Mobility of selected trace elements in Mediterranean red soil amended with phosphogypsum: experimental study

Lina Nafeh Kassir, Talal Darwish, Amin Shaban, Bruno Lartiges & Naim Ouaini

⚘ Springer

Springer

Mobility of selected trace elements in Mediterranean red soil amended with phosphogypsum: experimental study

**Lina Nafeh Kassir · Talal Darwish ·
Amin Shaban · Bruno Lartiges · Naim Ouaini**

Abstract Soil amendment by phosphogypsum (PG) application becomes of increasing importance in agriculture. This may lead, however, to soil, plant, and groundwater contamination with trace elements (TEs) inherently present in PG. Monitoring of selected TEs (Pb, Zn, Cu, and Cd) distribution and mobility in a Mediterranean red soil profile has been performed in soil parcels applied with PG over a 16-month period. Concentrations were measured in soil and plant samples collected from various depth intervals at different points in time. TEs sequential extraction was performed on soil and PG samples. Results showed soil profile enrichment peaked 5 months after PG application for Cd, and 12 months for Pb, Zn, and Cu. Rainwater, pH, total organic carbon, and cationic exchange capacity were the main controlling factors in TEs accumulation in soils. Cd was transferred to a soil depth of about 20 cm. Zn exhibited mobility towards deeper layers. Pb and Cu were accumulated in around 20–55-cm-deep layers. PG increased the solubility of the studied TEs; PG-applied soils contained TEs bound to exchangeable and acid-soluble fractions in higher percentages than reference soil. Pb, Zn, and Cu were sorbed into mineral soil phases, while Cd was mainly found in the exchangeable (bio-available) form. The order of TEs decreasing mobility was Zn>Cd>Pb>Cu. Roots and leaves of existed plants, *Cichorium intybus* L., accumulated high concentrations of Cd (1–2.4 mg/kg), exceeding recommended tolerable levels, and thus signifying potential health threats through contaminated crops. It was therefore recommended that PG should be applied in carefully established, monitored, and controlled quantities to agricultural soils.

L. N. Kassir · N. Ouaini
Faculty of Sciences, URA GREVE CNRS/USEK/UL,
University of Holy Spirit Kaslik,
BP 446, Jounieh, Lebanon

L. N. Kassir (✉) · B. Lartiges
Laboratoire Environnement et Minéralurgie
(LEM–ENSG/CNRS–INPL),
Institut National Polytechnique de Lorraine - Nancy,
BP 40-54 501, Pole de l'Eau, 15, Avenue du Charmois,
Vandoeuvre, France
e-mail: rmelkassir@darbeirut.com

T. Darwish · A. Shaban
Centre of Remote Sensing,
National Council for Scientific Research, CNRS,
P.O. Box 11-8281, Riadh El Solh,
11072260 Beirut, Lebanon

Introduction

Phosphogypsum (PG) is a by-product of the phosphate fertilizer industry that results from the wet process of phosphate rock. It may contain large amounts of trace elements (TEs), fluorine, and radionuclides (e.g., ^{226}Ra and ^{210}Po), which can be toxic to the environment (Rutherford et al. 1994; Burnett et al.

1999; Senesi et al. 1999), depending on the origin of the phosphate rock. Worldwide, there is a widespread production of PG, estimated at 100 to 280 Mt/year (Parreria et al. 2003).

Most of the PG produced worldwide is usually disposed of in stockpiles. Alternative practical options for eliminating this waste have been sought; its consumption in agriculture as soil amendment agent has been widely investigated (Conkline 1992; Arocena et al. 1995). PG is widely used with an estimated amount of about 150 Mt/year (Prud'home and Sukalac 2006).Thus, studies have been conducted on the use of PG in improving the soil composition to enhance crop yield (May and Mortvedt 1986; Mullins and Mitchell 1990), reducing soil erosion, and increasing the levels of available S and P (Zhang et al. 1998; Delgado et al. 2002). However, such practices are limited due to PG content of toxic TEs and radionuclides, the leaching processes of which may transfer them to the soil, hence to the food chain (Rutherford et al. 1994; Al-Masri et al. 1999; Al-Oudat 1999). Indeed, Al-Masri et al. (2004), indicated that Cu, Zn and Cd could be transferred from PG into water and subsequently to the soil horizons, which should be considered when PG is used as an amendment to agriculture soils.

TEs can accumulate in plants and groundwater, depending on their mobility (Kabata-Pendias and Pendias 2001). In fact, TEs can be associated with a range of soil components (e.g., organic matter, clays, Fe and Mn oxides, lattice of silicate or carbonate minerals) that have a different ability to hold or release TEs (Tessier et al. 1979; Ure et al. 1993; Alloway 1995). Determination of different forms and phases of a TE, referred to as speciation, is primordial to link with the potential bioavailability of this element.

The regulations in Lebanon allow the use of PG as soil amendment without any restrictions (2004 Law 444 of the Ministry of the Environment). No attention has been paid to its TEs content and the risk of their transfer to the food chain. Consequently, it would be of vital importance to evaluate the impact of soil amendment with PG and establish measures to ensure acceptable levels of TEs in the soil matrix and agriculture products. It would therefore be necessary to evaluate the presence of TEs in plants and thus in the food chain as a whole.

Earlier studies focused on the radiological effects of the PG in agriculture (Alcordo et al. 1999;

Papastefanou et al. 2006; Abril et al. 2008). A gap remains in understanding the effects of such amendment on TEs mobility and transfer in the soil profile. In Spain, for example, in studying the cumulative effect of the amendment of PG on the uptake of elements and isotopes by tomatoes (*Lycopersicum esculentum*), Abril et al. (2008) showed a possible direct effect of PG amendment in increasing Cd levels in tomato crops, which was less than the permissible limit (50 ppb).

A recent study on the effect of phosphate industry emissions on soils contamination showed that PG had the highest contribution in TEs input into the surface soil (Kassir et al. 2011). Results had suggested that soil contamination with TEs carried with PG (and phosphate) particulates could be potentially hazardous to plants and ground waters. Nevertheless, further investigations on the behaviors, forms, and dynamics of these TEs in the soil had been recommended to better assess their risk factors.

It follows that focus on the time variation aspect of TEs mobility following PG application on soil has been considered in this study. Furthermore, roots and aerial parts of plants in the studied PG-applied soil were also analyzed for TEs content at different time intervals.

This study aimed to (1) determine the concentrations of TEs (Cu, Pb, Zn, and Cd) distribution in soil profile after the application of PG, (2) evaluate the variation of TEs mobility with time, (3) measure TEs concentration in roots and aerial parts of the plant, and (4) determine the factors controlling TEs mobility and accumulation.

Materials and methods

Field site and soil sampling

The study area, where the experimental site was selected, is located off the Mediterranean east coast, in north Lebanon, and extends over 100 km^2 of agricultural lands. It is almost surrounded by mountainous land, notably from the east. The region has a Mediterranean climate with intensive precipitations between January and May (600–900 mm). Meteorological data for the sampling period (May 2008–November 2009) were obtained from the Meteorological Department at Lebanon airport. Residential,

commercial, or industrial buildings are rare in this area, while agriculture land (47.3% of the study area) is more widespread than natural vegetation. Agriculture is mainly dominated by plantations of olive trees, which is the main crop of the study area. According to Darwish et al. (2005), the study region was dominated by a well-drained red soil classified as an association of Gleyic and Vertic Luvisols. The texture of the soil is clay (sand 24%, silt 20%, and clay 56%) with a calcium carbonate content reaching 22%. Despite its clay loamy texture, the red Mediterranean soil is distinguished by a strong granular surface structure and porosity promoting intermediate and high soil permeability. Drainage is improved by dominant gravel content and the type of underlying lithological rock known for fissures and karsts development (Darwish and Zurayk 1997). The organic matter content is low (1.3%). Soil profile is constituted by three horizons (A, B, and C). The thickness of the A and B horizons is approximately 55 cm. Stoniness is common with 30% to 40%. Medium to coarse subangular and angular blocky aggregates represent the strong structure of the soil. Common fine to medium roots are also found. Common plants growing between olive trees were of *Cichorium intybus* species.

The field site composes of a land frame of about 256 m^2. The study plot was divided into 24 separate parcels of 1 m^2 each spread over a surface of 49 m^2 and separated by distances of 75 cm. Each parcel was delimited with a wood frame of $1 \times 1 \times 0.15$ m (length$\times$width$\times$height). To simulate the potential source of pollution originating from PG-amended soils, 1 kg of PG, collected from the Lebanese fertilizer plant, was dispersed on the soil surface in every parcel over a surface of 0.5 m$\times$0.5 m, without homogenization with the soil. This initial PG application was done in May 2008. A reference parcel was left without amendment.

Coring was carried out to a depth of 60 cm, using a high power (2,500 W) motor of type Cobra TT. The core shaft used was 100-cm long, 6 cm in diameter. The first sample was cored from the reference parcel (not amended with PG), labeled R. Then, sample coring had been successively performed in three different parcels labeled P_1, P_2, and P_3 at three different subsequent dates: T1=5, T2=12, and T3= 16 months after the initial application and sampling from the reference plot (T0). Sampling times with corresponding weather data (temperature, humidity, and rain) for each coring are indicated in Table 1. Samples were collected from the cored cylindrical soil blocks at 5-cm intervals to a depth of 20 cm, then 15-cm intervals to a final depth of 55 cm. Accordingly, plant roots and leaves were also collected, simultaneously with soil samplings, from each parcel.

Sample preparation and analytical methods

Soil samples were oven-dried at 50°C, sieved to pass a 2-mm sieve, and ground to a fine powder using an agate pestle and mortar. Vegetation samples were washed in ultra-pure water, dried at 60°C and ground to a fine powder using an agate pestle and mortar. Therefore, the following procedures were applied: I— soil pH was determined in a ratio of 1:5, soil/ionized water suspension, according to AFNOR X 31-103. II—total organic carbon (TOC) in soil samples was determined using elemental analyzer of type Flash EA1112 NC. III—cation exchange capacity (CEC) of the soil was measured by displacing the exchangeable cations with a solution of cobalthexamine chloride. The displaced cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) were determined by flame atomic absorption spectroscopy (AAS—Analytical Gena Zeenit 700) and the summation is the cation exchange capacity. IV—TEs were measured using inductively coupled plasma mass spectroscopy (ICP-MS X7) "ThermoFisher", after melting the samples and PG with lithium metaborate, and dissolution of the melt in diluted nitric acid. Analysis was conducted in an accredited laboratory SARM (CRPG, Nancy). V—vegetation and reference soil samples (IAEA-405) were accurately weighed to approximatly 0.25 g directly in microwave PTFE vessels and subjected to 1 mL H_2O_2 (30%) and 9 mL concentrated HNO_3 (65%). The digestion program itself consisted of a 10-min gradual increase in temperature to 200°C, a 15-min step at 200°C (1,000 W; 10^6 Pa), and then a stage of ventilation cooling. The digests were filtered through a 0.45-μm filter and analyzed using atomic absorption spectroscopy to determine the content of Pb, Zn, Cu, and Cd in roots and plant leaves.

Soil samples from depth intervals within 0–20 cm were mixed and homogenized for subsequent speciation along with samples from 20- to 35-cm and 35- to 55-cm intervals. The sequential extractions were carried out progressively on an initial weight of 5 g in

Table 1 Sampling times and between-sampling periods weather data

Time	Temperature (°C)		Relative humidity (%)		Wind		Rain (mm)	Cumulative rain (mm)
	Min	Max	Min	Max	dd (°)	ff (m/s)		
PG amend. (30 Apr 08)								
May 08	12.1	29.3	30	89	320	16	9.3	
June 08	17.1	31.9	26	89	60	16	0	
July 08	20.5	33.7	28	89	260	12	0	15.4
Aug 08	21.9	33.4	33	87	240	13	2	
Sep 08	20.7	31.5	38	86	300	15	4.1	
P1 sampling (30 Sep 08)								
Oct 08	14.1	35.8	27	91	280	13	75.7	
Nov 08	9.8	26.9	18	92	340	13	85.1	
Dec 08	4.1	23.5	32	94	340	23	167.9	
Jan 09	2.9	21.3	27	94	120	13	100.5	768
Feb 09	6.8	22.1	14	99	300	23	183.4	
Mar 09	6	26.5	21	98	90	22	115.8	
Apr 09	8.4	32.2	13	99	240	22	39.6	
P2 sampling (30 Apr 08)								
May 09	12.8	36.5	10	98	240	26	2.4	
June 09	16.2	36.3	24	99	230	14	1.6	4
July 09	19.8	36.7	16	96	260	17	0	
Aug 09	22.1	34.7	35	95	260	15	0	
P3 sampling (31 Aug 09)								

polypropylene centrifuge tubes of 50 mL. Five TEs fractions were separated in five steps as follows: I—exchangeable form (F1) with 40 mL of 1 MMg $(NO_3)_2$; II—acid-soluble form (F2) extracted by 40 mL of 1 M CH_3COONa adjusted to pH 5 with CH_3COOH; III—reducible form (F3) extracted by 20 mL of Na citrate (78.4 g/L) and 20 mL of $NaHCO_3$(9.82 g/L), then adding 1 g of $Na_2S_2O_4$ (80°C for 4 h); IV—oxidizable form (F4) extracted by adding 8 mL of HNO_3 (0.02 M) and 20 mL of H_2O_2 (35%) in small aliquots then 12 mL of 3.2 M CH_3COONH_4 in nitric acid (85°C for 2 h); and V—residual form (F5) extracted by 40 mL HNO_3 (65%). Each extraction step was followed by centrifugation of the mixtures at 5,000 rpm for 30 min, and the solutions were separated from the solid residues. Liquors were first filtered using a membrane filter of ester cellulose of 0.45 μm porosity. All the solutions were stored in polyethylene vials at 4°C after which it was analyzed by AAS to determine the content of Pb, Zn, Cu, and Cd in each extracted fraction. In order to monitor analytical accuracy and precision, reagent blanks and a standard sediment reference (IAEA-405) were analyzed (47.7:52.21, 74.8:81.2, 279:256.1, and 0.73:0.81 mg/kg—recommended/analyzed for Cu, Pb, Zn, and Cd, respectively). Another check of extraction procedure was made by comparing the sum of the five steps from the sequential extraction procedure with the total metal analysis from the digestion procedure and calculating of the percentage recovery of the sequential extraction procedure as follows:

Recovery %

$$= (F1 + F2 + F3 + F4 + F5/\text{total element analysis}) \times 100$$

Where F is the TE fraction.

Mineralogical analysis

X-Ray diffractograms (XRD) were recorded using a D8-Brucker diffractometer (cobalt radiation source, $\lambda = 1.788965$ Å). The diffractometer is equipped with $(\theta, 2\theta)$ goniometer and position-sensitive detector.

Reflections were collected in ambient conditions within [3–65°] 2θ range, with 0.036° step width and 3-s collecting time. Homogenized PG and ground reference soil samples, of about 500 mg each, were deposited on plexiglass discs, 2 cm in diameter, as sub-compacted powder forming 1-mm-thick layers.

Statistical analysis

ANOVA tests were performed on the samples data of TE concentrations and pH values obtained for the soil profile in all parcels. The objective of this statistical analysis was to test the influence of time and depth intervals on TEs uptake and spatial distribution along the soil profile. The data was therefore distributed in different levels of two categories: time (R, P1, P2, and P3) and depth (horizons 0–5 cm, 5–10 cm, etc.). When significant differences were found, a multiple comparison of mean values was carried out by the Walker–Duncan test ($P<0.05$). Normality of variances was examined by the Shapiro–Wilk test before running ANOVA. Correlation analyses (Pearson r) were carried out between TE concentrations in soil, soil characteristics, and TE concentrations in plant roots and leaves. All statistical analyses were performed using SPSS version 17.

Results

Soil background values: reference parcel

The mineralogical results (XRD) showed that the background soil contained quartz (SiO_2), calcite ($CaCO_3$), kaolinite, montmorillonite as clay minerals, anatase (TiO_2), and hematite (Fe_2O_3). The soil pH showed alkalinity (8.23 ± 0.12), and the cation exchange capacity (CEC) exhibited relatively high values (31.06 ± 0.5 cmol/kg of dry weight) with a dominance of calcium ions at the exchange sites. The TOC% was found low (3.17 ± 0.03).

The average background soil contained relatively low concentration in Cd (0.28 mg/kg) and high Zn concentration (101.41 mg/kg). As for Cu and Pb, their average concentrations were found to be 35.15 mg/kg and 11.57 mg/kg, respectively. No significant differences were found in TEs distribution with depth (down to 55 cm), except in the layer (35–55 cm) where Cu and Pb concentrations decreased (Table 2).

The chemical speciation of the studied TEs in the reference soil showed their main association with Fe and Mn oxides and hydroxides (reducible fraction F3) (64%, 45%, 43%, and 13% for Cd, Pb, Zn, and Cu, respectively) and inside the structure of clays (residual fraction F5) (63%, 56%, 23%, and 11% for Cu, Zn, Pb, and Cd, respectively). This partition of the studied elements is due to the soil nature (Luvisol) with a dominance of clays and iron oxides. In addition, Cu was accumulated in the oxidizable fraction (F4) (20%).

Characterization of PG amendment

XRD results of PG showed that the main peak recorded in the diffractogram was gypsum ($CaSO_4\cdot2H_2O$) and to a lesser extent bassanite ($CaSO_4\cdot1/2H_2O$) and anhydrite ($CaSO_4$). The measured pH value of 6.51 ± 0.5 showed slight acidity of the PG sample.

The total concentration of the studied elements (Cu, Zn, Pb, and Cd) in the Lebanese-manufactured PG showed that Zn was the most abundant TE (123.60 mg/kg), with the lowest concentration being for Pb (2.46 mg/kg). Copper and cadmium concentrations were found to be 5.13 and 3.44 mg/kg, respectively.

According to the sequential extractions of TEs in PG, however, results of PG speciation showed that the studied metals (Pb, Cu, Zn, and Cd) were generally present inside the gypsum lattice (F2) (30%, 47%, 28%, and 54%, respectively). Moreover, part of these TEs mass (30%, 18%, and 32% for Zn, Pb, and Cu, respectively) was bound with organic matter (F4) incorporated within the PG. In addition, Pb was also found in the residual fraction (F5) (46%), Cd in the reducible fraction (F3) (20%), and Zn in silica fraction (F5) (36%).

Variation of total concentrations in soil profile

To analyze the PG-originated TEs transfer in soil with time, the concentrations of Cd, Zn, Pb, and Cu in different soil horizons were plotted against time for the reference parcel R at T0 and incubated parcels P1, P2, and P3 (corresponding to T1=5-, T2=12-, and T3=16-month period). The time axis was started at the date when the PG was just applied on the study parcels; the corresponding metal concentrations at the

Table 2 Trace elements concentrations and pH values in parcels R, P1, P2, and P3 at different depth intervals with ANOVA test for concentration and pH variations (P is for significant difference with time and P' with depth)

Element	Depth (cm)	R±SD (mg/kg)	P1±SD (mg/kg)	P2±SD (mg/kg)	P3±SD (mg/kg)	P (ANOVA)	Parcel average	P' (ANOVA)
Cu	0–5	34.10±0.28	35.62±0.26	39.64±0.11	39.44±0.42	0.000**	37.20±0.27	0.035**
	5–10	36.96±0.13	38.73±0.11	39.49±0.23	38.25±0.32	0.000**	38.36±0.20	
	10–15	34.85±0.25	35.54 ±0.26	39.38±0.35	37.41±0.25	0.001**	36.80±0.28	
	15–20	36.10±0.78	36.71±0.8	39.90±0.32	32.12±0.48	0.001**	36.21±0.60	
	20–35	38.32±0.21	40.19±0.31	41.71±0.81	41.09±0.48	0.010**	40.33±0.45	
	35–55	30.54±0.33	43.07±0.28	39.26±0.18	40.62±0.28	0.000**	38.37±0.27	
	Depth average	35.15±0.33	38.31±0.34	39.90±0.33	38.16±0.37	0.025*	–	
Cd	0–5	0.28±0.04	0.56±0.05	0.38±0.04	0.32±0.03	0.045*	0.37±0.04	0.122
	5–10	0.27±0.05	0.60±0.03	0.42±0.04	0.27±0.04	0.033*	0.39±0.04	
	10–15	0.28±0.04	0.66±0.04	0.3±0.05	0.24±0.04	0.038*	0.37±0.04	
	15–20	0.28±0.03	0.55±0.04	0.32±0.03	0.29±0.02	0.041*	0.35±0.03	
	20–35	0.30±0.03	0.28±0.02	0.31±0.05	0.38±0.04	0.047*	0.31±0.04	
	35–55	0.24±0.04	0.36±0.05	0.34±0.02	0.34±0.04	0.046*	0.31±0.04	
	Depth average	0.28±0.04	0.5±0.04	0.35±0.04	0.31±0.04	0.000**	–	
Zn	0–5	98.61±1.20	109.16±1.47	118.37±2.64	107.58±3.01	0.001**	108.43±2.08	0.223
	5–10	97.08±3.90	114.94±1.64	116.63±1.17	100.39±2.28	0.002**	107.26±2.25	
	10–15	104.49±2.42	114.07±1.93	115.77±2.02	94.86±3.10	0.001**	107.30±2.37	
	15–20	104.87±1.93	108.00±2.54	112.58 ±3.22	88.69±3.12	0.001**	103.54±2.70	
	20–35	99.96±2.32	106.83±2.45	117.24±2.31	110.29±1.85	0.000**	108.58±2.23	
	35–55	103.42±2.66	110.66±2.77	113.98±2.66	106.25±2.90	0.000**	108.58±2.75	
	Depth average	101.41±2.41	110.61±2.13	115.76±2.34	101.34±2.71	0.000**	–	
Pb	0–5	11.86±0.13	12.78±0.12	17.60±0.11	16.37±0.23	0.012**	14.65±0.15	0.002**
	5–10	12.92±0.20	14.13±0.10	16.48±0.13	12.82±0.13	0.000**	14.09±0.14	
	10–15	12.10±0.16	12.54±0.18	16.46±0.16	11.37±0.19	0.000**	13.12±0.17	
	15–20	11.55±0.29	12.61±0.09	16.53±0.29	10.07±0.19	0.000**	12.69±0.22	
	20–35	11.72±0.10	12.57±0.30	14.56±0.23	12.68±0.30	0.001**	12.88±0.23	
	35–55	9.25±0.18	12.66±0.32	11.28±0.16	11.70±0.40	0.001**	11.22±0.27	
	Depth average	11.57±0.18	12.88±0.19	15.49±0.18	12.50±0.24	0.012**	–	
pH	0–5	8.23±0.17	7.56±0.13	7.82±0.06	7.87±0.05	0.019**	7.87±0.10	0.549
	5–10	8.27±0.21	7.69±0.04	7.94±0.07	7.94±0.11	0.043*	7.96±0.11	
	10–15	8.21±0.12	7.74±0.11	8.02±0.06	7.92±0.08	0.036*	7.97±0.09	
	15–20	8.20±0.14	7.72±0.06	8.00±0.03	8.15±0.08	0.018**	8.02±0.08	
	20–35	8.24±0.11	7.75±0.14	7.99±0.06	8.04±0.01	0.030*	8.01±0.08	
	35–55	8.31±0.04	7.93±0.02	8.04±0.04	8.07±0.03	0.001**	8.09±0.03	
	Depth average	8.24±0.13	7.73±0.08	7.97±0.05	8.00±0.06	0.000**	–	

* Significant difference at the 0.05 level, ** significant difference at the 0.01 level

different depths represent the soil background concentrations (Fig. 1 and Table 2). Moreover, Table 2 shows the statistical analyses performed on the samples data of TE concentrations and pH values obtained for the soil profile in all parcels. It includes the mean and standard deviation for each set of samples, and the P value for the parcels data collected for each soil horizon.

It could be seen from Fig. 1, for the overall depth, that TEs showed different periods for reaching their peak concentration values. Peaks for TEs occurred in P1 for Cd (in September) and P2 for Zn
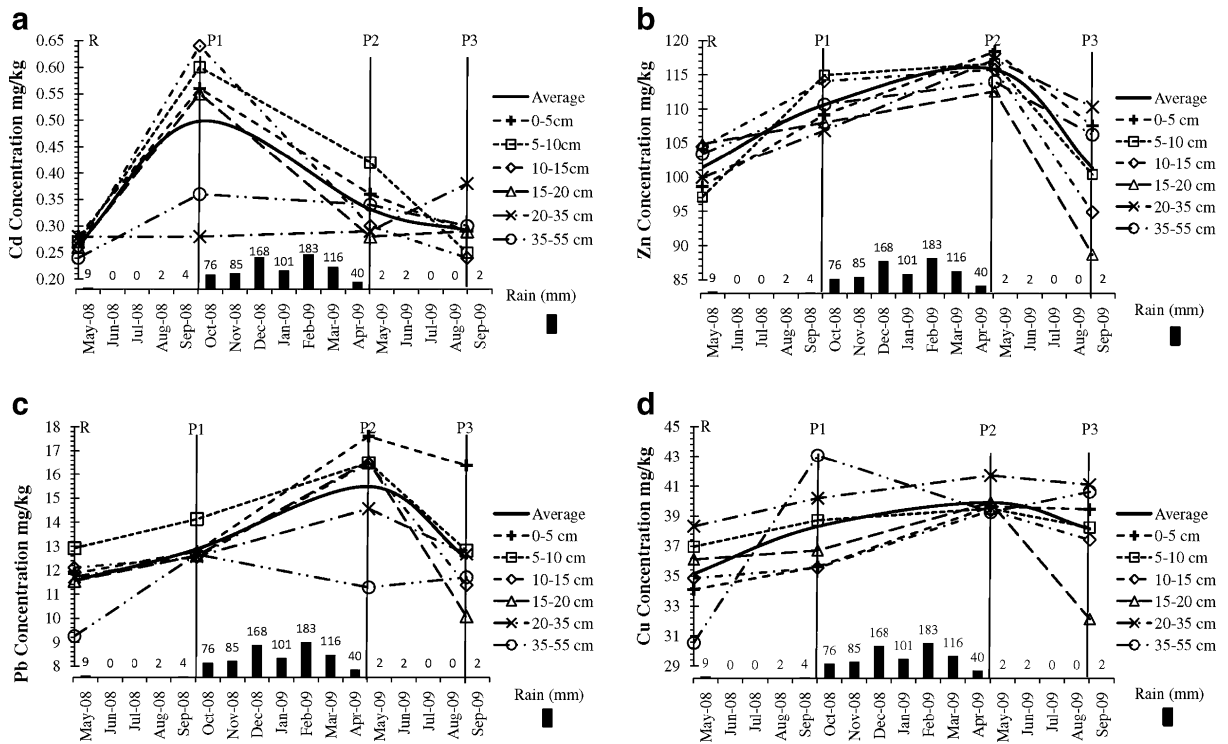
Fig. 1 **a–d** Time variation of trace element concentrations in the soil profile

and Pb (in April) before it decreased gradually with time (spring–summer) to reach a minimum value in P3 (in August) within the initial background range (Fig. 1a–c). The time variation of Cu concentrations over the studied depths exhibited a generally steady function (Fig. 1d) increasing at a slight rate with time.

Following PG amendment, a general increase of TEs concentration could be observed. During the rainy period (October–April), Cd concentration decreased (0.5 to 0.35 mg/kg) (Fig. 1a), whereas Zn, Pb, and Cu concentrations were generally increasing at almost all depths (110.61 to 115.76, 12.88 to 15.49, and 38.31 to 39.90 mg/kg, respectively) (Fig. 1b–d). However, in the deeper layers (35–55 cm), Pb and Cu concentrations decreased ($P < 0.01$) while Zn concentration showed no significant difference between parcels in this particular layer. Cd concentration displayed a significant difference ($P < 0.05$) between parcels (R, P1, P2, and P3) only in the upper layers (0–20 cm). A general remarkable decrease in TEs concentrations was observed over the study period in the layer (10–20 cm) particularly over the spring–summer period.

Metals mobility in soil

In order to assess the chemical form of TEs and thus their mobility and potential risk on the environment, speciation of Cu, Cd, Zn, and Pb were performed in all parcels (R, P1, P2, and P3).

The time variations of concentrations of TEs in the chemical fractions (F1, F2, F3, F4, and F5) at the different study depths (0–20 cm, 20–35 cm, and 35–55 cm) were plotted on separate charts for each of the considered metals (Cu, Cd, Zn, and Pb) over the study period, as shown in Fig. 2.

Cd speciation

Cd was associated with the acido-soluble and reducible fractions (F2 and F3) in the reference parcel in all depths. Exchangeable, oxidizable, and residual fractions (F1, F4, and F5) were negligible except for layer 35–55 cm where Cd was found in the residual fraction in a concentration of 0.069 mg/kg (Fig. 2a). Cd speciation in parcel P1 did not change significantly (Fig. 2b) while in parcels P2 and P3 a modification of Cd mobility could be observed (Fig. 2c, d). In fact, in
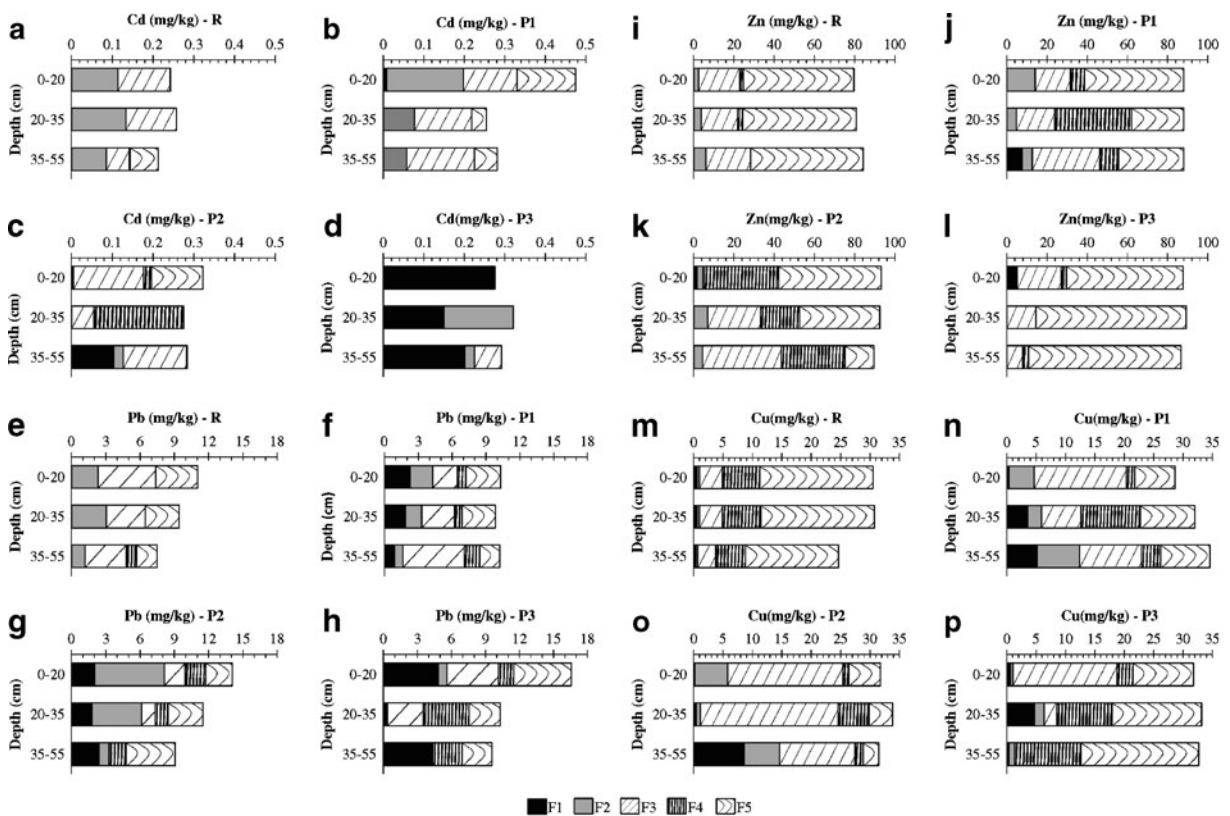
Fig. 2 **a–p** Time variation of trace element fraction concentrations in the soil profile

parcel P2, Cd was found to be related to the organic matter and sulfur (F4) at depth 20–35 cm in concentration of 0.22 mg/kg, and to the exchangeable fraction (F1) at depth 35–55 cm (0.276 mg/kg) (Fig. 2c). This fraction (F1), which is very mobile, was dominant in all depths at parcel P3 (0.276 mg/kg in 0–20 cm; 0.15 mg/kg in 20–35 cm; 0.201 mg/kg in 35–55 cm) (Fig. 2d). Moreover, in depth 20–35 cm, Cd in the acido-soluble fraction (F2) was relatively in equivalent quantity with exchangeable fraction (F1) (0.171 mg/kg) (Fig. 2d).

Pb speciation

Lead was mainly combined to carbonates (F2), iron and manganese oxides and hydroxides (F3), and to clays (F5) in the reference parcel in all depths. At natural abundance, the exchangeable (F1) and oxidizable fractions (F4) could be considered insignificant in all depths (Fig. 2e). At T1 (5 months after PG application), a change of Pb speciation was observed in P1 (Fig. 2f), with appearance of the exchangeable

(F1) and oxidizable (F4) Pb fractions in all depths (2.29 and 0.77 mg/kg at 0–20 cm; 1.87 and 0.68 mg/kg at 20–35 cm; 0.91 and 1.39 mg/kg at 35–55 cm in F1 and F4, respectively) (Fig. 2f). At T2 (12 months after PG application), the mobile fractions (F1 and F2) in parcel P2 were dominant and they decreased with depth. Pb was found to be in concentrations of 8.12 (the sum of Pb concentration in F1 and F2), 6.13, and 3.26 mg/kg at 0–20 cm, 20–35 cm, and 35–55 cm, respectively (Fig. 2g). At T3 (16 months after PG amendment), the amount of exchangeable Pb fraction (F1) in parcel P3 was significant at 0–20-cm and 35–55-cm depth (4.84 and 4.32 mg/kg, respectively) while Pb was found accumulated (4.02 mg/kg) in the organic matter and sulfur phase (F4) at 20–35-cm layer (Fig. 2h).

Zn speciation

The Zn reducible and residual fractions (F3 and F5) were dominant at T0 in the reference parcel R throughout the soil profile (Fig. 2i). F1, F2, and F4

were negligible in all soil horizons (<6 mg/kg). At T1 (parcel P1), more oxidizable zinc fraction (F4) accumulated in all layers (38.30 mg/kg), particularly in the intermediate layer (20–35 cm) (Fig. 2j). A decrease of the residual Zn fraction F5 was observed in deeper soil layers (20–35 cm) (from 56.45 mg/kg to 25.84 mg/kg). Moreover, the mobile fractions (F1 and F2) increased significantly in the upper and lower soil layers (14.16 mg/kg for F2 in 0–20 cm and 12.65 mg/kg for the sum of F1 and F2 in 35–55 cm) (Fig. 2j). At T2 (parcel P2), Zn was found mostly associated with the reducible, oxidizable, and residual fractions (F3, F4, and F5) in all layers except the surface where the reducible fraction was negligible (0.98 mg/kg) (Fig. 2k). The residual Zn fraction decreased with depth, whereas an increase in the reducible fraction was observed. At T3 (parcel P3), Zn reference speciation was practically restored, where the reducible and the residual fractions (F3 and F5) were again dominant in the soil control section under study (Fig. 2l).

Cu speciation

At T0, copper was mainly partitioned between reducible (F3), oxidizable (F4), and residual fractions (F5) in all layers of the reference soil (parcel R). It is obvious that the greatest quantity of copper was detected in the residual fraction in all depths (19.27, 19.34, and 15.81 mg/kg in 0–20 cm, 20–35 cm, and 35–55 cm, respectively). The exchangeable (F1) and the acid-soluble fractions (F2) were negligible (<1 mg/kg) (Fig. 2m). At T1 (parcel P1), these two fractions held a larger quantity of copper particularly in depth (35–55 cm) (5.16 and 7.24 mg/kg in F1 and F2, respectively). Copper quantity associated with the alumino-silicates fraction (F5) was less than in the reference soil (Fig. 2n) (it deceased from 15.81 to 19.34 mg/kg in R to 6.89–9.26 mg/kg). At T2 (P2), the reducible fraction F3 was found to be dominant in all depths (19.60, 23.43, and 12.86 mg/kg in 0–20 cm, 20–35 cm, and 35–55 cm, respectively) (Fig. 2o). The residual fractions (F5) held less quantity of copper than in parcel R. An increase of 11% in the mobile Zn fractions (F1 and F2) could be observed in the 35–55-cm layer of P2 comparing to the same depth in P1 (Fig. 2o). At the end of the experiment, Cu was partitioned in the reducible, oxidizable, and alumino-silicate fractions of the soil in P3 (Fig. 2p). However,

19% of Cu content was present in the mobile fraction (F1 and F2) in the layer 20–35 cm.

TEs concentration in plants

TEs concentrations in roots and leaves of plants collected from reference and amended parcels are presented in Fig. 3. TEs concentrations in leaves were relatively equal or higher than the corresponding concentrations in roots depending on the time of sampling. Zn exhibited highest concentrations in roots and leaves in all parcels (8–25 mg/kg), followed by Pb (7.5–10 mg/kg), Cu (6–7 mg/kg), and Cd (1–2.4 mg/kg). P2 plants contained the peak concentrations in Zn and Cd, and P1 in Pb and Cu.

Considering all studied parcels, significant differences (P<0.05) in TEs concentrations in roots and leaves were found between all parcels except Cu concentrations in leaves which showed no significant difference between parcels.

Making comparisons with the reference parcel, TEs (Cu, Pb, Zn, and Cd) contents in roots showed significant differences (P<0.05) between the reference and parcel P1. Only Cu concentration in roots displayed no significant difference between the reference and parcel P2. Cd content in roots exhibited significant difference between reference and parcel P1.

Pb, Zn, and Cd concentrations in leaves exhibited significant differences (P<0.05) between the reference and each of parcels P1 and P2. In addition, Cd concentration in leaves showed a significant difference (P<0.01) between the reference and parcel P1.

No significant difference was found in Cu concentration in leaves between the reference and parcel P1, P2, or P3.

Correlations

Results of Pearson correlations between TEs concentrations in soils, soil pH, CEC, and COT as well as between TEs contents in soils, roots, and leaves are presented in Table 3. Cd concentration in the soil was found to be negatively correlated to soil pH ($r=-0.90$, P<0.001), whereas Zn showed a positive correlation ($r=0.92$, P<0.001). Pb and Zn concentrations in the soil were positively correlated with soil's TOC and CEC ($r>0.90$, P<0.001 for Pb; $r>0.75$, P<0.05 for Zn).

Cd concentration in the soil was positively correlated with Cd and Cu concentrations in the roots ($r=0.882$,

Fig. 3 Time variation of
trace element concentrations
in plant roots and aerial
parts
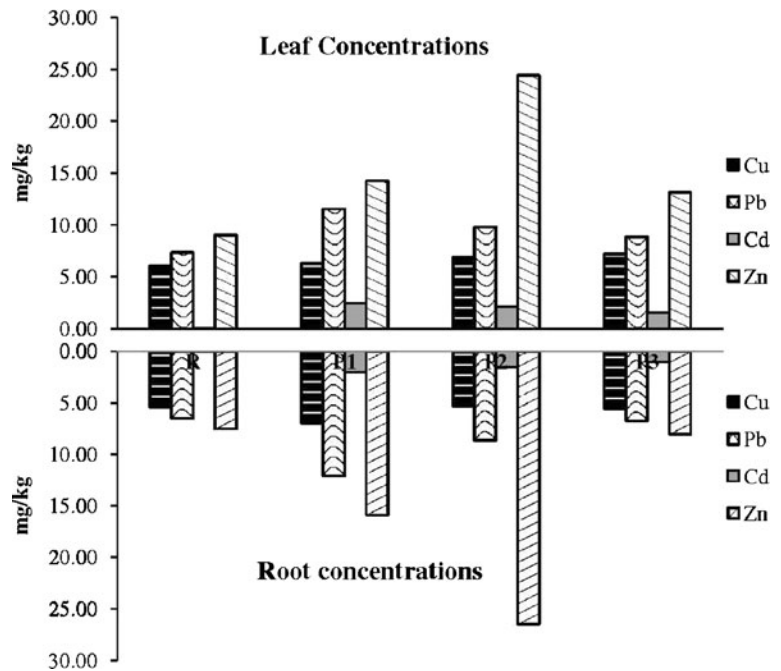
$P<0.005$ and $r=0.884$, $P<0.005$, respectively). Cu and Pb concentrations in the soil were positively correlated with Zn concentration in the roots ($r=0.763$, $P<0.05$ and $r=0.869$, $P<0.01$, respectively). Positive correlations were found between TEs (Pb, Zn, and Cd) in roots and leaves ($r>0.8$, $P<0.005$). In fact, a positive correlation was found between the concentrations of exchangeable Pb in the soil (F1) and plant leaves ($r=0.731$, $P<0.05$). The level of soil acid-soluble Cu (F2) was positively correlated with Cu content in plant roots ($r=0.727$, $P<0.05$). Zn acid-soluble and oxidizable fractions (F2 and F4) contents were positively corre-

lated with Zn content in roots ($r>0.85$, $P<0.01$) which was negatively correlated with Zn level in reducible fraction (F3) ($r=-0.78$, $P<0.05$).

Discussion

TEs in soil

Prior to PG amendment, the study area presented elevated Zn concentrations and slightly elevated Cu concentration when compared to the world agriculture

Table 3 Results of correlation: Pearson correlation

	pH	TOC	CEC	$Cu|_{root}$	$Cd|_{root}$	$Zn|_{root}$	$Pb|_{root}$	$Pb|_{leaf}$
$Cu|_{soil}$	–	–	–	–	–	**	–	–
$Cd|_{soil}$	(–)**	–	–	**	**	–	–	–
$Zn|_{soil}$	**	*	*	–	–	–	–	–
$Pb|_{soil}$	–	**	**	–	–	**	–	–
$Cu|_{soil,\ F2}$	–	–	–	**	–	–	–	–
$Pb|_{soil,\ F1}$	–	–	–	–	–	–	–	**
$Zn|_{soil,\ F2}$	–	–	–	–	–	**	–	–
$Zn|_{soil,\ F3}$	–	–	–	–	–	(–)**	–	–
$Zn|_{soil,\ F4}$	–	–	–	–	–	**	–	–
$Cd|_{leaf}$	–	–	–	–	**	–	–	–
$Zn|_{leaf}$	–	–	–	–	–	**	–	–
$Pb|_{leaf}$	–	–	–	–	–	–	**	–

(–) Negative correlation, – insignificant correlation

*$P<0.05$, significant correlation at the 0.05 level; **$P<0.01$, significant correlation at the 0.01 level

soils (20–30 mg/kg and 50 mg/kg for Cu and Zn, respectively) (Alloway 1995). Pb and Cd concentrations were within the range of agricultural and normal soils (10–30 mg/kg and 0.2–1 mg/kg for Pb and Cd, respectively) (Alloway 1995; Baize 1997). Moreover, if the comparison was performed with the arable soils from North Lebanon and Syria, Zn and Cu concentrations exceeded the reported background values (Lebanon—12±2 and 64±2 mg/kg; Syria—21.2±1.2 and 60.4±3.4 mg/kg for Cu and Zn, respectively) (Nsouli et al. 2004; Attar et al. 2011).

R–P1

The amendment of PG (pH=6.51±0.5) caused a pH decrease (in P1, the average pH dropped from 8.24±0.13 to 7.73±0.08) (Table 2). TEs cations became more soluble as pH decreased (Chopin and Alloway 2007) which explained the general increase of TE concentrations in P1 soil profile following the PG amendment (till 55 cm for Pb, Zn, and Cu, and 20 cm for Cd). This indicated that TEs were in a mobile phase and easily translocated down the profile, whereas Cd remained within the active root zone (Loganathan et al. 1995). Cd was found to be the TE most influenced by pH with a peak occurring in parcel P1. Earlier studies showed that the rate of accumulation of Cd in soils depends on soil properties such as pH (Kirkham 2006).

P1–P2

In the interval period P1–P2, during the winter season, Cd concentration decreased indicating the presence of Cd in a soluble phase readily leachable or absorbed by plants. Pb, Cu, and Zn concentrations constantly increased between surface and 35-cm depth, suggesting their continuous release from PG at the surface and accumulation in the mineral soil phases. However, Pb and Cu concentrations decreased below this depth, which could be due to their limited mobility in soil profile. Zn concentration remained fairly constant below 35 cm. In fact, Citeau et al. (2003) found that Zn could migrate to depth in soil solution as free ions (Zn).

P2–P3

In the period P2–P3 (spring–summer), TEs concentrations generally decreased relative to P2, but

remained higher than the background values, except for Zn which concentration dropped below the reference value in the 10–20-cm-deep layers. It would be important to point out the continuous plants absorption of TEs (particularly Zn) in the layer (10–20 cm) where active roots were extended.

TEs fractions in soil

Speciation of TEs was performed in order to assess their chemical form, and thus potential risk for vegetable and groundwater contamination. Fractions F1 (exchangeable) and F2 (acido-soluble) are considered as potentially mobile, while fractions F3 (reducible) and F4 (oxidizable) are relatively mobile depending on redox conditions. Fraction F5 (residual) is considered immobile (Ure et al. 1993).

The studied elements were mostly associated with Fe and Mn oxides (reducible fraction, F3) and clays (residual fraction, F5) in the reference plot.

R–P1

At T1, the studied elements revealed a higher mobility in the amended plot P1 than in the reference plot R. In R and P1 parcels, at the surface soil layer (0–20 cm), the amount of Zn, Pb, Cu, and Cd found in the mobile fractions (F1+F2) were 3% and 16%, 20% and 40%, 3% and 16%, and 46% and 61%, respectively. This increase was in the detriment of clays fraction (F5) in the case of Zn, on the account of Fe and Mn oxides (F3) in the case of Pb and Cd, and organic matter and sulfur (F4) in the case of Cu (69% and 56% for Zn, 45% and 22% for Pb, 53% and 34% for Cd, and 20% and 4% for Cu in the R and P1 parcels, respectively).This represents a relative shift of 13%, 20%, 13%, and 15% for Zn, Pb, Cu, and Cd, respectively, to the mobile fractions. Generally, this relative increase in the mobile fractions of TEs (except for Cd) was observed with soil depth (till 55 cm) of amended parcels comparing to R parcel. The mobility of Zn was mainly controlled by alumino-silicates (Spark et al. 1995). Fe and Mn oxides were the major constituents of mineral soils that react with Pb (Jaradat et al. 2006). Association of Cu to organic matter was well reported in the literature (Zaccone et al. 2007). Thus, clays, iron oxides, and organic matter were represented as the most susceptible to changes that result in an increase in TEs solubility.

P1–P2

In parcel P2 (after the wet period), and comparing to P1, the continuous increase of Pb content in the mobile fractions (14%, 12%, and 20% in 0–20, 20–35, 35–55 cm, respectively), compared to clays and iron oxides fractions, was due to Pb release associated with acid-soluble fraction of PG (30%) during rainy periods. Cd transferred from acid-soluble phase of PG (54%) was dissolved in soil profile and migrated to a depth of 55 cm, which explained the increment of 20% of Cd in the mobile phase when comparing to P1. Mobile Zn and Cu originating from PG (28% and 47%, respectively) were decreased in soil profile (till 55 cm for Zn and 35 cm for Cu) when compared to P1 and transferred to the oxidizable (Zn) and reducible fraction (Cu).

P2–P3

In summer, at T3, 16 months after the amendment of PG (parcel P3), Cd was retained in the mobile fraction (mainly exchangeable) in all depths (87%, 90%, and 77% in 0–15 cm, 15–35 cm, and 35–55 cm, respectively). In soils and sediments polluted with metal wastes, the greatest percentage of the total Cd was associated with the exchangeable fraction (Tessier et al. 1980; Kuo et al. 1983). Cu, Pb, and Zn associated with the oxidizable fraction (32%, 18%, and 30%, respectively) were released from PG (in dry condition) due to the high porosity of PG (Rabi and Mohamad 2006). These elements were adsorbed to soil constituents. With pH increase due to soil buffering capacity, Zn was finally intercepted by reactive negatively charged soil constituents such as phyllosilicates and iron oxides (Van Oort et al. 2006; Fernandez et al. 2007).

TEs mobility comparison

It could be construed that TEs mobility in the soil profile constantly varied due to changing factors, such as soil pH, COT, CEC, porosity, water flux, and plant roots exudation, which have different effects on the displacement of different TEs depending on their properties, concentrations, colloidal complexes, and occurring chemical phases (Carrillo-Gonzalez et al. 2006). Nevertheless, TE overall mobility during the study period could be compared by assessing the ratio

(R) of displaced TE from soil control volume—to its input to the control volume:

$$R = \text{Displaced Quantity}/\text{Input}$$
$$= (\text{Input} - \text{Retained})/\text{Input} = 1 - \text{Retained}/\text{Input}$$

Therefore,

$$R = 1 - E_r \rho V / C_{pg} M$$

Where,

E_r TE average retained enrichment (mg/kg)
ρ Soil density (kg/m^3)
V Soil control volume (m^3)
C_{pg} TE concentration in PG (mg/kg)
M PG added mass (kg)

Since M, ρ, and V are constant, this mobility comparison ratio could be simplified to:

$$R' = 1 - E_r / C_{pg} = 1 - (C_s - C_r)/C_{pg}$$

Where,

C_s TE average concentration in studied soil profile (control volume) (mg/kg) for all layers in parcels P1, P2, and P3
C_r TE average concentration in reference soil for all layers (mg/kg)

Comparing R' ratio for the studied TEs, the order of their mobility was found to be Zn (1.00)>Cd (0.99)>Pb (0.62)>Cu (0.41).

TEs transfer from soil to *C. intybus*

Accumulation ratio (element concentration in plant root to element concentration in soil) and transfer coefficient (element concentration in aerial part/element concentration in root) (Baker 1981; Kabata-Pendias and Pendias 2001; Madejon et al. 2002) were determined for the different studied elements (Table 4) in order to provide a better understanding of the relationship between TEs concentrations in soil and plants, and to investigate their potential transfer into the food chain.

Cd showed a high accumulation ratio in all parcels with an increment of approximately 25× with relation to reference values. Previous studies displayed that plants could accumulate high amounts of this element even when its concentration in the soil was low (Ciura

Table 4 Accumulation ratio and transfer coefficient of the studied elements for *Cichorium intybus* in the reference and amended parcels (P1, P2, and P3)

Parcels	Accumulation ratios				Transfer coefficient			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
R	0.14	0.14	0.56	0.07	1.14	1.12	1.16	1.14
P1	3.22	0.19	0.95	0.14	1.20	0.91	0.95	0.89
P2	3.79	0.13	0.52	0.21	1.40	1.20	1.13	0.92
P3	3.53	0.15	0.67	0.10	1.46	1.30	1.25	1.40

et al. 2005). However, in a balanced undisturbed soil, Cd in the control plot must have been well retained by the soil particles compared with Cd added with PG which seems to be more readily accessible to plants during its life cycle, and transfer from fertilizer to soil solution, root, and soil phase.

According to Ross criteria (Ross 1994), Cd concentration in roots was within the values of contaminated plants (0.03–3.8 mg/kg).

Pb exhibited accumulation ratios greater than Zn in all parcels, with increments in parcels P1 and P2 being approximately 2× higher than in control soil. This order disagrees with previous studies showing Zn as the most and Pb the least readily accumulated TE in vegetation (Kabata-Pendias and Pendias 2001; Chopin and Alloway 2007). This discrepancy resulted from diversity of factors such as differences in TEs speciation and the consequent variations in mobility and bioavailability, soil conditions, plants age and state of health, and element concentrations (Ross 1994; Kabata-Pendias and Pendias 2001; Batista et al. 2007). However, Pb and Zn concentrations (Fig. 3) did not exceed the minimum levels of contamination in plants reported by Ross (1994) (30–300 mg/kg for Pb; 100–400 mg/kg for Zn).

The accumulation ratio of Cu could be considered constant with time which probably is related to the plants regulation of the uptake of this essential micronutrient. Copper concentration (Fig. 3) was not above the minimum values for plants contamination (20–100 mg/kg) (Ross 1994).

As vegetation can only take up soluble TEs, these were absorbed by plants in mobile forms (i.e., exchangeable, acid soluble). Chicory root exudates (i.e., H+, acetic acid, organic acids, amino acid) could solubilize or mobilize TEs from the mineral and organic fractions in soil (Carrillo-Gonzalez et al. 2006). Therefore, roots promoted mobilization and uptake of exchangeable, acid-soluble, and oxidizable TEs (i.e., Pb in exchangeable fraction, Cu and Zn in acid-soluble, and Zn in complexed form).

According to Baker (1981), plants can be classified according to their transfer coefficients as accumulators (TC>1.5), indicators (TC from 0.5 to 1.5), and excluders (TC<0.1). Chicory was demonstrated to be a potential indicator plants for heavy metal contaminated soils (Simon et al. 1996; Aksoy 2008) particularly for Cd. Due to the high rate of Cd transfer, concentration of Cd in leaves was higher than in roots. According to Simon et al. (1996), Cd concentrations in all chicory plant parts grown in Cd-amended soils were substantially higher than in controls following the order leaf>root. Moreover, chicory leaves growing on soil amended with PG had approximately an average of 2.0 mg/kg of Cd in all parcels (Fig. 3), exceeds the normal levels (0.1–1 mg/kg), and exceeding the tolerable level (0.5 mg/kg) recommended for livestock (Chaney 1989).

Transfer coefficient of Cu, Pb, and Zn were relatively constant with time. Cu level in leaves was within the normal range (3–20 mg/kg) (Chaney 1989) and showed no significant difference between parcels and reference. Several studies have reported restricted transport of Cu from contaminated soils to aboveground parts in different species (Arduini et al. 1996; Ait Ali et al. 2002; Dominguez et al. 2008). Pb in leaves was above the normal levels (2–5 mg/kg) in all parcels and showing significant difference with the reference, but not exceeding the toxic level for livestock (30 mg/kg) (Chaney 1989).

Though Zn concentration in leaves presented a significant difference between parcels and reference, its concentration remained within the normal values (15–150 mg/kg) (Chaney 1989). In fact, Zn is a micronutrient whose absorption was closely regulated by plants (Madejon et al. 2007).

These results suggest that chicory showed a translocation of these elements from roots to leaves particularly for Cd that could present a food-chain hazard over the limited study period. In fact, Cd is the most predisposed TE in terms of crop accumulation from soil amendments (Carrillo-Gonzalez et al. 2006). Long-term application of PG and derived industrial materials can bring environmental and public health hazards.

Conclusion

The application of PG on soil slightly increased the TEs (i.e., Cu, Pb, Zn, and Cd) concentrations in soil profile, remaining within the natural thresholds. Rainwater and pH fluctuations due to intermittent soil wetting and drying and resulting soil conditions were found to be the main factors controlling the mobility and accumulation of TEs in the soil profile and soil plant continuum. Under balanced pedogenic conditions with minimal human interference, most of the TEs were associated with the iron and manganese oxides and hydroxides (F3) and clays (F5) in the reference parcel, with insignificant amount of exchangeable (F1) and oxidizable (F4) fractions. The amendment of PG caused a modification in the behavior, thus the mobility, of the studied TEs with time since they became predominantly associated with exchangeable (F1), acid-soluble (F2), and oxidizable (F4) fractions over the study period. Indeed, the studied elements were mainly linked to the mobile and oxidizable fractions of the PG. TEs associated with PG mobile fractions were released into the soil during the rainfall events with an exception to Cd (Fig. 1). On the other hand, the intermittent wetting and drying of the well-drained red Mediterranean soil and the high porosity of dry PG allowed the atmospheric oxygen infiltration into these contaminants, releasing the elements associated with the oxidizable fractions.

Over the study period (16 months), Cd was found mainly in the exchangeable fraction, whereas Zn was retained in the reducible and residual fractions after its movement to deep layers. Pb and Cu were accumulated as oxidizable and residual fractions. The soil had a capacity to bind metals in slightly mobile fractions due to its alkaline pH and clay texture.

The existed plants consisting of chicory species were found to accumulate high amounts of Cd in leaves, indicating that Cd could enter the food chain through crops grown on amended soils. In addition, chicory leaves are normally consumed as food by the local community, hence the risk of direct exposure to toxic TEs.

The application of PG slightly increased the concentration of Cd in soil, but remained within the natural limit. However, the agriculture application of PG could increase the availability of Cd to *C. intybus*, which is known to be an accumulator to this element.

Investigating the application of PG using other plant species would be of great importance. Further investigation should be carried out on Pb, Cu, and Zn when some soil variables that control TEs mobility are changed, such as pH, texture, structure, and organic matter contents.

References

Abril, J. M., Garcia-Tenorio, R., Enamorado, S. M., Hurtado, M. D., Andreu, L., & Delgado, A. (2008). The cumulative effect of three decades of phosphogypsum amendments in reclaimed marsh soils from SW Spain: 226Ra, 238U and Cd contents in soils and tomato fruit. *Science of the Total Environment, 403*, 80–88.

Ait Ali, N., Bernal, M. P., & Ater, M. (2002). Tolerance and bioaccumulation of copper in *Phragmites australis* and *Zea mays*. *Plant and Soil, 239*, 103–111.

Aksoy, A. (2008). Chicory (*Cichorium intybus* L.): a possible biomonitor of metal pollution. *Pakistan Journal of Botany, 40*(2), 791–797.

Al-Masri, M. S., Ali, A., Keitou, M., & Al-Hares, Z. (1999). Leaching of 226Ra from Syrian phosphogypsum. In W. A. Newton (Ed.), *Environmental radiochemical analysis*. London: Royal Society of Chemistry.

Al-Masri, M. S., Amin, Y., Ibrahim, S., & Al Bich, F. (2004). Distribution of some trace elements in Syrian phosphogypsum. *Applied Geochemistry, 19*, 747–753.

Al-Oudat, M. (1999) The effect of adding phosphogypsum to cracking soil on plant growth and radionuclides accumulation. Technical Report AECS-PR/FRSR205, Atomic Energy Commisson of Syria, Damascus.

Alcordo, I., Recheigl, J., Roessler, C., & Littell, R. (1999). Radiological impact of phosphogypsum applied to soils under bahiagrass pasture. *Journal of Environmental Quality, 28*, 1555–1567.

Alloway, B. J. (1995). *Heavy metals in soils* (2nd ed.). London: Blackie.

Arduini, I., Godbold, D. L., & Onnis, A. (1996). Cadmium and copper uptake and distribution in Mediterranean tree seedlings. *Physiologia Plantarum, 97*, 111–117.

Arocena, J. M., Rutherford, P. M., & Dudas, M. J. (1995). Heterogeneous distribution of trace elements and fluorine in phosphogypsum by-product. *Science of the Total Environment, 162*, 149–160.

Attar, L. A., Al-Oudat, M., Chemali, K., Ghany, B. A., & Kanakri, S. (2011). Case study: heavy metals and fluoride contents in the materials of Syrian phosphate industry and the vicinity of phosphogypsum piles. *Environmental Technology*. Available at http://www.informaworld.com/10.1080/09593330.2011.552531.

Baize, D. (1997). *Teneurs totales en éléments traces métalliques dans les sols (France). Références et stratégies d'interprétation*. Paris: INRA.

Baker, A. J. M. (1981). Accumulators and excluders—strategies in the response of plants to heavy-metals. *Journal of Plant Nutrition, 3*, 643–654.

Batista, M. J., Abreu, M. M., & Serrano Pinto, M. (2007). Biogeochemistry in Neves Corvo mining region, Iberian Pyrite Belt, Portugal. *Journal of Geochemical Exploration, 92*, 159–176.

Burnett, W. C., Schaefer, G., & Schultz, M. K. (1999). Fractionation of 226Ra in Florida phosphogypsum. In G. W. A. Newton (Ed.), *Environmental radiochemical analysis* (pp. 1–20). London: Royal Society of Chemistry.

Carrillo-Gonzalez, R., Simunek, J., Sauve, S., & Adriano, D. (2006). Mechanisms and pathways of trace element mobility in soils. In D. L. Sparks (Ed.), *Advances in agronomy, vol. 91* (pp. 111–178). San Diego: Academic.

Chaney, R. L. (1989). Toxic element accumulation in soils and crops: protecting soil fertility and agriculture food chains. In B. Bar-Yosef, N. J. Barrow, & J. Goldshmid (Eds.), *Inorganic contaminants in the vadose zone* (pp. 140–158). Berlin: Springer.

Chopin, E. I. B., & Alloway, B. J. (2007). Distribution and mobility of trace elements in soils and vegetation around the mining and smelting areas of Tharsis, Riotinto and Huelva, Iberian Pyrite Belt, SW Spain. *Water, Air, and Soil Pollution, 182*, 245–261.

Citeau, L., Lamy, I., Elsass, F., & Van Oort, F. (2003). Colloidal facilated transfer of metals in soils under different land use. *Colloids and Surfaces A, 217*, 11–19.

Ciura, J., Poniedzialek, M., Sekara, A., & Jedrszczyk, E. (2005). The possibility of using crops as metal phytoremediants. *Polish Journal of Environmental Studies, 14*(1), 17–22.

Conkline, C. (1992) Potential uses of phosphogypsum and associated risks: background information document for 40 CFR 61 Subpart R National Emission Standards for Radon Emissions from Phosphogypsum Stacks. Technical Report EPA 402-R 92-002, Washington, DC.

Darwish, T., Khawlie, M., Faour, G., Masri, T., Shaaban, A., & BouKheir, R. (2005) Land degradation in Lebanon: vulnerability of soil resources to desertification. Technical Report, Regional Workshop, United Nations, Islamic Republic of Iran.

Darwish, T., & Zurayk, R. (1997). Distribution and nature of Red Mediterranean Soils in Lebanon along an altitudinal sequence. *Catena, 28*, 191–202.

Delgado, A., Uceda, I., Andreu, L., Kassem, S., & Del Campillo, M. (2002). Fertilizer phosphorus recovery from gypsum-amended, reclaimed calcareous marsh soils. *Arid Land Research and Management, 16*, 319–334.

Dominguez, M. T., Maronon, T., Murillo, J. M., Schulin, R., & Robinson, B. H. (2008). Trace element accumulation in woody plants of the Guadiamar Valley, SW Spain: a large-scale phytomanagement case study. *Environmental Pollution, 152*, 50–59.

Fernandez, C., Labanowski, J., Cambier, P., Jongmeans, A. G., & Van Oort, F. (2007). Fate of airborne metal pollution in soils as related to agricultural management. 1. Zn and Pb distributions in soil profiles. *European Journal of Soil Science, 58*, 547–559.

Jaradat, Q. M., Massadeh, A. M., Zaitoun, M. A., & Maitah, B. M. (2006). Fractionation and sequential extraction of heavy metals in the soil of scrapyard of discarded vehicles. *Environmental Monitoring and Assessment, 112*, 197–210.

Kabata-Pendias, A., & Pendias, H. (2001). *Trace elements in soils and plants* (3rd ed.). Boca Raton: CRC.

Kassir, L. N., Lartiges, B., & Ouaini, N. (2011). Effects of fertilizer industry emissions on local soil contamination: a case study of phosphate plant on the east Mediterranean coast. *Environmental Technology* (in press).

Kirkham, M. B. (2006). Cadmium in plants on polluted soils: effect of soil factors, hyperaccumulation, and amendments. *Geoderma, 137*, 19–32.

Kuo, S. P., Heilman, E., & Baker, A. S. (1983). Distribution and forms of copper, zinc, cadmium, iron, and manganese in soils near a copper smelter. *Soil Science, 135*, 105–109.

Loganathan, P., Mackay, A. D., Lee, J., & Hedley, M. J. (1995). Cadmium distribution in grazed hill pastures as influenced by 20 years of phosphate fertilizer application and sheep grazing. *Australian Journal of Soil Research, 33*, 859–871.

Madejon, P., Murillo, J. M., Maranon, T., Cabrera, F., & Soriano, M. A. (2002). Bioaccumulation of As, Cd, Cu, Fe and Pb in wild grasses affected by the Aznalcollar mine spill (SW Spain). *Science of the Total Environment, 307*, 239–257.

Madejon, P., Murillo, J. M., Maranon, T., & Lepp, N. W. (2007). Factors affecting accumulation of thallium and other trace elements in two wild Brassicaceae spontaneously growing on soils contaminated by tailing dam waste. *Chemosphere, 67*, 20–28.

May, D., & Mortvedt, J. (1986). Crop response to soil applications of phosphogypsum. *Journal of Environmental Quality, 15*, 78–81.

Mullins, G. L., & Mitchell, C. C. (1990) Use of phosphogypsum to increase yield and quality of annual forages. Technical Report Publication No. 01-048-084, Florida Institute of Phosphate, Bartow.

Nsouli, B., Darwish, T., Thomas, J. P., Zahraman, K., & Roumie, M. (2004). Ni, Cu, Zn and Pb background values determination in representative Lebanese soil using the thick target PIXE technique. *Nuclear Instruments and Methods in Physics Research Section B, 219–220*, 181–186.

Papastefanou, C., Stoulos, S., Ioannidou, A., & Manolopoulou, M. (2006). The application of phosphogypsum in agriculture and the radiological impact. *Journal of Environmental Radioactivity, 89*, 188–198.

Parreria, A. B., Kobayashi, A. R. K., Jr., & Silvestre, O. B. (2003). Influence of Portland cement type on unconfined compressive strength and linear expansion of cement-stabilized phosphogypsum. *Journal of Environmental Engineering, 129*, 956–960.

Prud'home, M., & Sukalac, K. (2006). *Presentation on current and projected demand for phosphoric acid. Paper presented at the Joint Meeting of IAEA and the Florida Institute of Phosphate Research and Sukalak*. Paris: International Industries Association.

Rabi, J. A., & Mohamad, A. A. (2006). Parametric modelling and numerical simulation of natural convective transport of radon-222 from a phosphogypsum stack into open air. *Applied Mathematical Modelling, 30*, 1546–1560.

Ross, M. S. (1994). Sources and form of potentially toxic metals in soil–plant systems. In M. S. Ross (Ed.), *Toxic metals in soil–plant systems* (pp. 3–25). Chichester: Wiley.

Rutherford, P. M., Dudas, M. J., & Samek, R. A. (1994). Environmental impacts of phosphogypsum. *Science of the Total Environment, 99*, 1–38.

Senesi, G. S., Baldassare, G., Senesi, N., & Radina, B. (1999). Trace elements inputs into soils by antropogenic activities and implications for human health. *Chemosphere, 39*(2), 343–377.

Simon, L., Martin, H. W., & Adriano, D. C. (1996). Chicory (*Cichorium intybus* L.) and dandelion (*Taraxacum officinale* Web.) as phytoindicators of cadmium contamination. *Water, Air, and Soil Pollution, 91*, 351–362.

Spark, K. M., Wells, J. D., & Johnson, B. B. (1995). Characterizing trace metal adsorption on kaolinite. *European Journal of Soil Science, 46*, 633–640.

Tessier, A., Campbel, P. G. C., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry, 51*(7), 844–851.

Tessier, A., Campbell, P. G. C., & Bisson, M. (1980). Trace metal speciation in the Yamaoka and St. Francois Rivers (Quebec). *Canadian Journal of Earth Sciences, 17*, 90–105.

Ure, A. M., Quevauviller, P., Muntau, H., & Griepink, B. (1993). Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International Journal of Environmental Analytical Chemistry, 51*, 135–151.

Van Oort, F., Jongmans, A. G., Citeau, L., Lamy, I., & Chevallier, P. (2006). Metal transport dynamics in soils as revealed by microscale zinc and lead distribution patterns in subsurface horizons. *European Journal of Soil Science, 57*, 154–166.

Zaccone, C., Cocozza, C., D'Orazio, V., Plaza, C., Cheburkin, A. K., & Miano, T. M. (2007). Influence of extractant on quality and trace element content of peat humic acids. *Talanta, 73*, 820–830.

Zhang, X., Miller, W., Nearing, M., & Norton, L. D. (1998). Effects of surface treatment on surface sealing, runoff, and interril erosion. *Transactions of ASAE, 41*(4), 989–994.