ASSESSMENT OF ZINC MOBILITY IN CONTAMINATED SOILS AND MINING MATERIALS IN THREE STUDY SITES OF NORTHERN VIETNAM

Đánh giá tính di động của Zn ở các đất bị ô nhiễm và khai thác mỏ ở ba điểm nghiên cứu tại miền Bắc Việt Nam

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TÓM TẮT

Tính di động của Zn được đánh giá trong các mẫu đất được lấy trên đất nông nghiệp ở khoảng cách 10 m và 150 m so với các xưởng tái chế kim loại của hai làng nghề ở miền Bắc Việt Nam (Chỉ Đạo - Hưng Yên và Phùng Xá - Hà Tây cũ). Nghiên cứu tương tự cũng được tiến hành ở mỏ khai thác chì, kẽm Lang Hích, Đại Từ, Thái Nguyên. Ngoài xác định Zn tổng số, việc chiết rút lặp lại được tiến hành bằng với nước, $CaCl_2$ và EDTA. Hàm lượng Zn tổng số ở Chỉ Đạo (200 - 240 mg Zn kg^{-1}) thấp hơn ở Phùng Xá (580 - 640 mg Zn kg^{-1}). Hơn nữa, ở Chỉ Đạo, chỉ một phần nhỏ của Zn (2 - 4%) tồn tại ở dạng hòa tan dạng trao đổi, mức độ nguy hiểm chủ yếu cho môi trường liên quan đến hàm lượng chì cao trong đất của làng này. Ở Phùng Xá, một tỷ lệ khá cao của Zn tổng số có thể được giải phóng bởi các quá trình trao đổi ion (25 - 35%), chỉ ra mức độ nguy hiểm khá nghiêm trọng cho sức khỏe con người và sự nhiễm bẩn sản phẩm nông nghiệp thông qua sự hấp thụ của cây trồng. Hàm lượng Zn rất cao quan sát được ở mẫu chất lấy tại mỏ Lang Hích (50.000 mg Zn kg^{-1}) và phế thải rắn dạng hạt mịn (7.000 mg Zn kg^{-1}) được chứa tại thung lũng cạnh mỏ; phần trao đổi thấp (0,3%), nhưng Zn có thể trở nên di động trong tương lai do sự hòa tan của axit đối với những nguyên liệu này. Hàm lượng Zn trong đất liền kề mỏ thấp hơn nhiều (250 mg Zn kg^{-1}), với tỷ lệ thấp của các dạng hòa tan và trao đổi (≤1% so với Zn tổng số).

Từ khoá: Kim loại nặng trong đất, ô nhiễm đất, ô nhiễm kim loại nặng.

SUMMARY

The mobility of zinc was assessed in soil samples collected at 10 and 150 m far from metal recycling craft villages of Northern Vietnam (Chi Dao and Phung Xa). A similar study was conducted in mining materials and in soil samples collected closely to the Lang Hich mine. Besides total Zn measurements, repeated extractions were performed with H_2O, $CaCl_2$, and EDTA. The total Zn content was lower in Chi Dao (200 - 240 mg Zn kg^{-1}) than in Phung Ha (580 - 640 mg Zn kg^{-1}). Moreover, in Chi Dao, only a small fraction of Zn (2 - 4%) occurs in soluble and exchangeable forms, the main environmental hazard being linked to the high Pb content in the soils of this village. In Phung Xa, a high proportion of total Zn can be released by ion exchange processes (25 - 35%), which represents a serious risk to human health and to the contamination of the food chain through plant uptake. Very high Zn content was observed in the calcareous mine substratum at Lang Hich (50,000 mg Zn kg^{-1}) and in the fine-grained residues (7,000 mg Zn kg^{-1}) stored in a neighboring valley; the exchangeable fraction is low (0.3%), but Zn can be mobilized at mid- and long term by acid dissolution of these materials. The Zn content in the neighboring soil is much lower (250 mg Zn kg^{-1}), with a low fraction (≤1%) in soluble and exchangeable forms.

Key words: Heavy metal in soils, soil pollution, heavy metal pollution.

1. INTRODUCTION

In many rural communes of Vietnam situated in the vicinity of urban and industrial areas metal recycling craft villages have developed parallelly to traditional farming activities. Such activities contribute to the diversification of income sources for farm households and create new job opportunities to the local available workforce. However, as for any industrial activity, risk assessment should be taken into consideration for possible environmental contamination, more especially in agricultural areas which constitute the starting point of the food chain. Great care should be taken in the vicinity of small factories handling heavy metals whose high toxicity was well established. The same holds true for mining areas where extraction of heavy metals is carried out leading to by-product storage in the neighbouring soils.

The present study focused on zinc contamination in the field plots close to metal recycling craft villages and to zinc and lead mining. The total Zn content in soils and mining materials only provide a partial view of environmental hazards because heavy metals can exist in many different forms which are more or less mobile and therefore more or less likely to enter the food chain and to affect human health. The assessment of heavy metal mobility is, therefore, needed to make a more confident diagnosis of effective contamination levels. Various laboratory procedures were proposed to differentiate the metal forms in soil materials. They are based on extractions with different reagents which are expected to selectively mobilize different metal sources. A great deal of papers was published on selective and sequential extractions of heavy metals (e.g. Tessier et al, 1979; Ure, 1996; Cappuyns et al., 2006 ; Davidson et al., 2006 ; Pueyo et al., 2008 ; Torri & Lavado, 2009) and a recent thorough study was published by Rao et al (2008). In this research, we attempted to assess the more mobile Zn forms released by simple dissolution and by ion exchange from mineral and organic constituents. Three case studies in Northern Vietnam were presented in this paper and provide complementary data to previous researches (Ho Thi Lam Tra and Nguyen Huu Thanh, 2003; Nguyen Huu Thanh et al., 2006).

2. MATERIALS AND METHODS

Study sites and soil sampling

Three study sites were selected based on expected Zn contamination in their neighboring environment. Composite samples, as a mixture of five subsamples, of soil or mining materials were gathered from the 0-15 cm layer in each investigated plot at the end of January 2009.

Chi Dao village (Hung Yen province)

Chi Dao village is situated at 25 km east to Hanoï city, of the Red River Delta. This village is specialized in recycling lead from used batteries. This activity causes pollution hazard when the batteries are emptied and rinced with water; indeed the electrolyte contains various metals such as zinc and antimony. The battery bodies are usually stored in open air, and sometimes used to build walls and courtyards, the residual metals of which can be leached by rain and scattering to neighbouring fields. Two mixed top soil samples were collected in a distance at 10 and 150 m from a dump of old batteries (named CD-10 and CD-150 respectively). These plots are used for paddies but they were left fallow at the time of soil sampling.

Phung Xa village (Ha Tay province)

Phung Xa village, 25 km West of Hanoï city, is also specialized in metal recycling, namely zinc for galvanization of pipes and other steel pieces to protect them from corrosion. After dipping the steel elements into the bath of zinc, they are cleaned with water and the washing solution is discharged which can contaminate the surrounding area. Top soil samples were taken in plots at 10 and 150 m from the discharge of a galvanization factory (named PX-10 and PX-150 respectively). These fields were under fallow at the time of sampling.

Lang Hich mine (Thai Nguyen province)

The Lang Hich mine, situated in a hilly area 80 km far from the North of Hanoï city, is exploited for zinc and lead resources. The heavy metal ores are included in paleozoic limestone. The extraction process involves rock crushing and sieving by flotation, and the residual wet gangue is poured out in a neighbouring valley. Three mixed samples were collected around the mine: the first one (LH-GE) was taken nearby the exit of one of the mine galeries on rubble material covered by sparse vegetation; the second sample (LH-FR) was

collected on the fine-grained residues stored in the neighbouring valley; and the third mixed sample (LH-S) was collected from a soil plot at 10 m distance from the edge of this waste area.

Physico-chemical analyses

The collected samples were dried at 50°C and crushed to pass through a 2 mm sieve. Physico - chemical characteristics were carried out according to widely used laboratory procedures described in the extended soil analysis book by Page et al. (1996). The following characteristics were measured: particle size distribution (dispersion with ion-exchange resins, wet sieving for separating the sand fraction, and pipette method for separating the silt and clay fractions), pH of soil-water and soil-KCl suspensions (1:5 ratio), electrical conductivity (EC) of soil-water suspension (1:5 ratio), organic carbon (C_{org}, Walkley and Black method), total nitrogen (N_{tot}, Kjeldahl method), total phosphorus (P_{tot}, extraction with aqua regia), exchangeable Ca, Mg, K and Na and cation exchange capacity (CEC, extraction of exchangeable cations by 1M NH$_4$Ac, pH 7, desorption of NH_4^+ by 1M KCl), extractable H and Al for soils with $pH_{H2O}<7$ (extraction with 1M KCl), carbonate content for soils with $pH_{H2O}>7$, free Fe and Al oxides (DCB method). The total content in macro and micro elements was measured by ICP-AE spectrophotometry on liquid extracts after alkaline melting (with Li-metaborate and Li-tetraborate at 950°C) for macro elements and triacid attack (with HNO$_3$, HF, and HClO$_4$) for micro elements.

Selective extractions were used for assessing the zinc "mobility" in the collected samples, namely extraction with deionized water, extraction with CaCl$_2$ 0.01M, and extraction with Na$_4$-EDTA 0.05M, at 1:10 soil:solution ratio. After stirring the suspensions for 22 hours, they were centrifuged and filtered, and zinc was measured in the extracts by ICP-AE spectrophotometry. The extraction procedure was then repeated four times on the wet soil remaining in the centrifuge tubes.

3. RESULTS AND DISCUSSION

Sample characterization

The characteristics of the seven samples are presented in Table 1. Two samples from Chi Dao village showed similar physico-chemical properties as well as two samples from Phung Xa village. Three samples collected surrounding the Lang Hich mine were quite different. The clay content is about 35% in Chi Dao and 25% in Phung Xa. All four soil samples of these villages were slightly acidic and their CEC was in the range of 10 cmolc kg^{-1}. Two villages differed from each other by the trace element content in the collected samples. The soils from Phung Xa were more charged with Zn and Cr, whereas the soils from Chi Dao were much more charged with Pb and Cu. The total Zn content decreased only slightly with the distance from the presumed pollution source.

The pH values of Lang Hich soil samples were close to 8, which is related to the calcareous geological substrate in this mining area. Two samples coming from the exploited rock with more or less processing (LH-GE and LH-FR) have high carbonate content, whereas the neighboring soil (LH-S) is only slightly calcareous. This might be due to the surface contamination by the mined materials. The particle size analysis of these three samples was to be examined knowing that carbonate minerals were not dissolved prior to granulometric fractionation. Therefore, the clay fraction certainly contains much carbonate; this is corroborated with the low CEC values which would be expected to be higher if the fine-grained fraction mostly accounted for by clay minerals. High values of "exchangeable" calcium is also related to the same feature; CaCO$_3$ was partly dissolved in the extraction procedure with NH$_4$-acetate, so that the released Ca cannot be fully attributed to the exchange complex. Very high Zn and Pb content is found in the two samples collected from mining materials, and logically these heavy metals are much more concentrated in the raw rubble at the exit of the mine gallery (LH-GE) than in the fine-grained wastes (LH-FR) rejected after the extraction process. The soil plot only 10 m far from these wastes is slightly polluted by Zn and Pb, which corroborates with its low carbonate content also likely due to trace contamination with mine dust.

The total content in Ca, Mg, K, and Na is expressed in cmolc kg^{-1} (Table 1) for comparison with exchangeable forms; TRB (total reserve in bases) is the sum of these cations. TRB is very high in LH-GE and LH-FR samples, due to high total Ca content derived from the limestone substratum which obviously not only contains calcite but also dolomite as inferred from the total Mg content.

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Table 1. Physico-chemical charasteristics of the seven studied soil samples

Sample[a]	CD-10	CD-150	PX-10	PX-150	LH-GE	LH-FR	LH-S
Sand (%)	14.5	6.1	15.3	9.4	51.6	67.2	39.7
Silt (%)	53.0	55.2	60.7	60.9	25.5	26.8	28.8
Clay (%)	32.5	38.7	23.9	29.7	22.8	6.0	31.6
C_{org} (%)	1.9	2.9	4.6	2.9	3.1	0.7	1.1
N_{tot} (%)	0.17	0.24	0.31	0.26	0.20	0.01	0.10
P_{tot} (%)	0.10	0.11	0.06	0.04	0.17	0.02	0.04
pH_{H2O}	6.1	5.7	5.5	5.2	7.7	8.2	7.7
pH_{KCl}	5.3	4.6	4.8	4.5	7.4	8.6	6.6
CO_3^{2-} (%)	-	-	-	-	18.4	37.4	0.2
CE ($\mu S\ cm^{-1}$)	415	146	600	482	175	278	96
Ca_{ex} (cmolc kg^{-1})	8.94	7.74	7.66	6.96	23.01	34.94	8.20
Mg_{ex} (cmolc kg^{-1})	2.23	1.91	1.94	1.64	1.77	1.28	0.95
K_{ex} (cmolc kg^{-1})	0.13	0.15	0.18	0.15	0.09	0.05	0.14
Na_{ex} (cmolc kg^{-1})	0.64	0.28	0.83	1.15	0.07	0.16	0.06
CEC (cmolc kg^{-1})	9.56	9.32	10.23	7.21	4.71	0.20	3.76
H_{ex} (cmolc kg^{-1})	0.16	0.08	0.52	0.62	-	-	-
Al_{ex} (cmolc kg^{-1})	0.04	0.14	0.14	0.16	-	-	-
Fe_{DCB} (g kg^{-1})	20.7	17.2	9.2	8.9	20.6	1.3	29.7
Al_{DCB} (g kg^{-1})	1.24	0.96	0.48	0.49	1.21	0.07	3.84
Ca_{tot} (cmolc kg^{-1})	22.4	19.7	21.0	19.8	472.5	1238.6	13.0
Mg_{tot} (cmolc kg^{-1})	53.0	50.9	31.4	34.4	248.9	411.8	31.0
K_{tot} (cmolc kg^{-1})	48.9	48.1	31.5	37.1	29.9	15.7	36.7
Na_{tot} (cmolc kg^{-1})	25.6	20.7	21.9	19.9	2.5	2.8	3.2
TRB (cmolc kg^{-1})	150	140	106	111	754	1669	84
Fe_{tot} (g kg^{-1})	40.8	37.9	22.1	21.6	35.6	9.0	38.7
Al_{tot} (g kg^{-1})	73.5	81.4	50.0	59.0	31.0	14.5	48.7
Mn_{tot} (g kg^{-1})	0.84	0.25	0.24	0.16	1.40	1.00	0.36
Si_{tot} (g kg^{-1})	313	299	339	342	168	63	358
Ti_{tot} (g kg^{-1})	5.27	5.86	5.35	6.23	2.04	0.54	4.51
Zn_{tot} (mg kg^{-1})	243	200	639	584	49 757	6 918	246
Pb_{tot} (mg kg^{-1})	1 363	1 001	37	33	18 821	3 561	155
As_{tot} (mg kg^{-1})	16.2	12.8	5.2	10.4	74.2	30.2	16.2
Cd_{tot} (mg kg^{-1})	0.3	0.2	0.3	0.3	270.8	35.2	0.9
Cr_{tot} (mg kg^{-1})	71.0	77.9	218.2	132.9	37.1	14.3	48.3
Cu_{tot} (mg kg^{-1})	101.1	200.5	39.2	40.3	82.9	26.7	17.9
Ni_{tot} (mg kg^{-1})	36.4	38.0	22.4	26.0	43.2	9.0	12.9

[a]CD-10 and CD-150: Chi Dao, at 10 and 150 m from presumed contamination source; PX-10 and PX-150: Phung Xa at 10 and 150 m from presumed contamination source; LH-GE, LH-FR, and LH-S: Lang Hich on rubble at mine gallery exit, on fine-grained mining residues, and in neighboring soil

Table 2. Zn extracted with different reagents (results of five successive extraction runs, E1 to E5) and cumulated values (cumul) for the five extraction runs per soil mass unit and as a percentage of total Zn content

		Sample[a]	CD-10	CD-150	PX-10	PX-150	LH-GE	LH-FR	LH-S
H_2O extracts									
	E1	mg kg^{-1}	0.19	0.47	9.23	15.54	3.73	0.34	0.08
	E2	mg kg^{-1}	1.03	1.16	2.53	2.10	3.65	0.23	0.22
	E3	mg kg^{-1}	1.50	1.49	2.10	2.37	3.84	0.11	0.59
	E4	mg kg^{-1}	1.43	1.38	2.17	2.37	5.47	0.25	0.78
	E5	mg kg^{-1}	1.60	1.49	1.85	2.07	8.50	0.18	0.85
	cumul	mg kg^{-1}	5.75	5.99	17.89	24.45	25.19	1.11	2.53
	cumul	% Zn$_{tot}$	2.36	2.99	2.80	4.18	0.05	0.02	1.03
$CaCl_2$ extracts									
	E1	mg kg^{-1}	1.40	2.71	58.81	93.11	24.92	4.42	0.14
	E2	mg kg^{-1}	1.37	1.85	37.45	51.16	21.55	4.10	0.15
	E3	mg kg^{-1}	0.87	1.51	27.98	29.83	30.87	3.90	0.11
	E4	mg kg^{-1}	0.70	1.06	21.25	17.94	28.12	3.83	0.14
	E5	mg kg^{-1}	0.78	0.90	16.58	12.08	24.82	3.51	0.12
	cumul	mg kg^{-1}	5.12	8.02	162.1	204.1	130.3	19.76	0.66
	cumul	% Zn$_{tot}$	2.10	4.01	25.3	34.9	0.26	0.29	0.27
EDTA extracts									
	E1	mg kg^{-1}	43.73	16.32	334.6	265.1	9 533	966	41.46
	E2	mg kg^{-1}	10.75	3.97	45.51	30.07	4 922	269	6.03
	E3	mg kg^{-1}	3.97	1.77	10.32	8.36	2 506	202	2.27
	E4	mg kg^{-1}	3.06	2.10	5.89	4.76	1 828	178	1.55
	E5	mg kg^{-1}	2.15	1.14	5.49	4.43	1 620	159	1.17
	cumul	mg kg^{-1}	63.67	25.29	401.8	312.7	20 408	1 774	52.48
	cumul	% Zn$_{tot}$	26.2	12.6	62.8	53.5	41.0	25.6	21.3
Total Zn	Zn$_{tot}$	mg kg^{-1}	243.3	200.1	639.5	584.4	49 757	6 918	246.4

[a]*CD-10 and CD-150: Chi Dao, at 10 and 150 m from presumed contamination source; PX-10 and PX-150: Phung Xa at 10 and 150 m from presumed contamination source; LH-GE, LH-FR, and LH-S: Lang Hich on rubble at mine gallery exit, on fine-grained mining residues, and in neighboring soil*

Other properties listed in Table 1 are not be discussed further in this paper because most of them are less relevant in the present study on Zn pollution and mobility. Other research works on the same samples could be carried out in the future and might benefit from our detailed characterization. However, we will refer to some of these properties when needed to support our interpretation of the results on Zn mobility.

Zinc mobility

The results of the five successive Zn extractions by H_2O, $CaCl_2$, and EDTA are presented in Table 2 from which the cumulative extracted Zn and its percentage with respect to the total Zn content were calculated. The total Zn values are recalled in the last line of this table to facilitate the discussion.

The Zn concentration of samples from Chi Dao and Lang Hich did not show sharp decrease in values in the successive H_2O extracts, whereas clearly higher values were noticed in the first H_2O extraction on the two soils from Phung Xa. These soils have also higher electrical conductivity (Table 1), indicating high soluble salt content, including Zn salts, that are easily solubilized in the first extraction run. In further extractions for all seven materials, the low variations of Zn concentration might result from the requilibration of added water with less soluble Zn minerals that are far from being exhausted in this procedure. The Zn concentration in the successive $CaCl_2$ washings showed steady decreasing values for the soils from Chi Dao and Phung Xa, which is most likely due to the progressive removal of exchangeable Zn by renewed Ca solutions, involving Ca-Zn competition for the exchange sites. In the mined materials from Lang Hich (LH-GE and LH-FR), the Zn concentration in the $CaCl_2$ extracts did not change clearly with repeated washings. This might be related first to their high carbonate content; the released Zn is likely coming mainly from Zn forms occluded in a calcareous gangue that partly dissolves in $CaCl_2$ solutions; only small amounts of exchangeable Zn can be expected because of the low CEC values of these samples. The soil from Lang Hich (LH-S) releases very small amounts of Zn in the successive $CaCl_2$ extractions because of its low CEC value and low Zn content. As far as the EDTA extractions are concerned, all samples show sharply decreasing Zn concentration in the

successive extracts; EDTA clearly proves to be a very efficient reagent to mobilize a given Zn fraction which will be considered below.

In the following discussion, we concentrate on comparisons between the cumulative values of extracted Zn for the different samples and on the Zn forms that are expected to be mobilized by each of the three reagents having regard to the total Zn content.

The Zn amount extracted with water of Phung Xa soils was higher than Chi Dao ones. The difference is not only due to higher easily soluble salt content in Phung Xa as mentioned above, but also to the higher total Zn content in these soils, which results in similar percentage of Zn extracted with water regarding total Zn content in the four soils (2.4 to 4.2%). This Zn fraction could be easily mobilized by rain, and rather high Zn concentrations are expected to be found in runoff water in the study fields of Phung Xa. Also, if these plots are submerged for rice cultivation, high Zn concentration can likely be found in drainage water, which can represent an awkward source of pollution for the neighbouring environment and for human health. In the mining materials from Lang Hich, the percentage of Zn mobilized by water only amounts to 0.02 and 0.05% of the total Zn content. However, as the raw rubble at the mine exit has a very high Zn content, the Zn amount that can be mobilized just by rain is a delicate question mainly for the mine workers who handle the original Zn ore. The Zn concentration in the leaching water of the fine-grained residues after ore processing and of the neighbour soil is lower than in all other studied samples.

The Zn amount extracted with $CaCl_2$ can logically be understood as the sum of soluble Zn and the Zn from the exchange complex that can be desorbed by Ca in the conditions of the experiments (low $CaCl_2$ concentration, high solution : soil ratio, five extraction runs). However, in the soils from Chi Dao, the amounts of Zn that are extracted with water and with $CaCl_2$ are nearly similar. This may be due to the fact that the amounts of Zn extracted in the two procedures (5.1 to 8 mg kg^{-1}, i.e. 0.016 to 0.025 cmolc kg^{-1}) represent only a very small fraction of the exchange capacity (CEC = 9.6 and 9.3 cmolc kg^{-1} for these two soils). The difference in the two procedures is that $CaCl_2$ is more efficient than water to extract Zn in the first extraction runs because of the competing effect of Ca for the

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exchange complex, and also likely because of the salt effect on the pH of the extract. The pH values were about 0.8 to 1 unit lower in $CaCl_2$ extracts than in H_2O extracts (data non shown), which can result in some dissolution of alkaline Zn forms in the presence of $CaCl_2$. As compared to the total Zn content, the forms mobilized by water or $CaCl_2$ remain low, which corroborates the fact that Zn in the soils from Chi Dao is most likely included in minerals and does not mainly originate from the exchange complex.

In the soils from Phung Xa, the amounts of Zn released by $CaCl_2$ are much higher than the amounts extracted with water; in terms of charge equivalent, the exchangeable Zn displaced by Ca represents 0.50 and 0.63 cmolc kg^{-1} for CD-10 and CD-150 samples respectively, i.e. 4.9 and 8.7% of the cation exchange capacity. And the exchangeable Zn accounts for 25 and 35% of the total Zn content in these samples, which is by far higher than in the other five samples. We can assert, than in the study plots of Phung Xa, huge quantities of Zn can be mobilized just by cation exchange processes and consequently by cation fertilizers such as potassium and magnesium. Exchangeable cations are the most available nutrient forms for plant uptake, so that we can expect high Zn concentration in the growing vegetation and high contamination hazard of the food chain.

In the samples from Lang Hich, the Zn extracted with $CaCl_2$ represents less than 0.3% of the total Zn content. For the soil sample (LH-S), the same comments can be made as well as two soils from Chi Dao. In the mining materials, despite much higher values of total Zn than in Phung Xa, the Zn released by $CaCl_2$ is lower because most part of Zn is occluded in calcareous material, as discussed above, and is not in an exchangeable form. The much higher efficiency of $CaCl_2$ to extract Zn as compared to water should be attributed to the dissolution of carbonate minerals by the salt effect of the $CaCl_2$ reagent (increasing mineral solubility due to increasing ionic strength and consequent decreasing ion activity coefficients) and also by the enhanced deprotonation of variable charge constituents such as organic matter.

The EDTA molecule, with four carboxylic groups, is a very efficient chelating agent for polyvalent cations. Therefore, it acts as a sink for cations such as Ca and Zn (of most interest in the present study) when these cations are released into the solution phase. This results in a very large increase of Ca- and Zn-mineral solubility. Also, the cation exchange processes are much affected by introducing EDTA in the solution. As the stability of Zn-EDTA complex is higher than the stability of Ca-EDTA complex (Skoog and West, 1982), Zn is selectively desorbed with respect to Ca. The EDTA molecules also compete with the humic substances to pick up cations from the exchange sites of these organic components. It is expected that part of the Zn linked to organic constituents was not desorbed by Ca at the low concentrations used in this study.

For all samples, the Zn extracted with EDTA is much higher than with $CaCl_2$. The effect is the most spectacular for the samples from Lang Hich for which the amount of Zn extracted with EDTA is around 100 times greater than the amount of Zn extracted with $CaCl_2$. This is clearly due to an enhanced dissolution of carbonate minerals in the presence of EDTA and to consequent release of Zn which is trapped by EDTA. The lowest relative effect of EDTA, compared to $CaCl_2$, is noticed in the soils from Phung Xa (extraction of Zn is only 2.5 ad 1.5 times greater with EDTA than with $CaCl_2$). This is a clear confirmation that, in these soils, a much higher proportion of Zn than in the other materials is adsorbed by the exchange complex and is rather easily displaced by Ca. In the soils from Chi Dao, EDTA is also clearly more efficient than Ca for releasing Zn, which supports the comments made on the similarity of the amounts of Zn extracted with water and $CaCl_2$. An important fraction of Zn should be associated wih Zn-minerals and much less to the exchange complex. As far as contamination hazards are concerned, the EDTA reagent could be compared to root exudates, although the chelating efficiency of organic acids released in the rhizosphere is expected to be somewhat lower because they contain less carboxylic groups than EDTA molecules (review in Dakora and Phillips, 2002). Moreover, the concentrations of root exudates with respect to soil mass is much lower than the amount of EDTA involved in successive extractions employed. Nevertheless, the fraction of Zn released by EDTA can give some indication of potentially mobilizable Zn at long term in plots covered by vegetation, and long term contamination risk of the food chain.
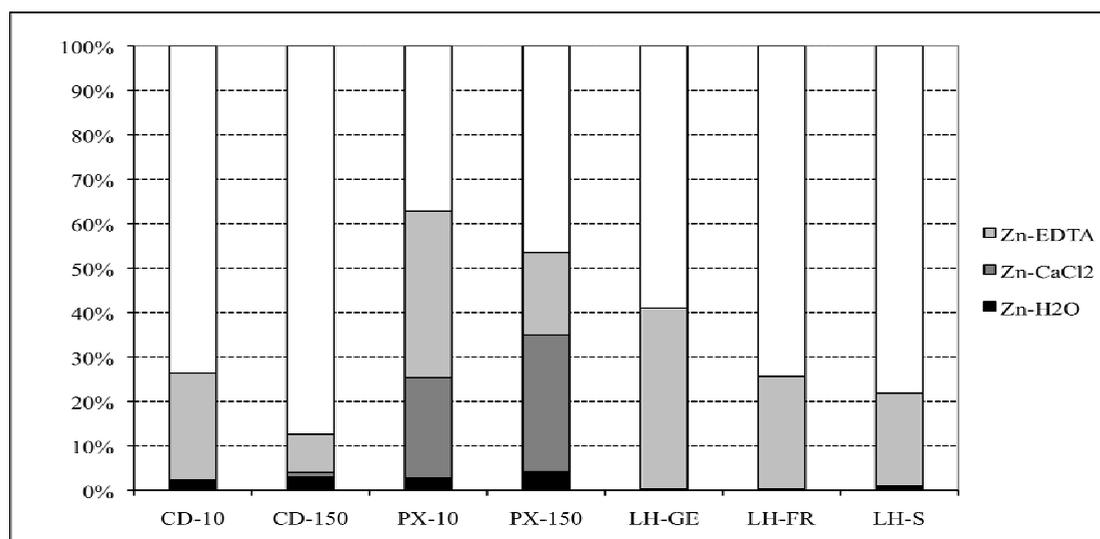
Figure 1. Zn fractions specifically mobilized par H₂O, CaCl₂, and EDTA as a percentage of total Zn content in the 7 studied samples (CD-10 and CD-150: Chi Dao, at 10 and 150 m from presumed contamination source; PX-10 and PX-150: Phung Xa at 10 and 150 m from presumed contamination source; LH-GE, LH-FR, and LH-S: Lang Hich on rubble at mine gallery exit, on fine-grained mining residues, and in neighboring soil)

Figure 1 summarizes our data of the selective Zn extractions with respect to total Zn content, in terms of the specific fractions mobilized by the three reagents, i.e., beside Zn specifically mobilized by water, we consider that Zn specifically moblized by $CaCl_2$ = total Zn_{CaCl2} - total Zn_{H2O}, and Zn specifically mobilized by EDTA = total Zn_{EDTA} - total Zn_{CaCl2}. This figure clearly shows the proportions of total Zn that can be considered as highly mobile (Zn-H₂0), slowly mobilizable (Zn-CaCl₂), and potentially long-term mobilizable (Zn-EDTA). This figure will help to draw the conclusions below.

4. CONCLUSIONS

In Chi Dao village, the Zn amounts that can be mobilized from soils in short and long term is lower than in Phung Xa and in the mining materials from Lang Hich, mainly due to the lower total Zn content of which only a small fraction occurs in soluble and exchangeable forms. This does not mean that the environmental risks linked to battery recycling are limited. Indeed, very high Pb concentrations are detected in the surrounding soils, as well as high Cu concentrations. Further studies

should concentrate on the mobility of these elements.

The results on the soils from Phung Xa raises a serious question of Zn contamination hazard for the soil environment and human health, as inferred from the amount of exchangeable Zn and from its proportion in the total Zn content. The waste waters coming from the local Zn-coating enterprises should not be released to the environment without any purification process. Another environmental risk is linked to the high Cr concentrations in these soils.

In the mining materials of the Lang Hich mine, even if the exchangeable Zn fraction might be considered as negligible, it is not to forget that the total Zn content is very high of which a significant fraction can be released to the environment in the long term. This stresses on the need to carefully consider the problem of the storage of mine rubble and processing by-products to avoid Zn release when they are exposed to natural acid sources. The vegetation growing on these materials involves evident risks of food chain contamination. These mining materials also raise the question of environmental pollution by Pb and Cd heavy metals which are also found in high concentration in the mine substratum.

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