

Note

Distribution of cadmium in a cultivated soil in Brittany, France

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ABSTRACT: Cadmium (Cd) can be potentially toxic to the environment, and its bioavailability is related to the chemical forms it occurs in the soils. The distribution of Cd into the solid phase and its availability was investigated in a cultivated soil in Brittany, France. Cd sequential extraction was performed using a modified Tessier's sequential extraction protocol. Total content of Cd (n = 22 samples) ranged from 0.13 to 0.37 mg kg⁻¹. Long term history of organic and mineral fertilizers application increased Cd concentration in the surface horizon. The fate of Cd was correlated with soil available P₂O₅ concentration and pH. The regression analysis (linear and non-linear) and Principal Component Analysis revealed the synergistic effect of P₂O₅ in the retention of Cd in cultivated soils. The following fractions' sequence was observed: bounded to Fe and Al oxides + phosphates > exchangeable > bound to organic matter ≈ residual fraction.

Key words: Cd, soil pollution, Tessier protocol, sequential extraction

Distribuição de cádmio em solo cultivado na Bretanha, França

RESUMO: O cádmio (Cd) pode ser tóxico no ambiente e sua biodisponibilidade está relacionada às formas químicas em que os metais se encontram no solo. Apresenta-se a distribuição deste metal na fase sólida de um solo cultivado na Bretanha, França, assim como fatores que influenciam sua disponibilidade. Foi realizada a extração sequencial do Cd utilizando o método Tessier, modificado. A concentração total de Cd, avaliada em 22 amostras, variou de 0,13 a 0,37 mg kg⁻¹. O uso contínuo de fertilizantes orgânicos e minerais aumentou a concentração de Cd no horizonte superficial do solo. A distribuição do Cd foi relacionada à concentração de P₂O₅ disponível e ao pH. Análises de regressão (linear e não linear) e a Análise de Componentes Principais mostraram efeito sinérgico do P₂O₅ na retenção de Cd nos solos cultivados. O fracionamento apresentou a seguinte sequência: ligado a óxidos de Fe e de Al + fosfatos > trocável > ligado à matéria orgânica ≈ residual. Palavras-chave: Cd, poluição do solo, método Tessier, extração sequencial

Introduction

Trace metals, as Cd, are potentially toxic to the environment, and their behavior is related to the chemical associations that occur in soils. Thus, the mobility and bioavailability of the metals depend strongly on the physical and chemical properties of the soils. Trace metals can be associated with soil fractions: the exchangeable fraction, considered quickly available; the fraction bound to carbonates, susceptible to changes of pH in soil; the fraction associated to iron and manganese oxides, thermodynamically unstable under anoxic conditions; the organic matter fraction, that can be degraded, leading to a release of soluble trace metals; the residual fraction that is not available by oxy-reduction reactions or solubilization, and presents fewer environmental risks (Tessier et al., 1979).

In agricultural areas, Cd accumulates in soils due to application of mineral (mainly phosphates) and organic fertilizers (Campos et al., 2005; Bizarro et al., 2008; Raven and Loeppert, 1997; Levasseur, 2002). Cd may be uptaken by crops or transported to waters. Cd transport from agricultural areas occurs mainly in acidic soils (Mortvedt and Osborn, 1982; Mendes et al., 2006; Reuss et al., 1978).

Lime application is an important management practice to immobilize trace metals because it increases the pH and favors the adsorption of the metals over the oxides and carbonates surface. Lime may also reduce the Cd exchangeable fraction and increase the fractions bound to organic matter and oxides, and residual fractions (Melo et al., 2008; Silveira et al., 2008; Matos et al., 1996). The percent of clay, surface area, and percentage of iron oxides were used to predict the amount of Cd sorbed in the soil (Korte et al., 1976).

The concentration of total Cd in surface soil amended with phosphates can be highly correlated to total phosphorus concentration (Mulla et al., 1980). The addition of phosphates reduces Cd availability (Pierangeli et al., 2004; Abou-Zied, 2007; Campbell et al., 2006). The Cd association with the solid phase of soil occurs mainly through cation exchange reactions or specific adsorption. The dominance of the exchangeable and bound to organic matter fractions in surface horizons is due to the negative charges than in the subsurface horizon (Gomes et al., 1997). In subsurface horizons exhibiting low organic matter concentrations, Cd fractions are primarily associated with oxides and residual fractions.

Assuming that much soil geochemical properties and agricultural practices can modify the trace metal behavior and affect their availability, the aim of the study was to determine soil Cd concentration and distribution into the solid phase in surface and subsurface horizons of a cultivated soil.

Material and Methods

The research was developed with soil samples collected in the west of Brittany, France (Figure 1), a region dominated by intense agriculture and cattle farm operations. The Typic Hapludalf soil in this study represents the typical soil type of the region, with a loamy cover and schist substrate (Curmi and Widiatmaka, 1995). Samples were collected along a linear toposéquence located in a cultivated area in Ploudiry. The area consisted of 8 ha receiving long-term (over 20 years) repeated applications of pig slurry and high rates of mineral fertilizers. The studied toposéquence, with 270 m and 6% slope, begins on the top of the hill slope (48°28'9.08" N, 4°6'34.64" W; Figure 1) and finalized at the end of the cultivated area in the middle/end slope (48°28'10.5" N, 4°6'45.57" W).

Twenty-two samples, distributed on 11 points (separated by 25-30 m), were collected from two continuous horizons identified in the field: the tilled top soil horizon, denominated SH (surface plowed horizon, 0-35 cm, 11 samples), and the subsurface horizon denominated DH ("deep" horizon, under the plowed horizon, 35-50 cm, 11 samples) (Figure 2). The samples were collected with a dutch auger and the outside parts of each sample, in contact with the metal, were rejected. The samples, each one with about 0.5 kg, were disposed in recipients previously decontaminated with HCl 10%, at a 4°C. The samples were dried at 105°C in a forced air oven. Cadmium fractionation was performed according to a modified Tessier's protocol (Table 1). This method (Tessier et al., 1979) is largely used to fractioning metals in soils (Rao et al., 2008) and was validated by other authors (Frentiu et al., 2008).

Separations were performed by centrifuging (3,000 rpm) for 30 min and the supernatant was analyzed for Cd. The residue was washed with 50 mL of ultrapure water and this supernatant was discarded. All glassware used for the extractions was previously soaked in 14% HNO₃ (v/v) and rinsed with ultrapure water. The extracts were analyzed using a graphite furnace atomic ab-



Figure 1 – Location of the toposéquence studied in the west of Brittany, France. Source: image obtained from Google Earth™ (earth.google.com), modified (Accessed Febr. 26, 2010).

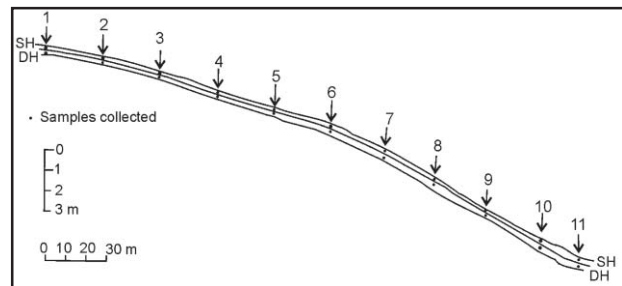


Figure 2 – Profile of the toposéquence studied and location of the samples collected.

Table 1 – Protocol adopted for Cd fractioning in soil.

FRACTION	(1)*exchangeable(EXCH)	(2)*Fe and Mn oxides(OXID)	(3)*organic matter(OM)	(4)**residual(RES)
Sample	6.5 g dry soil	residue of (1)	residue of (2)	residue of (3)
Reagents and conditions of the extraction	50 mL MgCl ₂ 1 M (pH 7), 1 h, room temperature continuous shaking	125 mL 0.04 M NH ₂ OH.HCl solution 25% CH ₃ COOH 6 h, 96 ± 4°C, periodic shaking	6 mL 0.02M HNO ₃ + 31.25 mL H ₂ O ₂ , 2 h, 85 ± 3°C, periodic shaking, 18 mL H ₂ O ₂ 30%, 85 ± 3°C, 3 h, periodic shaking. After attain room temperature: 31 mL CH ₃ COONH ₄ in solution 20%HNO ₃ - dilut the sample to 100 mL with ultra-pure water, 30 min, room temperature, continuous shaking	dry mineralization after calcinations at 450°C; ash dissolved with HCl

*Extractions made in the Laboratory of Soils of the "INRA/Science du Sol", Rennes, France; solutions determined in the laboratory of COOPAGRI BRETAGNE, Landerneau, France. **Extraction and determination made in the laboratory of COOPAGRI BRETAGNE.

sorption spectrometer (GFAAS) with Zeeman correction, wavelength 228.8 nm for the Cd and detection limit 0.01 mg kg⁻¹. The carbonate fraction was not analyzed as a specific fraction (as advocated by the Tessier's protocol) due to the acidic character of the soil. This procedure was suggested by Matos et al. (1996) for acidic soils. Since Cd was under the detection limit in the used reagents, no blank correction was necessary. In five samples, the total and the available P₂O₅ were analyzed before and after the oxides extraction (metals bounded to Fe and Mn oxides, fraction 2). As phosphates were dissolved in this fraction, the metals associated to the phosphates were released to the extracted solution of fraction 2.

Other analysis performed: granulometry; pH (water and KCl); organic matter – O.M. (organic carbon Anne); cations exchange capacity – CEC; available phosphates - P₂O₅ (Dyer) and free iron – Fe-free (Méhra-Jackson). The analytical methods are described in Baize (2000 a).

Statistical analyses (Principal Component Analysis and regression analysis, using the software Statistica 5.0) were conducted to evaluate the distribution of Cd in the soil horizons.

Results and Discussion

Surface and subsurface soil samples exhibited different concentrations of O.M., P₂O₅ and CEC (Table 2). The P₂O₅ concentration in SH was greater than in DH. The phosphate increasing into the surface horizon due to the organic and mineral fertilization in the top of the soils, associated to the low mobility of the phosphate applied, are reported by many authors (Hountin et al.,

1997; Gomes et al., 1997; Berwanger et al., 2008). Highest values of CEC in the SH are certainly related to the highest O.M. and clay concentrations. The pH and Fe concentrations are not different between the two horizons.

The values of Cd in the fractions ranged of 0.01 to 0.21 mg kg⁻¹. The mean values of the fractions also suggested the difference between the horizons. Lower total Cd concentration was found in the deep horizon (DH), and the mean is comparable to the mean obtained in non cultivated soils in France: 0.16 mg kg⁻¹ (Baize, 2000 b). Results indicate no Cd contamination in the subsurface horizon.

There was no difference in the Cd-res fraction between the horizons. This result indicates no anthropogenic contribution to the residual fraction. On this way, no difference was found in the Cd-OM fraction suggesting a low Cd retention by organic matter. Other metals, as Cu and Zn, are more retained by de organic matter than Cd (Bertoncini and Mattiazzo, 1999). The proportional fractions of Cd show that in the both horizons predominates Cd bound to Fe and Mn oxides. This fraction includes the Cd bounded to the phosphates.

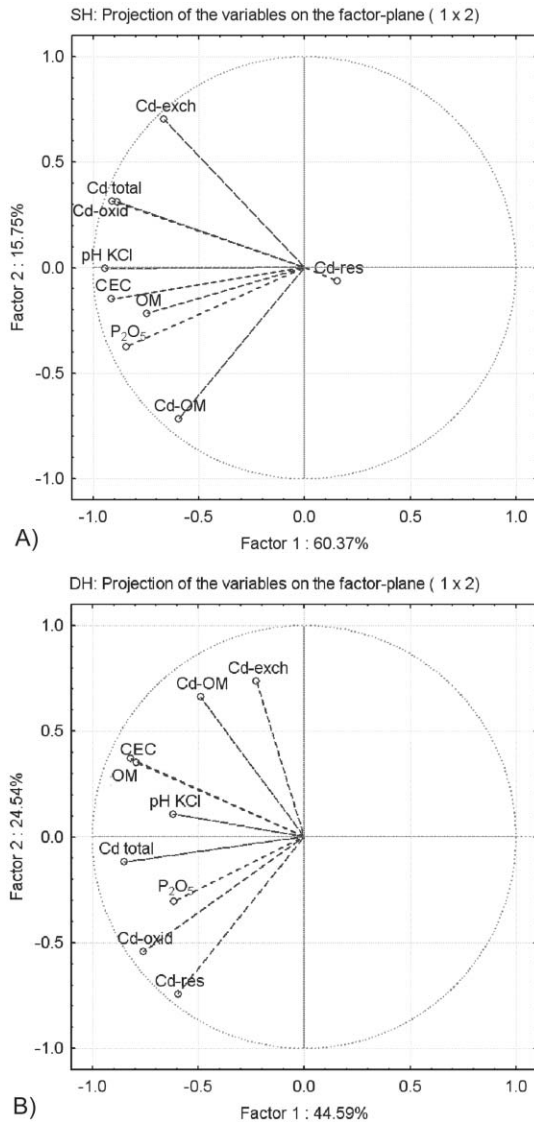
There was no relation between the granulometry fractions, free-Fe and pH (water) with other physicochemical parameters or with the Cd fractions in the cultivated area (SH and DH) ($p < 0.01$). A positive correlation between O.M. and CEC was found in both sample groups ($p < 0.05$; SH: +0.83; DH: +0.98).

These observations contributed to the selection of the parameters for the Principal Component Analysis – PCA (Figure 3). The PCA reduces the number of vari-

Table 2 – Mean values and Standard Deviation of the parameters analyzed into the samples of two horizons (SH – surface horizon; DP – deep horizon). Means with different letters in the same lines differ ($p < 0.01$. T-test).

Parameter	SH (n = 10)		DH (n = 11)	
	mean	S.D.	Mean	S.D.
sand (g kg ⁻¹)	227 ^{NS}	37	271	94
silt (g kg ⁻¹)	612 ^{NS}	39	621	112
clay (g kg ⁻¹)	161 ^a	15	108 ^b	36
pH (in water)	6.24 ^{NS}	1.51	6.06	0.69
pH (in KCl)	5.47 ^{NS}	0.54	5.10	0.51
O.M. (%)	3.36 ^a	0.38	1.41 ^b	0.62
P2O5 (mg kg ⁻¹)	815 ^a	610	83 ^b	73
CEC (meq kg ⁻¹)	113 ^a	11	63 ^b	15
Fe (%)	1.435 ^{NS}	0.061	1.316	0.200
Cd-exch (mg kg ⁻¹)	0.085 ^a (27%)	0.032	0.040 ^b (21%)	0.031
Cd-oxid (mg kg ⁻¹)	0.166 ^a (53%)	0.042	0.090 ^b (47%)	0.045
Cd-OM (mg kg ⁻¹)	0.037 ^{NS} (12%)	0.016	0.031 (16%)	0.022
Cd-res (mg kg ⁻¹)	0.026 ^{NS} (8%)	0.008	0.032 (16%)	0.031
Cd-total (mg kg ⁻¹)	0.314 ^a (100%)	0.074	0.193 ^b (100%)	0.080

^{NS}=Not significant. Cd-exch = exchangeable fraction; Cd-oxid = Cd bound to Fe and Mn oxides; Cd-OM = Cd bound to Organic Matter; Cd-res = residual fraction; Cd-total = total concentration of Cd.



Variable contributions - Include condition: local = "SH"		
	Factor 1	Factor 2
pH KCl	0.163803	0.000014
OM	0.102235	0.032948
P ₂ O ₅	0.130694	0.098525
CEC	0.153684	0.015557
Cd-exch	0.081597	0.348557
Cd-oxid	0.145105	0.068691
Cd-OM	0.065393	0.362425
Cd-res	0.004334	0.002743
Cd-total	0.15315 6	0.070540

Variable contributions - Include condition: local = "SH"		
	Factor 1	Factor 2
pH KCl	0.095565	0.005399
OM	0.167242	0.062232
P ₂ O ₅	0.094314	0.041580
CEC	0.156951	0.056213
Cd-exch	0.012862	0.246255
Cd-oxid	0.144328	0.133689
Cd-OM	0.059947	0.198409
Cd-res	0.088518	0.249908
Cd-total	0.180275	0.006315

Figure 3 - Principal Component Analysis diagrams for variables and their contribution for the first two axes. (A) SH - surface horizon; (B) DH - deep horizon.

ables from the original data to some factors (or principal components) and indicates groups of data that present similar behavior. The two principal components selected are able to account for 69% of the total variance presented. In the SH (Figure 3A), the soil parameters selected (pH KCl, O.M., P₂O₅ and CEC) and Cd-oxid and Cd-total concentrations define 60% of the variance of the data indicated by the first factor. In the DH (Figure 3B), however, the P₂O₅ concentration and the pH have no significant contributions. The data variance may be better explained by the O.M. content and CEC. In addition, the Cd-oxid and Cd-total data have also a notable contribution in the Factor 1.

The pH around 6 in the cultivated area and the presence of Cd associated to the phosphates originated from mineral and organic fertilizers, explain the great proportion of Cd-oxid in the SH compared to the subsurface

horizon. The importance of the Fe and Al oxides in the retention of the trace metals by specific adsorption or co-precipitation mechanisms was shown by Gomes et al. (1997).

Pierangeli et al. (2004) showed that the presence of phosphates in soils contributes to reduce Cd bioavailability. These authors also indicated that other trace metals (Cu and Pb) are preferably sorbed by the soil compared to Cd. On the other hand, repeated pig slurry application in the cultivated area may have saturated the phosphate adsorption sites in the soil, which also promoted phosphorus desorption (Berwanger et al., 2008). Thus, the Cd bounded to the phosphates may be transported to other environments as lowlands or rivers.

Bertoncini and Mattiazzi (1999) observed the potential for Cd to be lost with the percolation of soluble organic-metal complexes. The authors presented the fol-

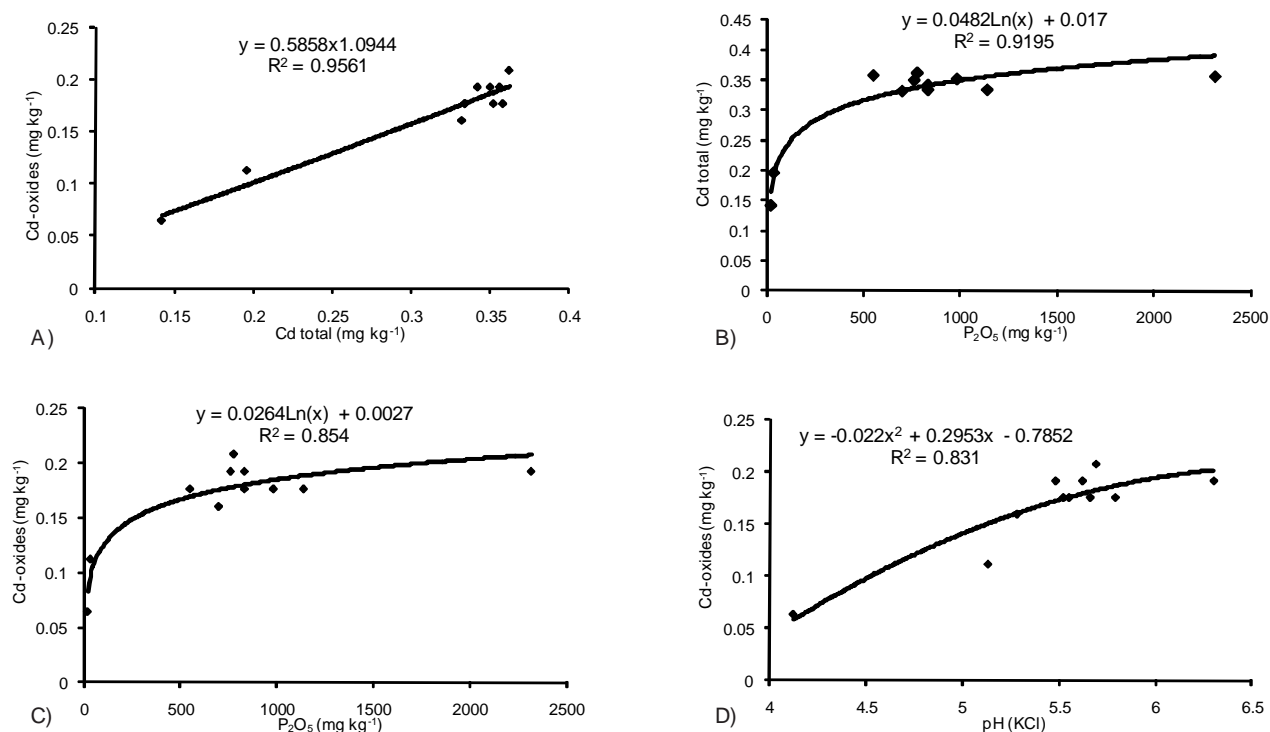


Figure 4 – Total or fractions cadmium concentration in the soil as a function of parameters for the surface horizon – SH. (Regression analysis: $p < 0.05$).

lowing order of compatibility and intensity of the adsorption of trace metals by active sites of humic acids (when in low concentration): $\text{Cu} > \text{Zn} > \text{Cd}$.

In SH, the total-Cd and Cd-oxide concentrations present a high regression coefficient (Figure 4A). In agreement with the equation of the dependence, the Cd-oxide fraction is around 58% of the total Cd concentration. The retention as Cd-oxide fraction is also pH-dependent (Figure 4D). The logarithmic relationships between the total Cd (4B) and Cd oxides (4C) with the P_2O_5 values reveal a synergistic effect of P_2O_5 on Cd retention in soil at the surface horizon. Therefore, the highest control of the Cd concentration and distribution in cultivated soil is associated with the P_2O_5 presences. The behavior was not identified in the DH horizon ($R^2 > 0.75$). Moreover, when considering the use of organic or mineral phosphate fertilizers, the accumulation of Cd in the top horizon of soil may increase.

Conclusions

The Cd distribution in cultivated soils followed the sequence: bounded to Fe and Mn oxides + phosphates > exchangeable > bounded to O.M. \approx residual fraction. In the surface horizon, Cd concentration was highly correlated to available P_2O_5 and soil pH. In the deep horizon (under the plowed horizon), O.M. and CEC are the most important properties to explain the distribution of Cd into the soil. Cadmium concentration associated with total, exchangeable and bounded to oxides fractions were relatively lower than in the surface horizon.

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