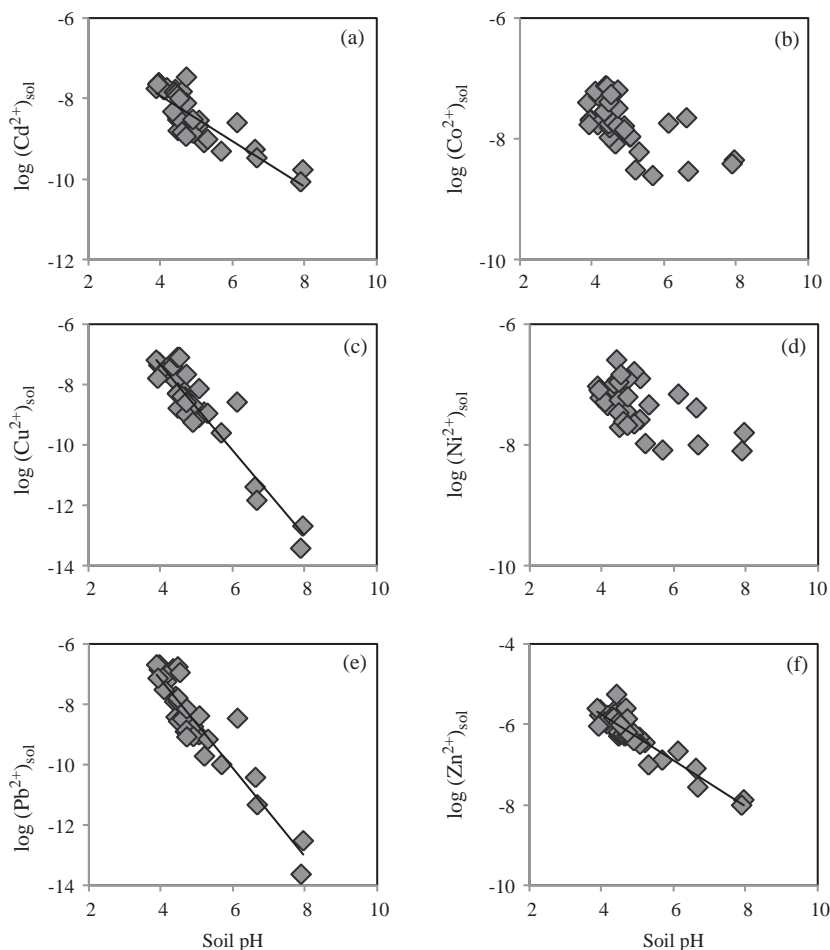


Figure 4 Relationship between free metal ion (FMI) concentration ($\log (M^{2+})_{sol}$) in soil solution and soil pH for Cd (a), Co (b), Cu (c), Ni (d), Pb (e) and Zn (f). The lines represent the relationship between $\log (M^{2+})_{sol}$ and soil pH for the entire pH range.

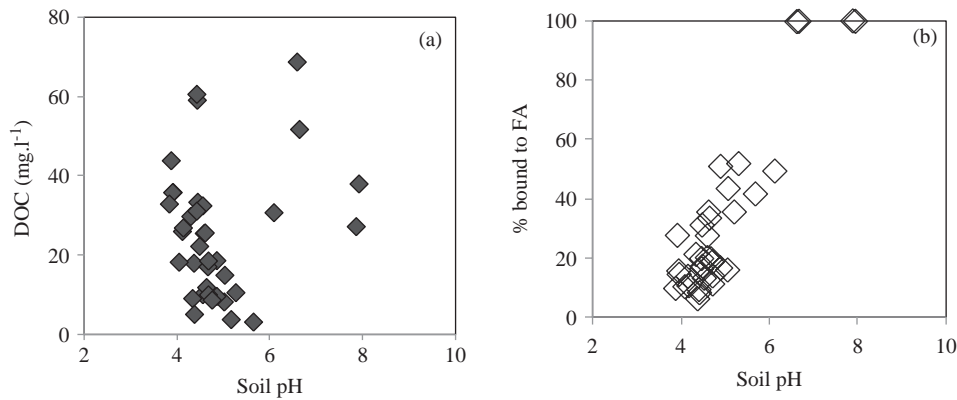


Figure 5 (a) Relationship between dissolved organic carbon (fulvic acids: FA) in soil solution and soil pH. (b) Relationship between the percentages of lead associated with dissolved organic matter and soil pH (WHAM-VI output data).

et al., 2003; Pedrot *et al.*, 2008). Because various types of colloids (organic and organo-metallic, association of DOC and Fe (III) hydroxides) can be found in soil solution, different affinities between the present elements and these colloids can thus be assumed. In our study, no distinction could be made between TM complexing with DOC or Fe hydroxides, although a large affinity of Cr for iron oxides was evident. Chromium extractability was correlated only with Fe content, and in soil solution the correlation between Fe and Cr was the strongest ($r^2 = 0.88$, $n = 37$), which confirmed the association between the two elements in soil solution. Antimony was also less significantly correlated with DOC than with Fe in soil solution. This indicated a greater affinity of Sb for Fe hydroxides than for DOC in soil solutions. Antimony affinity for DOC in soil solution depends on its oxidation state (III or V) (Filella *et al.*, 2002). Affinity of Sb for Fe (III) hydroxides has been already observed in other soils (Mitsunobu *et al.*, 2006).

Ability of soil properties to predict TM dynamics in soils

These results for weakly contaminated forest soils lead to simple metal-specific models, based on a limited number of soil properties that could accurately predict both TM partitioning (extractability) and solubility. The partitioning of the elements studied showed an obvious similarity: the same dependence on soil pH (<6) for extractability and solubility was observed. TM partitioning in soils depends on element affinity for solid (OC, iron oxides) and dissolved (DOC, iron hydroxides) phases. TM (Cd, Ni, Zn and Pb) extractability could be predicted by soil pH (below pH 6 for Pb) and OC and Fe content in the case of Cd, Co, Ni and Zn. Cr extractability could be predicted by soil Fe content alone.

In soils of pH < 6, pH combined with OC content (for Cd, Co, Cr, Ni and Zn) or Fe content (for Cu, Cr, Pb and Sb) predicted accurately total metal concentration in soil solution. For less acidic pH values, soil properties alone were less effective in predicting total metal concentration in soil solution because processes occurring in soil solution mainly controlled TM solubility and speciation. In the case of Cu, Cr, Sb and Pb, including DOC

concentration in the regressions improved prediction of the total concentration for the whole pH range.

TM partitioning between FMI and soil depended on soil pH at all pH values. pH alone and combinations of pH and OC for Cd, Co and Ni, and pH and Fe for Pb accurately predicted FMI in the soil solutions. The efficiency of the prediction (variance) was similar to that previously obtained for FMI concentration prediction in soil solutions (Tipping *et al.*, 2003; Pampura *et al.*, 2007; de Vries *et al.*, 2007), when considering 'reactive' metal content in soil, and soil solution pH. Therefore, for these French forest soils, simple transfer functions could be used for FMI prediction in soil solution. No information was needed about soil solution pH and total metal content in soils.

In summary, in this study, total metal content was a significant property with which to predict total metal concentration in soil solution only for Cu, Cr, Sb and Pb, and was never significant for FMI prediction. According to Watmough *et al.* (2005), total metal content in soils with small inputs does not vary to a large extent, and has thus a weak influence on metal concentration in solution.

Risk assessment and critical limits

An original aspect of our study was to consider separately the behaviour of TM in soil solution for pH > 6: forest soils of this pH range are rarely investigated (Römkens & Salomons, 1998; Sauvé *et al.*, 2003). Even if taken into account, these pH conditions are not generally considered separately, even if for some elements a different behaviour is observed (Watmough *et al.*, 2005). Our results showed that relatively large total concentrations in soil solutions of Cr, Cu, Pb and Sb were measured at pH > 6. Moreover, soil solutions were filtered (<0.22 μm) and consequently, only small colloids were included in the analysis (1–0.22 μm). The measured concentration would be greater if colloidal concentrations of up to 1 μm were considered. Total concentrations in soil solution should therefore be considered for TM mobility in soil profile and leaching to surface and ground waters (Citeau *et al.*, 2003; Pedrot *et al.*, 2008).

Critical limits are based on FMI concentration (Lofts *et al.*, 2004) as TMs are mostly available in FMI form (Florence *et al.*, 1982) in aquatic ecosystems. Availability of certain small organo-metallic complexes has been shown by Brandt *et al.* (2008). Moreover, small colloids carrying TM can be dissociated or ingested by living organisms (van Gestel, 2008) and this might lead to a significant toxic effect, particularly in alkaline soils. In such soil conditions, FMI certainly under-estimates TM toxicity in soil solutions, and TM critical limits for soil organisms cannot be estimated only on this basis (Bur *et al.*, in press). The observed increase of total TM concentration at pH values > 6 through complex formation with organo-mineral colloids can not be neglected when considering TM impact on ecosystems. These data will be integrated into critical load data bases to improve critical load calculations, which have been already tentatively made at a national scale for lead (Probst *et al.*, 2003b).

Conclusions

In this study, TM (Cd, Co, Cr, Cu, Ni, Pb, Sb and Zn) partitioning between total, CaCl₂ extractable and soil solution in relation to soil properties was investigated in some French forest soils under the influence of long-range atmospheric pollution. The main findings are as follows. TM abundance in soil was Zn > Cr > Pb > Ni > Cu > Co > Sb ≫ Cd. Metal concentrations were within the range of background values in mineral layers, but in northern, eastern and central sites, surface organic layers have been impacted by atmospheric inputs (EF > 2 for Zn, Cd, Sb and Pb). TM extractability and solubility strongly depended on the element. In soil solution, metal concentration was in the order Zn > Ni > Cu > Pb > Co > Cr > Cd > Sb, whereas regarding extractability, metal could be classified as follows: Cd > Cu > Zn > Co > Ni > Pb > Cr. Differences in metal concentrations were noted between extractable and soluble fractions, especially for pH > 6. Under these conditions, CaCl₂ extraction could not be considered strictly as a proxy for soil solution composition in the case of forest soils with small TM inputs.

TM partitioning in forest soils between total, extractable and soluble phases mainly depended on soil pH. Nevertheless, TM behaviour in soils was different in acidic (pH < 6) and less acidic conditions. In these weakly contaminated soils, competition between protons and metallic cations for adsorption sites mainly controlled TM behaviour at pH < 6. In soil solution, FMI concentration for Cd, Cu, Pb and Zn was significantly correlated to soil pH over the whole pH range. Organic carbon and Fe content were the main metal adsorption components in forest soils. At pH > 6, complexing with DOC and Fe (III) hydroxides increased Cu, Cr, Sb and Pb total concentrations.

Simple models based on soil pH and including some soil sorbing phases (OC, Fe), predicted effectively TM partitioning. TM extractability was predicted by pH only for pHs < 6 and by pH and soil Fe for the whole pH range. Fe content alone explained Cr extractability. Total metal concentration in solutions was modelled by soil pH, OC content (Cd, Co, Cr, Ni and Zn) and

Fe content (Cu, Cr, Ni, Pb and Sb). Total metal concentration in soil is an important property to predict total metal concentration in solution only for Cu, Cr, Ni, Pb and Sb. More precise predictions were obtained at pH < 6, and for less acidic pH, soil solution composition had a stronger influence on TM solubility and speciation. Including DOC concentration improved total metal concentration prediction in soil solution for the whole pH range. In contrast, FMI concentration in soil solution was efficiently simulated for all pH values using only a few simple soil properties (pH and OC for Cd, Co and Ni, and Fe for Pb).

Neutral to alkaline conditions should be considered separately in order to accurately predict total metal concentration in solutions from forest soils. Small colloids (organic carbon or hydroxides) were efficient at complexing metals, and they increased concentrations in soil solution as shown for Cu, Cr, Sb and Pb. The increase in concentration order was Pb > Cr > Sb > Cu > Cd > Co > Ni > Zn. Because risk assessments are presently based only on FMI concentrations, TM impact on soil organisms may be under-estimated for these pH conditions. Critical load assessment must thus take this into account in the future.

Acknowledgements

This project was supported by ADEME (French Agency for Environment) and received logistic support from the ONF (French Forest board). Laure Gandois received a fellowship from ADEME. The authors warmly thank the ONF staff (Vincent Borthelle, Jean-Pierre Chassagne, Joël Clamart, Gilles Fournel, Jean Luc Fiol, René Gregoire, Alain Jacquemard, François Mouchot, Florence Pertile, Pierre Trithardt and Jérôme Vany) for invaluable help during field work and Erwin Ulrich for facilitation, Manuel Nicolas (ONF-INRA Nancy) for help in soil sampling, Gael Durbe and Alain Alric (EcoLab, Université de Toulouse, UPS-CNRS-INP) for help in field work and technical assistance in the laboratory, Daniel Boutaud and Jean Claude Harrichourry for centrifugation device design and production, Frederic Candaudap (LMTG, Université de Toulouse, UPS-CNRS-IRD) for ICPMS analysis assistance and Frederic Julien (EcoLab, Université de Toulouse, UPS-CNRS-INP) for major anion analysis. Two anonymous reviewers are thanked for their helpful comments.

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