INSTITUT NATIONAL POLYTECHNIQUE DE LORRAINE
ÉCOLE DOCTORALE : *RP2E*
Laboratoire de *LEM*

THÈSE

Présentée et soutenue publiquement le 13/12/2012
pour l'obtention du grade de Docteur de l'INPL
(Spécialité : Géosciences)

par

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Les métaux lourds dans les engrais phosphatés et les sulfates rejetés par les industries des fertilisants: Recherche sur leur transfert et leur mobilité dans les sols libanais

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Remerciements

Cette thèse a été réalisée en codirection au sein de deux laboratoires: Laboratoire d'Environnement et Minéralurgie (LEM) à Nancy et laboratoire de Saint-Esprit de Kaslik (USEK) au Liban.

Je souhaite tout d'abord exprimer ma gratitude envers l'agence universitaire francophone (AUF) pour leur aide financière pendant la préparation de cette thèse.

Tout le long de mon chemin dur, j'ai été accompagnée par de nombreux amis sans lesquels il m'aurait été impossible d'accomplir ce projet de travail. En premier lieu, je tiens à exprimer ma profonde gratitude à mon co-directeur de thèse, Prof. Naim Ouaini, d'être toujours disponible et pour la confiance qu'il m'a toujours témoignée. Merci pour croire en moi.

Je souhaite également remercier Prof. Bruno Lartiges pour me donner la chance d'être présente dans un laboratoire comme le LEM, et pour ses conseils.

Mes remerciements vont également à Bernard Legube et à Margot Munoz d'avoir accepté de juger et d'améliorer ce travail. Un remerciement particulier à Guillaume Echevarria qui a jugé mes travaux scientifiques et m'a donné l'espoir et la confiance de continuer jusqu'au bout.

Je souhaite remercier le directeur de laboratoire Fabien Thomas, mon directeur Frédréric Villiéras pour son support, son encouragement, son aide précieuse et son humanité touchante ainsi que tous les membres du LEM qui m'ont toujours chaleureusement accueilli en particulier ; Guerric Olivier qui a été toujours à l'écoute de mes demandes concernant l'analyse de Diffraction des Rayons-X, Odiles Barres pour l'analyse Infra-Rouge, Delphine Martin pour son aide informatique et Jdid el Aïd pour la réservation des séances de MEB et ses *conseils précieux, à mes sincères amis Jean-aimé Mbey et Noémie d'etre à mes cotés dans les moments les plus difficiles.*

Je suis reconnaissante à Antoine ElSemrani pour initier cette thèse. J'adresse mes remerciements les plus profonds aux Prof. Rosette Ouaini et Hanna Chbib pour le temps qu'ils m'ont accordé, leur encouragement pendant la phase la plus dure de la thèse.

J'aimerais vivement remercier l'équipe des assistantes dans le laboratoire de l'USEK qui m'ont aidé durant mes travaux de thèse et en particulier Marie-Josee Zacca, Savio Karam et Elie Ahmar pour leur aide précieuse durant l'échantillonnage des parcelles à Bsarma.

Je remercie mes parents qui m'ont toujours motivé et encouragé dans les moments les plus durs. Sans leur support, je n'aurais pas pu y arriver. Cette thèse est dediée à l'ame de mon père qui est décédé 3 mois avant ma soutenance.

Enfin, un mot pour mes deux enfants, Moudrek et Moustafa qui ont bien supporté mes longues périodes d'absence en étant responsables et compréhensibles. Ils m'ont donné la force pour continuer.

Je réserve une mention particulière à mon très cher mari qui m'a soutenu le long de mon chemin et m'a aidé à affronter mes difficultés professionnelles. Une grande partie de ce travail te revient.

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Introduction Générale

Les éléments traces métalliques sont présents naturellement dans le sol à des concentrations faibles et sont relativement peu mobiles. Les industries, les retombées atmosphériques, le rejet des déchets urbains et industriels ainsi que les pratiques agricoles contribuent à l'augmentation des éléments traces dans le sol jouant le rôle d'un système accumulateur. . Particulièrement, les industries des engrais chimiques posent un problème sérieux pour l'environnement dû aux émissions de particules polluants, aux déchets solides rejetés et aux effluents liquides déchargés dans le milieu aquatique. Ainsi l'air, l'eau et le sol sont bien affectés et peuvent être pollués. Cette pollution provient principalement de la manipulation des matières premières (transport, stockage et traitement), de stockage des déchets et de type des effluents rejetés. En fait, la roche phosphate utilisée comme matière première dans la fabrication des engrais phosphatés, suivant son origine, contient des concentrations élevées des métaux lourds (Brigden et al., 2002). Ces métaux lourds sont en partie transférés aux engrais phosphatés et aux sous-produits formés comme le sulfate de calcium dihydraté connu sous le nom de phosphogypse (Rutherford et al., 1994). Seulement 15% des déchets de phosphogypse sont recyclés et les 85% sont rejetés dans l'environnement (IFA, 1998). La poussière émise par le stockage de ces déchets et sa déposition sur le sol peut constituer une source de contamination du sol.

Le risque associé aux éléments traces métalliques contenus dans le phosphogypse et les engrais phosphats appliqués sur le sol dépend de leur mobilité en d'autres termes de leur passage en solution pour être transférés aux plantes ou pollués en profondeur l'eau souterraine. Cette mobilité n'est pas stable au cours du temps dépendant de plusieurs paramètres physico-chimiques comme le pH, le potentiel redox, la teneur en matière organique (Kabata-Pendias, 2004). Parmi les métaux traités en commun dans plusieurs études et contenus dans la roche phosphate, les engrais phosphatés et le phosphogypse (Cr, Cu, Zn, Pb, Ni, U, Cd, Sr), nous avons sélectionné 4 éléments (Cd, Pb, Cu et Zn) pour l'évaluation de leur mobilité dans le sol agricole et ceci pour deux raisons principales : leur toxicité et leur propriété géochimique différentes. Le cadmium et le plomb constituent un risque important pour la santé humaine vu leur toxicité à long terme pour les plantes et l'homme alors que le zinc et le cuivre sont des éléments nutritifs essentiels pour les plantes mais qui à des concentrations élevées peuvent devenir nuisibles pour celles ci. D'autre part, Zn et Cd sont considérés comme des éléments relativement mobiles dans le sol. Le zinc peut migrer facilement dans le profil du sol et polluer l'eau souterraine alors que le Cd peut être absorbé facilement par les plantes. Sa translocation vers les organes consommés des végétaux est favorisée par certaines espèces végétales, dont la chicorée (Simon et al., 1996 ; Aksoy, 2008). Le cuivre et le plomb sont fixés par les constituants du sol donc relativement peu mobiles, le cuivre est connu par sa grande affinité pour la matière organique et le plomb pour les oxyhydroxydes de fer et de manganèse. Cependant, ces 4 éléments contribuent majoritairement à la contamination du sol.

Les effets toxiques des éléments traces dépendent principalement des quantités accumulées et de leurs formes chimiques dans le sol. L'existence des éléments traces sous des formes solubles, échangeables, incluses dans les minéraux, précipitées ou complexées définit le potentiel polluant et son impact sur la qualité des sols et des eaux ainsi que la toxicité pour les plantes et les autres organismes.

Notre étude se situe sur l'évaluation de la contamination du sol par des éléments traces (Cr, U, Zn, Cu, Pb, Ni, Cd, Sr) métalliques provenant des déchets rejetés par les industries et l'application des engrais phosphatés, et d'étudier la mobilité des éléments sélectionnés (Cu, Pb, Zn et Cd) dans le sol.

Objectifs de l'étude

Le présent travail de recherche tourne autour de deux axes principaux : (1) étudier la source, la distribution des éléments traces dans les sols autour des industries des engrais chimiques, (2) évaluer la mobilité des éléments traces dans le profil de sol en réalisant un amendement du phosphogypse et des engrais phosphatés sur un site contrôlé et surveillé, étant donné qu'ils sont une source de contamination du sol.

L'objectif général de l'étude se décline en 3 sous-objectifs :

(1) Evaluation de la contamination du sol autour de l'industrie des fertilisants chimiques provenant des poussières émises à proximité.

(2) Suivre et comprendre l'évolution temporelle de la distribution et la mobilité des éléments traces métalliques dans un profil du sol épandu par du phosphogypse.

(3) Suivre et comprendre l'évolution temporelle de la distribution et la mobilité des éléments traces métalliques dans un profil du sol épandu par des engrais phosphatés aini que le transfert des éléments traces aux plantes cultivées dans les deux cas est également évalué au cours du temps.

Structure de l'étude

L'étude est divisée en 5 chapitres. Le ***chapitre 1*** comprenant une synthèse bibliographique qui permet de comprendre les impacts environnementaux de l'industrie des engrais phosphatés avec les études réalisées sur la valorisation du phosphogypse et des engrais phosphatés comme amendement sur le sol.

Le ***chapitre 2*** decrit les sites étudiés de point de vue géographique et géologique.

Le ***chapitre 3*** visant à répondre au sous-objectif 1, les ***chapitres 4 et 5*** aux sous-objectifs 2 et 3.

Les chapitres 3, 4 et 5 sont présentés sous forme d'articles, parmi lesquels les deux premiers ont été publiés et le troisième a été accepté.

Article 1

Ce chapitre a pour but d'évaluer la contamination du sol provenant des engrais phosphatés et des déchets rejetés par les usines des fertilisants chimiques (sous-objectif 1). Ceci a été réalisé sur les échantillons prélevés d'un site industriel qui est le site de Selaata. Tout d'abord, nous avons sélectionné une méthode de calcul des flux des métaux lourds provenant de la poussière de la roche phosphate, du phosphogypse et des engrais phosphatés et appliqué cette méthode sur notre site. Puis nous avons réalisé une corrélation entre les flux calculés (théorique) et les métaux lourds dans les échantillons du sol (expérimental) ainsi qu'une corrélation entre ces métaux et les éléments majeurs (phosphore) permettant de comprendre les sources de contamination du sol autour de l'industrie. En outre, les risques attribués à l'industrie des engrais chimiques sur le milieu continental ont été évalués en étudiant la spéciation des métaux lourds dans la roche phosphate, le phosphogypse et les engrais phosphatés.

Articles 2 et 3

Ces 2 chapitres ont pour but de suivre et de comprendre l'évolution temporelle de la distribution et de la mobilité des métaux lourds dans un profil du sol épandu par le phosphogypse (chapitre 4, sous objectif 2) et les engrais phosphatés (chapitre 5, sous objectif 3). Ces 2 chapitres ont été réalisés sur les échantillons du sol prélevés d'un terrain expérimental agricole situé à Bsarma de type "*luvisol*" jusqu'à une profondeur de 55 cm. L’intervalle de temps entre les prélèvements a été choisi suivant les saisons pour prendre en considération l’influence des précipitations sur la distribution des métaux lourds dans le profil du sol épandu (phosphogypse et engrais phosphatés). Un suivi parallèle de la mobilité des métaux lourds dans le profil du sol épandu a été réalisé. Dans cette étude, le végétal est le témoin biologique permettant de montrer le transfert des métaux lourds du sol au végétal en étudiant le risque associé via la chaîne alimentaire. Le végétal poussant dans le site Bsarma est du type Chicorée utilisée dans la salade.

1 Synthèse Bibliographique

1.1 Les éléments traces métalliques

1.1.1 Notion d'éléments traces métalliques

Les métaux lourds sont des éléments ayant une masse volumique supérieure à 5g/cm^3. Ce terme est utilisé couramment pour désigner les éléments ayant une toxicité avérée pour l'Homme. Certains de ces métaux lourds, sont des oligo-éléments qui à faibles doses sont bénéfiques mais qui peuvent devenir toxiques à concentration élevée comme le cuivre, le zinc et le manganèse etc. En revanche, le cadmium, le nickel, le plomb, le chrome, le mercure, l'arsenic sont toxiques au delà d'une certaine dose dans l'organisme. Cependant, en Science du sol, il convient de parler des « éléments traces métalliques (ETM) » (au nombre de 68) qui sont ceux présents dans la lithosphère en concentration inferieure à 0,1% (Baize 1997). Cette appellation a été choisie dans le cadre de ce projet qui traite de la contamination du sol.

1.1.2 Différentes sources des éléments traces métalliques

Les ETM dans le sol ont 2 origines : naturelles et anthropiques. L'origine naturelle provient de l'héritage de la roche mère des minéraux contenant des métaux géogènes. Après altération biogéochimique de la roche mère dépendant de la composition chimique de celle-ci, de sa porosité, du climat et de la faune et de la flore, les minéraux primaires sont libérés qui à leur tour en s'altérant vont former les minéraux secondaires ou minéraux transformés appelés aussi minéraux néogènes. Baize (1997) définit le fond géochimique naturel comme la concentration d'un élément chimique dans un sol, résultant des évolutions naturelles, géologiques et pédologiques, en dehors de tout apport d'origine humaine. Cependant, la majeure source des ETM est d'origine anthropique. Les métaux dans le sol provenant d'apports anthropiques peuvent provenir de la pollution atmosphérique, la pollution industrielle et des pratiques agricoles. La pollution atmosphérique se fait sous forme de rejets directs à partir des sites producteurs, ou bien par retombées aériennes après la dispersion des métaux lourds dans l'atmosphère. On estime que 68% de plomb et 38% de cadmium provenant des retombées atmosphériques contribuent à l'enrichissement moyen annuel des sols (Feix and Wyart 1998). Evidemment, la principale source de Pb atmosphérique est la combustion de l'essence pour les voitures à moteur. Ces rejets du plomb par les gaz d'échappement sont une cause de la contamination des sols situés à proximité des grands axes routiers (Nriagu and Pacyna 1988). Concernant le Cd atmosphérique, sa source est principalement industrielle. L'estimation de Cd atmosphérique par les usines des fertilisants chimiques est de 1,7g/T de fertilisant (Pacyna 1984). En outre, l'industrie chimique et métallurgique est la source principale de la pollution du sol par le zinc et le plomb (Pacyna 1984).

D'autres sources peuvent à long terme engendrer une accumulation excessive des métaux dans le sol nuisant aux cultures et même s'étendre à toute la chaîne alimentaire telle que les engrais, les sous- produits industriels, les composts et les boues d'épuration utilisés comme amendement en agriculture et contenant des concentrations des métaux lourds assez élevées. Parmi les fertilisants inorganiques ce sont les engrais phosphatés qui sont les plus riches en métaux lourds (Cd, Cu, Cr, Ni, Zn) (Pacyna 1984), c'est pour cette raison qu'ils ont pris un grand intérêt dans ce projet de travail depuis leur fabrication dans les industries jusqu'à leur amendement sur les sols.

Il est important de distinguer entre la part des ETM d'origine géogènes et celle d'origine anthropique dans les sols pour évaluer le degré de contamination du sol. C'est pour cela qu'il est fondamental de connaître le fond géochimique de la région à étudier ou d'établir une comparaison par rapport à un site de référence. La comparaison peut se faire par rapport à des références illustrées dans le Tableau 1.1. De plus, les guides de Canada (CCME 1999) ont fixé un seuil de concentration des éléments traces dans les sols agricoles de 64 ; 1,4 ; 63 ; 70 ; 200 ; 200 ; et 50 mg/kg pour Cr, Cd, Cu, Pb, Sr, Zn et Ni respectivement. La législation de la majorité des régions dans le monde n'ont pas donné une valeur limite pour l'Uranium, pourtant l'Allemagne a fixé son seuil à 5mg/kg (Norge Geologiske Undersokelse (NGU)).

Tableau 1. 1 Teneurs en métaux lourds (mg/kg) dans les sols au monde présentés selon différents auteurs

Elément	***Min., moyenne, max. de la moyenne de la surface du sol au monde (mg/kg) (A Kabata-Pendias and Pendias 2001)***	***Gamme de teneurs habituelles (mg/kg) (Baize 1997)***	***Sols agricoles du monde (Alloway 1995)***
Ni	6-24-92	2-60	50
Cu	6-24-80	2-20	20-30
Zn	17-67-236	10-100	50
Pb	8-29-67	9-50	10-30
Cd	-	0,05-0,45	0,2-1

1.2 Industrie des engrais phosphatés

1.2.1 Fabrication des engrais phosphatés

L'apatite ou la roche phosphate $Ca_{10}F_2(PO_4)_6$ est solubilisée par action de l'acide sulfurique H_2SO_4 ou de l'acide phosphorique H_3PO_4 pour produire respectivement du simple superphosphate (SSP) ou du triple superphosphate (TSP):

$$Ca_{10}\,F_2\,(PO_4)_6 + 7H_2SO_4 + 6{,}5\,H_2O \rightarrow \underbrace{3Ca(H_2PO_4)_2.H_2O}_{SSP} + 7CaSO_4.\tfrac{1}{2}H_2O + 2HF$$

$$Ca_{10}\,F_2\,(PO_4)_6 + 14H_3PO_4 + 10H_2O \rightarrow \underbrace{10Ca\,(H_2PO_4)_2.H_2O}_{TSP} + 2HF$$

Pour former l'acide phosphorique, l'apatite est attaquée par l'acide sulfurique dans un rapport stœchiométrique différent que celui utilisé pour produire le SSP, en donnant comme sous-produit le phosphogypse ($CaSO_4.2H_2O$) et de l'acide fluorhydrique (HF):

$$\underbrace{Ca_{10}\,F_2\,(PO_4)_6}_{Apatite} + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + \underbrace{10\,(CaSO_4.2H_2O)}_{Phosphogypse} + 2HF$$

Cette réaction chimique est appelée processus humide.. Les différentes étapes de la fabrication des engrais phosphatés sont illustrées dans la Figure 1.1.

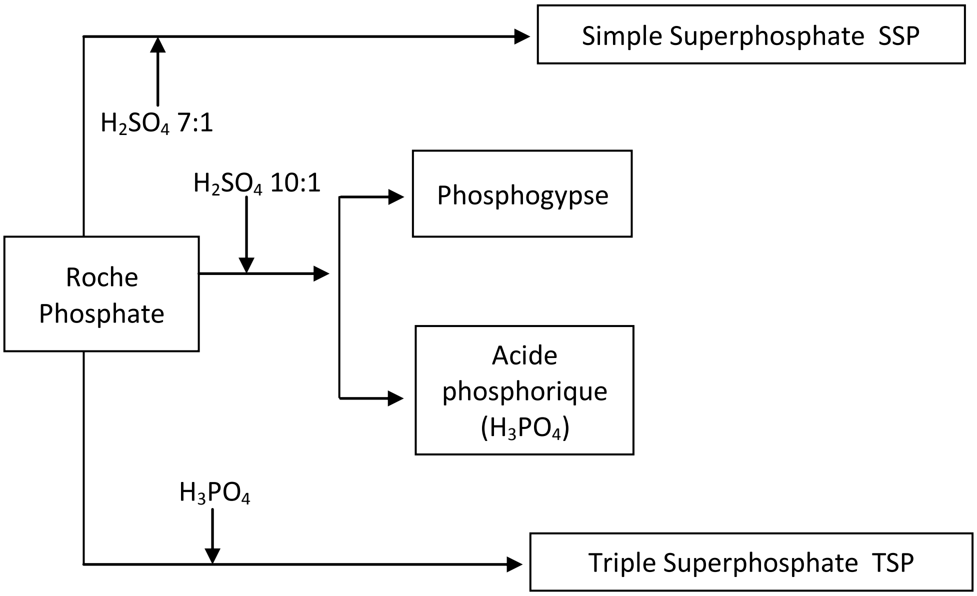

Figure 1. 1 Fabrication des engrais phosphatés dans l'industrie à partir de la roche phosphate (PNTTA 2000)

1.2.2 *Impacts environnementaux des industries des engrais phosphatés*

Le problème principal lié aux industries des engrais phosphatés est la présence des impuretés, comme les métaux lourds et les radionucleïdes, dans la roche phosphate utilisée comme matière première. Durant le processus de fabrication, des quantités signifiantes de ces impuretés sont transférées de la roche phosphate aux fertilisants et à l'acide phosphorique. Le reste est présent dans le phosphogypse (Brigden et al. 2002). Les roches phosphates d'origine sédimentaire contiennent des concentrations plus élevées d'impuretés (les éléments traces) que les roches igneuses (Van Kauwenbergh, 2002). Comme moyenne, la roche phosphate contient 11, 25, 188, 32, 10 et 239 mg/kg de As, Cd, Cr, Cu, Pb et Zn respectivement (He et al. 2005). Le phosphogypse peut contenir des quantités assez élevées des éléments traces, du fluor et des éléments radioactifs causant ainsi un risque pour l'environnement (Rutherford et al. 1994; Burnett et al. 1999; Senesi et al. 1999). Celui-ci est soit déchargé sous forme de suspension dans la mer méditerranéenne soit stocké à terre (IFA-UNDP 1998). la zone côtière méditerranéenne de plusieurs pays comme la Tunisie, l'Algérie et la Maroc, la Syrie est affectée par ces déchargements (Guillaumaut et al. 1996; Azouazi et al. 2001; Kacimi et al. 2006; Al-Masri et al. 1999b) qui sont responsables de l'entrée de plus de 1300 tonnes par an de mercure, cadmium et plomb dans la mer méditerranéenne (UNEP/MAP 2008). Cependant une étude récente en Syrie impliqué dans l'étude de l'influence du phosphogypse, éliminés dans des stocksà côté de l'industrie des fertilisants chimiques, a montré que la concentration des éléments traces (Cu, Pb, Zn, Cd et Cr) dans le sol est dans les limites tolérables en Syrie, ceci est dû selon les auteurs à la faible concentration de ces éléments dans les échantillons du phosphogypse (Attar et al. 2011). Au Liban, une industrie des engrais chimiques est localisée au nord du pays dans une région appelée Selaata. Cette usine, située à l'est de la zone côtière méditerranéenne, produit 230 000 T de SSP et 31 000 T de TSP par an (Al-Hajj and Muscat 2000; Yager 2005). Donc le processus de fabrication de 261 000 T de fertilisants à l'usine de Liban dégage en total 0,11 T/an et 0,4 T/an de Pb et Cd respectivement (en estimant que Pb et Cd atmosphérique provenant de l'usine des fertilisants est de 0,42g/T et 1,7g/T respectivement selon Pacyna, 1984). Cette quantité est dispersée dans l'atmosphère sous forme particulaire ou retombées sur le sol. Par ailleurs, cette usine utilise plus que 840 T par jour de la roche phosphate (Abboud-Abi Saab and Dargham 1998) d'origine sédimentaire (Bridgen et al., 2002) et décharge 950 T par jour du phosphogypse dans la mer méditerranéenne (Abboud-Abi Saab and Atallah 1996; Tebodin 2000).

Comme conséquent du déchargement de ce déchet dans la mer, plusieurs études ont mis l'accent sur la pollution marine (Al-Masri et al. 1999a; Al-Masri et al. 2000; Alcaraz Pelegrina and Martinez-Aguirre 2001; Othman and Al-Masri 2007), des eaux de surface, des eaux souterraines par les éléments radioactifs (^{222}Rn et ^{226}Ra) et des écoulements des eaux (eaux de ruissellement et lixiviat) provenant du terril de phosphogypse (Duenas et al. 2007; Canete et al. 2008). Quand ce déchet entre dans l'environnement marin, une altération de la structure du sédiment conduisant à une sérieuse dégradation de l'écosystème benthique peut avoir lieu dans les lieux proches de l'industrie (Nakhle 2003). En période sèche, un vent plus ou moins violent peut disperser la poussière de phosphogypse stocké à terre. Cette poussière peut contenir du gypse, des fluorures, des éléments radioactifs, des métaux lourds. Ces impuretés peuvent être déposées sur le sol, accumulées dans le sol et par suite absorbés par les plantes pour être transférées aux chaînes alimentaires.

Pollution atmosphérique

Dans une industrie de fertilisants phosphatés, les sources fugitives de dégagement de poussière proviennent de la manipulation de la matière première (roche phosphate et soufre), des processus de fabrication (séchage et granulation de produits), de la manipulation des produits finis (engrais phosphates granulés), du stockage à l'air libre du déchet (phosphogypse) et de la roche phosphate, et du transport de ces matières par les camions en dehors de la zone industrielle (Figure 1.2). Une fraction de la poussière fugitive émise est déposée principalement sur une distance d'environ 1 kilomètre, puisque le mélange vertical peut atteindre des altitudes élevées (jusqu'à 30 m) à cette distance pour des conditions atmosphériques stables (Countess et al. 2001); au delà de 1Km c'est la déposition humide et l'interaction de la force du gravité agissant sur les particules avec les forces de suspension de vent qui ont lieu sur une échelle principalement globale. Une étude expérimentale élaborée de l'émission de la poussière de la roche phosphate et des fertilisants phosphatés a été effectuée par Lundgren and Rangaraj (1988),

La plupart de la déposition des particules de poussière se produit près de la surface, où la plume de la poussière agit l'un sur l'autre avec des végétations et d'autres obstacles. Quand la plume de la poussière fugitive imprègne les verrières végétatives, le dépoussiérage est augmenté par l'impaction et l'interception de substances particulaires présentées par les feuilles et les branches des plantes. En outre, la majeure partie de la poussière déposée à proximité de l'industrie est attribuée aux particules grosses de poussière (d > 20 μm), dû à leur inertie plus élevée, et par suite une plus grande vitesse de déposition. Les particules émises fines (d < 10 µm) sont principalement transportées dans l'atmosphère à une distance lointaine. L'impact des particules localement déposées (roche phosphate, phosphogypse et engrais phosphatés) sur le sol et contaminées avec des métaux lourds n'a pas été considéré dans des études antérieures. En fait, le dégagement de poussière a été étudié afin d'évaluer sa contribution aux pollutions atmosphériques et par conséquent la déposition régionale des particules fines (Countess et al. 2001; Noll and Aluko 2006). Dans ce contexte, de nombreuses études sont reportées aux particules fines (d < 10 µm) (Lin et al. 1994; Etyemezian et al. 2003). Dans ce travail, le degré de contamination de sol par la déposition locale des particules de poussière émises au cours du processus des engrais phosphatés a été étudié.

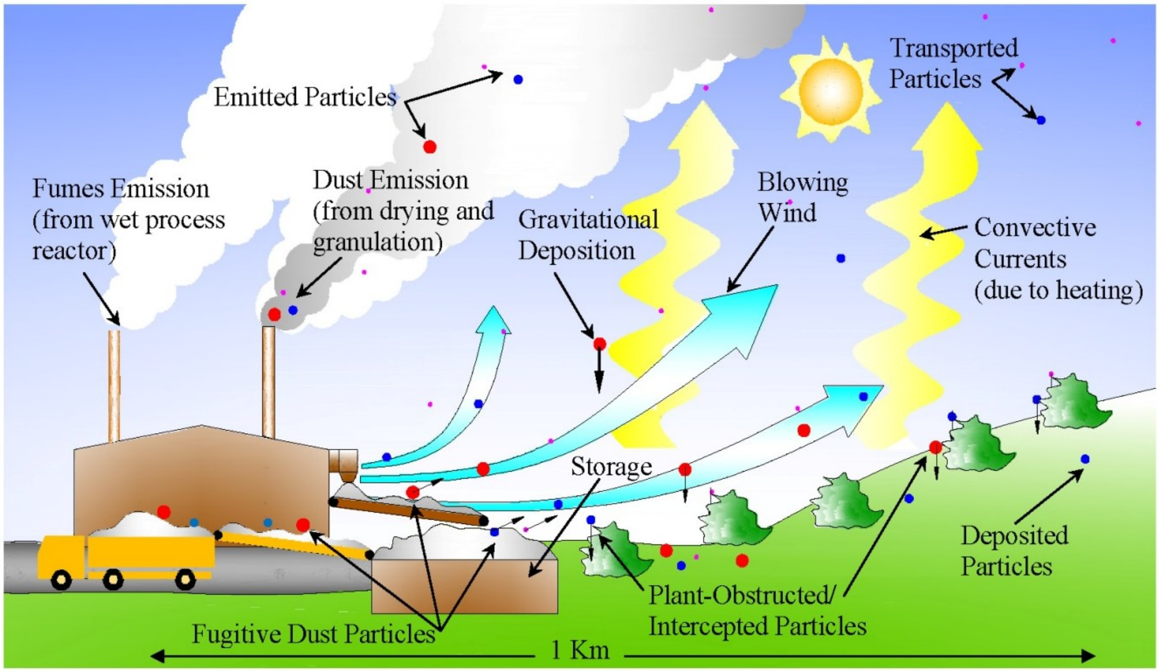

Figure 1. 2 Déposition locale de la poussière émise autour des industries des engrais phosphatés

1.3 Mobilité et biodisponibilité des éléments traces métalliques

1.3.1 *Mobilité des ETM*

Selon Juste (1988), "la mobilité d’un élément désigne son aptitude à passer d’un compartiment du sol où il est retenu avec une certaine énergie dans un autre où il est retenu avec une moindre énergie", le compartiment ultime étant la phase liquide représentée par la solution du sol. Deux compartiments peuvent être décrits dans le sol : la matrice solide formée par la fraction minérale et organique et la solution du sol, une phase aqueuse, constituée par des ions et des colloïdes organiques et inorganiques. La fraction minérale du sol étant composée par les minéraux primaires, les minéraux secondaires (par exemple kaolinite, montmorillonite, illite) et oxydes et hydroxydes de fer, d'aluminium et de manganèse, la fraction organique ou matière organique du sol est constituée par des substances complexes et biodégradables dont la majorité comprend les acides humiques et les acides fulviques différenciés par leur taille et leur solubilité à différents pH. Dans le sol, les éléments traces peuvent être: (1) échangeables sur le complexe argilo-humique, (2) précipités sous forme minérale, (3) adsorbés sur les oxy- hydroxydes de Fe, Al et Mn, (4) complexés ou inclus dans les molécules organiques, (5) inclus dans les réseaux cristallins des minéraux primaires et secondaires (Baize 1997). Dans la solution du sol, les éléments traces peuvent être sous forme des ions libres, des formes complexées avec la matière organique dissoute ou des formes associées aux phases colloïdales. Donc la mobilité des éléments traces dépend de leur interaction avec les compartiments du sol : la matrice solide et la solution du sol. Leur distribution entre la phase solide et la phase liquide ou leur solubilisation (leur passage de la phase solide à la phase liquide) constitue la clé pour mieux comprendre leur sort et leur transport dans le sol (Ross 1994; Adriano 2001). La mobilité des éléments traces dépend de plusieurs facteurs tels que le pH, le potentiel redox, la teneur en matière organique, leurs formes physico-chimiques ou spéciation, les fertilisants ou amendement du sol (Carrillo-Gonzalez et al. 2006) conditionnant leur disponibilité pour les végétaux et leur mobilité par transfert dans la solution du sol.

1.3.1.1 Evaluation de la mobilité des ETM

Il est donc indispensable d'évaluer la localisation des éléments traces dans les différentes phases organiques ou minérales afin de prévoir leur mobilité dans le sol du fait que la concentration totale est un indicateur médiocre de la mobilité des éléments traces (Tessier et al. 1979; Ure et al. 1993; Chopin et al. 2008). Nous avons recherché dans ce projet à identifier et à quantifier les différentes phases porteuses des ETM dans le sol se référant au terme de « spéciation géochimique ». Comme la spéciation des éléments traces dans le sol n'est pas stable (Kabata-Pendias 2004), nous avons également étudié sa cinétique suite à l'épandage du phosphogypse et des engrais phosphatés sur un terrain expérimental

Des approches chimiques en littérature sont utilisées pour évaluer la mobilité des métaux lourds : les extractions sélectives et les extractions séquentielles. Dans les extractions sélectives, l'échantillon du sol est soumis à un seul réactif. Ce type d'extraction est plutôt utilisé dans le but d'estimer la fraction biodisponible des métaux lourds dans le sol (Tack and Verloo 1996). Elle est plus rapide qu'une extraction séquentielle (Menzies et al. 2007) mais elle ne donne aucune indication sur les diverses associations des métaux lourds avec les différentes phases géochimiques présentes dans le sol. Notre choix s'est donc concentré sur les extractions séquentielles qui sont basées sur l'utilisation des réactifs sélectifs d'agressivité croissante choisis pour solubiliser différentes phases géochimiques responsables de retenir la plus grande partie des métaux lourds. Cette approche va nous permettre de connaître les fractions du sol auxquelles les métaux sont liés et par suite évaluer leur mobilité dans le sol. Plusieurs schémas d'extraction ont été utilisés dans les sols et les sédiments dans la littérature dont le protocole de (Tessier et al. 1979) a été largement appliqué. Celui-ci partage les éléments en 5 fractions géochimiques qui sont : la fraction échangeable, carbonates (acido-soluble), réductible (oxydes de Fe et Mn), oxydable (matière organique ou sulfures) et résiduelle (silicates). Le Tableau 1.2 résume les différents réactifs utilises dans la littérature pour l'extraction séquentielle afin d'extraire les 5 fractions géochimiques.

Ces méthodes d'extraction séquentielle sont souvent critiquées en littérature par le manque de sélectivité des réactifs (Kim and Fergusson 1991), la ré-adsorption et la redistribution des métaux solubilisés durant l'extraction (Kheboian and Bauer 1987; Belzile et al. 1989; Raksasataya et al. 1996; Burnett et al. 1999; Chopin et al. 2008). L'efficacité des réactions dépend des conditions opératoires : le temps d'extraction, le type d'agitation, la masse de l'échantillon et la méthode du rinçage. Plusieurs auteurs ont remarqué une dissolution incomplète des oxydes de fer durant l'extraction de la fraction réductible du schéma de Tessier conduisant à une surestimation de la fraction résiduelle. (Barona and Romero 1996; Gleyzes et al. 2002). Cependant, l'extraction séquentielle a prouvé sa valeur dans le domaine de la géochimie. Elle apporte des informations opérationnelles sur la mobilité des métaux, informations inaccessibles par d'autres méthodes. Combinée à d'autres résultats, l'extraction séquentielle peut nous aider à bien expliquer la localisation des métaux dans les phases du sol le long du profil et par conséquent comprendre leur mécanisme de transfert.

Tableau 1. 2 L'extraction séquentielle des éléments traces présents dans les sols et les sédiments dans la littérature

Fraction	Réactif	Auteur
Échangeable	$MgCl_2$	(Tessier et al. 1979; Kuo et al. 1983)
	KNO_3	(Gupta et al. 1990)
	$BaCl_2$	(Meguellati et al. 1982)
	$Mg(NO_3)_2$	(Shuman 1979)
Acido-soluble (liée aux carbonates)	CH_3COONa+ CH_3COOH	(Tessier et al., 1979; Meguellati et al., 1982)
	CH_3COOH	(Farrah and Pickering 1993)
Réductible (liée aux oxydes et hydroxydes de Fe, Mn)	$Na_2S_2O_4$+ Na-Citrate+ Acide citrique	(Tessier et al. 1979; Mehra and Jackson 1960)
	$NH_2OH.HCl$ + CH_3COOH	(Tessier et al., 1979)
	$(COOH)_2 + (COONH_4)_2$	(McLaren and Crawford 1973; Ma and Uren 1995; Farrah and Pickering 1993)
	$NH_2OH + CH_3COOH$	(Meguellati et al. 1982)
Oxydable (liée à la matière organique et aux sulfures)	$HNO_3 + H_2O_2$ + CH_3COONH_4	(Tessier et al., 1979)
	$Na_4P_2O_5$	(Garcia-Miragaya et al. 1986)
Résiduelle	$HF+HClO_4$	(Tessier et al., 1979)
	HNO_3	(Ribeiro and Mexia 1997; Hudson-Edwards 1997)

1.3.1.2 Interaction entre les phases minérales et les ETM

Les oxydes et hydroxydes, la matière organique du sol et les minéraux secondaires aluminosilicatés sont les principaux minéraux sorbant les métaux dans le sol. On appelle sorption l'ensemble des mécanismes réversibles qui engendrent le transfert d'une espèce métallique de la phase aqueuse vers la phase solide. Les principaux processus de sorption des métaux lourds sur les phases minérales du sol sont illustrés dans la Figure 1.3 qui peuvent être résumés en 4 mécanismes :

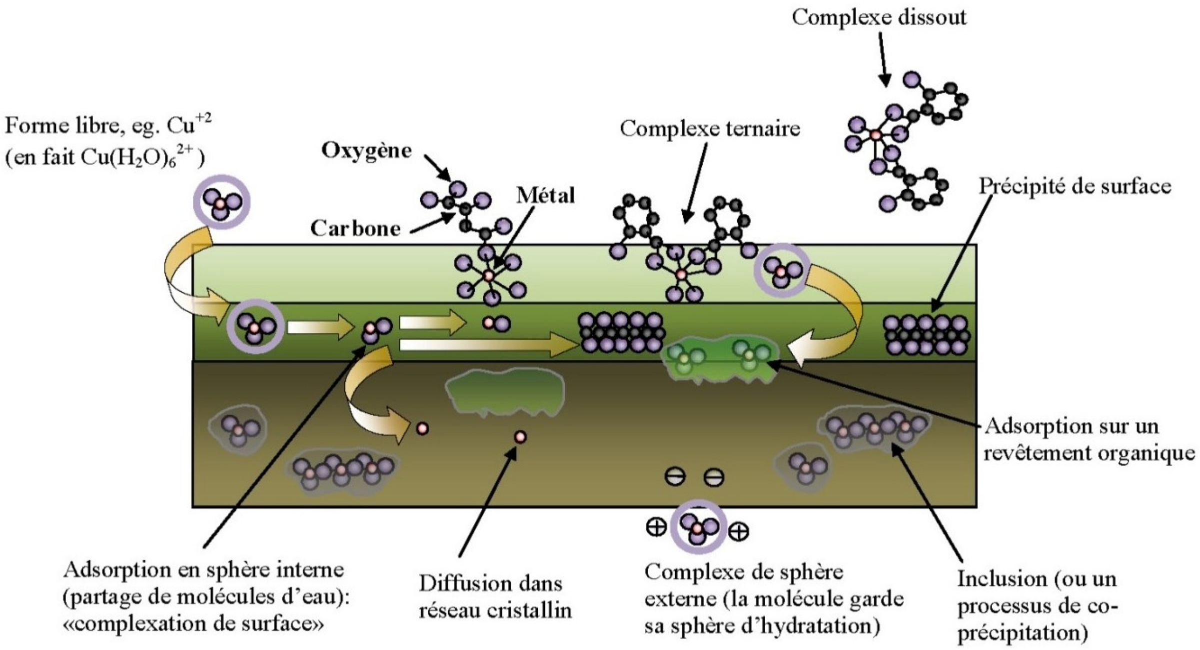

Figure 1. 3 Processus de sorption des métaux lourds sur des phases minérales (Dubertret 1953)

1) L'adsorption non spécifique des métaux à la surface des minéraux ou échange ionique provient des interactions électrostatiques des cations en solution. Dans ce mécanisme, l'espèce métallique forme avec la surface un complexe de sphère externe.

2) L'adsorption spécifique où le métal est saisi plus fortement à la surface des ligands du sol par une liaison covalente, ce qui résulte à la formation des complexes de sphère interne ou adsorption spécifique.

3) L'absorption du métal à l'intérieur des particules qui implique la diffusion du métal par exemple dans le réseau cristallin.

4) La précipitation de surface est caractérisée par la croissance d'une phase tridimensionnelle se produisant à la surface d'une phase solide minérale préexistante.

Les minéraux argileux ou phyllosilicates sont impliqués dans le type d'interaction électrostatique ou échange ionique du fait qu'ils possèdent une charge de surface permanente négative résultant des substitutions isomorphiques dans la structure. Alors que les hydroxyles en bordure des aluminosilicates, les hydroxyles des oxydes métalliques, les groupements carboxyles et phénols de la matière organique sont plutôt impliqués dans le type complexation dépendant du pH. Les oxy-hydroxydes métalliques (Fe et Mn) ainsi que les aluminosilicates amorphes jouent un rôle important dans les réactions d'adsorption spécifique. Cependant certains métaux peuvent former avec les ligands de surface des liaisons de nature électrostatique.

Le Tableau 1.3 montre les résultats des recherches variés étudiant la sorption des métaux sur les phases minérales et les constituants du sol. D'après ces recherches, Pb et Cu présentent une affinité plus grande que Zn et Cd pour les constituants du sol, cependant l'ordre de l'affinité de la sorption reste dépendant des propriétés du métal, du type de la surface et des conditions de l'expérience.

Tableau 1. 3 L'affinité relative des métaux pour les phases minérales et les constituants du sol

Les constituants du sol	***L'Ordre de la sorption***	***Références***
Goethite	Cu>Pb>Zn>Co>Cd	(Forbes et al. 1976)
Fe oxide	Pb>Cu>Zn>Cd	(Forbes et al. 1976)
Soil Minerals	Pb>Cu>Zn>Cd	(Elliott et al. 1986)
Kaolinite	Cd>Zn>Ni	(Puls and Bohn 1988)
Montmorillonite	Cd=Zn>Ni	(Puls and Bohn 1988)

1.3.1.3 Comportement géochimique des éléments traces sélectionnés

Parmi les éléments traces étudiés, nous en avons sélectionné quatre (Cd, Zn, Cu et Pb), présentant des comportements géochimiques différents ainsi une mobilité différente.

1.3.1.3.1 Le cuivre

Le cuivre est retenu dans le sol par un mécanisme d'adsorption spécifique et d'échange d'ion. Dans un sol calcaire, le cuivre est adsorbé spécifiquement sur la surface de $CaCO_3$ contrôlant la concentration de Cu en solution. Cavallaro and McBride (1981) ont proposé que le cuivre peut être adsorbé par un processus d'échange d'ion sur la bordure des minéraux argileux dans un sol non calcaire. D'autres études ont prouvé que l'adsorption de cuivre sur la montmorillonite diminuait quand le pH augmentait en présence des ligands organiques solubles. Une quantité maximale de Cu en solution est adsorbée sur l'argile à pH = 5.5 mais quand le pH augmente, son adsorption diminue ce qui est l'opposé de la relation générale entre l'adsorption des métaux et le pH. Les auteurs ont conclut que Cu rentrait en compétition avec le H^+ pour la complexation avec la matière organique quand le pH diminuait. Donc le Cu complexé avec la matière organique augmente avec le pH et par conséquent son adsorption sur la montmorillonite diminue. C'est pour cela que dans un sol contenant de la matière organique dissoute assez signifiante, une élévation du pH peut augmenter la mobilité de Cu dû à sa complexation avec les ligands organiques et assure son transport dans le profil du sol. Dans plusieurs études récentes, le cuivre a bien montré sa grande affinité pour la matière organique (Zaccone et al. 2007).

1.3.1.3.2 Le zinc

Dans des conditions acides et oxydantes, le zinc est le cation le plus soluble et le plus mobile ce qui lui rend le microélément le plus phytotoxique après l'aluminium et le manganèse (McBride 1994). Alors que dans des conditions alcalines, il est plutôt lié aux carbonates, oxydes de Fe et de Mn et aux aluminosilicates (Jaradat et al. 2006). Le zinc peut migrer dans le profil du sol sous forme d'ions libres en solution étudié dans un *in situ* lysimètre pour un sol sableux et légèrement acide (Citeau et al. 2003). Pourtant, il est intercepté par les constituants négatifs du sol comme les phyllosilicates et les oxydes de fer (Van Oort et al. 2006; Fernandez et al. 2007).

Des études macroscopiques de sorption de Zn ont montré qu'il peut être adsorbé sur les oxydes et hydroxydes de Fe et de Mn (Stahl and James 1991) et sur les aluminosilicates (Huang and Rhoads 1989; Spark et al. 1995) et que son adsorption augmente avec le pH. Cependant, à un pH alcalin et à des concentrations élevées de Zn, la précipitation devient le mécanisme le plus important qui contrôle la solubilité de Zn (Sadiq 1991). Une diffusion de Zn dans les micropores des oxydes de fer est observée qui est responsable de son immobilité dans le sol (Manceau et al. 2000).

1.3.1.3.3 Le cadmium

L'adsorption est le mécanisme prédominant contrôlant la concentration de Cd en solution. Dans les sols et les sédiments pollués un grand pourcentage de Cd est adsorbé par un mécanisme d'échange d'ion (Tessier et al. 1980; S. P. Kuo et al. 1983). La chimie de cadmium dans le sol est contrôlée par les propriétés du sol comme la quantité de la matière organique et notamment le pH (Kirkham 2006). Une étude à Canada a montré que la matière organique jouait un rôle très important dans la partition du Cd entre la matrice du sol et la solution du sol (Jeng and Singh 1995). Les auteurs ont prouvé que les sols forestiers organiques avaient une grande affinité de sorber le cadmium, 30 fois plus élevée que les phases minérales du sol. De plus, dans des conditions acides, la solubilité de Cd augmente et c'est la forme ionique Cd^{+2} devient prédominante. D'après plusieurs études le cadmium est fixé aux fractions solubles et échangeables (Tuins and Tels 1990; Li and Thornton 2001).Quand le pH augmente (supérieur à 6), le cadmium est adsorbé par la matrice solide du sol ou précipité. Le Cd peut former des complexes solubles avec des ligands inorganiques comme le Cl^{-}, ce qui augmentait la mobilité de Cd dans une colonne de sol étudié par Doner (1986).

Des résultats contradictoires ont été obtenus concernant la mobilité de Cd dans le profil du sol. (Loganathan et al. 1995) ont trouvé que le cadmium ajouté à un sol non perturbé restait dans les premiers centimètres de la surface du sol où les racines des plantes sont présentes. Ils ont conclut que la mobilité de cadmium dans le profil du sol est lente et qu'il est peu probable que le cadmium pollue les eaux souterraines. En revanche, certaines études ont proposé que dans un sol sableux, le cadmium devient mobile et constitue donc un risque pour les eaux souterraines (Lebourg et al. 1988). Une étude récente a montré que le cadmium est très mobile et peut migrer sous forme d'ion libre dans le profil du sol (Citeau et al. 2003).

1.3.1.3.4 Le plomb

Le plomb est un métal peu mobile dans le profil du sol (Nasreddine et al. 2010) dû à sa réactivité avec les argiles, les phosphates et la matière organique réduisant ainsi sa solubilité dans le sol. Pour un pH supérieur à 6, le plomb est soit adsorbé sur la surface des argiles ou forme des complexes carbonates. Lebourg et al. (1987) ont trouvé dans sept sols de la région Calais de France que Pb^{+2} est prédominant pour un pH inferieur à 6,5 alors qu'il est associé aux carbonates quand le pH augmente. De plus de sa liaison avec les carbonates dans un pH alcalin, le plomb peut être également fixé dans les oxydes de Fe et de Mn (Sheppard and Thibaut 1992; Jaradat et al. 2006).

Les Fe- colloïdes jouent un rôle très important dans la migration de Pb dans le profil du sol (Citeau et al. 2003). Même des observations sur la localisation de Pb dans des revêtements en fer en horizons profonds des sols contaminés ont été mentionnées (Van Oort et al. 2006; Fernandez et al. 2007). En présence de la matière organique dissoute, la mobilité de Pb augmente dans le sol (Manceau et al. 2000).

1.3.2 *Biodisponibilité des ETM*

La biodisponibilité définit l'aptitude d'un élément à passer d'un compartiment quelconque du sol à un être vivant (végétal, animal, bactérie). Dans une parcelle donnée, la biodisponibilité d'un élément peut être évaluée par la mesure de sa concentration dans les plantes (Baize, 1997) qui représentent effectivement le réactif d'extraction qui traduit le mieux la biodisponibilité réelle, car elle intègrerait tous les facteurs liés aux sols et à l'élément (Juste, 1988).

1.3.2.1 Accumulation des éléments traces dans les végétaux

Les végétaux contiennent des éléments traces pour des concentrations inferieures à 0,01% de leur matière sèche. Parmi ces éléments, le Cu et Zn sont considérés des micronutriments essentiels pour la vie des plantes alors que le Cd, Cr et Pb ne sont pas des éléments essentiels qui, selon leur concentration, peuvent être classifiés toxiques pour les plantes. Même le Cu et Zn en dépassant un certain seuil peuvent devenir toxiques. Les végétaux constituent une voie d'entrée dans la chaîne alimentaire en particulier la chaîne alimentaire humaine surtout les produits végétaux consommés (Epinards, Chicorée, Artichaut, Asperges…) qui contribuent dans l'apport quotidien des éléments traces pour une population adulte au Liban de 48,7%, 46,8%, 10,8% et 5,1% pour Pb, Cd, Cu et Zn respectivement (Nakhle 2003). D'où l'intérêt d'évaluer et de suivre l'évolution de l'accumulation des éléments traces dans les végétaux particulièrement pour le Pb et le Cd. L'accumulation des éléments traces diffère selon l'espèce, les variétés dans la même espèce végétale et même selon la partie du végétal étudié (racine ou parties aériennes).

Kuboi et al. (1986) classifie les plantes en 3 catégories selon leur degré d'absorption des éléments traces : faiblement accumulatrices comme les légumineuses, moyennement accumulatrices comme les Graminées, Liliacées, Cucurbitacées et Ombellifères et les plantes fortement accumulatrices comme les Chénopodiacées, les Crucifères, les Composées. Les feuilles des végétaux sont des accumulatrices efficaces des métaux contrairement aux fruits et légumes (Adriano 2001). De nombreuses études ont examiné le transfert des éléments traces des racines vers les parties aériennes, en calculant le rapport de la concentration des éléments traces dans les racines et celle dans les parties aériennes, dans l'objectif d'évaluer le potentiel du transfert des éléments traces dans la chaîne alimentaire (Baker 1981; Kabata-Pendias and Pendias 2001; Madejon et al. 2002). Ce rapport est appelé coefficient de transfert (CT). Ce transfert reste dépendant de la mobilité du métal, sa concentration dans le sol, le type et l'âge des plantes (Ross 1994; Kabata-Pendias and Pendias 2001; Batista et al. 2007). Des études ont montré un transport restreint de Cu des sols contaminés dans les parties aériennes de plusieurs types de plantes (Arduini et al. 1996; Ait Ali et al. 2002; Dominguez et al. 2008). Les plantes de la famille *Brassicaceae* ont montré une accumulation limitée de Zn dans les parties aériennes indiquant un transport régularisé dans ce type de plantes (Madejon et al. 2007). Selon leur coefficient de transfert, Baker, (1981) a classifié les plantes en des plantes accumulatrices (CT > 1.5), indicatrices (CT de 0.5 à 1.5), et exsudatrices (CT < 0.1). Dans notre projet, la plante « Chicorée » est considéré comme indicateur de la contamination du sol par les éléments traces métalliques et particulièrement le cadmium (Simon et al. 1996; Aksoy 2008). De plus, Simon et al. 1996 ont dosé la concentration de Cd dans la Chicorée cultivée sur des sols amendés de Cd (11,2 kg par hectare appliqué durant une période de 5ans). Ils ont trouvé que l'accumulation de Cd était plus élevée dans les feuilles de chicorée que dans les racines.

Pour évaluer le degré de la contamination des plantes, éventuellement leur risque pour la chaîne alimentaire, les concentrations obtenues doivent être comparés par rapport à une plante « contrôle » ou des références présentes dans la littérature. La concentration normale des éléments traces dans les feuilles des plantes, les niveaux des éléments considérés phytotoxiques et la concentration maximale tolérable par le bétail sont représentés dans le Tableau 1.4.

Tableau 1. 4 Concentration des éléments traces dans les plantes normales, contaminées, phytotoxiques et maximale tolérable par le bétail par différents auteurs (Chaney 1989; Malavolta 1994; Ross 1994)

Les éléments traces	***Concentration normale dans les plantes en mg/kg***[a]	***Concentration dans les plantes contaminées*** [b]	***Concentration phytotoxique dans les plantes en mg/kg***[c]	***Concentration maximale tolérable par le bétail*** [a]
Cd	0,1- 1	0,03 – 3,8	3-8	0,5
Cu	3-20	20-100	60-125	300
Pb	2-5	30-300	-	30
Zn	15-150	100-400	70-400	1000

[a]Chaney, 1989 ; [b]Ross, 1994 ; [c]Kabata-Pendias et Pendia, 1992

1.3.2.2 Facteurs influençant la biodisponibilité

Le pH joue un rôle très important dans la biodisponibilité influençant la spéciation des éléments traces en solution. En effet, l'accumulation de Cd et son absorption par les plantes augmente quand le pH diminue (Kuo et al. 2004). Une tendance linéaire entre le pH et l'absorption de Cd est observée dans la littérature (Tudoreanu and Phillips 2004). Les racines des plantes jouent un rôle vital dans la transformation et la spéciation des éléments traces dans le sol (Koo et al. 2005). Les exsudations racinaires des substances variables et des composés de masse moléculaire faible comme l'acide acétique, l'acide oxalique et des acides aminés peuvent modifier le pH de l'ambiance racinaire et par conséquent augmenter la biodisponibilité des éléments (Mortvedt 1991). De plus, ces acides organiques peuvent complexer les ions métalliques en les rendant plus mobiles et biodisponibles. L'âge est un facteur également impliqué dans la biodisponibilité des éléments traces; avec le temps et comme résultat des processus chimiques à long terme dans le sol et physiques comme la diffusion, la biodisponibilité des éléments peut être réduite. Cependant, il est difficile de savoir le taux d'un métal âgé car plusieurs paramètres puissent intervenir et affecter les processus de l'âge d'un métal comme le pH, la température, l'humidité du sol, sa concentration dans le sol (Lock and Janssen 2003). D'autres facteurs influencent la biodisponibilité des éléments traces comme la capacité d'échange cationique (CEC), le potentiel redox et la température. D'une manière générale, les éléments traces sont plus retenus quand le CEC augmente par suite leur mobilité et leur biodisponibilité diminuent. Les réactions redox peuvent affecter la concentration des éléments en solution. En générale, les conditions oxydantes favorisent la rétention des éléments dans le sol alors que les conditions réductrices contribuent à la solubilisation des surfaces des hydroxydes ferriques par exemple et par conséquent la libération des éléments qui y sont adsorbés. Cependant, la précipitation des éléments peut avoir lieu dans ces conditions par formation des sulfures. L'état de redox dans le sol est étroitement lié à l'activité des microorganismes. La minéralisation augmente pendant les saisons chaudes (quand la température s'élève), ce qui aboutit au passage des éléments traces des complexes qui y sont associés vers la solution du sol.

1.4 Amendement du sol par les Fertilisants phosphatés et le phosphogypse

L'application des engrais phosphatés et l'amendement du sol par le phosphogypse peuvent perturber le cycle des éléments traces et par suite modifier leur spéciation du fait qu'ils contiennent des quantités significatives des métaux dépendant de l'origine de la roche phosphate et du processus utilisé.

La concentration des éléments traces dans les engrais phosphatés peut varier entre 50-600 mg/kg; 0,5-40 mg/kg; 9-100 mg/kg; 90-1500 mg/kg; 10-60 mg/kg; 5-70 mg/kg pour Zn, Pb, Cd, Cr, Cu et Ni respectivement (Adler, 2001). Le Cd est l'élément qui a pris le plus grand intérêt en terme de son accumulation dans les cultures provenant des fertilisants et de l'amendement du sol (McLaughlin et al. 1999). La teneur des ETM dans le phosphogypse est dans une gamme variant entre 6-103 mg/kg ; 6-315 mg/kg ; 0,8- 40 mg/kg ; 2-43 mg/kg ; 6-135 mg/kg ; 3-7 mg/kg pour Cu, Zn, Cd, Ni, U, Pb respectivement provenant de différentes sources (Afrique du Sud, Tunisie, Syrie, Florida, Espagne, Idaho) (May and Sweeney 1984; Malan 1988; Rouis and Bensalah 1990; Luther et al. 1993; Al-Masri et al. 2004; Perez-Lopez et al. 2007). Une fois déposés sur le sol, les éléments traces ou contaminants peuvent s'accumuler dans le sol par les mécanismes de sorption diminuant ainsi leur mobilité ou passer dans la solution du sol constituant un risque pour les eaux souterraines et la flore. Ils peuvent aussi être immobilisés par précipitation en sels (Figure 1.4).

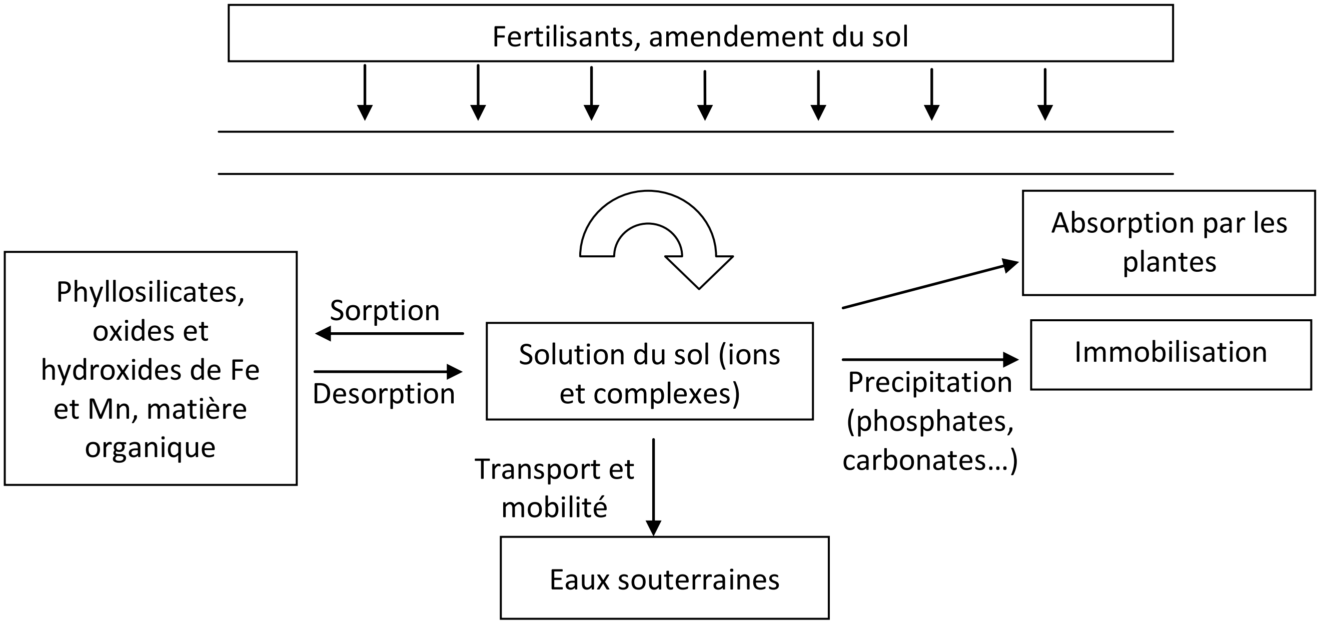

Figure 1. 4 Le sort des ETM déposés sur le sol suite à l'amendement du sol par les fertilisants et le phosphogypse

Il est largement reconnu que l'amendement des phosphates (fertilisants phosphatés, roche phosphate, acide phosphorique) et des sous-produits industriels comme le phosphogypse (Garrido et al. 2005) stabilisent les contaminants dans le sol (Lindsay 1979; Hettiarachchi et al. 2001; Geebelen et al. 2002; Cao et al. 2004; Brown et al. 2005; Chen et al. 2007; Kumpiene et al. 2009).

1.4.1 *Etudes réalisées sur la valorisation des engrais phosphatés en agriculture*

L'application des engrais phosphatés a été largement utilisée dans de nombreuses régions du monde. Par exemple l'application des fertilisants phosphatés à un taux de 600 kg/ha/an sur les sols Brésiliens acides, n'augmente pas la concentration des métaux lourds (Cd, Cr, Cu, Ni, Pb et Zn) dans le sol d'atteindre des niveaux nuisibles à court et moyen terme. En fait leur addition *via* les engrais phosphatés est surtout moins que les valeurs annuelles limites tolérables en Brésil (Malavolta, 1994). Du fait de sa toxicité pour les animaux et l'Homme (Kirkham 2006) et de sa forte corrélation avec les phosphates (Mortvedt and Beaton 1995), le cadmium a fait l'objet de nombreuses d'études dans la littérature. Pour évaluer l'effet environnemental de Cd dans les fertilisants phosphatés, des expériences à long terme, considérées plus significatives, ont été établies. Morvedt (2005) résume les résultats obtenus de l'application du TSP, provenant de la roche phosphate de Florida, plus que 50 ans pour un taux annuel du P variant entre 15-30 kg/ha. Il a conclu qu'une augmentation minimale de la concentration totale de Cd dans le sol se produit à court terme. Une étude à Norvège soutient ce résultat en montrant que bien que le Cd tend à s'accumuler dans les échantillons sélectionnés et traités après 70 ans d'expérience sur des engrais phosphatés, le taux de son augmentation est lent (Singh and Myhr 1997). L'application des engrais phosphatés (0,03-12 g ha^{-1}) augmente considérablement le Cd extrait (Enamorado et al. 2009) alors que Singh and Myhr (1997) n'ont pas trouvé un tel effet dans leur étude à Norvège, bien qu'une tendance à avoir une concentration de Cd plus élevée dans le sol est observée dans les parcelles recevant une quantité supérieure des fertilisants phosphatés. En général, l'augmentation de la concentration de Cd en solution suite à l'application des engrais phosphatés est attribuée à une diminution du pH et une force ionique élevée (Grant et al. 2002). En effet, Lambert et al. (1989) ont évalué la solubilité de Cd et Zn après l'application des engrais phosphatés (MAP) en mesurant leur concentration dans l'eau du sol extrait. Ces applications ont été réalisées sur un terrain cultivé à des taux et concentrations différents des métaux et ceci pour une période de 3 ans. Pour évaluer l'application à long terme des engrais phosphatés, une simulation au laboratoire a été réalisée en ajoutant une dose unique équivalente à 15 ans d'application. Les résultats ont montré qu'en augmentant le taux des engrais phosphatés et en utilisant ceux qui contiennent plus de Cd, la concentration du Cd dans l'extrait du sol augmente sur le terrain et au laboratoire alors que celle de Zn ne peut pas être relié à la concentration de Zn dans les engrais ou le taux d'application.

Des résultats contradictoires ont été obtenus en littérature sur la concentration de Cd dans les plantes. En effet, sur un terrain expérimental, l'application des engrais phosphatés, en induisant un apport de Cd allant de 0,07-28 g/ha/an, a conduit à une augmentation de la concentration de Cd dans les plantes (Guttormsen et al. 1995), alors que l'addition de Cd à des taux allant de 0,3-1,2 g/ha/an n'a pas abouti (Singh and Myhr 1997) à un résultat pareil. Cette contradiction provient de plusieurs facteurs comme le type des fertilisants utilisés, la concentration de Cd, le taux des fertilisants, l'espèce de la plante, les propriétés du sol et les conditions du climat (Singh et Myhr, 1997). De plus une compétition entre le Cd et le Zn est souvent établie. En fait, une concentration élevée de Zn dans la solution du sol réduit l'absorption de Cd par les plantes

(McLaughlin et al. 1995; Grant and Bailey 1997). Ces deux métaux peuvent rentrer en compétition pour l'adsorption des particules du sol et l'absorption par les plantes, cette compétition dépend de la concentration de ces 2 éléments dans le sol, dans la solution du sol et dans les fertilisants. En outre, l'application sur le sol des niveaux élevés des engrais phosphatés diminue la concentration de Zn dans les tissus des plantes due à l'interaction entre le phosphore et le zinc dans le sol. Une réduction dans l'adsorption de Cd observée en présence des phosphates est attribuée à la formation de complexes Cd-P en solution.

1.4.2 *Etudes réalisées sur la valorisation du phosphogypse comme amendement*

La production de chaque tonne d'acide phosphorique est accompagnée de la production de 4.5 tonnes de sulfate de calcium (US EPA 2000). Jusqu'au présent, la production du phosphogypse dans le monde est plus de 100 à 280 Mt /an (Parreria et al. 2003). Des études ont valorisé le phosphogypse en agriculture comme amendement pour les sols (Conkline 1992; Arocena et al. 1995) en particulier pour les sols calcaires et les sols acides (Rutherford et al. 1994). Il est considéré comme stabilisateur chimique pour améliorer les propriétés du sol surtout les sols salins qui sont impropres à la culture (Degirmenci et al. 2007). De plus, il est amendé sur les sols dans le but de réduire l'érosion du sol, augmenter la disponibilité de soufre et de phosphore (Zhang et al. 1998; Delgado et al. 2002) et augmenter la fertilité des sols agricoles (May and Mortvedt 1986; Mullins and Mitchell 1990).

Cependant, des études ont mis l'accent sur l'effet cumulatif de l'amendement du phosphogypse au cours des trois dernières décennies dans une région de marais en Espagne appelée Lebrija et son impact en agriculture (Alcordo et al. 1999; Papastefanou et al. 2006; Abril et al. 2008). De plus, Abril et al. (2008) et Enamorado et al. (2007) ont étudié les effets du phosphogypse sur l'absorption des éléments et des isotopes Cd, Pb, U, ^{226}Ra et ^{210}Po par les tomates du type *Lycopersicum esculentum* Mill L. dans différents fermes commerciales. Les résultats ont montré un effet direct possible entre l'amendement du phosphogypse et l'augmentation de la concentration de Cd dans les tomates. La concentration de l'U, ^{226}Ra et ^{210}Po est au dessous de la limite de détection. Dans cette même région, Perez- Lopez et al. (2006) ont montré l'importance de quantifier les éléments traces mobiles et toxiques ajoutés à chaque hectare comme résultat de l'amendement du phoshogypse et l'effet cumulatif des trois décennies d'application, vu que la majorité des éléments traces sont associés à la fraction mobile du phosphogypse. La quantité des éléments traces mobiles estimée à 1,2 x 10^3 t de Sr, 20 t de Cr, 9 t de Zn, 7 t de Cu, 6 t de Pb, 5 t de Cd, 3 t de Ni et 1,4 t d'U peut avoir été ajoutée à une surface de 140 km^2 comme résultat de trois décennies d'application du phosphogypse. Al-Masri et al. (2004), en étudiant la distribution des métaux lourds dans le phosphogypse syrien, ont montré que Cu, Zn et Cd peuvent être transférés aisément du phosphogypse à l'eau distillée et par suite ceci doit être pris en considération quand le phosphogypse est utilisé comme amendement sur les sols agricoles.

D'autre part, les résultats de l'amendement du phosphogypse sur un sédiment alluvial d'une rivière à Mississippi sous un contrôle du potentiel redox et pH ont montré que le phosphogypse a réduit la solubilité d'Al et par suite sa toxicité pour les plantes qui poussent dans les sédiments (pH=7) (Burnett et al. 1999). D'autres études ont montré que l'addition du phosphogypse sur les sols induit la formation et la rétention des polymères hydroxy d'aluminium qui peuvent stimuler la capacité de rétention des éléments toxiques dans le sol (PNTTA 2000) même il peut régulariser la mobilité de Pb, Cd et Cu dans les sols acides (Pacyna 1984). Aguilar- Carrillo et al. (1998) ont même évalué l'efficacité du phosphogypse dans l'immobilisation de Cd, As et Tl dans les sols acides.

2 Démarche Expérimentale

2.1 Les sites d'échantillonnage

Pour répondre au mieux aux objectifs de cette étude, deux sites ont été choisis au Liban, l'un industriel et un autre agricole utilisé comme un terrain expérimental pour le suivi de la distribution verticale et de la mobilité des éléments traces dans le profil du sol, étant donné que les engrais phosphatés et le phosphogypse constituent une source de contamination du sol par les éléments traces. D'un point de vue géographique, les 2 sites se situent au nord du pays. Le site industriel où se trouve l'industrie des fertilisants chimiques, à 55 km Nord de la capitale Beyrouth, est localisé à l'Est de la mer méditerranéenne dans une région appelée Selaata. Il est constitué par une plaine triangulaire traversée d'Est en Ouest par les cours de Nahr al-Jawz qui coule au pied du plateau. L'autre est situé à 18 km Nord-Est de Selaata, dans une région appelée Bsarma, un village situé à l'Est du plateau Koura loin de toute influence industrielle et où le site peut être contrôlé et surveillé. De plus, ce site est connu par ses activités agricoles. D'un point de vue géologique, ce sont les roches sédimentaires non clastiques, les dépôts colluviaux du Quaternaire et les dépôts alluviaux qui ont formé le sol à Selaata et Bsarma respectivement (Darwich et al., 2004). Deux séries alluviales paraissent exister dans la région de Bsarma : des alluvions à abondante matrice argileuse rougeâtre incluant des galets de basalte pourris (hétérométriques) et une formation aux éléments à la fois homométriques de calibre modeste et d'émoussé médiocre. Ces alluvions ont constitué d'épandage sur le plateau Koura (Sanlaville, 1977). Le même type du sol « *Luvisol* » est identifié pour les deux sites, ce type du sol est caractérisé par un lessivage des oxydes de fer et de manganèse associés avec les argiles.

L'usine des engrais chimiques fonctionne depuis une cinquantaine d'années en rejetant ses déchets (en particulier le phosphogypse) dans l'environnement sans aucune restriction de la part de la législation Libanaise. Les études antérieures se sont concentrées sur la pollution marine autour de l'industrie sans donner aucun intérêt sur leur impact continental.

Le terrain expérimental choisi, de surface 256 m^2, a été limité par un siège métallique afin d'éviter toute intervention extérieure au site. A l'intérieur, il est divisé en 24 parcelles chacune avec une surface de 1m^2 par un quadrillage en bois de (longueur x largeur x hauteur) (1x1x0,15m) afin de délimiter la surface et minimiser une contamination externe par ruissellement, 12 parcelles ont servi à l'étude du phosphogypse (PG) et les 12 autres pour l'étude des engrais phosphatés (EP). Les parcelles occupent une surface de 64 m^2. Elles sont numérotées de 1 à 11 (Figure 2.1). La douzième parcelle reste intact, servant de témoin (T) utilisé comme référence tout le long de l'étude.

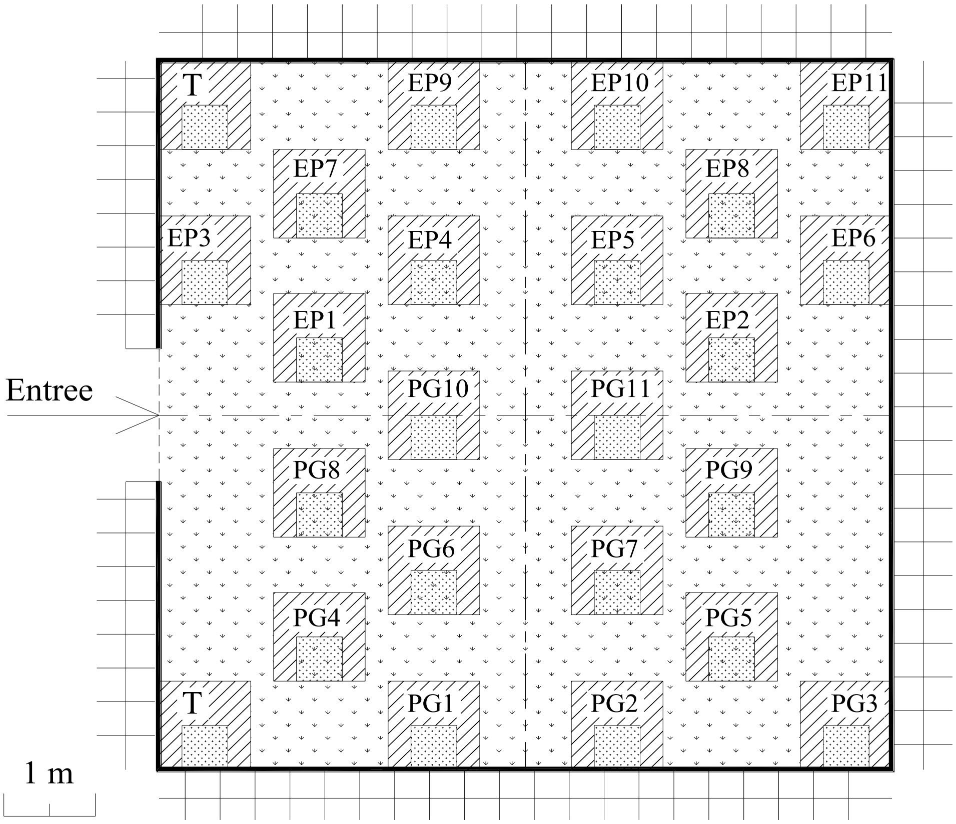

Figure 2. 1 Terrain Expérimental à Bsarma

L'epandage a été realise sur une surface de 0,25 m^2 pour une dose de 1kg de phosphogypse et 2 kg des engrais phosphates. Cette quantite est loin des pratiques agricoles utilisees au Liban (1860/kg/ha/an) dans l'objectif de simuler l'impact des engrais phosphates sur le sol à long terme. Les différents prélèvements ont été réalisés sur les parcelles épandues par le phosphogypse et les engrais (SSP) espacées par des temps et saisons variables. Puisque l'amendement du phosphogypse a été realise pendant une periode seche et sur la surface sans homogeneisation, un arrosage au demarrage était necessaire pour assurer le transfert des particules du phosphogypse au sol.

La figure ci-dessous montre une coupe verticale modèle au niveau de la surface de la parcelle épandue avec la carotte pénétrant dans le profil du sol.

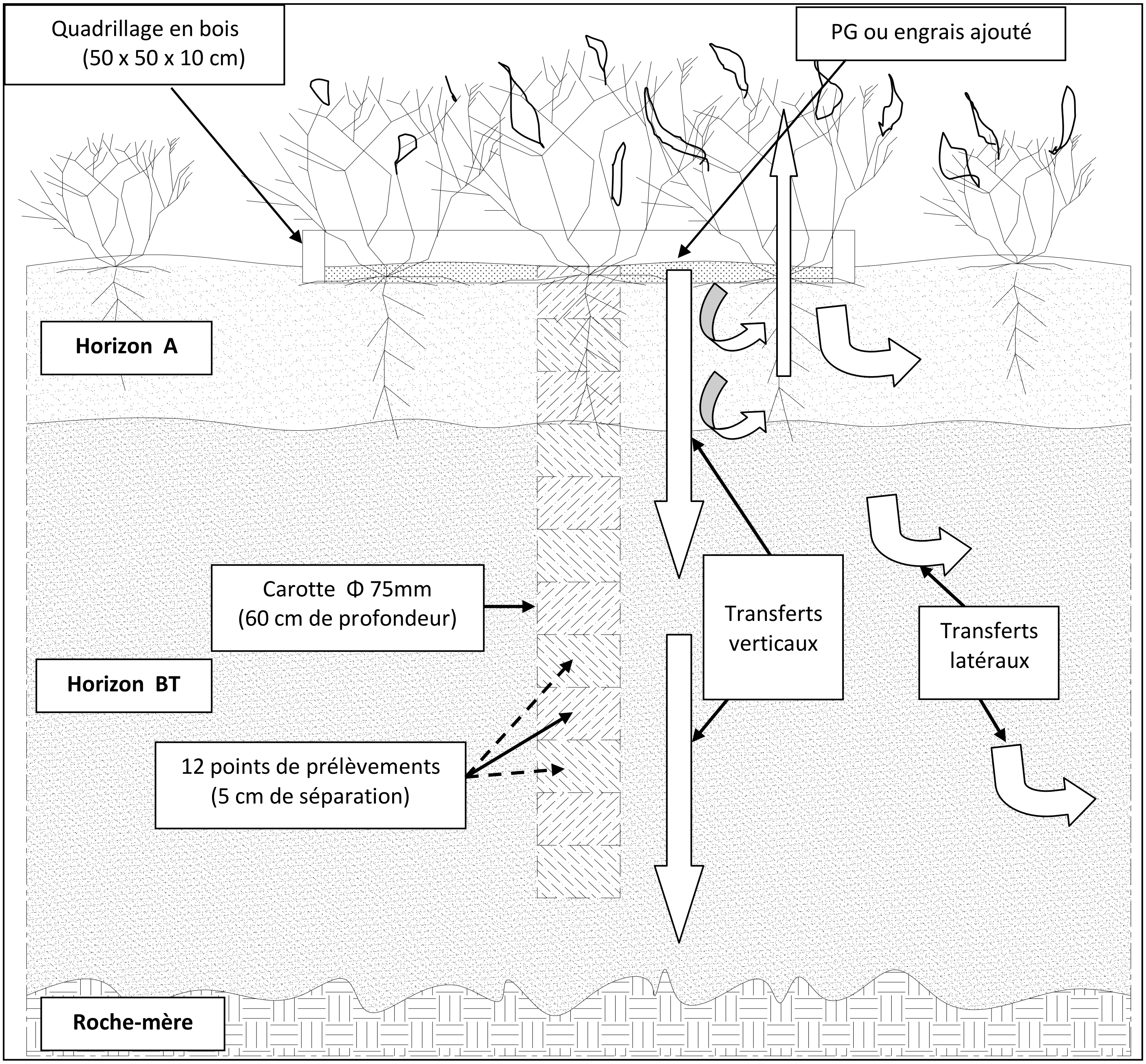

Figure 2. 2 Coupe verticale au niveau du carottage d'une parcelle épandue

Celui-ci est formé en surface d'un horizon A de couleur foncée à teneur relativement élevée en matière organique et à activité biologique maximale. C'est un horizon qui peut être soumis à l'influence marquée d'une intervention anthropique. Puis l'horizon BT dit argillique ou encore argilo-illuvial situe sous l'horizon de surface. Il est caractérisé par un enrichissement en colloïdes argileux et oxydes de fer repartis notamment en revêtements orientés sur les faces des agrégats structuraux. La roche-mère ou les matériaux originels sont des matériaux argileux.

Deux types de transferts peuvent se produire à partir de la surface, les transferts verticaux et les transferts latéraux. Dans un sol de type « *Luvisol* », une migration des apports agricoles associés aux argiles et aux hydroxydes de fer des horizons superficiels (horizons éluviaux) aux horizons profonds (horizons illuviaux) peut avoir lieu par lessivage. Ces éléments peuvent être absorbés par les racines des plantes. Le lessivage peut être latéral entraînant les particules dans des horizons particuliers en dehors de la zone d'épandage.

La concentration totale des métaux a été dosée dans les plantes cultivées dans les parcelles pour avoir une indication ou une estimation de l'absorption de ces métaux par les plantes et son évolution avec le temps. En d'autres termes, pour bien évaluer si un transfert a eu lieu aux plantes au cours du temps pouvant constituer un risque pour la chaîne alimentaire, dés que les plantes cultivées sont du type *Cichorium Intybus* (Chicorée) utilisé fréquemment dans le régime alimentaire local.

3 Effects of fertilizer industry emissions on local soil contamination: A case study of phosphate plant on the east Mediterranean coast

(Article 1)

Résumé de l'article I

Dans une industrie des engrais phosphatés, l'émission de poussière fugitive est originaire de la manipulation de la matière première (roche phosphate) et des produits finaux, du transport et de stockage à l'air libre du déchet généré lors de leur production (le phosphogypse). Du fait que cette poussière émise est contaminée par les métaux lourds, elle peut causer un danger pour l'environnement et particulièrement pour le milieu continental. Notre objectif principal est d'évaluer l'impact des poussières émises de l'industrie des engrais phosphatés sur le sol à proximité et les risques qui y sont associés Pour bien comprendre le transfert de ces polluants de l'atmosphère sur la surface de sol et leur mobilité, nous avons mis en œuvre la technique de l'extraction séquentielle pour identifier les phases porteuses des éléments traces dans les poussières émises de la roche phosphate, des engrais phosphatés et du phosphogypse. En parallèle, les échantillons de surface (0-15cm) prélevés à proximité de l'industrie et à une distance de 1 km ont été analysés pour calculer la concentration totale des éléments traces (Cd, Cr, Cu, Pb, Zn, Sr, U et Ni) et éléments majeurs ainsi qu'une référence située dans une région rurale loin de l'émission. L'ordre de magnitude sur les flux éléments traces (Cd, Cr, Cu, Pb, Zn, Sr, U et Ni) déposés sur le sol et provenant de la roche phosphate, de phosphogypse et des engrais phosphatés a été calculé.

L'extraction séquentielle des éléments traces dans les trois sources (roche phosphate, engrais phosphatés et phosphogypse) a montré que le pourcentage moyen de Zn, Cu, Ni et Cd est à 50 % dans les fractions échangeables et acido-soluble. Le plomb et l'uranium sont plutôt associés aux argiles alors que le strontium et le chrome sont présents dans la fraction oxydable. La concentration moyenne des éléments traces dans les sites de prélèvement est de 392,5; 182,7; 156,4; 55,3; 43; 42,8; 16,7; 1,9 (mg/kg) pour Sr, Zn, Cr, Ni, Pb, Cu, U et Cd respectivement. Si la comparaison se fait par rapport à la référence (< 0.01; 92; 15; 1.2; 22; 35; < 0.01; < 0.01 (mg/kg) pour Sr, Zn, Cr, Ni, Pb, Cu, U et Cd respectivement), un enrichissement en ses éléments au niveau des sites est remarqué notamment pour le Sr, Cr, U, Ni et Cd. Mais si la comparaison se fait par rapport aux normes canadiennes à l'exception de l'uranium qui a été fixé par rapport aux normes Allemagnes (200; 200; 64; 50; 70; 63; 5; 1.4 (mg/kg) pour Sr, Zn, Cr, Ni, Pb, Cu, U et Cd respectivement), la concentration moyenne de cuivre, du plomb et du zinc au niveau des sites est au dessous des normes. Il est important à signaler que la concentration de ces métaux atteint des valeurs bien élevées au niveau de quelques sites dépendant de leur localisation par rapport a l'industrie.

La distribution spatiale de la concentration du phosphore au niveau des sites a montré qu'ils sont classés en deux groupes, ceux qui sont situés au sud et au sud-est de l'industrie dont la concentration est légèrement supérieure à celle de la référence (groupe I), l'autre localisé au Nord-Est de l'industrie dans la direction dominant du vent et dont la concentration est énormément supérieure à celle de la référence (groupe II). De même que l'enrichissement en éléments traces au niveau des sites suit le même modèle, dans la direction du vent dominant, ce qui suggère une corrélation entre le phosphore et les éléments traces des sites à l'exception de Cu et Pb dont l'enrichissement en ses éléments est élevée dans quelques sites du groupe I et notamment ceux qui sont localisés le long de la route. En effet, les corrélations menées entre les éléments traces et les éléments majeurs ont montré que le phosphore (élément de base des engrais phosphatés, roche phosphate et phosphogypse) est le principal porteur de l'uranium, strontium, cadmium et chrome. Le Cu et le Pb ne montrent pas une corrélation ni avec le phosphore ni avec le calcium alors que le Ni se trouve associé avec le fer. Ce qui donne qu'une autre source contribue à l'élévation de Cu et Pb dans certains sites qui est dû probablement aux échappements des voitures et des camions. Pour le Ni, puisqu'il est associe aux fractions labiles des sources d'émission (engrais phosphatés, roche phosphate et phosphogypse), il est peut-être transféré au sol puis fixé par les oxydes de fer.

Dans l'objectif de confirmer l'idée que l'enrichissement des éléments traces proviennent des poussières émises de l'industrie, les flux des métaux sont calculés. Il apparaît que le phosphogypse contribue à un dépôt de poussière le plus élevé (73%) suivi par la roche phosphate (21%) et les engrais phosphatés (6%). Ce sont les grosses particules (> 20 cm) de poussière qui se déposent sur le sol autour de l'industrie à une distance de 1 Km. Les métaux lourds associés à ces produits montrent un important apport de flux déposés allant de Sr, Zn, Cr, U, Ni and Cd dans un ordre décroissant. En outre, une fonction croissante est remarquée entre les flux des métaux calculés et la moyenne de leur concentration au niveau des sites.

Par conséquent, les poussières émises par l'industrie des fertilisants chimiques contribuent à l'enrichissement des sites par les éléments traces et ceci dans la direction du vent dominant et à une distance de 1 km

Effects of fertilizer industry emissions on local soil contamination: A case study of phosphate plant on the east Mediterranean coast

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Published in ***Environmental Technology***; 2012, Vol. *33*, Issue 8, p 873-885, doi:10.1080/09593330.2011.601765

Abstract

Fugitive dust emission, transport and deposition from phosphate fertilizer industries may exhibit an environmental hazard to the surrounding environment, particularly to soil. This study is to evaluate such hazard by investigating the fate of airborne pollutants, their transfer from atmosphere to soil surface, and their contamination potential.

Elements concentrations were measured in soil samples. Elemental analyses were carried out using ICP-AES and ICP-MS. Trace elements speciation using sequential extraction method was performed on the industry's raw material (apatite), product and waste (phosphate fertilizer and phosphogypsum). Local atmospheric dry deposition estimating model was formulated. Sample data statistical analyses were performed.

Measured phosphorus was accumulated considerably in the north-east of the industry, mainly due to the prevailing wind and associated dry deposition. Results exhibited considerably above-threshold enrichments in potentially toxic, bio-available trace elements (Cd, Zn) (2.5-6.9, 295-506 mg kg^{-1}) and radionuclide (U, 20-98.69 mg kg^{-1}) within a major deposition area. Speciation results revealed Zn and Cd occurring predominantly in mobile phases within the pollution-source materials. Dry deposition calculation showed extensive input fluxes of Sr, Zn, Cr, U, Ni and Cd. Significant correlation was established between measured trace elements concentrations and their calculated deposition fluxes. Phosphorus species were the principal carriers of trace elements in soils.

Phosphate industry poses serious soil pollution hazard, with deposited contaminants being potentially hazardous to plants and ground waters. This study serves as a basis to assess the phosphate industries risk impact on the soil, while it introduces combined analytical methodologies for such assessment.

Keywords: *phosphate industry; dry deposition; soil contamination; trace elements; speciation*

3.1 Introduction

When contaminated dust particulates are emitted to the atmosphere, they can be transported by wind and deposited on soils, thus spreading the pollution over large distances. The phosphate fertilizer industry is recognized to be one of the main emitters of such contaminated dust (DEQ 2005). Indeed, both raw material and primary by-product, i.e. phosphate rock (PR) ore and phosphogypsum (PG), contain large amounts of trace elements and fluorine, which can be toxic to the environment (Burnett et al. 1999; Senesi et al. 1999). The vast majority of PG waste is disposed of into the surrounding environment of fertilizer industries either as dry or wet stacking, or is simply discharged into the sea or local water bodies (IFA-UNDP 1998).

Most studies dealing with the environmental impacts of PG disposal have focused on marine pollution (Alcaraz Pelegrina and Martinez-Aguirre 2001; Al-Masri et al. 2000; Al-Masri et al. 1999b; Othman and Al-Masri 2007). Indeed, the coastal zone of many Mediterranean countries, i.e. Tunisia, Algeria, Morocco, Lebanon, and Syria, has been afflicted with serious pollution problems generated by the disposal of gypsum by-product (Azouazi et al. 2001; Guillaumaut et al. 1996; Kacimi et al. 2006). According to UNEP, such disposal is responsible for an input of more than 1,300 tons year^{-1} of mercury, cadmium and lead into the Mediterranean Sea (UNEP/MAP 2008). Other studies considered the effect of PG disposal in stockpiles and ponds on ground waters (Rutherford et al. 1995; Canete et al. 2008; Duenas et al. 2007). A recent study (Attar et al. 2011) investigated the environment potential contamination with heavy metals and fluorides in the vicinity of PG stockpiles.

In contrast, little information is available about the pollution generated by the atmospheric dry deposition of phosphate and PG particulates in the vicinity of fertilizer industries.

The aim of this study is to investigate the effects of windborne contaminants contained in PG and phosphate mineral particulates emitted in the atmosphere from fertilizer industry on the surrounding soils. These effects include the extent of soil enrichment in trace elements relative to the background of the region and threshold values, and the associated hazards imposed on the soil environment. Such hazards are inherent in the contaminants mobility that depends on trace elements carriers, as well as on their behaviour and interaction with the soil constituents. Hence, trace elements total concentrations in soils surrounding the industry, and their chemical species in the contamination source were determined. Relationships between major and trace elements in the soil were examined as an approach for identifying species of trace elements carriers.

In order to relate the quantified soil contaminations to the industry's processes, correlation between soil contaminants and the industry's processed materials composition was determined. In addition, to substantiate the idea that soil contamination effect was caused by the industry's emission, it was prudent to assess the extent of dust particulates deposition and the respective trace elements input fluxes into the soil of the study area; correlation between trace elements soil input by dry deposition and their concentrations in the soil was examined.

A conventional phosphate plant, located on the Mediterranean coast 55 km north of Beirut city, was suitably selected for the case study. In fact, this industry has been established since 1957, and the sedimentary PR processed by this plant originates mainly from Syria (Brigden et al. 2002), which contains relatively high concentrations of trace elements as well as radio-nuclides (Cowart and Burnett 1994; Abboud-Abi Saab and Atallah 1996). It follows that, the considered phosphate plant has been processing contaminated raw materials for an extended period of time sufficient to make the assessment of its impact on the surrounding environment reliable. Furthermore, the plant is surrounded by open land field which makes it suitable for the study objective to investigate the effects of phosphate plant on local soils contamination.

3.2 Materials and Methods

3.2.1 Study Area

The study area spreads over about 0.8 km^2 around the fertilizer industry (Figure 3. 1). The factory footprint shows two sections, the main unit located along the coastal zone which produces sulphuric acid, phosphoric acid and phosphate fertilizer (PF), and the annexed factory where granular TSP is obtained from a slurry-granulation process. Phosphogypsum (PG) by-product is stored next to the raw material (phosphate rock) storage area (Figure 3. 1). Two wet scrubbers are used to control the emissions of fugitive dust and gases generated from acidulation, granulation, and drying. Scrubbers exhaust is expelled into the atmosphere through two chimneys. Some contaminated dust is nevertheless released into the surrounding environment from the open air storing and handling (unloading, grinding, curing, loading, etc.) the raw material, product, and by-product.

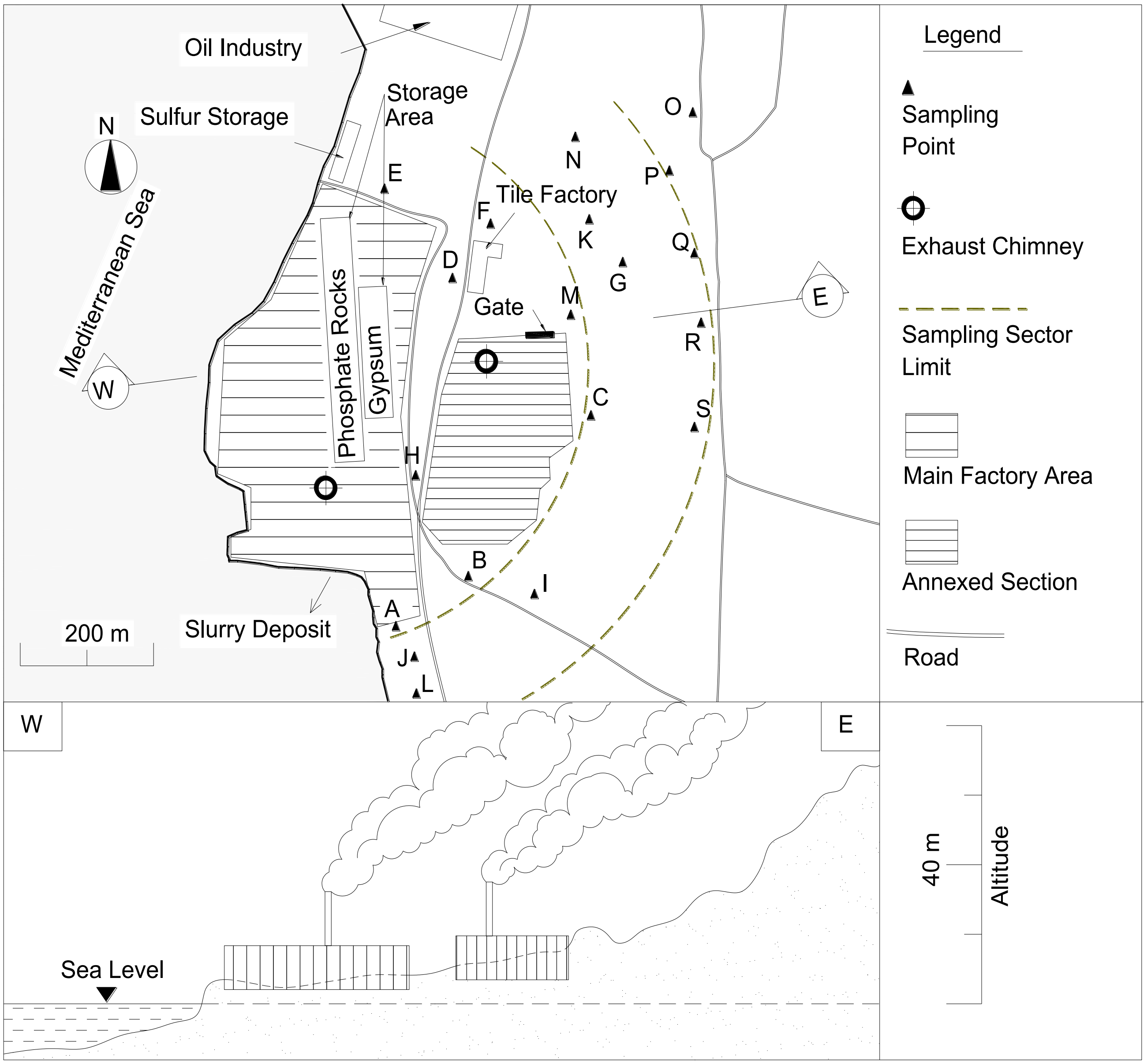


Figure 3. 1 Localization of the study area and sampling sites

The yearly production of the plant is about 230 000 tons of SSP (single super phosphate), 31000 tons of TSP (triple super phosphate), and 160 000 tons of phosphoric acid (Al-Hajj and Muscat 2000; Yager 2005). It uses more than 840 tons of phosphate rocks per day (Abboud-Abi Saab and Dargham 1998). Around 1250 tons of by-products (phosphogypsum) are disposed of by dry stacking on land for further use as cement additive.

A tile factory and an oil industry are located northeast and north of the study area, respectively.

The general topographical profile of the area is depicted by an east-west section view (Figure 3. 1). Starting from sea-shore, the land elevation increases at a rate of about 1.5% in the east direction to reach a level of about 7 m at the industrial zone eastern limit (500 m from the coast-line), and then it further increases at a rate of 3% to reach an elevation of 15 m at the sampling region limit. The average slope becomes then steeper (10%) towards inland. However, water runoff is minimal with the vegetation cover containing mixed shrubs and few dispersed growing trees such as *Quercus calliprinos* (Abi-Saleh 1978). Groundwater shallow aquifer exists among the alluvial deposits and sand accumulations. The water table in this aquifer doesn't exceed 5-30 m in depth across the study area; depending on the inland distance from the coast line (Dubertret 1953).

The climate of the region is Mediterranean, with heavy rains in the winter season (January to May), and dry to arid conditions in the remaining seven months of the year. The average annual rainfall is about 823 mm, varying from 600 to 900 mm along the coastal zone (Department of Meteorology 2010). The prevailing wind is south westerly (Windfinder Website). The soil of the study area is reported in the Lebanese soil map as an association of Haplic and Leptic Luvisols (Darwish et al. 2005).

3.2.2 *Sample Collection and Analysis*

Nineteen sampling sites (tagged from A to S) were selected in the study area at various distances and orientations from the fertilizer industry (Figure 3. 1). Sampling sites A, B, C, D, E, F, H, and M are scattered in the close vicinity of the factory – where the water table is high – whereas G, I, J, K, L, N, O, P, Q, R and S are situated along a land stretch between 600 and 800 meters from the industry, at relatively higher altitude – and lower water table. Vegetation density generally increases with distance from the plant, and it is remarkably high near sites O and R, where clustered shrubs are found. A sampling reference site was also selected in a rural region located 7.10 Km south of the industry. Surface soil samples (0–15 cm) were cored (internal section of 10 cm) at each site, and homogenized after removing stones and plants. Samples were oven-dried at 50^{o}C for 12 hours, and sieved.

The soil pH was estimated after re-suspension of samples in de-ionized water with a 1:5 ratio (AFNOR X 31-103).

The concentration of major and trace elements in soil samples, phosphate rock, and phosphogypsum by-product, were measured (in two repetitions) by ICP-AES and ICP-MS, respectively, after melting 200 mg sample with 600 mg $LiBO_3$ in a Pt-Au crucible, and dissolving the melt with 1N HNO_3. Ignition loss was determined after heating the samples at 980°C for 3 hours. Reagent blanks and reference soil samples (IAEA-405) were analyzed in order to verify the validity and accuracy of the analytical measurements. Analysis was conducted at SARM (CRPG, Nancy).

A five-stage sequential extraction method was performed on PR, PG and PF samples using modified Tessier sequential extraction (Tessier et al. 1979). The extractable contents of trace elements, from an initial 5 g aliquot, were determined as follows: (1) exchangeable fraction (F_1) was extracted with 40 mL of 1 M $Mg(NO_3)_2$ (Shuman 1979); (2) acid soluble (F_2) with 40 mL of 1 M CH_3COONa adjusted to pH 5 with CH_3COOH; (3) reducible (F_3) with 20 mL Na-citrate (78,4g L^{-1}) and 20 mL $NaHCO_3$ (9.82g L^{-1}), and then adding 1g of $Na_2S_2O_4$ (80°C for 4h) (Mehra and Jackson 1960); (4) oxidizable (F_4) with adding 8 mL HNO_3 (0.02M) 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 2h); and (5) residual (F_5) with 40 mL HNO_3 (65%) (Hudson-Edwards 1997; Ribeiro and Mexia 1997). Each extraction step was followed by centrifugation at 5000 rpm for 30 minutes. The centrifugates were then analyzed for trace elements by Atomic Absorption Spectroscopy (AAS) (Analytical Gena Zeenit 700). Reagent blanks and certified reference samples (IAEA-405) were also analyzed in order to monitor analytical accuracy and precision.

Statistical analyses were performed on the experimental data in order to introduce a level of confidence to the interpretations inferred from data correlations and comparisons. Correlation analysis (Pearson r) between trace and major elements, and t-test for means equality between results of grouped samples were carried out. All statistical analyses were performed using SPSS Version 17.

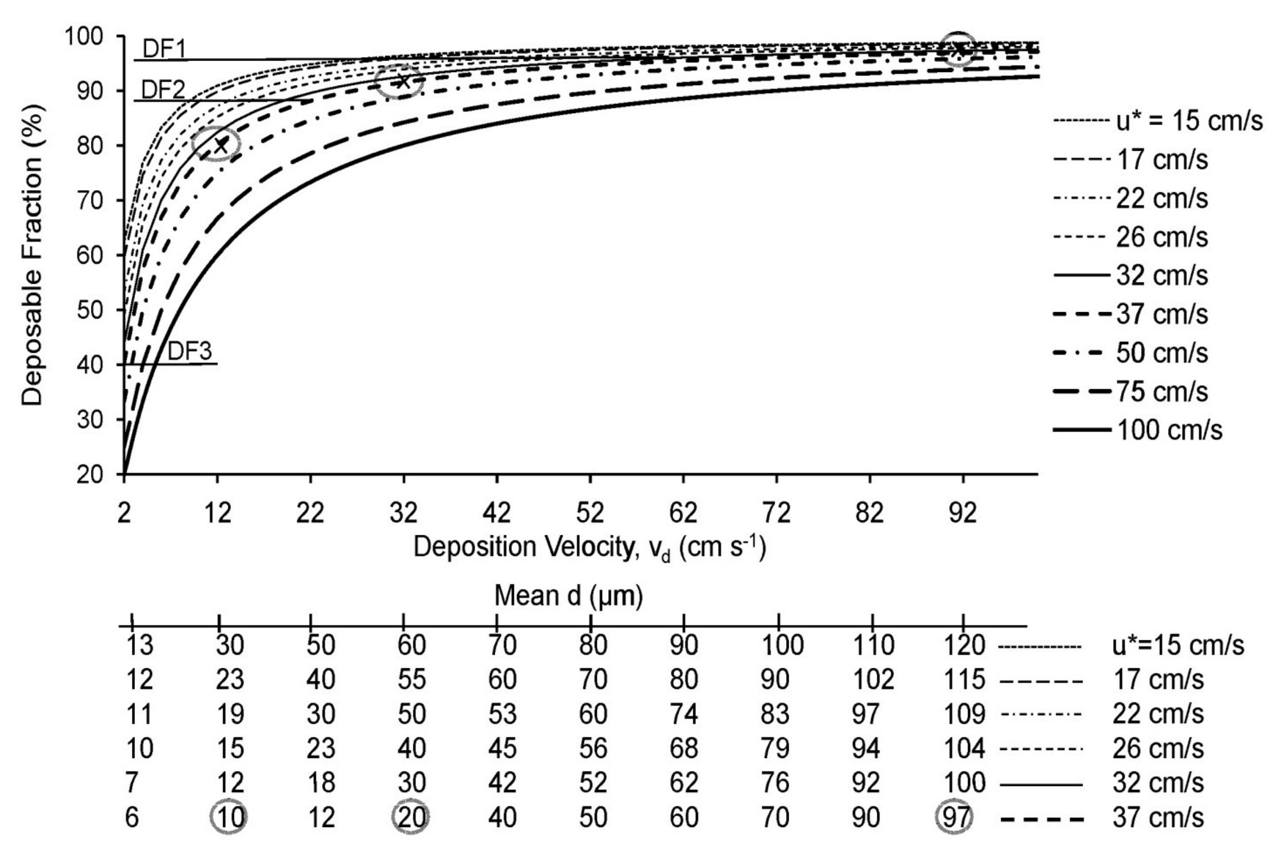
3.2.3 *Dry Deposition Model*

Since fugitive dust emission, transport, and deposition are not limited to a confined boundary and depend on a continuum of constantly changing factors including, but not limited to, meteorological conditions, frequency and nature of handling operations, the topographical, structural, and vegetative features of the source surrounding area, accurate assessment of these emissions could not be practically feasible, and only order of magnitude estimations would be expected.

The fugitive dust emission rate can be estimated by using applicable emission factors obtained from published related works (Lundgren and Rangaraj 1988), whereas the rate of deposited fraction (D_F) can be deduced from the transportable fraction ($T_F = 1 - D_F$) of fugitive dust, given by $T_F = 0.08U^*(V_d+0.08U^*)^{-1}$ (Countess et al. 2001; Etyemezian et al. 2003). Therefore,

$$D_F = 1 - 0.08U^*(V_d + 0.08U^*)^{-1} \qquad (1)$$

Where U^* and V_d are the friction velocity (cm s^{-1}) and dry deposition velocity (cm s^{-1}), respectively. Friction velocity is defined as the square root of the viscous drag to air density ratio, U^* (m s^{-1}) = (τ (kg m s^{-2} m^{-2}) / ρ (kg m^{-3}))$^{1/2}$, which is a measure of turbulent dispersion and buoyant mixing generated by wind speed and atmospheric stability factors. Under stable atmospheric conditions, U^* does not exceed 50 cm s^{-1}; high friction velocities exceeding 120 cm s^{-1} generate sand storm in arid region (Etyemezian et al. 2003). The deposition velocity is a function of many variables including the particulate size and density, roughness height, and meteorological conditions (Countess et al. 2001); coarse airborne dust particulates (1-100 µm) exhibit higher deposition velocity, due to their higher inertia and gravitational settlement velocities (Noll and Aluko 2006). Therefore, for a given value of U^*, the deposable fraction can be determined from equation (1) for different deposition velocities, hence for different corresponding particulate sizes, since the factors other than particle size affecting V_d are tied with U^*. Plotted results for applicable U^* values are shown in Figure 3. 2. The particulate sizes corresponding to the different combinations of (V_d, U^*) are obtained from particulates (ρ = 1g cm^{-3}) deposition velocity measurements reported by (Lin et al. 1994). These measurements could be applicable to PR, PF, PG, and S particulates having comparable densities (~ 1g cm^{-3}).



13	30	50	60	70	80	90	100	110	120	u*=15 cm/s
12	23	40	55	60	70	80	90	102	115	17 cm/s
11	19	30	50	53	60	74	83	97	109	22 cm/s
10	15	23	40	45	56	68	79	94	104	26 cm/s
7	12	18	30	42	52	62	76	92	100	32 cm/s
6	10	12	20	40	50	60	70	90	97	37 cm/s

Figure 3. 2 Dust particulate deposable fraction as a function of friction velocity (U*) and deposition velocity (Vd) with corresponding particulate aerodynamic diameter (d) (ρ = 1 g cm-3)

The fugitive dust deposition rate can be obtained from the following equation,

$$D_R = E \times R \times (D_{F1} \times \%d_1 + D_{F2} \times \%d_2 + D_{F3} \times \%d_3) \qquad (2)$$

Where,

D_R = Deposition rate

E = Emission factor

R = Handled rate of the dust emitting source

D_{F1}, $D_{F2,}$ and $_{DF3}$ denote the deposable fractions of particles with aerodynamic diameters of d_1, d_2, and d_3, respectively, where: $20 < d_1 < 97$ µm, $10 < d_2 < 2\ 0$ µm, and $d_3 < 10$ µm.

$\%d_1$, $\%d_2$ and $\%d_3$ represent the particulates mass size-distribution of the emitting source (PR, PF, PG or sulphur).

The deposition rate (T_e) of a trace element (TE) can then be determined as follows;

$T_e = PR\ D_R \times [TE]_{PR} + PF\ D_R \times [TE]_{PF} + PG\ D_R \times [TE]_{PG}$ (3)

Where $[TE]_{PR}$ designates the trace element concentration in PR (phosphate rock), $[TE]_{PF}$ in PF (phosphate fertilizer), and $[TE]_{PG}$ in PG (phosphogypsum).

Using Figure 3. 2, it can be shown that for an average friction velocity U^* of 37 cm s^{-1} (a reasonable average value for the region atmospheric conditions), particulates having aerodynamic diameters between 20 and 97µm (d_1) would acquire deposition velocities between 32 and 92 cm s^{-1}, and their corresponding deposable fractions would range from 92 to 97% with a mean average of about 95% (D_{F1}). Similarly, the mean average deposable fractions (D_{F2} & D_{F3}) for particulates with aerodynamic diameters d_2 and d_3 would be 88% and 40%, respectively.

The dust emission from the industry's exhaust stacks is controlled by the use of wet suppression. In such a case, 80% control efficiency (20% of uncontrolled emission) of dust suppression may be used for the exhaust emission (DEQ 2005).

3.3 Results and Discussion

3.3.1 *PR, PG, and PF Trace Elements Content and Speciation*

Results for trace elements content and speciation in PR, PG, and PF are shown in Table 3. 1. In order to obtain a combined value representing the concentration of a trace element in the overall emitted particulates, weighted average of that trace element concentration in the emission materials was obtained based on the industry's consumption and production of raw material, product and by-products. Trace elements contents in PG were within the range obtained by Al-Masri (Al-Masri et al. 2004) for Syrian phosphogypsum, with the exception of Pb and Cu that exhibited lower concentrations in the present study case, which could be due to some differences in processing the raw material. It should be noted this result similarity is attributed to the fact that the industry raw material (phosphate rock) is outsourced by the industry from Syria.

Table 3. 1 Trace elements total concentration (mg kg-1) in phosphate rock (PR), phosphogypsum (PG), and phosphate fertilizer (PF), and % distribution (weighted) over various fractions (F1, F2, F3, F4 and F5)

	Cr	*Cu*	*Cd*	*Pb*	*Sr*	*U*	*Zn*	*Ni*
PR	157.10	6.97	7.13	3.02	1479.00	23.68	257.20	57.71
PG	74.27	5.13	3.44	2.46	1132.00	10.82	123.60	26.89
PF	98.45	16.63	6.18	2.65	1108.00	27.25	199.30	66.85
Average[a]	105.16	8.56	5.23	2.68	1230.10	18.79	182.60	46.13
F_1	7.35	11.57	9.99	10.39	2.30	6.68	21.52	37.24
F_2	10.69	44.62	41.46	19.11	7.36	8.01	20.84	12.46
F_3	12.38	1.51	19.11	6.32	19.60	0.00	2.81	0.00
F_4	41.85	29.64	1.49	12.49	43.39	0.00	22.83	22.80
F_5	22.50	12.85	21.29	58.07	23.03	79.33	30.85	21.60

Note: Mean values are shown, N=2. Upper and lower values are within ±8% of the mean.

[a] Average total concentration or fraction of trace element in PR, PG and PF is weighted according to their handled quantity in the phosphate fertilizer plant (840[b], 1250[c], and 715[d] tons day^{-1} for PR, PG, and PF respectively)

[b] (Abboud-Abi Saab and Dargham 1998)

[c] Considering that the industry produces around 160,000 tons of phosphoric acid per year (Al-Hajj and Muscat 2000), around 2200 tons of phosphogypsum are generated per day (5 tons for every ton of phosphoric acid) (US EPA 2000) of which 950 tons are disposed of in the Mediterranean sea (Abboud-Abi Saab and Atallah 1996)

[d] (Al-Hajj and Muscat 2000)

Among the fractionated trace metals, Cd, Zn and Ni occurred considerably in the mobile forms within the combined deposition source (Table 3. 1), thus they were likely to be readily mobile in the soil horizons, and to become associated with ground water contamination. However, further investigation on the behaviour, forms and dynamics of these elements in the soil would be required to affirm this conclusion.

Cr and Cu association with mobile fractions was rather significant, whereas Pb occurred mainly in the residual fraction, F_5.

3.3.2 *Major Elements*

In many soil samples, the average contents in SiO_2, Al_2O_3, and Fe_2O_3 (Table 3. 2), fell in the range of typical concentrations found in Luvisols (FAO 1999). CaO and P_2O_5 were found in notably higher than typical concentrations, which could be attributed to phosphorus and calcium input into the soils from the phosphate industry.

The major elements contents in PR were within comparable ranges with those in PG, except for phosphorus, a main constituent of PR. Silicon was the major impurity in both materials, and was found in the range of 7-8.8%, as opposed to 0.1-0.7% for Al, Fe, Mg, and Na, and less than 0.1% for Mn and K. The phosphate content in PG (13%) was notably high and most likely attributed to un-reacted PF.

The measurements of the pH of soil sampling indicate the buffer behaviour of soils. They show a neutral-alkaline pH fluctuating between 7.03 and 7.57.

3.3.3 *Phosphorus Distribution*

The total phosphorus content (Table 3. 2) is quite variable ranging from 0.6% to about 6-10% P_2O_5 at most sampling sites, and even reaching a surprisingly high P_2O_5 total of 29.07% at M. Actually, M is located close to the entrance of the phosphate fertilizer granulation unit, and accidental spills during fertilizer handling is likely to occur.

Figure 3. 3 depicts the spatial distribution of phosphorus concentrations over the study area.

Table 3. 2 Major elements contents (%) in all sampling sites, phosphate rock (PR), and phosphogypsum (PG)

Site	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*MnO*	*MgO*	*CaO*	*Na_2O*	*K_2O*	*P_2O_5*	*LOI*
Ref.	35.32	8.25	3.30	0.06	1.08	2.93	0.72	1.69	0.04	42.73
A	20.24	4.23	4.45	0.06	2.44	31.75	0.33	0.50	2.38	32.94
B	16.83	4.15	3.99	0.05	1.82	36.38	0.18	0.35	1.75	33.65
C	36.83	9.42	8.42	0.10	2.86	15.77	0.33	0.74	0.63	23.19
D	8.78	2.36	2.24	0.03	1.26	40.28	0.54	0.23	7.46	31.35
E	24.78	5.66	5.31	0.06	2.61	26.48	0.45	0.55	11.65	20.54
F	20.60	6.26	4.45	0.07	1.15	33.23	0.24	0.47	2.94	29.30
K	37.45	10.88	7.14	0.11	1.39	13.78	0.53	0.87	6.03	20.00
G	48.87	13.40	8.64	0.18	0.96	8.85	0.27	0.99	2.65	13.20
N	24.25	5.96	4.23	0.06	1.56	28.26	0.31	0.57	7.93	24.85
O	37.26	1.25	6.39	0.11	1.11	15.87	0.29	0.84	1.77	23.63
P	32.08	8.58	5.15	0.07	0.88	21.69	0.25	0.61	3.52	25.69
Q	20.72	5.22	3.86	0.06	0.94	30.04	0.25	0.47	9.60	27.48
R	26.58	6.72	5.11	0.10	1.03	24.42	0.23	0.73	0.65	33.06
S	42.86	10.82	8.04	0.11	1.50	19.41	0.32	0.90	0.77	25.16
M	7.15	0.60	0.32	0.01	0.29	48.30	0.41	0.01	29.07	12.43
L	51.78	13.71	10.07	0.01	0.67	28.60	0.31	1.29	1.01	14.79
H	6.60	1.87	1.29	0.02	0.57	13.92	0.75	0.15	10.26	63.47
I	24.82	7.12	5.11	0.10	1.17	27.20	0.21	0.73	1.15	31.22
J	34.90	7.33	5.96	0.07	1.72	22.31	0.17	0.59	1.30	24.39
Average	27.55	6.61	5.27	0.07	1.36	25.61	0.34	0.61	5.40	26.86
PR	8.82	0.42	0.19	0.00	0.74	46.96	0.47	0.02	28.21	9.36
PG	7.02	0.25	0.11	0.00	0.38	38.16	0.33	0.01	13.02	16.90

Note: Mean values are shown, N = 2. Upper and lower values are within ±9% of the mean.

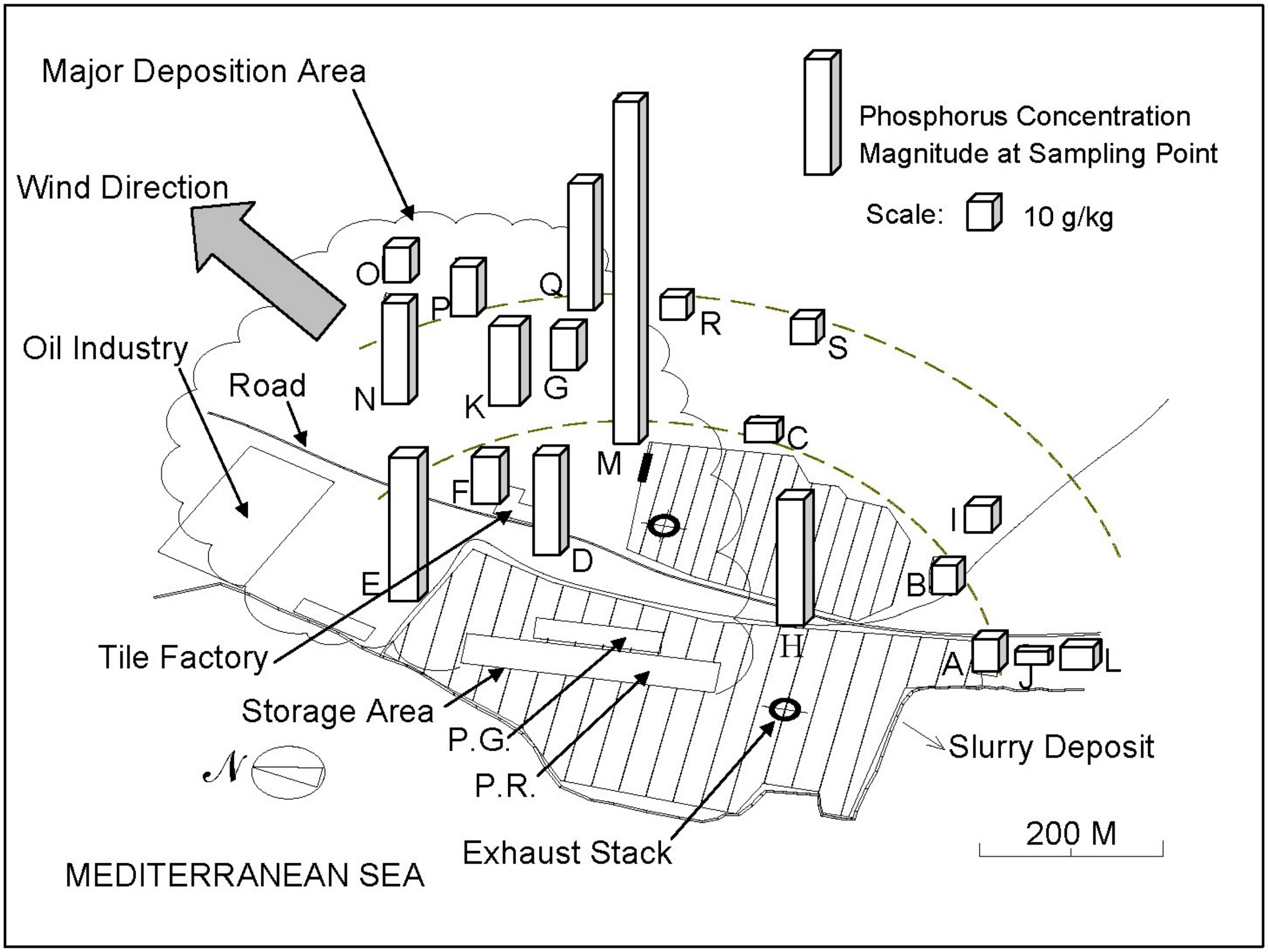


Figure 3. 3 Phosphorus concentration magnitude in sampling sites

Two groups of soil samples can be readily distinguished according to their phosphorus content; those roughly situated to the east-southeast of the factory with a P level rather higher than the background surface soil (Group I: A, B, C, I, J, L, R, S), and those located to the north-east of the fertilizer industry (Group II: D, E, F, G, H, K, N, O, P, Q) with dramatically higher phosphorus concentrations. The area delimited by the latter group is located downstream of the potential phosphorus emission sources, i.e. open-to-air storage of phosphate ore and PG by-product, and wet scrubber exhausts, in the dominant wind direction. This pattern strongly suggests that the emission of fugitive dust particulates from the fertilizer industry is responsible for the excess of phosphorus in those soil samples. Furthermore, the total phosphorus content of those soil samples tend to decrease downwind of the sources, except at sampling sites F and G where higher phosphorus concentrations should be expected. However, F is located just behind the tile factory which then acts as an obstacle to the wind flow, whereas G is situated downhill of Q, the topographical feature determining an enhanced particulates collection efficiency.

3.3.4 *Concentrations of Trace Elements*

a) U, Sr, Cd, Cr, and Zn

Table 3. 3 presents total trace element concentrations results in all sampling sites and in the region background, and displays the trace elements permissible limits set by CCME-CEQG (Kabata-Pendias and Pendias 2001). The data shows wide variations, element as well as site wise. To facilitate results reading, site enrichments (mg kg^{-1}) are determined from Table 3. 3 (by subtracting the reference background concentration from the total site content), and plotted in separating the two site groups in Figure 3. 4. Logarithmic scale is used to account for the wide data range.

Table 3. 3 Trace element contents (mg kg-1) in all sampling sites

Site	*Cr*	*Cd*	*Cu*	*Pb*	*Sr*	*U*	*Zn*	*Ni*
Ref.	15.00	<0.01	35.00	22.00	<0.01	<0.01	92.00	1.20
A	112.50	1.37	17.55	47.08	365.30	7.46	93.96	49.29
B	107.80	1.60	71.24	134.53	351.20	6.40	213.40	52.03
C	167.80	0.65	33.85	28.77	300.70	2.91	102.70	79.06
D	105.40	2.73	66.55	35.51	526.60	23.68	219.20	36.79
E	226.30	3.85	124.80	90.63	650.40	38.09	418.80	102.90
F	116.60	1.42	25.41	23.38	391.20	9.45	97.09	50.16
K	192.30	2.54	27.41	34.67	388.10	21.14	133.90	77.15
G	179.40	1.35	33.13	21.58	238.00	7.50	124.00	71.24
N	143.70	3.08	74.54	62.82	474.20	20.25	506.50	54.86
O	158.20	1.04	65.06	40.60	217.00	5.14	34.60	68.37
P	135.30	1.43	25.75	38.57	269.90	10.81	125.20	51.78
Q	147.00	3.53	24.69	39.93	577.40	20.65	207.40	41.56
R	110.70	0.57	30.41	46.90	142.70	2.19	86.57	45.25
S	157.80	0.61	26.61	51.11	121.50	2.96	104.40	61.65
M	337.10	6.91	23.72	6.08	1475.00	98.69	282.00	39.59
L	198.90	0.58	50.48	40.03	105.90	3.05	166.80	85.37
H	94.30	2.93	17.54	15.59	358.30	31.67	134.30	18.47
I	98.73	0.45	38.30	23.69	200.80	1.55	126.20	44.12
J	182.80	0.22	37.20	36.21	303.70	5.24	295.00	22.06
Average	156.454	1.940	42.855	43.036	392.521	16.781	182.738	55.353
Permissible Limit[a]	64	1.4	63	70	200	5[b]	200	50

Note: Mean values are shown, N=2. Upper and lower values are within ±7.5% of the mean

[a] Canadian Soil Quality Guideline, agricultural land (CCME 1999)

[b] Uranium concentration threshold in soils is not covered by legal regulations in the vast majority of countries in the world. In German soil protection guides, it is set to 5 mg kg^{-1}
(Norge Geologiske Undersokelse (NGU))

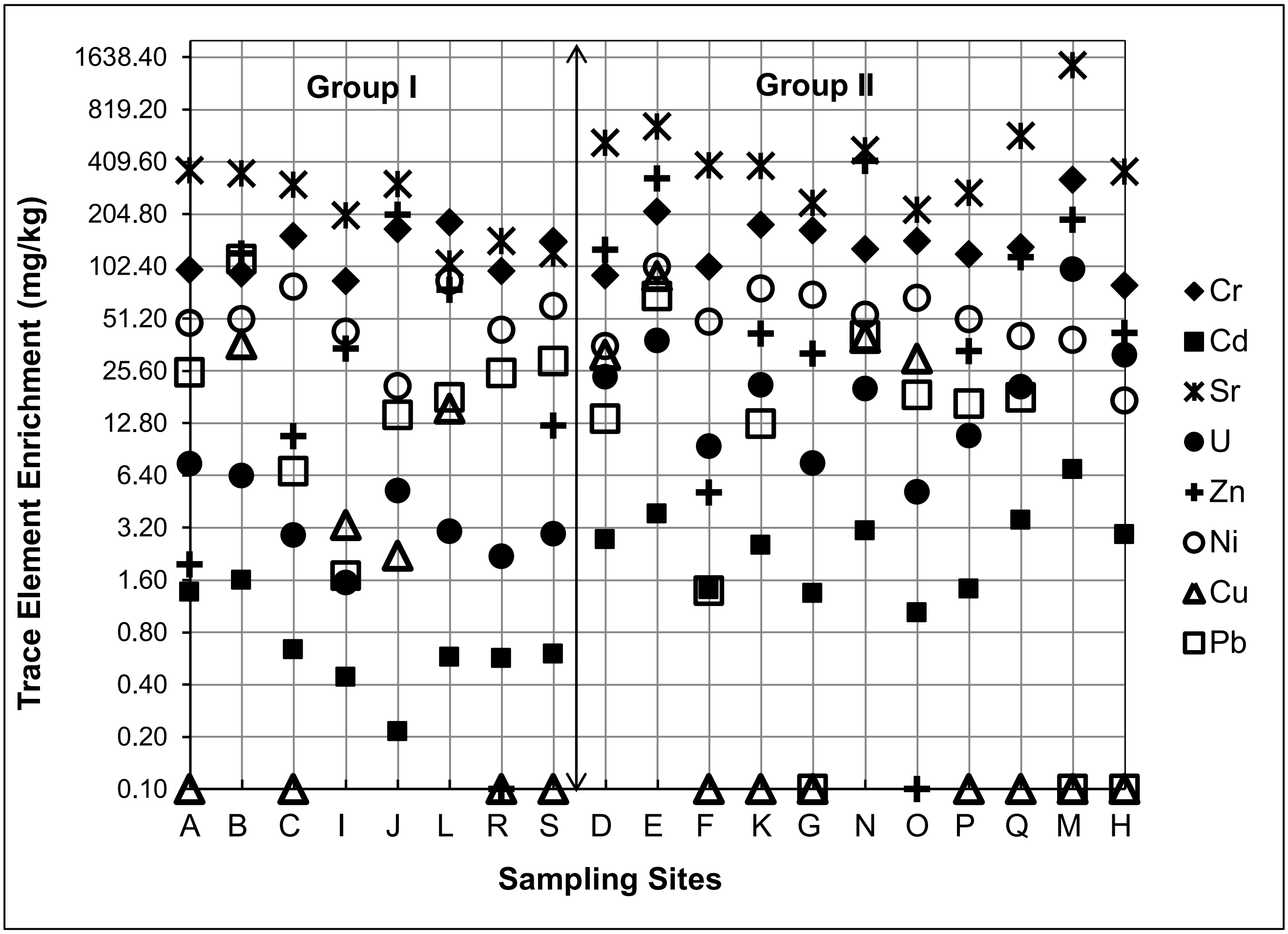


Figure 3. 4 Trace element enrichments in Group I and Group II sampling sites

It can be seen from Figure 3. 4 that all GI and GII soil samples were enriched in trace elements (with some exceptions for Cu, Pb and Zn in few sites) when compared to the respective background contents. In addition, they exhibited higher concentration ranges when compared to the worldwide mean averages reported for superficial soil horizons (Kabata-Pendias and Pendias 2001).

It can be noticed from Figure 3.s 3 and 4 that the trace elements (except Cu and Pb) and phosphate concentration peaks occurred in the same sites (D, E, K, N, Q & M); in other words, the trace element and phosphate spatial distributions followed similar patterns, suggesting a governing correlation existed between them. In fact, considering all sampling sites, statistical test results showed that U, Sr, Cd, Cr, and Zn were significantly correlated with phosphorus concentrations (Table 3. 4).

Table 3. 4 Correlation (Pearson P M) between major and trace elements in all sampling sites (N = 19) – Correlation coefficient r and p-value

Element	**Fe_2O_3** **r** **p**	**MgO** **r** **p**	**CaO** **r** **p**	**P_2O_5** **r** **p**
Cr	0.036	-0.121	0.202	0.672^{**}
	0.882	0.621	0.407	0.002
Cd	-0.672	-0.259	0.504^{*}	0.970^{**}
	0.002	0.284	0.028	0.000
Cu	0.038	0.396	0.152	0.049
	0.879	0.093	0.535	0.844
Pb	0.052	0.480^{*}	0.170	-0.223
	0.834	0.038	0.486	0.360
Sr	-0.662	-0.177	0.634^{**}	0.956^{**}
	0.002	0.469	0.004	0.000
U	-0.644	-0.316	0.508^{*}	0.991^{**}
	0.003	0.188	0.026	0.000
Zn	-0.288	0.178	0.360	0.463^{*}
	0.232	0.466	0.130	0.046
Ni	0.667^{**}	0.409	-0.273	-0.162
	0.001	0.082	0.259	0.508
P_2O_5	-0.669	-0.337	0.510^{*}	-
	0.002	0.158	0.026	-

**Positive correlation is significant at the 0.01 level (2-tailed)
*Positive correlation is significant at the 0.05 level (2-tailed)

Furthermore, Pearson's correlation test between trace elements average concentrations for all sites (Table 3. 3) and their weighted averages in the dry deposition source (PR, PG and PF)

(Table 3. 1) revealed strong correlation (r = 0.930) with P-value of 0.0008. Moreover, a jump in concentrations of most of these elements can be observed as crossing from GI to GII regions (Figure 3. 4), i.e. as approaching the main phosphate deposition area. In fact, when comparing the mean concentration for each element between the two groups, statistically significant differences were found, with higher means for group II sites (Table 3. 5). It follows that, the correlation between these trace elements and phosphate distributions in the study area, their relationship with the deposition source concentrations in trace elements, and their biased enrichments in the main phosphate deposition area, imply that soil enrichments in these trace elements was originated from the deposition of dust particulates emitted from the fertilizer industry.

Table 3. 5 Comparison between GI (south & southeast sites) and GII (north & northeast sites) element concentration (mg kg-1) means and p-value for t-test of means equality ($p < 0.05$ implies significant difference)

El.	*GI Mean (mg kg^{-1})*	*GII Mean (mg kg^{-1})*	*t-test p (2-tailed)*
Cr	142.13	166.87	0.33
Cd	0.76	2.80	0.00**
Cu	38.21	46.24	0.50
Pb	51.04	37.21	0.35
Sr	236.48	506.01	0.03*
U	3.97	26.10	0.02*
Zn	148.63	207.54	0.26
Ni	54.85	55.72	0.93
P_2O_5	1.21	8.44	0.01**

When the comparison is performed with the region background concentrations (Figure 3. 4), it seems that sites D & E, located north-east and north of the industry, close to the storage area, exhibiting considerably high concentrations in trace elements, are mostly influenced by the storage area and the prevailing wind. Site F, despite its close location northeast of the industry, showed relatively low enrichment in trace elements compared to sites D and E, due to the presence of a barrier, the tile factory structure, in front of this site.

Sr, U and Cd concentrations in all sampling sites were considerably higher than the local reference, with more important enrichments in the north-eastern sites (GII) (Figure 3. 4). In many instances, Cd and U concentrations (2.5-6.9 & 20-98.69 mg kg^{-1}, respectively) (Table 3. 3) were found to be remarkably exceeding the permissible limits (1.4 & 5 mg kg^{-1}). Cr exhibited high enrichments in all sampling sites (93-322 mg kg^{-1}), thus exceeding considerably the permissible threshold (64 mg kg^{-1}).

Zn low enrichment in sites R and O could be most probably attributed to the dense vegetation layer at these sites, absorbing the soil Zn thus lowering its concentration. In fact, speciation results (Table 3. 1) showed Zn existed considerably in mobile fractions (F_1, 21.52 %; F_2, 20.84%) within the combined deposition source (PR, PG and PF). Furthermore, Zn in alkaline soils could still extensively occur in the mobile, bio-available, soluble form, due to its ability to create mineral-organic compounds and anion complexes (Baranowski et al. 2002). It follows that the soil contamination with Zn, remarkably exceeding the allowed limits (200 mg kg^{-1}) in some sites (E, 418.8; N, 506.50; and J, 295 mg kg^{-1}), could be potentially hazardous to plants as well as to ground waters.

A related study involved mainly with the influence of Syrian PG stockpiles on the surrounding ecosystem has been undertaken by Attar (Attar et al. 2011). Results showed studied trace elements (Cu, Pb, Zn, Cd, and Cr) concentrations in soils surrounding the PG piles area were within the Syrian permissible limits; this was due, according to the author, to the low contents of these elements in the studied PG pile samples. These contents were actually much lower than those found in the present study's PG samples, which could be attributed to differences in the PR origins within the two main Syrian phosphate ore mines located in different geological areas (Attar et al. 2011). Differences in the wet process could also result in different PG compositions. In fact, PG samples in this study exhibited relatively high phosphate content (13%) originating from un-reacted PF in the wet process. Nevertheless, the source of contamination in this study was the fugitive dusts emitted from the combined industry's processed phosphate ore, PF products, and PG waste.

b) Ni

Ni exhibited high enrichments in all sampling sites (49-335 mg kg^{-1}) (Figure 3. 4), exceeding permissible limit (50 mg kg^{-1}) (Table 3. 3). On the other hand, high Ni concentrations in soil were not found to be correlated with phosphate concentrations, despite Ni relatively high content in the phosphate source (Table 3. 1). However, this does not necessarily mean that Ni in the soil was not originated from the phosphate source. In fact, Ni was found to be strongly correlated with iron (Table 3. 4), which suggests that deposited Ni, occurring substantially in mobile fractions (F_1, 37.24%; F_2, 12.46%) (Table 3. 1), within the combined deposition source (PR, PG, & PF), had been leached into the soil and got adsorbed by, or coprecipitated with iron oxides. Indeed, the affinity of Ni to Fe in soil is well reported in the literature, suggesting that this metal is specially associated with iron oxides and hydroxides (Hernandez et al. 2003; Sterckman et al. 2004).

c) Pb and Cu

The weak Cu-P and Pb-P correlations (Table 3. 4) in all sampling sites, in addition to Cu & Pb low concentrations in the phosphate source (Table 3. 1) relative to their high enrichments in many sites (Figure 3. 4), suggest that Pb and Cu in the study soil have other sources than the mere atmospheric deposition, disrupting their correlations with phosphate. This deduction can be further supported by the following observations.

Concentrations of Pb, Cu, and Cd in PR, PG, or PF displayed comparable values (Table 3. 1) within a relatively low range (2.7-16.6 mg kg^{-1}). However, Pb and Cu enrichments (18–113 and 15– 90 mg kg^{-1}, respectively) in many sampling sites (B, D, E, N, O, L) (Figure 3. 4) were unexpectedly much higher than those of Cd (1–3.8 mg kg^{-1}), suggesting that sources other than the atmospheric deposition contributed to the increase of concentrations of Cu and Pb in the study area soil, provided the accumulation possibility of Pb and Cu was eliminated. In fact, sampling sites in the main deposition area showed insignificant enrichments in Pb and Cu (G & H for Pb and Cu, and F, K, P & Q for Cu) (Figure 3. 4); thereby, the accumulation scenario for Pb and Cu could be excluded. This may lead to the assumption that Pb and Cu soil enrichments were mainly attributed to exhaust emissions of trucks (Nriagu and Pacyna 1988) transporting materials in connection with the industry – The content of metals in diesel vehicle engine exhaust have been assessed by Wang et al. (2003); Pb and Cu contents are 40.6 and 55.4 µg m^{-3}, and their concentrations in diesel fuel are 2.04 and 2.78 mg l^{-1}, respectively. In fact, it can be noted that samples collected near roadsides around the industry (e.g. B, E, N, and O), showed relatively high enrichment in Pb (112, 69, 41, and 19 mg kg^{-1}) and Cu (36, 90, 40, and 30 mg kg^{-1}) (Figure 3. 4). It should be noted that other studied trace metals content in truck exhaust (10.7, 88.6, 51.1, 14.4, 111.0 µg m^{-3} for Cd, Cr, Ni, Sr and Zn, respectively) (Wang et al. 2003), has also contributed to their increase in sites near roads, which can be inferred from Figure 3. 4, as the concentrations of these metals are relatively higher at near-road sites, relative to their positions with respect to the main dry deposition area.

On the other hand, the surface horizon low enrichments in Cu and Pb at some GII sites (not near roads) don't exclude the phosphate plant contribution in these metals input into the soil. In fact, their relatively low contents in the deposition source where they occurred in moderate percentages in the mobile fraction (Table 3. 1) contributed largely to their weak presence in these main phosphate deposition sites.

3.3.5 ***Correlations***

All relationships between major (P, Mg, Ca, Al, Si and Fe) and trace elements (U, Sr, Cd, Cr, Pb, Zn, Cu and Ni) in the sampling sites are shown in Table 3. 4.

It can be inferred from the previous section and Table 3. 4 correlations that phosphate is a principal carrier of U, Sr, Cd, Cr, and Zn, whereas iron species are the final carriers of Ni. In fact, it has been reported that phosphate species enriched in uranium are entrapped in calcium phosphate minerals by isomorphic substitution (Pfister et al. 1976). Cadmium is strongly related to phosphates, as it has been reported in the literature (Mortvedt and Beaton 1995).

It is noticed from Table 3. 4 that some trace elements (U, Sr and Cd), correlated to phosphate, are strongly correlated to calcium as well, which is the natural consequence of Ca-P correlation ($r = 0.510$ and $p = 0.026$) initiated from the phosphate compounds (PR and PF). The correlation between Sr and Ca concentrations could be related to their leaching into a soil solution by the same mechanisms, so they could enter in exchange competition for the carbonate or sulphate ions (Koss and Kim 1990).

All sites illustrated fairly strong correlations between Pb and Mg concentrations (Table 3. 4). This correlation could be due to the association of Pb to clay (Mg being a constituent of clay) and to major elements (divalent cations e.g. Mg) in competition with Pb for cationic exchange, resulting in Pb mobilization when Mg concentration increases in soil solution.

3.3.6 *Order of Magnitude of Dust Deposition Rate and the Respective Trace Elements Inputs into the Study Area Soil*

Dust deposition rate and trace elements input flux estimations were implemented using the carried out dry deposition model formulation; the respective results were summarized in Table 3. 6.

An average of about 106 tons year^{-1} of dust particulates polluted with trace elements are deposited in the study area, yielding an average deposition flux of around 318 g m^{-2} year^{-1}. It can be seen that PG has the greatest contribution to dust deposition (about 73%), followed by PR (21%) and PF (6%) – with just about 0.6% for sulphur. In addition, most of the total deposition rate in the vicinity of the industry is attributed to coarse dust particles (d > 20 µm), with 95% deposable fraction. Whereas 60% of the fine emitted particles (d < 10 µm) are transported beyond the study region into the higher atmosphere.

The deposition fluxes of trace elements associated with PR, PG and PF (Table 3. 1) showed an important input rate of Sr, Zn, Cr, U, Ni and Cd (in descending order) into the study area soil (Table 3. 6). For instance, in the world's remote regions, the elements Cd and Cr are deposited in amounts less than 10 mg ha^{-1} year^{-1} (0.001 mg m^{-2} year^{-1}) (Senesi et al. 1999), whereas, in the present case, they were locally deposited at rates of 1.379 and 29.373 mg m^{-2} year^{-1}, falling in the range of their deposition rate in heavily industrialized regions of North America (0.02-6.5 & 0.16-47.3 mg m^{-2} year^{-1} for Cd & Cr respectively) (Senesi et al. 1999). The same could be said about other trace elements (found in phosphate rock) deposited in the study area; that is the order of magnitude of their deposition rate is comparable to the respective trace elements input range into the soil of heavily industrialized regions (Table 3. 7). However, Pb showed an exception with a relatively lower input.

Strontium deposition was considerably high in comparison to other trace elements, owing to both its elevated concentrations in PR and PG having high deposable fractions of their emitted particulates. On the other hand, the contribution of the dust particulates deposition to Cu and Pb inputs into the soil appeared to be relatively low.

It can also be noted that PG had the greatest contribution in total trace elements input (321 mg m^{-2} yr^{-1}) into the soil of the study area, followed by phosphate rock (131 mg m^{-2} yr^{-1}) and phosphate fertilizer (27 mg m^{-2} yr^{-1}).

Correlation test between trace elements average concentrations for all sites (Table 3. 3) and their average fluxes in the deposition area (Table 3. 6) revealed strong correlation (Pearson r = 0.921) with p-value of 0.001; which supports the experimental results for soil concentrations in trace elements, and emphasizes the connection between the phosphate plant's fugitive emission and soil contamination with trace elements.

Table 3. 6 Calculations summary for dust particulates deposition and trace elements input rates

Particulate size (µm)	**Average deposable fraction, D_F (Figure 3. 2)**	**Dust PM mass size-distribution**[a, b]				**Totals**
		PR[a]	**PF**[a]	**PG**[b]	**S**[a]	
20 < d_1 < 98	0.95	60%	30%	65%	0%	-
10 < d_2 < 20	0.88	30%	30%	25%	0%	-
d_3 < 1 0	0.4	10%	40%	10%	0%	-
d < 5	0.1	-	-	-	100%	-
Emission Factor, E (g kg^{-1})		0.1362[a]	0.0465[a]	0.2680[f]	0.0877[a]	-
Handled product rate, R (tons day^{-1})		840[c]	715[d]	1250[e]	240[g]	3045
Fugitive dust emission, E x R (kg day^{-1})		114	33	335	21	503
Deposition rate, D_R, (Eq. 2) (kg day^{-1})		100	24	295	2	421
Dep. rate in major dep. area (tons yr^{-1})[h]		22	5	65	1	93
Stack controlled emission (kg day^{-1})[i]		0	7	67	0	74
Stack dust deposition (tons year^{-1})		-	1	13	-	14
Total dust deposition (tons year^{-1})		22	6	78	1	107
Major Deposition area (m^2)[j]		-	-	-	-	335000
Deposition average flux (g. m^{-2} year^{-1})		66	18	233	1	318
Cr deposition rate (kg yr^{-1})[k]		3	1	6	-	10
Cr Average flux (mg m^{-2} yr^{-1})		10	2	17	-	29
Cu deposition rate (kg yr^{-1})		0.2	0.1	0.4	-	0.7
Cu Average flux (mg m^{-2} yr^{-1})		0.5	0.3	1.2	-	2
Cd deposition rate (kg yr^{-1})		0.2	0	0.3	-	0.5
Cd Average flux (mg m^{-2} yr^{-1})		0.5	0.1	0.8	-	1.4
Pb deposition rate (kg yr^{-1})		0.1	0	0.2	-	0.3
Pb Average flux (mg m^{-2} yr^{-1})		0.2	0.1	0.6	-	0.9
Sr deposition rate (kg yr^{-1})		33	7	88	-	127
Sr Average flux (mg m^{-2} yr^{-1})		97	20	264	-	381
U deposition rate (kg yr^{-1})		0.5	0.2	0.8	-	1.5
U Average flux (mg m^{-2} yr^{-1})		2	1	2	-	5
Zn deposition rate (kg yr^{-1})		6	1	10	-	17
Zn Average flux (mg m^{-2} yr^{-1})		17	4	29	-	50
Ni deposition rate (kg yr^{-1})		1	1	2	-	4
Ni Average flux (mg m^{-2} yr^{-1})		4	1	6	-	11
Total trace elements average flux		131	27	321	-	479

[a] (Lundgren and Rangaraj 1988) reported dust particles mass size-distributions and average total plant-wide emission factors for PF, PR & sulphur

[b] The dust particles mass size-distribution for phosphogypsum (ρ = 0.9 ~ 1 g cm^{-3}) was roughly estimated using SEM images obtained for a random phosphogypsum sample

[c] (Abboud-Abi Saab and Dargham 1998)

[d] (Al-Hajj and Muscat 2000)

[e] Considering that the industry produces around 160,000 tons of phosphoric acid per year (Al-Hajj and Muscat 2000), around 2200 tons of phosphogypsum are generated per day (5 tons for every ton of phosphoric acid) (US EPA 2000), of which 950 tons are disposed of in the Mediterranean sea (Abboud-Abi Saab and Atallah 1996)

[f] Deduced from (DEQ 2005)

[g] 87,650 tons of sulphur are used to yield 265,000 tons of H_2SO_4 required to produce 160,000 tons of phosphoric acid per year

[h] Number of "dry" days with south-westerly wind is considered (i.e. 220 days/ year) (Windfinder Website ; Department of Meteorology 2010)

[i] 20% of uncontrolled emission (DEQ 2005)

[j] Major deposition area was calculated from Figure 3. 3 (approximated by the area of a 60° arc with 800-m radius). Local dry deposition would take place mainly within a downwind distance of about 1 Km, since vertical mixing can reach high elevations (up to 30 m) at this distance for neutral to stable atmospheric conditions (Countess et al. 2001). In fact, this could be inferred from the distribution of the deposited phosphorus (Figure 3. 3), fading away beyond 800-meter downwind distance; a major deposition area (Figure 3. 3) can be delimited according to this distribution pattern, and deposition fluxes can then be readily calculated.

[k] Using trace element concentrations given in Table 3. 1

Table 3. 7 Trace elements soil deposition flux (mg m-2 year-1) comparison – Study area versus remote regions (South Pole, North Norway, North West Canada), and rural, metropolitan and industrialized regions in Europe and North America (Senesi et al. 1999)

Element	*Remote Regions*	*Europe*	*North America*	*Study Area*
Cd	<0.0001	0.08-97.80	0.02-6.50	1.4
Cr	<0.001-0.040	0.16-22.10	0.16-47.30	29
Cu	0.002-0.160	1.30-772.60	0.79-173.40	2
Pb	0.04-0.72	8.50-53.60	7.10-2050	0.9
Sr	-	-	-	381
Ni	0.08-0.13	0.63-18.90	1.60-18.90	11
Zn	0.002-0.630	2-2523	78.80-268	50
U	-	-	-	5

3.4 Conclusions

In order to evaluate the potential hazard of phosphate fertilizer industry emissions on soil contamination with trace elements, analytical methods were combined to investigate their concentrations and distribution in the vicinity of the industry, and the main mechanism of their transfer to soil surface. Trace elements forms in the source materials (PR, PG and PF) were investigated by speciation.

Results of trace elements speciation in PR, PG, and PF (deposition source) suggested soil contamination with deposited Zn and Cd could be potentially hazardous to plants and ground waters. Nevertheless, further dedicated investigation on the behaviour, forms and dynamics of trace elements in the soil would be required to better assess their risk factors.

Elevated levels of trace elements (Sr, Cr, Ni, Zn, U, and Cd) and phosphorus were found to be located near the storage area, in the centre, and northeast of the industry; with trace elements-polluted phosphate and phosphogypsum dusts drifted by the prevailing wind into a major deposition area, being the most important risk factor. In many instances, highly toxic trace elements concentrations exceeded the permissible limits set by CCME (Kabata-Pendias and Pendias 2001) for agricultural soils.

Sources other than the atmospheric deposition (e.g. trucks exhaust) seem to have contributed to the increase of Cu and Pb concentrations in the study area. Cu and Pb enrichments were elevated only in sites close to roadsides.

An order of magnitude estimation of fugitive dust particles deposition rate showed a considerable amount of dust accumulation in the major deposition area. The associated trace elements deposition rates revealed relatively high input fluxes of Sr, Zn, Cr, U and Ni, in descending order. The inputs of nearly all investigated trace elements were comparable to their deposition rates in heavily industrialized regions.

A significant correlation was established between measured trace elements concentrations in soil and their calculated deposition fluxes. Relationships between major and trace elements showed phosphorus species were the principal carriers of trace elements in the study area soil.

Acknowledgements

This study was supported by (CSR-USEK). We wish to thank the staff of SARM (CRPG -UPR 80) where chemical analyses were carried out. Eng. R. Kassir is acknowledged for his helpful contribution in achieving this work.

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

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(Article 2)

Résumé de l’article II

Le phosphogypse, sous-produit de l'industrie des engrais phosphatés formé de sulfate de calcium hydraté, est utilisé comme amendement sur les sols agricoles. Cependant, ce sous-produit peut contenir des éléments traces affectant les eaux souterraines et les plantes. Notre étude se focalise sur l'impact de l'amendement du phosphogypse sur les sols méditerranéens rouges. Dans cet objectif un terrain expérimental a été réalisé à Bsarma et divisé en parcelles de 1 m^2 chacune sur lesquelles 1kg du phosphogypse a été appliqué sur une surface seulement de 0.25 m^2. Le carottage a été réalisé jusqu'à une profondeur de 55 cm sur les parcelles épandues par du phosphogypse et espacées par le temps et par les saisons durant une période de 16 mois. La carotte est découpée chaque 5 cm pour subir des analyses minéralogiques et chimiques. Une parcelle est restée sans amendement servant de témoin. La caractérisation minéralogique et chimique du sol Bsarma a montré qu'il est formé de Quartz, Kaolinite, Calcite, Montmorillonite et Hématite. Les concentrations de Cd, Zn, Cu et Pb sont 0,28; 102,07; 36,02 et 12,43 mg/kg respectivement. Les éléments traces sont plutôt associés aux deux fractions réductible et résiduelle. Quant au produit d'épandage, les éléments sont majoritairement liés aux fractions acido-soluble et oxydable. Les résultats de DRX et de MEB ont montré que le phosphogypse est formé principalement de sulfate de calcium.

Suite à l'application du phosphogypse, la concentration des éléments traces (Cd, Zn, Cu et Pb) augmente jusqu'à atteindre un pic pour le Cd, 5 mois après l'épandage et pour le Zn, Cu et Pb, 12 mois après l'épandage. La concentration de Cd diminue en fonction des précipitations alors que celle de Zn, Cu et Pb augmente. La concentration des éléments traces rejoint relativement celle de la référence, 16 mois après l'épandage.

La distribution des éléments traces (Cd, Zn, Cu et Pb) dans les différentes fractions géochimiques (échangeable, acido-soluble, réductible, oxydable et résiduelle) du profil du sol référence et amendé par du phosphogypse en fonction du temps a montré que la solubilisation de Cd a augmenté, 5 mois après l'épandage, dans le profil 0-20cm suite à la diminution de pH. Avec les précipitations, la fraction échangeable apparaît dans le profil 35-55cm, 12 mois après l'épandage, pour devenir prédominante 16 mois après l'épandage dans tout le profil du sol.

Le Zn est associé à la fraction acido-soluble en quantité plus grande dans le profil 0-20cm avec la diminution du pH, 5 mois après l'épandage. Avec les précipitations, la fraction oxydable apparaît. A la fin de l'étude, il est lié à la fraction réductible et à la fraction résiduelle.

La fraction échangeable apparaît pour le plomb dans tout le profil du sol et avec le temps avec une concentration plus grande de Pd dans le profil 0-20cm et 35-55cm 16 mois après l'épandage. Pour le cuivre, cette fraction apparaît en profondeur (20-35cm) dans les parcelles épandues par le phosphogypse. Cependant, 16 mois après l'épandage, il est plutôt lié aux fractions oxydables et résiduelles.

La variation temporelle des concentrations en éléments traces dans les racines et les plantes de type chicorée "*Cichorium Intybus*" cultivées dans ce terrain a montré que la concentration de ces éléments a augmenté 5 mois après l'épandage dans les racines ainsi que dans les feuilles notamment pour le Cd, cette augmentation continue pour le Zn et le Cd dans la deuxième parcelle 12 mois après l'épandage pour diminuer à la fin de l'étude à l'exception de Cd qui reste élevée dans les feuilles des plantes (2 mg/kg de Cd comme moyenne dans les parcelles épandues par du phosphogypse) dépassant les valeurs normales (0,1-1 mg/kg).

En conclusion, l'application du phosphogypse sur les sols agricoles a augmenté la solubilisation des éléments étudiés par l'apparition de la fraction échangeable et la fraction acido-soluble en profondeur (jusqu'à 55 cm). Le cadmium devient très mobile 16 mois après l'épandage où il se trouve majoritairement associé à ces 2 deux fractions dans le profil du sol alors que le Zn, Pb et Cu sont plutôt liés aux phases minérales du sol (oxydes de fer et de manganèse et argiles). Le pH et les précipitations sont les principaux facteurs contrôlant la mobilité des éléments étudiés.

Le risque associé à l'épandage du phosphogypse est l'accumulation de Cd dans les feuilles des plantes de Chicorée consommées par l'homme dépassant les valeurs normales d’où un risque de transfert aux chaînes alimentaires.

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

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Published in ***Environmental Monitoring and Assessment***; 2012, *Vol. 184*, Issue 7, p 4397-4412, doi:10.1007/s10661-011-2272-7.

Abstract

Soil amendment by phosphogypsum (PG) application becomes of an 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 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 five 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 soil depth of about 20cm. Zn exhibited mobility towards deeper layers. Pb and Cu were accumulated in around 20-55cm 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.

Keywords: *transfer factor; trace elements; phosphogypsum; soil amendment; accumulation coefficient*

4.1 Introduction

Phosphogypsum (PG) is a by-product of the phosphate fertilizer industry 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 stock piles. 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/y (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. 1999a; 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 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 be therefore 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 PG had the highest contribution in TEs input into the surface soil (Kassir et al. 2012). Results had suggested 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.

4.2 Materials and Method

4.2.1 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 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 1x1x0.15m (length x width x 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 0.5m x 0.5m, 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 (2500 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 was indicated in Table 4. 1. Samples were collected from the cored cylindrical soil blocks at 5cm intervals to a depth of 20 cm, then 15cm intervals to a final depth of 55cm. Accordingly, plant roots and leaves were also collected, simultaneously with soil samplings, from each parcel.

Table 4. 1 Sampling times and between-sampling periods weather data

Time	*Temperature (°C)*		*Relative (%) Humidity*		*Wind*		*Rain*	*Cumulative Rain*
	Min	**Max**	**Min**	**Max**	**dd (°)**	**ff (m/s)**	**(mm)**	**(mm)**
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	
Mars 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 09)								
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)								

4.2.2 *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 the 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 accuratly 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 (1000W; 10^6Pa) and then a stage of ventilation cooling. The digests were filtered through a 0.45µm and analyzed using an Atomic Absorption Spectroscopy to determine the content of Pb, Zn, Cu and Cd in roots and plant leaves.

Soil samples from depth intervals within 0-20cm were mixed and homogenized for subsequent speciation along with samples from 20-35cm & 35-55cm intervals. The sequential extractions were carried out progressively on an initial weight of 5 g in polypropylene centrifuge tubes of 50 mL. Five TEs fractions were separated in 5 steps as follows: I- exchangeable form (F1) with 40 mL of 1 M $Mg(NO_3)_2$; 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 Na-citrate (78,4g/L) and 20 mL $NaHCO_3$(9.82g/L), then adding 1g of $Na_2S_2O_4$ (80°C for 4h); IV- oxidizable form (F4) extracted by adding 8 mL HNO_3 (0.02M) 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 2h); V- residual form (F5) extracted by 40 mL HNO_3 (65%) . Each extraction step was followed by centrifugation the mixtures at 5000 rpm for 30 minutes 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 / Total element analysis) x 100

Where, F is the TE fraction.

4.2.3 *Mineralogical Analysis*

X-ray Diffractograms (XRD) were recorded using D8-Brucker diffractometer (cobalt radiation source, $\lambda = 1.788965$ Å). The diffractometer is equipped with (θ, 2θ) 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 forming1mm-thick layers.

4.2.4 *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 0-5cm, 5-10cm, 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.

4.3 Results

4.3.1 *Soil Background Values: Reference Parcel*

The mineralogical results (XRD) showed that the background soil contained Quartz (SiO_2), Calcite ($CaCO_3$), Kaolinite, Montmorillonite as clays 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 55cm), except in the layer (35-55cm) where Cu and Pb concentrations decreased (Table 4. 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%).

Table 4. 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)

El.	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	
	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	0.035**
	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	
	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	0.122
	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	
	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	0.223
	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	
	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	0.002**
	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 0.01 level *Significant difference at the 0.05 level

4.3.2 *Characterization of PG Amendment*

XRD results of PG showed that the main peak recorded in the diffractogram was Gypsum ($CaSO_4.2H_2O$) and to a less extent Bassanite ($CaSO_4.1/2\ H_2O$) 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%).

4.3.3 *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 different depths represent the soil background concentrations (Figure 4.1 and Table 4. 2). Moreover, Table 4. 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 Figure 4. 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 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 (Figs.1a, 1b and

1c). The time-variation of Cu concentrations over the studied depths exhibited generally a steady function (Figure 4. 1d) increasing at slight rate with time.

Following PG amendment, a general increase of TEs concentration could be observed. During rainy period (October - April), Cd concentration decreased (0.5 to 0.35 mg/kg) (Figure 4. 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) (Figs. 1b, 1c and 1d). However, in the deeper layers (35-55cm), 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 (0-20cm). A general remarkable decrease in TEs concentrations was observed over the study period in the layer (10-20cm) particularly over the spring-summer period.

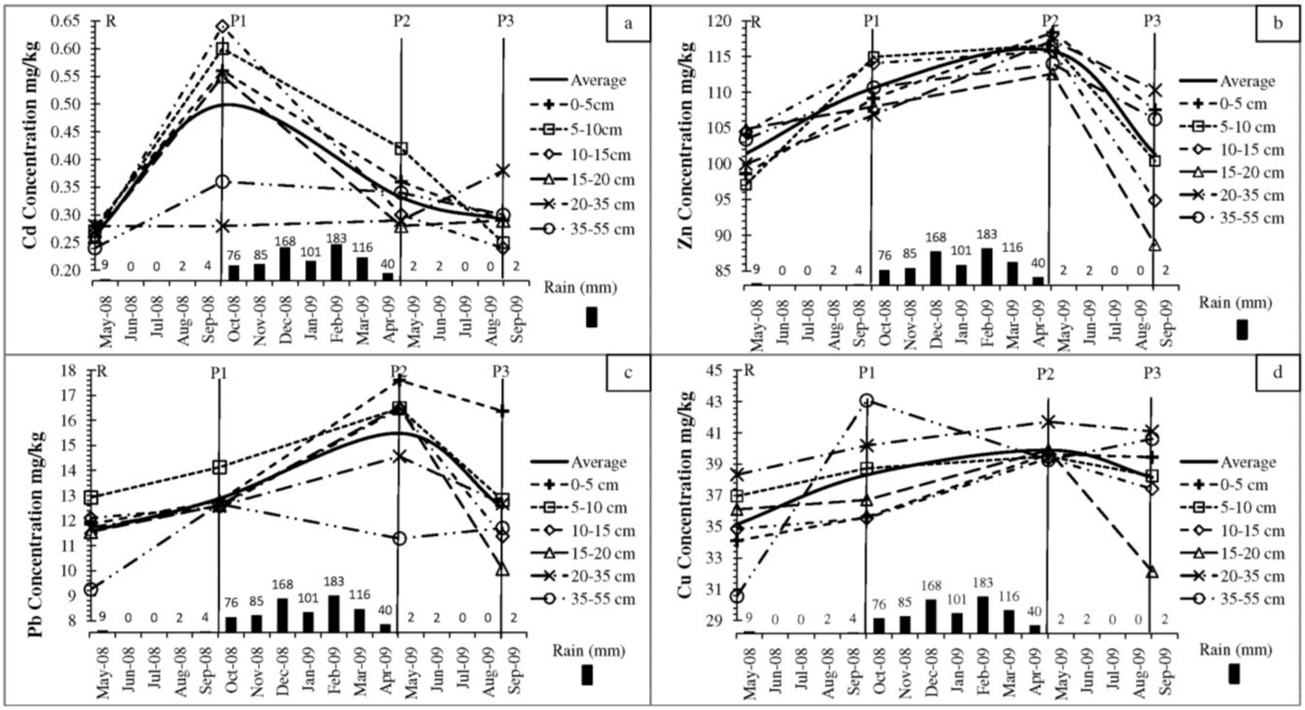

Figure 4. 1 Time-variation of trace element concentrations in the soil profile

4.3.4 *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 & F5) at the different study depths (0-20cm, 20-35cm, and 35-55cm), were plotted on separate charts for each of the considered metals (Cu, Cd, Zn & Pb) over the study period, as shown in Figure 4. 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 (Figure 4. 2a). Cd speciation in parcel P1 didn't change significantly (Figure 4. 2b) while in parcels P2 and P3 a modification of Cd mobility could be observed (Figure 4. 2c and 2d). In fact, in parcel P2, Cd was found to be related to the organic matter and sulfur (F4) at depth 20-35cm in concentration of 0.22 mg/kg, and to the exchangeable fraction (F1) at depth 35-55 cm (0.276 mg/kg) (Figure 4. 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 20-35cm; 0.201 mg/kg in 35-55cm) (Figure 4. 2d). Moreover, in depth 20-35cm, Cd in the acido-soluble fraction (F2) was relatively in equivalent quantity with exchangeable fraction (F1) (0.171 mg/kg) (Figure 4. 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 (Figure 4. 2e). At T1 (five months after PG application), a change of Pb speciation was observed in P1 (Figure 4. 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 20-35cm; 0.91 and 1.39 mg/kg at 35-55 cm in F1 and F4 respectively) (Figure 4. 2f). At T2 (twelve 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 0-20cm, 20-35cm and 35-55 cm respectively (Figure 4. 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 (Figure 4. 2h).

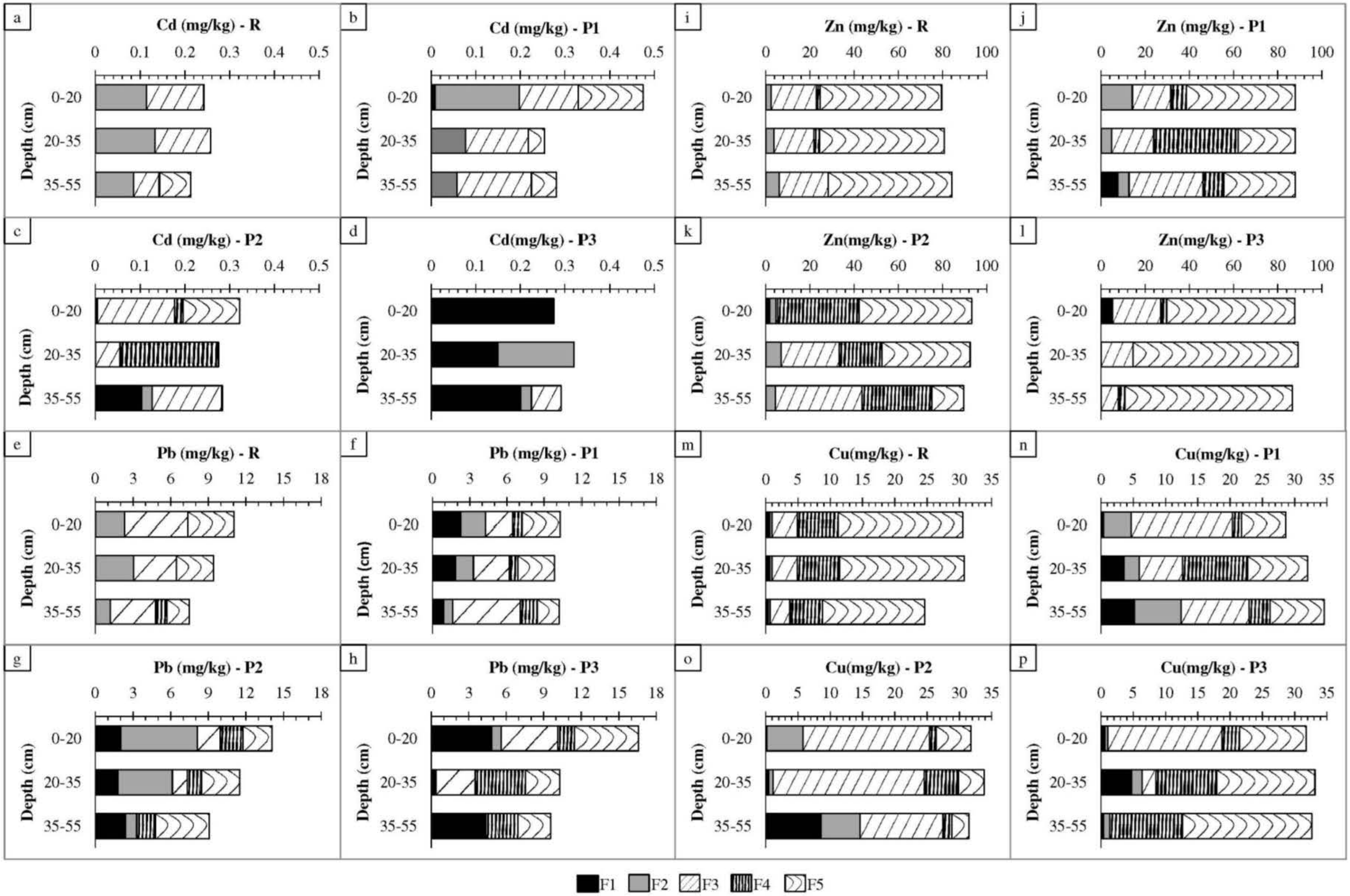

Figure 4. 2 Time-variation of trace element fraction concentrations in the soil profile

Zn speciation

The Zn reducible and residual fractions (F3 and F5) were dominant at T0 in the reference parcel R throughout the soil profile (Figure 4. 2i). F1, F2 and F4 were negligible in all soil horizons (< 6mg/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) (Figure 4. 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) (Figure 4. 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) (Figure 4. 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 (Figure 4. 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's 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, 20-35cm, and 35-55cm respectively). The exchangeable (F1) and the acid-soluble fractions (F2) were negligible (< 1 mg/kg) (Figure 4. 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 (Figure 4. 2n) (it deceased from 15.81- 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, 20-35cm, and 35-55cm respectively) (Figure 4. 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 (Figure 4. 2o). At the end of the experiment, Cu was partitioned in the reducible, oxidizable and alumino-silicate fractions of the soil in P3 (Figure 4. 2p) . However, 19% of Cu content was present in the mobile fraction (F1 and F2) in the layer 20-35cm.

4.3.5 *TEs Concentration In Plants*

TEs concentrations in roots and leaves of plants collected from reference and amended parcels were presented in Figure 4. 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 (8-25mg/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 & Cd, and P1 in Pb & 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 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.

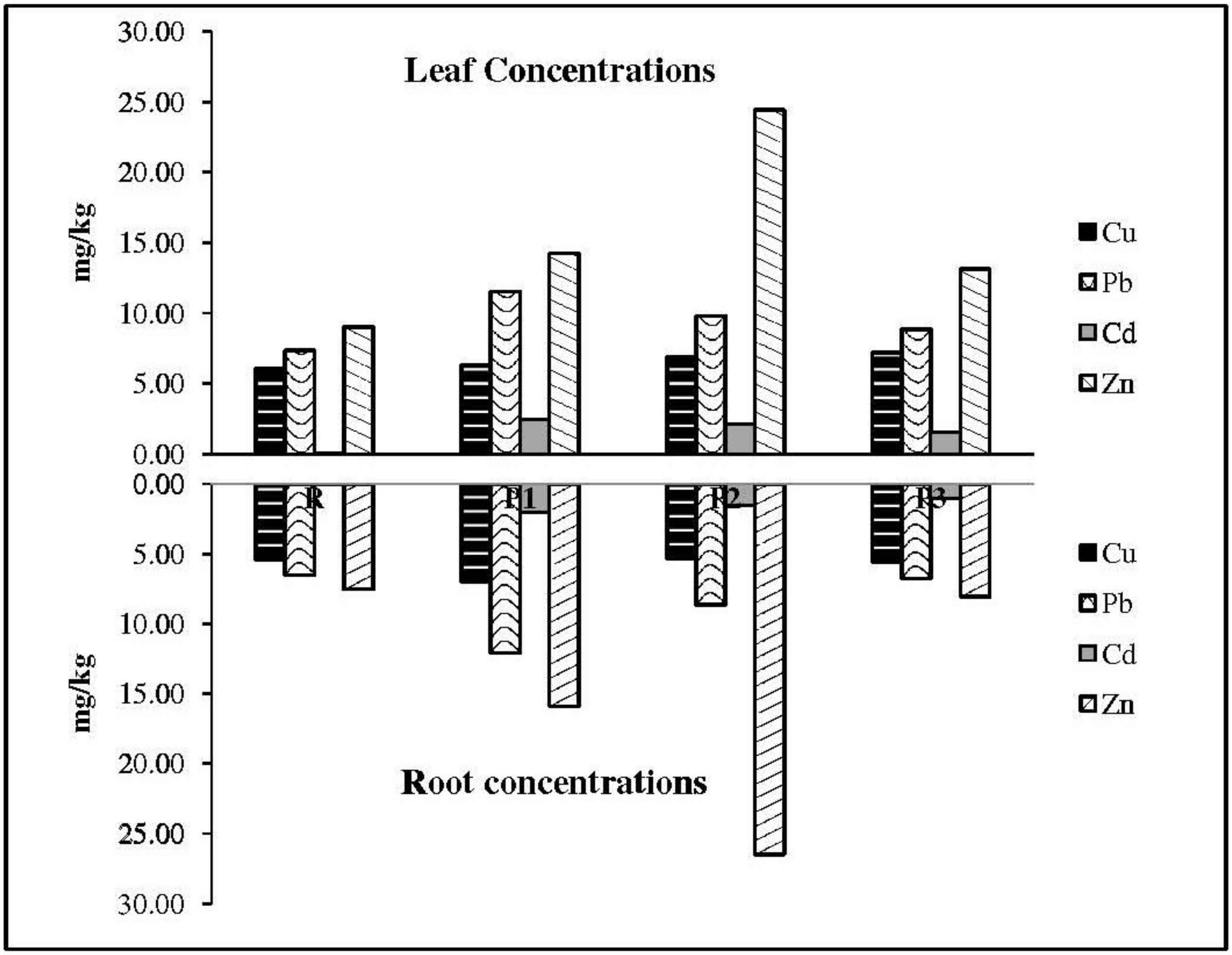

Figure 4. 3 Time-variation of trace element concentrations in plant roots and aerial parts

4.3.6 *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 4. 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).

Table 4. 3 Results of Correlation: Pearson Correlation

	pH	COT	CEC	Cu$\vert_{\text{root}}$	Cd$\vert_{\text{root}}$	Zn $\vert_{\text{root}}$	Pb $\vert_{\text{root}}$	Pb $\vert_{\text{Leaf}}$
Cu $\vert_{\text{soil}}$	-	-	-	-	-	**	-	-
Cd $\vert_{\text{soil}}$	(–)**	-	-	**	**	-	-	-
Zn $\vert_{\text{soil}}$	**	*	*	-	-	-	-	-
Pb $\vert_{\text{soil}}$	-	**	**	-	-	**	-	-
Cu $\vert_{\text{soil, F2}}$	-	-	-	**	-	-	-	-
Pb $\vert_{\text{soil, F1}}$	-	-	-	-	-	-	-	**
Zn $\vert_{\text{soil, F2}}$	-	-	-	-	-	**	-	-
Zn $\vert_{\text{soil, F3}}$	-	-	-	-	-	(–)**	-	-
Zn $\vert_{\text{soil, F4}}$	-	-	-	-	-	**	-	-
Cd $\vert_{\text{Leaf}}$	-	-	-	-	**	-	-	-
Zn $\vert_{\text{Leaf}}$	-	-	-	-	-	**	-	-
Pb $\vert_{\text{Leaf}}$	-	-	-	-	-	-	**	-

* $p < 0.05$, significant correlation at the 0.05 level
** $p < 0.01$ significant correlation at the 0.01level
(–) Negative correlation
\- Insignificant correlation

Cd concentration in the soil was positively correlated with Cd and Cu concentrations in the roots ($r = 0.882$, $p < 0.005$ 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 correlated with Zn content in roots ($r > 0.85$, $p < 0.01$) which was negatively correlated with Zn level in reducible fraction (F3) ($r = - 0.78$, $p < 0.05$).

4.4 *Discussion*

4.4.1 *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 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; 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 4. 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, & 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 35cm. 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 (10-20cm) where active roots were extended.

4.4.2 *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 P1than in the reference plot R. In R and P1 parcels, at the surface soil layer (0-20cm), 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, 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 55cm) of amended parcels comparing to R parcel. The mobility of Zn was mainly controlled by aluminosilicates (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 represented 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, 35-55cm 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 55cm, 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 35cm 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, 15-35cm and 35-55cm 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).

4.4.3 *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 = Displaced Quantity/ Input = (Input – Retained) / Input = 1 – Retained / Input

Therefore,

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

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).

4.4.4 *TEs Transfer from Soil to Cichorium 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. 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 x) 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 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.

Table 4. 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

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 x) 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; A Kabata-Pendias and Pendias 2001; Batista et al. 2007). However, Pb and Zn concentrations (Figure 4. 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 (Figure 4. 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 (Figure 4. 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.

4.5 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 (Figure 4. 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 Cichorium 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.

Acknowledgements

This study was supported by (CSR-USEK). We wish to thank the staff of SARM (CRPG -UPR 80) where chemical analyses were carried out. Eng. R. Kassir is acknowledged for his helpful contribution in achieving this work.

5 *Mobility and bioavailability of selected trace elements in Mediterranean red soil amended with phosphate fertilizers: Experimental study*

(Article 3)

Résumé de l'article III

L'impact de l'application des engrais phosphatés sur les sols agricoles à long terme a été évalué par de nombreuses études puisqu'ils contiennent des éléments traces pouvant être transférés au sol et par suite aux plantes. D'où la nécessité d'évaluer la mobilité des éléments au cours du temps et jusqu'à une profondeur de 55 cm. Le même terrain de Bsarma divisé en parcelles est utilisé pour l'amendement des engrais phosphatés sur la même surface mais avec une quantité plus grande (2 kg/0,25 m^2). C'est une quantité loin des pratiques agricoles dans l'objectif de simuler l'effet de l'amendement des engrais phosphatés à long terme. Le même protocole de carottage a été réalisé avec une alternance des saisons humides et sèches durant une periode de 15 mois.

La caractérisation minéralogique et chimique du sol Bsarma a montré qu'il est formé de Quartz, Kaolinite, Calcite, Montmorillonite et Hématite. Les concentrations de Cd, Zn, Cu et Pb sont 0,28; 102,07; 36,02 et 12,43 mg/kg respectivement. Les éléments traces sont plutôt associés aux deux fractions réductible et résiduelle. Quant au produit d'épandage, les éléments sont majoritairement liés aux fractions échangeable et acido-soluble. Les résultats de DRX et de MEB ont montré que les engrais sont formés majoritairement de $Ca\ (H_2PO_4)_2$ avec de sulfate de calcium anhydre.

La concentration totale des éléments étudiés (Cd, Zn, Pb et Cu) dans le profil du temps en fonction des précipitations et au cours du temps a montré qu'elle atteint un pic 4 mois après l'épandage avec les fortes précipitations et la diminution de pH pour diminuer après pendant la saison sèche pour rejoindre relativement les valeurs de la référence, 15 mois après l'épandage. Cependant le Cd montre un comportement différent pendant la saison sèche, sa concentration ne semble pas diminuer tout en restant constant suggérant une accumulation de celui-ci dans le profil 0-20cm.

La distribution des éléments traces (Cd, Zn, Cu et Pb) dans les différentes fractions géochimiques (échangeable, acido-soluble, réductible, oxydable et résiduelle) du profil du sol référence et amendé par des engrais en fonction du temps a montré qu'après solubilisation de Cd et apparition de la fraction échangeable ,4 et 11 mois après l'épandage dans le profil 0-20cm, il se trouve associé à la fraction réductible et résiduelle à la fin de l'étude (15 mois après l'épandage) dans le profil du sol. Tandis que pour le Zn, Pb et Cu, leur solubilisation et leur présence dans la

fraction échangeable dans le profil au cours de temps persiste pour les trois éléments, en ayant une quantité moindre dans ces 2 fractions 11 mois après l'épandage, où ils sont liés à ces 2 fractions jusqu'à une profondeur de 55 cm, 15 mois après l'épandage, proposant une mobilité plus grande que celle de la référence contrairement au Cd.

La variation temporelle du facteur de transfert des éléments traces dans les plantes a montre que le Cd possède le facteur de transfert le plus élevé suivi de Cu, Pb et Zn. Cependant ce facteur augmente 4 mois et 11 mois après l'épandage pour le Cd pour diminuer a la fin de l'étude. Ce qui est en accord avec les résultats de la spéciation où le Cd est lié à la fraction acido-soluble et échangeable dans le profil 0-20cm et par conséquent plus disponible pour les plantes.

De même, le facteur de transfert de Cu augmente 4 mois après l'épandage où il est présent dans les deux fractions échangeable et acido-soluble en quantité plus grande dans le profil 0-20cm. Puis ce facteur diminue en accord avec les résultats de la spéciation pour augmenter 15 mois après l'épandage où le cuivre est associé à la fraction échangeable dans ce même profil. Pour le plomb, son facteur de transfert est élevé 15 mois après l'épandage contrariant les résultats de la spéciation où il est présent dans ces deux fractions disponibles non pas dans le profil 0-20cm mais 20-35cm, ceci peut-être dû à ce que les racines peuvent être étendues plus que 20cm. Le Zn a le facteur de transfert le plus petit qui peut être expliqué par sa compétition au niveau des racines avec d'autres éléments comme le Cu et le Cd. Malgré le facteur de transfert élevé de Cd dans les plantes, sa concentration moyenne (0,8 mg/kg) dans la Chicorée ne dépasse pas les valeurs normales (0,1-1 mg/kg), par conséquent ne montrant aucun risque alimentaire. Cependant, les résultats de MEB des parcelles épandues par les engrais ont montré la présence de fluorine en profondeur nécessitant plus d'investigation a ce propos.

En conclusion, l'application excessive des engrais phosphatés sur les sols agricoles Libanais a augmenté la concentration totale des éléments traces pour rejoindre relativement ceux de la référence. Contrairement à l'application du phosphogypse, le Cd se trouve lié 15 mois après l'épandage aux particules du sol (oxydes de fer et de manganèse et argiles) alors que le Zn, Cu et Pb sont plus mobiles (présents dans les fractions labiles, échangeables et acido-solubles). Le pH et les précipitations restent les principaux facteurs contrôlant la mobilité des éléments étudiés.

L'accumulation des éléments étudiés dans les plantes ne montrent aucun risque alimentaire restant dans les valeurs admissibles. Le risque lié à l'application des engrais sur les sols est la présence de la fluorine dont sa détection par le MEB nécessite des techniques et des investigations plus approfondies.

Mobility and bioavailability of selected trace elements in Mediterranean red soil amended with phosphate fertilizers: Experimental study

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Published in ***Geoderma;*** 2012, Vol. 189, p 357–368; DOI 10.1016/j.geoderma.2012.05.017

Abstract

Trace Elements (TEs) distribution and mobility were monitored in a typical profile of Mediterranean red soil massively amended with Phosphate Fertilizers (PFs), over a period of fifteen months. Samples of soil (across a depth of 55 cm) and entire plants (roots and shoots), collected at different points in time, in addition to PF samples, were analyzed for TEs (Cu, Cd, Zn, and Pb) concentrations, sequentially extracted, and examined under a Scanning Electron Microscopy (SEM) coupled with an Energy Dispersive X-ray Spectrometer (EDX). Results showed peaks in TEs mean concentrations (Cu: 43.13, Cd: 0.52, Zn: 116.36, and Pb: 14.92 mg kg-1) in the soil profile four months following PF application, but they did not reach harmful levels. Sequential extractions revealed that the studied TEs were transferred from residual to exchangeable fractions in the amended soil profile (except for Cd), which may consequently lead to their transfer to the saturated zone. The order of TEs mobility was: Zn>Cd >Cu>Pb. Amended-soil plants, Cichorium Intybus L, accumulated higher TEs concentrations (Cu: 9.67, Cd: 0.37, Zn: 13.81, and Pb: 2.58 mg kg-1) than the reference plants, but they remained within normal reported levels for plants (Cu: 3-20, Cd: 0.5-1.0, Zn: 15-150, and Pb: 2-5 mg kg-1). Soil-plant transfer factor was notably affected by PF application, with highest acquired values being for Cd. Evidence of fluorine presence was detected by SEM in the amended soil, which should be a matter of concern in PFs application.

Keywords: *trace elements; phosphate fertilizers; soil amendment; mobility; trace elements uptake; transfer factor*

5.1 Introduction

Large application of fertilizers has been practiced on arable lands, to improve crop production and recover inherent and induced soil nutrients deficiency. Contamination of agricultural soils with trace elements (TEs), such as Cd, Pb, Zn and Cu, and with fluorine can occur as these elements are transferred during manufacturing from phosphate rock to phosphate fertilizers (PFs) (Camelo et al. 1997). Cd and Pb are unessential elements, having no specific biological functions. They are considered toxic elements, whereas Zn and Cu are micronutrients that could become toxic when exceeding certain limits. Concentrations of Zn, Cu, Cd and Pb can vary in the ranges of 50-600; 10-60; 9-100; 0.5-40 mg kg^{-1} in PFs (Adler 2001), depending on the origin of phosphate rock . Generally, sedimentary phosphate rocks (e.g. Apatite) contain higher concentrations of TEs than igneous rocks (Van Kauwenbergh 2002).

The effect of continuous application of PFs has been assessed in long term experiments conducted in many studies worldwide (Adriano 1986; Malavolta 1994; Guttormsen et al. 1995; Jeng and Singh 1995; Loganathan et al. 1995; McLaughlin et al. 1996; Morvedt 2005). Cd has been the most concerned element in PFs application, since it can accumulate in relatively large amounts in soil and plants, which could be harmful to human health (McLaughlin et al. 1996; Kirkham 2006). Lambert et al. (2007) studied the solubility of Cd and Zn, following the application of PFs in different rates and with different concentrations of these two elements. They found that when both the application rate of PFs and Cd concentration in PFs increased, the content of Cd in soil extracts increased, whereas such relationship was not confirmed for Zn (i.e. increasing the PF application rate and using PF with higher Zn concentration did not result in increased Zn level in soil). Furthermore, a competition between Zn and Cd was reported, leading to Cd increase in the soil extracts. Morvedt (2005) found that a minimal increase of Cd total concentration in soil occurred in short term, leading to higher absorption of this element by leaf vegetables compared to maize or wheat. A study in Norway established that Cd tend to accumulate in the soil after long term (70 years) and abundant treatment with PFs (Jeng and Singh 1995). Applying PFs at a rate inducing a Cd input of 0.07-28 g ha^{-1} y^{-1} in an experimental field, increased Cd uptake by cultivated plants (Guttormsen et al. 1995)–For locally manufactured PF containing Cd in a concentration of 6.18 mg kg^{-1}, the equivalent PF rate is 11.32-4350 kg ha^{-1} y^{-1}. On the other hand, different studies showed that applying PF with a Cd input of 0.3-1.2 g ha^{-1} y^{-1}(equivalent to locally made PF rate of 48.50-194.20 kg ha^{-1} y^{-1}) did not lead to such result (Singh and Myhr 1997). The average use of fertilizers on arable lands in Lebanon is1860 kg ha^{-1} y^{-1}(Farajalla et al. 2010).

Earlier studies showed that PFs application in recommended rates on Brazilian soils did not increase TEs concentrations to hazardous levels, in short and medium terms (Malavolta 1994; De Conceicao and Bonotto 2006). These studies pointed out that the cause of such "safe" increase could not be related to PFs application.

On the other hand, a recent study carried by Kassir et al. (2012) revealed that Cd was the most susceptible element in Mediterranean red soil and associated Chicory plants, when soil was amended with phosphogypsum by-product obtained from PFs processing. In addition, a study on the impact of phosphate fertilizer industry on local soil contamination showed deposited contaminants contained in the industry's emissions were potentially hazardous to plants and ground waters (Kassir et al. 2012).

To evaluate the potential risk of TEs in PF-amended soils, quantification of different forms and phases of TEs, referring to their speciation, must be performed, in order to assess their mobility in the soil profile, influencing their availability to plants and their transport to groundwater, and thus to food and ecological chains. Extraction procedure (or sequential extraction) has been commonly used in the literature, whereby ascending aggressive reagents are applied to solubilize five different chemical forms (exchangeable, acid-soluble, reducible, oxidizable and residual) (Tessier et al. 1979; Ure et al. 1993). The release or the seizing of TE in a defined phase depend on soil properties such as pH and other sosil properties (Kabala and Singh 2001).

The main purpose of this work is to assess the effects of PFs amendment on Mediterranean red soil, in order to reveal any associated environmental hazards, and thus possible contingency measures could be established. Therefore, in relation to soil mineralogical composition, four objectives were set: (1) to determine the total concentrations of TEs in the amended-soil profile, and their variation with time, (2) to evaluate TEs mobility in amended soil using sequential chemical fractionation (3) to determine the TEs concentration variation in the amended-soil plant roots and shoots, and (4) to carry out microscopic analyses of soil samples in attempts to spot TEs mineralogical species and other suspected minerals of environmental concern, such as fluorine, in the amended soil matrix.

5.2 Materials and method

5.2.1 Field survey and soil sampling

The study area, where the experimental site was selected, is located off the east Mediterranean coast, in north Lebanon (Figure 5. 1), and it 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 Beirut airport. Residential, commercial or industrial sites are rare in this area; while, agricultural land (47 % of the study area) is more widespread than natural vegetation.

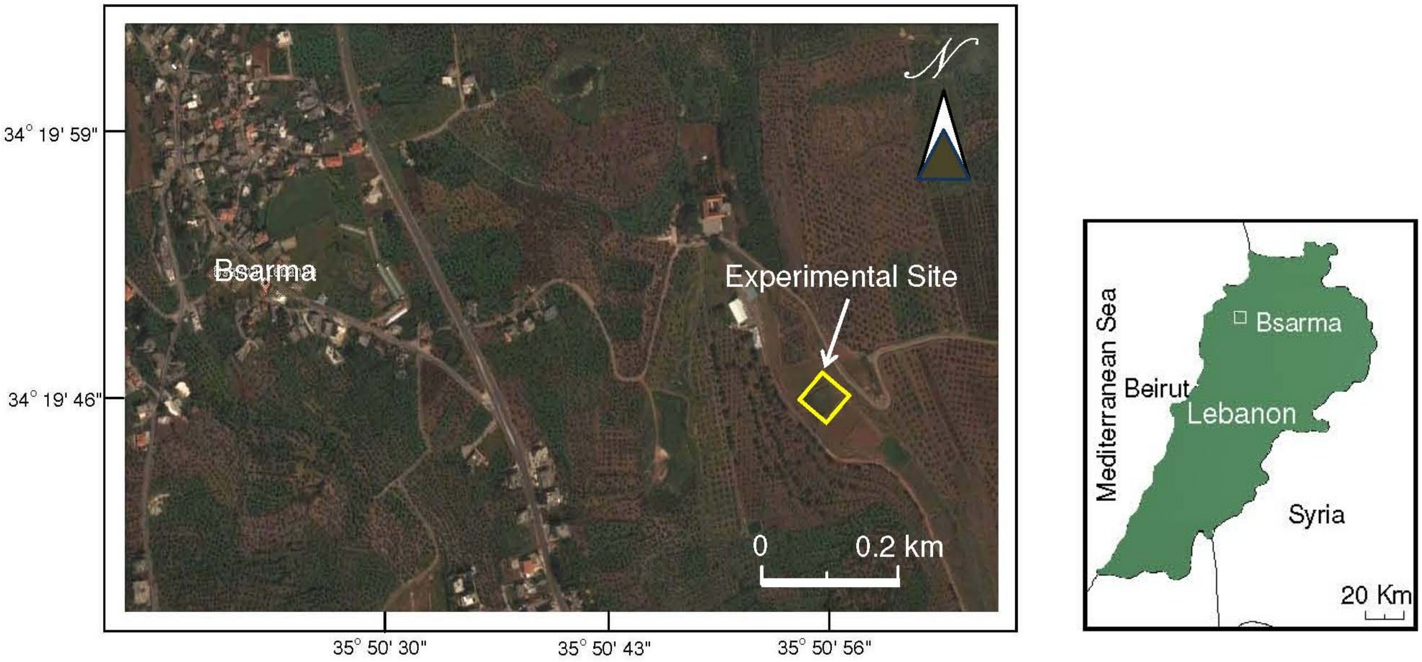


Figure 5. 1 Experimental site localization map

Agriculture is mainly dominated by plantation of olive trees, which is the main crop of the study area. According to Darwish et al. (2005), the studied region is dominated by well drained red soil classified in association with Gleyic and Vertic Luvisols. The texture of the soil is clayey (sand 24%, silt 20%, and clay 56%) with a calcium carbonate content reaching 22 %. Despite its loamy texture, the Mediterranean red soil is distinguished by a solid granular surface structure and porosity promoting intermediate and high soil permeability. Drainage course is improved by dominant gravel content and the type of underlying rocks, which are known for fissures and karsts (Darwish and Zurayk 1997). Soil profile is constituted of three horizons (A, B and C).The soil is relatively deep with a thickness of A and B horizons reaching 55 cm. Stoniness is common with 30 to 40%. Medium to coarse subangular and angular blocky aggregates represent the strong structure of the soil. The organic matter content is relatively low (1.3%). Common fine to medium roots are also found. The common plants growing between olive trees were of *Cichorium intybus* species.

The experimental site consisted of a land of 256-m^2 area. A study plot (7m x 7m) was divided into 24 individual parcels of 1 m^2 each, separated by distances of 75 cm. Each parcel was delineated with a wooden frame of 1x1x0.15m (length x width x height). The plot was fenced and gated as to restrict its accessibility, and prevent possible cattle intrusion.

To simulate the potential source of pollution originating from PF-amended soils, an opulent amount of 2 kg of PF, collected from the Lebanese fertilizer plant, was uniformly scattered on the soil surface in every parcel over a surface of 0.5m x0.5m without mixing with the soil. This is equivalent to applying PF at an intensity of 8 kg m^{-2} (80000 kg ha^{-1}), about forty times higher than the fertilizer yearly use of 1860 kg ha^{-1} on arable soils in Lebanon (Farajalla et al. 2010). The purpose of this abundant application was to subject the soil to a leveraged state of influence induced by PFs application, so as extreme ecological responses to such stimulus could be reached and measured. The initial PF application was done in October 2008. A reference parcel was left without amendment.

Coring was carried out to a depth of 60 cm, using a high power (2500 W) motor of type Cobra TT. The core shaft used was 100-cm long, 6-cm in diameter. The first soil sample was cored from the reference parcel (i.e. not amended with PFs) labeled as R. Then, sample coring had been successively performed in three different parcels labeled as P1, P2 and P3 at three different subsequent dates: T1, T2, and T3–four, eleven, and fifteen months, respectively, after the initial application and sampling from the reference plot R at T0, allowing a full plant growing cycle. Sampling times with corresponding weather data (temperature, humidity and rain) for each coring campaign is indicated in Table 5. 1. Samples were collected from the cored cylindrical soil blocks at 5cm intervals to a depth of 55cm. Plant roots (extending to a depth of about 20 cm) and leaves were also collected simultaneously with soil samplings, from each parcel.

Table 5. 1 Sampling times and weather data during periods between samplings

Time	*Temperature (°C)*		*Relative Humidity (%)*		*Wind Maximal*		*Rain*	*Cumulative Rain*
	Min	Max	Min	Max	dd (°)	ff (m/s)	(mm)	(mm)
Amendment								
Oct. 08	14.1	35.8	27	91	280	13	75.7	
Nov. 08	9.8	26.9	18	92	340	13	85.1	429.2
Dec. 08	4.1	23.5	32	94	340	23	167.9	
Jan. 09	2.9	21.3	27	94	120	13	100.5	
P1								
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	342.8
Mai 09	12.8	36.5	10	98	240	26	2.4	
Jun. 09	16.2	36.3	24	99	230	14	1.6	
Jul. 09	19.8	36.7	16	96	260	17	0	
Aug.09	22.1	34.4	34	88	240	11	0	
P2								
Sep. 09	19.8	32.4	37	87	280	17	2	
Oct. 09	15.3	36.6	28	88	300	15	72	327.4
Nov. 09	10.1	26.3	17	94	320	14	81.2	
Dec. 09	3.9	22.7	35	91	380	18	172.2	
P3								
Jan. 10	3	20.4	29	93	180	12	118.3	

5.2.2 *Sample preparation and analytical methods*

Soil samples were cleaned from roots and stones, oven-dried at 50°C, sieved to pass a 2 mm sieve, and ground to a fine powder using an agate pestle and mortar, while vegetation samples were washed in ultra-pure water, dried at 60°C and ground to a fine powder using an agate pestle and mortar.

Soil pH

Soil pH was determined in a ratio of 1 : 5 (soil : ionized water suspension) according to AFNOR X 31-103.

Soil and PF Total Concentrations

TEs in soil and PF samples were measured using an Iris Advantage ERS Inductively Coupled Plasma Mass Spectroscopy (ICP-MS X7) “ThermoFischer”, after melting the samples with lithium metaborate, and dissolution of the melt in diluted nitric acid. Analysis was conducted in an accredited laboratory SARM (CRPG, Nancy).

Vegetation Analysis

Vegetation samples were accurately weighed to 0.25 g directly in microwave PTFE vessels, and then subjected to 1 mL H2O2 (30%) and 9 mL concentrated HNO3 (65%). The digestion program itself consisted of a 10 min gradual increase in temperature to 200oC, a 15 min step at 200oC (1000W; 106Pa) and then a stage of ventilation cooling. The digests were filtered through a 0.45µm and analyzed using an Atomic Absorption Spectroscopy (AAS) “Analytical Gena Zeenit 700” to determine the content of Pb, Zn, Cu and Cd in roots and plant leaves.

Speciation of Soil & PF Samples

A five-stage sequential extraction method was performed on soil and PF samples using modified Tessier sequential extraction (Tessier et al. 1979). Soil samples from each of 0-20cm, 20-35cm, and 35-55cm depth intervals were mixed and homogenized. The extractable contents of trace elements, from an initial 5 g aliquot, were determined; five TEs fractions were separated in five steps as follows:

(1) Exchangeable fraction (F1) was extracted with 40 mL of 1 M $Mg(NO_3)_2$ (Shuman 1979);

(2) acid soluble fraction (F2) with 40 mL of 1 M CH_3COONa adjusted to pH 5 with CH_3COOH;

(3) reducible fraction (F3) with 20 mL Na-citrate (78,4 g L-1) and 20 mL $NaHCO_3$(9.82 g L-1), then adding 1g of Na_2S2O4 (80 ^{o}C for 4h) (Mehra and Jackson 1960);

(4) oxidizable fraction (F4) by adding 8 mL HNO_3 (0.02M) 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 ^{o}C for 2h); and

(5) residual fraction (F5) was extracted with 40 mL HNO_3 (65%) (Hudson-Edwards 1997; Ribeiro and Mexia 1997).

Each extraction step was followed by centrifugation of the mixtures at 5000 rpm for 30 minutes, 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 ^{o}C pending subsequent analyses. Analyses were carried out by AAS to determine the content of Pb, Zn, Cu and Cd in each extracted fraction.

Quality Control

In order to monitor the accuracy and precision of the used analytical methods, reference materials SRM2711 (Soil), CMI7004 (Soil), and NCS DC73349 (Bush Branches & Leaves) were analyzed for Cu, Pb, Zn and Cd total concentrations, using the same described methods for soil and vegetation sample analyses. Results were within -9.57% to +10.95% of the reference mean values.

The accuracy of the sequential extraction procedure was assessed by comparing the sum of the five TE fractions obtained from the procedure with the total TE concentration. The percent recovery of the sequential extraction procedure was calculated as follows:

Recovery % = (F1 + F2 + F3 + F4 + F5 / Total element analysis) x 100, where F is the TE fraction.

5.2.3 *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 a (θ, 2θ) goniometer and a position sensitive detector. Reflexions were collected in ambient conditions within the [3-65°] 2θ range, with a step width of 0.036° and a 3s collecting time. About 500 mg of homogenized phosphogypsum, ground reference soil samples were deposited as sub-compacted powder within a thin layer of 1mm thickness onto a plexiglass disc 2 cm in diameter.

Electron microscopy observations were performed with a S-2500 Hitachi SEM (Scan Electron Microscopy) equipped with a Kevex 4850-S EDX (energy dispersive X-ray spectrometer). Trace elements carriers were identified from elemental analysis of individual particles. Stoichiometric ratios were first calculated from atomic percentages given by EDX spectra, and then compared with known mineralogical compositions. For SEM imaging and microanalysis, the powder sample was re-suspended in ethanol under ultrasonication, and a drop of suspension was evaporated on a carbon-coated copper grid (EuroMEDEX, Mesh200).

Samples for SEM-EDX examination were sprinkled onto 2 cm^2 plates and carbon coated. Backscattered Electron Imaging (BEI) was used to identify the particles of interest. In that mode, brightness is related to the average atomic number of materials, and the mineral particles appear as bright spots within the matrix of sediments. The relative abundance of a given heavy metal carrier can then be assessed by conducting systematic microanalysis of bright spots. It should nevertheless be noted that this procedure largely overlooks mineral phases with low atomic number elements. In order to increase the emission of backscattered electrons, the SEM microscope was generally operated with a beam current of 3 pA and an accelerating voltage of 20 keV.

5.2.4 *Statistical Analysis*

ANOVA tests were performed on the samples data of trace and major element concentrations and pH values obtained for the soil profile in all parcels. The data was distributed in different levels of two categories; time (T0, T1, T2, and T3, corresponding to parcels R, P1, P2, and P3) and depth (horizons 0-5cm, 5-10cm, 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 analysis (Pearson r) was carried out between trace and major elements, TE concentrations and soil characteristics. All statistical analyses were performed using SPSS Version 17.

5.3 Results and Discussion

5.3.1 *Soil Background values: Reference Parcel*

The mineralogical results (XRD) showed that the background soil contained Quartz (SiO_2), Calcite ($CaCO_3$), clay minerals (Montmorillonite, Kaolinite), Anatase (TiO_2) and Hematite (Fe_2O_3). The soil pH showed alkaline range (8.23±0.12), and the cation exchange capacity (CEC) exhibited relatively high values (31.06± 0.5 cmol kg^{-1} of dry weight) with a dominance of calcium ions at the exchange sites.

The average background soil contained relatively low Cd concentration (0.30 ± 0.02 mg kg^{-1}) and high Zn concentration (103.35± 6.72 mg kg^{-1}). As for Cu and Pb, their average concentrations were found to be 35.84 ± 2.33 mg kg^{-1} and 11.50 ± 0.75 mg kg^{-1}, respectively. No significant differences were found in TEs distribution with depth (till 55cm), except in layer (30-55 cm) where Cu and Pb concentrations decreased with respect to upper layers (Table 5. 2).

It follows that, the study area presented elevated Zn total concentrations and slightly elevated Cu concentration when compared to the world agriculture soils (20-30 mg kg^{-1} and 50 mg kg^{-1} for Cu and Zn, respectively) (Alloway 1995). Pb and Cd concentrations were within the range of agricultural and normal soils (10-30 mg kg^{-1} and 0.2-1 mg kg^{-1} for Pb and Cd; respectively) (Alloway 1995; Baize 1997). Moreover, the total Zn and Cu concentrations exceeded the background values (12±2 and 64±2 mg kg^{-1} for Cu and Zn, respectively) reported for the arable soils of North Lebanon (Nsouli et al. 2004). In general, the natural occurrence and concentration of the studied elements were homogenous with depth. However, Cu and Pb concentrations decreased in the deeper layer (30-55cm).

Chemical speciation of the studied TEs in the reference soil showed they were mainly associated with Fe and Mn oxides and hydroxides (reducible fraction F3) (64, 45, 43 and 13 % for Cd, Pb, Zn and Cu respectively) and bound to 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 swelling-shrinking clays and iron oxides, which agrees with the findings of previous works (Lamouroux et al. 1968; Darwish et al. 1988; Sayegh et al. 1990). In addition, Cu was accumulated in the oxidizable fraction (F4) (20%), in agreement with other findings reported in the literature (Kuo et al. 1983; Zaccone et al. 2007).

Table 5. 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)

	Depth (cm)	**R±SD (mg/kg)**		**P1 ±SD (mg/kg)**		**P2±SD(mg/kg)**		**P3±SD(mg/kg)**		**p (ANOVA)**	**Parcel Average**	**±SD**	**p' (ANOVA)**
Cu	**0-5 cm**	38.29	±3.52	40.54	±3.73	19.08	±1.75	36.08	±3.32	**0.008****	33.5	±3.08	0.144
	5-10	37.05	±3.41	39.36	±3.62	34.44	±3.17	29.95	±2.75	0.153	35.2	±3.24	
	10-15	36.03	±3.31	36.81	±3.38	35.74	±3.29	37.89	±3.48	0.916	36.62	±3.37	
	15-20	36.88	±3.39	48.45	±4.45	36.24	±3.33	37.57	±3.45	0.078	39.79	±3.66	
	20-25	38.47	±3.54	48.45	±4.45	39.37	±3.62	38.47	±3.54	0.142	41.19	±3.79	
	25-30	38.47	±3.54	44.78	±4.12	37.89	±3.48	38.65	±3.55	0.333	39.95	±3.67	
	30-40	30.77	±2.83	44.78	±4.12	36.35	±3.34	42.65	±3.92	0.054*	38.64	±3.55	
	40-50	30.77	±2.83	41.88	±3.85	41.17	±3.78	43.3	±3.98	0.078	39.28	±3.61	
	Depth Average	35.84	±3.29	43.13	±3.96	35.04	±3.22	38.07	±3.50	**0.000****	38.02	±3.49	
Cd	**0-5 cm**	0.3	±0.03	0.41	±0.04	0.83	±0.08	0.59	±0.05	**0.002****	0.54	±0.05	**0.000****
	5-10	0.31	±0.03	1.05	±0.10	0.4	±0.04	0.52	±0.05	**0.001****	0.57	±0.05	
	10-15	0.31	±0.03	0.86	±0.08	1.28	±0.12	0.95	±0.09	**0.002****	0.85	±0.08	
	15-20	0.3	±0.03	0.37	±0.03	0.32	±0.03	0.31	±0.03	0.218	0.32	±0.03	
	20-25	0.32	±0.03	0.37	±0.03	0.28	±0.03	0.27	±0.03	0.073*	0.31	±0.03	
	25-30	0.32	±0.03	0.39	±0.04	0.3	±0.03	0.34	±0.03	0.156	0.34	±0.03	
	30-40	0.27	±0.02	0.39	±0.04	0.26	±0.02	0.3	±0.03	**0.032****	0.3	±0.03	
	40-50	0.27	±0.02	0.31	±0.03	0.36	±0.03	0.27	±0.02	0.080*	0.3	±0.03	
	Depth Average	0.3	±0.03	0.52	±0.05	0.5	±0.05	0.44	±0.04	0.066*	0.44	±0.04	
Zn	**0-5 cm**	99.46	±9.14	108.4	±9.96	52.73	±4.85	105.9	±9.73	**0.009****	91.62	±8.42	**0.030****
	5-10	99.84	±9.18	134	±12.32	94.59	±8.70	83.43	±7.67	**0.024****	102.97	±9.46	
	10-15	106.2	±9.76	122.7	±11.28	131.8	±12.12	124.4	±11.44	0.276	121.28	±11.15	
	15-20	107.5	±9.88	112.9	±10.38	98.13	±9.02	97.73	±8.98	0.417	104.07	±9.57	
	20-25	101.6	±9.34	112.9	±10.38	99.35	±9.13	99.6	±9.16	0.509	103.36	±9.50	
	25-30	101.6	±9.34	115.2	±10.59	100.6	±9.25	101.1	±9.29	0.454	104.63	±9.62	
	30-40	105.3	±9.68	115.2	±10.59	94.61	±8.70	107.3	±9.86	0.339	105.6	±9.71	
	40-50	105.3	±9.68	109.6	±10.07	105.4	±9.69	109.6	±10.07	0.942	107.48	±9.88	
	Depth Average	103.4	±9.50	116.4	±10.70	97.15	±8.93	103.6	±9.53	**0.004****	105.12	±9.66	
Pb	**0-5 cm**	13.22	±1.22	13.49	±1.24	7.11	±0.65	12.56	±1.15	**0.012****	11.6	±1.07	**0.022****
	5-10	12.82	±1.18	13.45	±1.24	12.48	±1.15	10.83	±1.00	0.269	12.39	±1.14	
	10-15	11.87	±1.09	12.64	±1.16	17.23	±1.58	13.2	±1.21	**0.045****	13.73	±1.26	
	15-20	11.76	±1.08	21.24	±1.95	13.83	±1.27	13.84	±1.27	**0.010****	15.17	±1.39	
	20-25	11.79	±1.08	21.24	±1.95	14.12	±1.30	13.72	±1.26	**0.010****	15.22	±1.40	
	25-30	11.79	±1.08	12.86	±1.18	13.33	±1.23	12.95	±1.19	0.631	12.73	±1.17	
	30-40	9.38	±0.86	12.86	±1.18	13.06	±1.20	12.53	±1.15	0.079*	11.96	±1.10	
	40-50	9.38	±0.86	11.61	±1.07	13.28	±1.22	12	±1.10	0.087*	11.57	±1.06	
	Depth Average	11.5	±1.06	14.92	±1.37	13.06	±1.20	12.7	±1.17	**0.006****	13.05	±1.20	

pH	**0-5 cm**	8.23	±0.76	7.4	±0.68	6.98	±0.64	7.01	±0.64	0.352	7.41	±0.68	0.116
	5-10	8.23	±0.76	7.4	±0.68	6.98	±0.64	7.01	±0.64	0.352	7.41	±0.68	
	10-15	8.27	±0.76	7.11	±0.65	7.1	±0.65	7.37	±0.68	0.392	7.46	±0.69	
	15-20	8.2	±0.75	6.74	±0.62	6.6	±0.61	7.1	±0.65	0.208	7.16	±0.66	
	20-25	8.2	±0.75	7.74	±0.71	7.1	±0.65	7.76	±0.71	0.548	7.7	±0.71	
	25-30	8.23	±0.76	8.1	±0.74	7.57	±0.70	8	±0.74	0.822	7.98	±0.73	
	30-40	8.23	±0.76	8.1	±0.74	7.57	±0.70	8	±0.74	0.822	7.98	±0.73	
	40-50	8.25	±0.76	7.95	±0.73	7.98	±0.73	7.9	±0.73	0.961	8.02	±0.74	
	Depth Average	8.23	±0.76	7.57	±0.70	7.24	±0.67	7.52	±0.69	**0.000****	7.64	±0.70	

* Significant difference at the 0.10 level
** Significant difference at the 0.05 level

5.3.2 *Characterization of PF amendment*

XRD results of PF showed that the main peak recorded in the diffractogram was calcium phosphate ($Ca(H_2PO_4)_2.H_2O$) and to less extent Anhydrite ($CaSO_4$). The presence of $CaSO_4$ in PF is the result of the acidulation of phosphate rock with H_2O and H_2SO_4.The PF sample showed an acidic pH value of 2.63 ±0.8.

TEM elemental mapping of PF showed particles of phosphorus, sulfur and calcium. Ca was associated with sulfur (Ca/S=1) and with phosphorus (Ca/P=0.5). Particles of gypsum ($CaSO_4$) and acidulated P-fertilizers ($Ca(H_2PO_4)_2$) were thus identified.

The total concentration of the studied elements (Cu, Zn, Pb and Cd) in the Lebanese manufactured PF showed that Zn was the most abundant TE (199.3 mg kg^{-1}), with the lowest concentration being for Pb (2.66 mg kg^{-1}). Copper and cadmium concentrations were found to be 16.62 and 6.18 mg kg^{-1}, respectively. These results were generally within the average metal concentrations analyzed from a total of 196 European PFs (Cd, 7.4; Zn, 166; Pb, 2.9 mg kg^{-1}) (Nziguheba and Smolders 2008).

Results of PF speciation showed that the studied metals (Zn, Cd, Cu and Pb) were mainly present in the exchangeable fraction (F1) (60%, 41.9%, 40.7% and 38% respectively). They were also found in the acid-soluble fraction (F2) (27.7%, 10.4%, 19% and 34.7%; respectively). Moreover, part of these TEs mass (27% and 23.6% for Pb and Cd; respectively) was bound with reducible fraction (F3).

5.3.3 *Variation of Total Concentrations in the Soil Profile*

Table 5. 2 shows the results of total concentrations and pH measurements obtained for the soil profile in all parcels, along with the statistical analyses performed on the samples data, including the mean and standard deviation for each set of samples, and the p-value for the parcels data collected for each soil horizon.

To analyze the PF-originated TEs transfer in soil with time, the concentration of Cd, Zn, Pb, and Cu were plotted against time for the reference parcel R at T0 and incubated parcels P1, P2 and P3 (corresponding to T1=4-, T2=11- and T3=15-month periods) (Figure 5. 2)—To simplify the tracking of the profiles variations, the eight layers in each parcel were grouped in three depth zones: upper (0-20 cm), intermediate (20-35 cm), and lower zone (35-55 cm); zone TE concentration was taken as the average content of TE in the zone layers—The time axis was started at the date when the PF was just applied on the study parcels; the corresponding metal concentrations at the different depths represent the soil background concentrations.

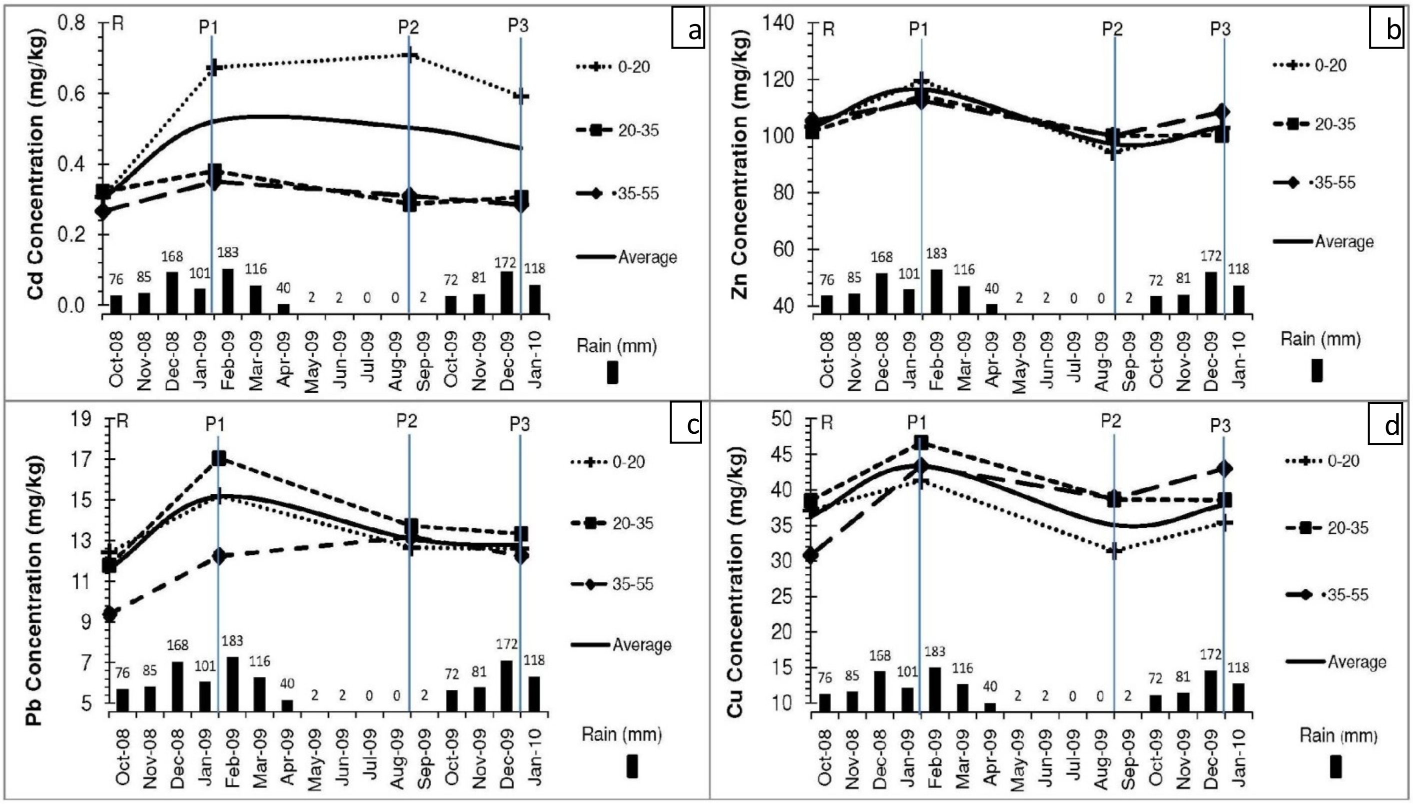


Figure 5. 2 Time-variation of TEs concentrations in the soil profile – Reference parcel R (T=0); PF-amended parcels P1 (T1 = 4 months); P2 (T2 = 11 months); and P3 (T3 = 15 months)

Generally, a similar trend was observed for the studied TEs. For the overall profile, peak concentrations of TEs (Cu: 43.13, Cd: 0.52, Zn: 116.36, and Pb: 14.92 mg kg^{-1}) occurred four months after amendment (in January, parcel P1). Then, TEs average total concentration decreased between parcels P1 and P2 (February-August) to finally reach near background values in parcel P3 (December) (Figure 5. 2). However, Cd average concentration remained relatively constant between parcels P1- P3 (0.44 to 0.52 mg kg^{-1}). Changes in Cd concentration between parcels occurred only in the upper layers (0-20 cm) (0.31 to 0.71 mg kg^{-1}), thus not reaching deeper layers (Figure 5. 2a), indicating possible in situ release and recovery. A soil enrichment of about 0.30 mg/kg (~100% enrichment) in Cd remained in P3 (11 months after PF application) in the upper zone (0-20 cm). Layer 35-55cm showed an increase in Pb content between P1 and P2 (February-August) (Figure 5. 2c). Practically, with the exception of Cd, slight variations in TE total concentrations occurred between P2 and P3 (August-December), where the TEs content in the soil approached the background levels, indicating the direct effect of PF on the soil profile took place mainly during around a year following PF application. No evidence of released TEs accumulation in the soil was observed by the end of the sampling period (15 months after PF application)–Except for Cd which was somewhat accumulated in the upper layers (0-20 cm). However, Cd content in this layer was decreasing between P2 and P3, and by extrapolation, it would eventually reach the background level.

A decrease of soil pH following the PF amendment was detected from the surface (0-5cm) till layer 15-20 cm that showed the lowest value with slightly acidic pH (6.6 ± 0.2) in parcels P1 and P2 (Table 5. 2).

Statistically, the fluctuation of TEs concentration in all depths with time proved a significant difference in the average concentration between parcels for Cu, Zn and Pb. The upper layers of the parcels (down to 25 cm) showed a significant difference with time for Cd (Table 5. 2).

As a result of local and temporary pH decrease after PFs amendment, and heavy rainfall during October-January, TEs average concentrations increased in the soil profile to reach their highest values in parcel P1 (Figure 5. 2). However, despite the relatively massive quantity of PFs amendment, their concentration remained below the permissible limits of TEs in agricultural soils (Cu: 63, Cd: 1.4, Zn: 200, and Pb: 70 mg kg^{-1}) (CCME 1999). TEs were transferred from PF and moved downward through the soil profile with incoming rain water creating temporary leaching conditions. Generally, the continuous rainfall between parcels P1 and P2 (particularly between January and April) caused TEs dilution, and thus a significant decrease in Zn, Cu, and Pb average concentrations was observed in the soil profile, and this trend persisted in the period between April and August, due to TEs uptake by growing plants. However, Cd nearly constant average concentration in the soil profile between parcels P1 and P2 indicated its accumulation in the soil matrix (Figure 5. 2a). In the period between September and December (P2-P3), the drying-wetting cycle of the soil caused the re-augmentation of Zn and Cu average concentrations in the soil profile. However, a different behavior was observed for Pb and Cd that showed a slight decrease of their average concentration between P2 and P3 (13.06 and 12.70 mg kg^{-1} for Pb, 0.50 and 0.44 mg kg^{-1} for Cd in P2 and P3, respectively) (Table 5. 2),indicating possible uptake by plants or leaching toward the saturated zone.

5.3.4 *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). TEs speciation results for soil samples taken from parcel P1 are presented in Table 5. 3, with replicates, averages, and standard deviations. TE recovery, measured total concentration, and percent recovery are also shown in Table 5. 3.

The TE content obtained by adding the sequentially extracted fractions (TE recovery) was to some extent lower than the actual value found by TE total concentration analysis. Significantly low recoveries were found only for Pb and Cd (62% & 66%) in parcel P1. The difference between recovered and actual TE total concentrations is due to the fact that the used sequential speciation method is subject to some inherent drawbacks. In fact, the re-adsorption of metals during the sequential extractions has been widely reported in other works that used sequential extractions for soil (Harrison et al. 1981; Ramos et al. 1994), and this process together with re-precipitation could take place during the extractions resulting in lower recovery values. A number of authors have established that the dissolution of iron oxides was incomplete during the reductive step of Tessier's scheme, leading to an overestimation of the residual fraction (Gleyzes et al. 2002; Kheboian and Bauer 1987).

The results of TE chemical fractions (F1, F2, F3, F4 & F5) concentrations in the different parcels, at the different study layers (0-20cm, 20-35cm, and 35-55cm), were plotted on separate charts for each of the considered metals (Cd, Pb, Zn & Cu), as shown in Figure 5. 3.

In the reference plot, most of the studied elements were stable and associated with the reducible and residual fractions (F3 and F5). Moreover, in the reference parcel (R), Cd and Pb were bound to acid-soluble fraction (F2). Previous studies showed that in alkaline soil, Pb was fixed to the iron and manganese oxide and carbonate fractions (Tuins and Tels 1990; Sheppard and Thibaut 1992; Jaradat et al. 2006). Copper appeared mainly in the iron and manganese oxide and residual fraction (Castillo-Carrion et al. 2007).

Table 5. 3 Fractionated TEs concentrations, recovery, and measured total concentration in the soil profile of parcel P1

Horizon	F1		F2		F3		F4		F5		Recovery	SD	Measured Total Conc.	SD	% Recovery
	Rep.1	Rep.2	Rep.1	Rep.2	Rep.1	Rep.2	Rep.1	Rep.2	Rep.1	Rep.2					
	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD					
Cd - P1 (T = 4 months)															
0-20 cm	< D.L.[a]	< D.L.	0.19	0.27	0.12	0.16	0.06	0.09	< D.L.	< D.L.	0.44	0.07	0.67	0.04	66.27
	< 0.005	—	0.23	0.04	0.14	0.02	0.07	0.01	< 0.005	—					
20-35	< D.L.	< D.L.	0.11	0.15	0.08	0.06	0.07	0.06	< D.L.	< D.L.	0.27	0.03	0.38	0.02	69.74
	< 0.005	—	0.13	0.02	0.07	0.01	0.06	0.01	< 0.005	—					
35-55	< D.L.	< D.L.	< D.L.	< D.L.	0.09	0.06	0.26	0.17	< D.L.	< D.L.	0.29	0.06	0.35	0.03	83.71
	< 0.005	—	< 0.005	—	0.08	0.01	0.216	0.04	< 0.005	—					
Pb - P1 (T = 4 months)															
0-20 cm	1.72	2.22	1.32	1.73	1.82	2.53	2.34	3.47	4.33	5.44	13.46	1.93	15.20	0.99	88.50
	1.97	0.25	1.52	0.20	2.18	0.36	2.90	0.56	4.88	0.55					
20-35	1.10	1.53	0.54	0.72	3.12	3.95	3.75	4.59	0.97	0.81	10.55	1.22	17.05	1.11	61.86
	1.32	0.22	0.63	0.09	3.54	0.42	4.17	0.42	0.89	0.08					
35-55	< D.L.	< D.L.	2.73	2.28	2.71	2.20	2.33	2.86	2.22	1.72	9.52	1.00	12.24	0.80	77.81
	< 0.005	—	2.50	0.23	2.46	0.25	2.59	0.26	1.97	0.25					
Zn - P1 (T = 4 months)															
0-20 cm	4.01	2.93	< D.L.	< D.L.	42.32	32.94	45.22	36.27	17.45	12.67	96.91	12.09	119.50	7.77	81.09
	3.47	0.54	< 0.005	—	37.63	4.69	40.74	4.48	15.06	2.39					
20-35	< D.L.	< D.L.	0.21	0.16	22.45	16.72	78.33	62.95	4.98	3.13	94.46	11.51	114.05	7.41	82.83
	< 0.005	—	0.19	0.02	19.58	2.87	70.64	7.69	4.05	0.93					
35-55	< D.L.	< D.L.	< D.L.	< D.L.	74.43	62.27	9.03	7.03	15.03	11.95	89.87	8.62	112.40	7.31	79.96
	< 0.005	—	< 0.005	—	68.35	6.08	8.03	1.00	13.49	1.54					
Cu - P1 (T = 4 months)															
0-20 cm	4.52	3.42	7.22	9.70	10.77	7.83	6.76	5.31	10.02	14.89	40.22	6.42	41.29	2.68	97.41
	3.97	0.55	8.46	1.24	9.30	1.47	6.03	0.73	12.46	2.44					
20-35	11.23	8.28	3.55	2.83	5.22	4.14	5.88	4.70	12.03	16.05	36.96	4.97	46.62	3.03	79.28
	9.75	1.48	3.19	0.36	4.68	0.54	5.29	0.59	14.04	2.01					
35-55	6.67	5.04	2.65	3.75	6.98	8.58	10.55	7.55	18.26	13.18	41.60	6.20	43.33	2.82	96.01
	5.86	0.82	3.20	0.55	7.78	0.80	9.05	1.50	15.72	2.54					

[a] < D.L.: Value is below the AAS detection limit (0.001-0.005 depending on the studied element)

Cd speciation

At T0, Cd was associated with the acid-soluble and reducible fractions (F2 and F3) in the reference parcel at all depths. Exchangeable, oxidizable and residual fractions (F1, F4 and F5) were generally negligible in soil profile (Figure 5. 3a).

At T1 (four months after PF application), Cd amounts were doubled (0.23 mg kg^{-1}) in the acid-soluble fraction F2 (Figure 5. 3b) in layer 0-20 cm. Furthermore, Cd related to the oxidizable fraction (F4) appeared in all depths of the soil profile of parcel P1, or at T1 (0.07, 0.06 and 0.22 mg kg^{-1} at 0-20; 20-35 and 35-55cm, respectively).

At T2 (eleven months after PF application), in parcel P2, Cd was found associated mainly with the exchangeable fraction (F1) (0.33 mg kg^{-1}–65 %) at layer 0-20cm, and to oxidizable fraction (F4) in layers 20-35 (0.20 mg kg^{-1}–87 %) and 35- 55cm (0.20 mg kg^{-1}–69 %) (Figure 5. 3c). Thus, Cd concentration increased in the mobile fraction (exchangeable) at 0-20 cm and in the oxidizable fraction at 20-35 and 35-55cm.

At T3 (fifteen months after PF amendment), the reducible and residual fractions were dominant (F3:96% at 35-55 cm, and F5: 73 % at 0-20 cm) (Figure 5. 3d).

The change in Cd speciation over the study period can be attributed to phosphate fertilizer application decreasing soil pH in parcels P1 and P2 at the surface layer (0-20cm). It is well reported that under acid conditions, Cd was found accumulated in the exchangeable fraction and acid soluble fraction (F1 and F2) (Li and Thornton 2001; Castillo-Carrion et al. 2007). In the end of our study, under alkaline soil conditions, Cd was adsorbed to iron and manganese oxides, organic matter, and clays structure.

Pb speciation

Pb was mainly combined to carbonates (F2), iron and manganese oxides and hydroxides (F3) and to clays (F5) in the reference parcel (R) in all depths. At natural abundance, the exchangeable (F1) and oxidizable fractions (F4) could be considered insignificant in all depths (Figure 5. 3e).

At T1 (five months after PF application), a change of Pb speciation was observed in P1 with the appearance of the exchangeable (F1) and oxidizable (F4) Pb fractions (1.97 mg kg^{-1}–15% and 2.90 mg kg^{-1} – 22% at 0-20 cm; 1.32 mg kg^{-1}–12% and 4.17 mg kg^{-1}–40% at 20-35cm; <1 mg kg^{-1}–<1% and 2.59 mg kg^{-1}–27% at 35-55 cm, in F1 and F4, respectively) (Figure 5. 3f). Layer

35-55 cm of parcel P1 contained Pb in a concentration of 2.50 mg kg^{-1} (26.30%) in the acid-soluble fraction (F2). Pb revealed an increase of 15% and 13% at 0-20 and 20-35 cm, respectively, in the exchangeable fraction F1 of parcel P1

At T2 (eleven months after PF application), the reducible and oxidizable fractions (F3 and F4) in parcel P2 were dominant (Figure 5. 3g).

At T3 (fifteen months after PF amendment), Pb was associated with the reducible and alumino-silicates fractions (F3, 1.74 mg kg^{-1}–17% and F5, 8.78 mg kg^{-1}–84%) in the surface layer (0-20m), and mainly to acid-soluble (F2) (8.44 mg kg^{-1}–81%) and exchangeable fractions (F1) (8.67 mg kg^{-1}–88%) in layers 20-35 and 35-55cm, respectively (Figure 5. 3h). Hence, Pb solubility increased in layers 20-35 and 35-55cm.

The appearance of Pb in the exchangeable fraction F1 in parcels P1 and P2 (acid pH) is in agreement with different studies (Castillo-Carrion et al. 2007). It can be ascribed to the input of phosphate fertilizer with speciation results showing that 38% of Pb occurred in the exchangeable fraction F1. Pb binding to oxidizable fraction F4 has been reported in the literature (Chaney et al. 1988), generally in the detriment of the residual fraction (F5). The presence of complexing and organic ligands and competing cations, decreasing Pb sorption, could substantially enhance its mobility (Puls et al. 1991; Kotuby-Amacher and Gambrell 1988), which may lead to reinstating, to some extent, the exchangeable fraction F1 (P3 layer 35-55 cm).

Zn speciation

Zn reducible and residual fractions (F3 and F5) were dominant in the reference parcel R throughout the soil profile (Figure 5. 3i). F1, F2 and F4 were negligible in all soil horizons (< 6 mg kg^{-1}).

At T1 (parcel P1), more oxidizable zinc fraction (F4) accumulated in all layers, particularly in the upper and intermediate layers (40.74 mg kg^{-1}–42% and 70.64 mg kg^{-1}–75% in layers 0-20 and 20-35 cm, respectively) (Figure 5. 3j).

At T2 (parcel P2), Zn was found mostly associated with residual fractions (F5) in all layers (55.59 mg kg^{-1}–71%, 66.01mg kg^{-1}–70%, and 82.40 mg kg^{-1}–92%, in layers 0-20, 20-35 and 35-55 cm, respectively) (Figure 5. 3k). Zn was sorbed mainly in clay fraction.

At T3 (parcel P3), Zn mobility was modified, where Zn in the exchangeable and acid soluble fractions (F1 and F2) was in relatively higher concentrations of 21.90 mg kg^{-1}–26%, 31.94 mg kg^{-1}–37%, and 24.40 mg kg^{-1}–27% at 0-20, 20-35 and 35-55 cm, respectively (Figure 5. 3l). Zn solubility increased, comparing with parcel P2, in the detriment of residual fraction (at 0-20 and 35-55 cm) and reducible fraction (at 20-35cm) (net shifts of 14%, 15% and 27% at 0-20, 20-35 and 35-55 cm, respectively, were observed from Fe/Mn oxides and clay fractions to the mobile fractions (F1 and F2).

Phosphate fertilizer application varied Zn speciation in the soil horizons where the greatest proportion of Zn resided in the oxidizable fraction (F4) in parcel P1, in the detriment of the residual fraction (F5). This can be related to the soil organic matter's affinity for soluble Zn (Kabata-Pendias and Pendias 1984), which was released into soil solution from the applied PF containing high proportion (60%) of the metal’s exchangeable fraction F1. The increase of fractions F1 and F2 in P3 may be related to the formation of zinc complexes with inorganic and organic ligands, affecting Zn adsorption reactions with the clay minerals by altering its chemical species (McLean and Bledsoe 1992).

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 at all depths (19.27mg kg^{-1}–63%, 19 mg kg^{-1}–63% and 15.81 mg kg^{-1}–64% in 0-20 cm, 20-35cm, and 35-55cm, respectively). The exchangeable (F1) and the acid-soluble fractions (F2) were negligible (< 1 mg kg^{-1} and < 4 mg kg^{-1}, respectively) (Figure 5. 3m).

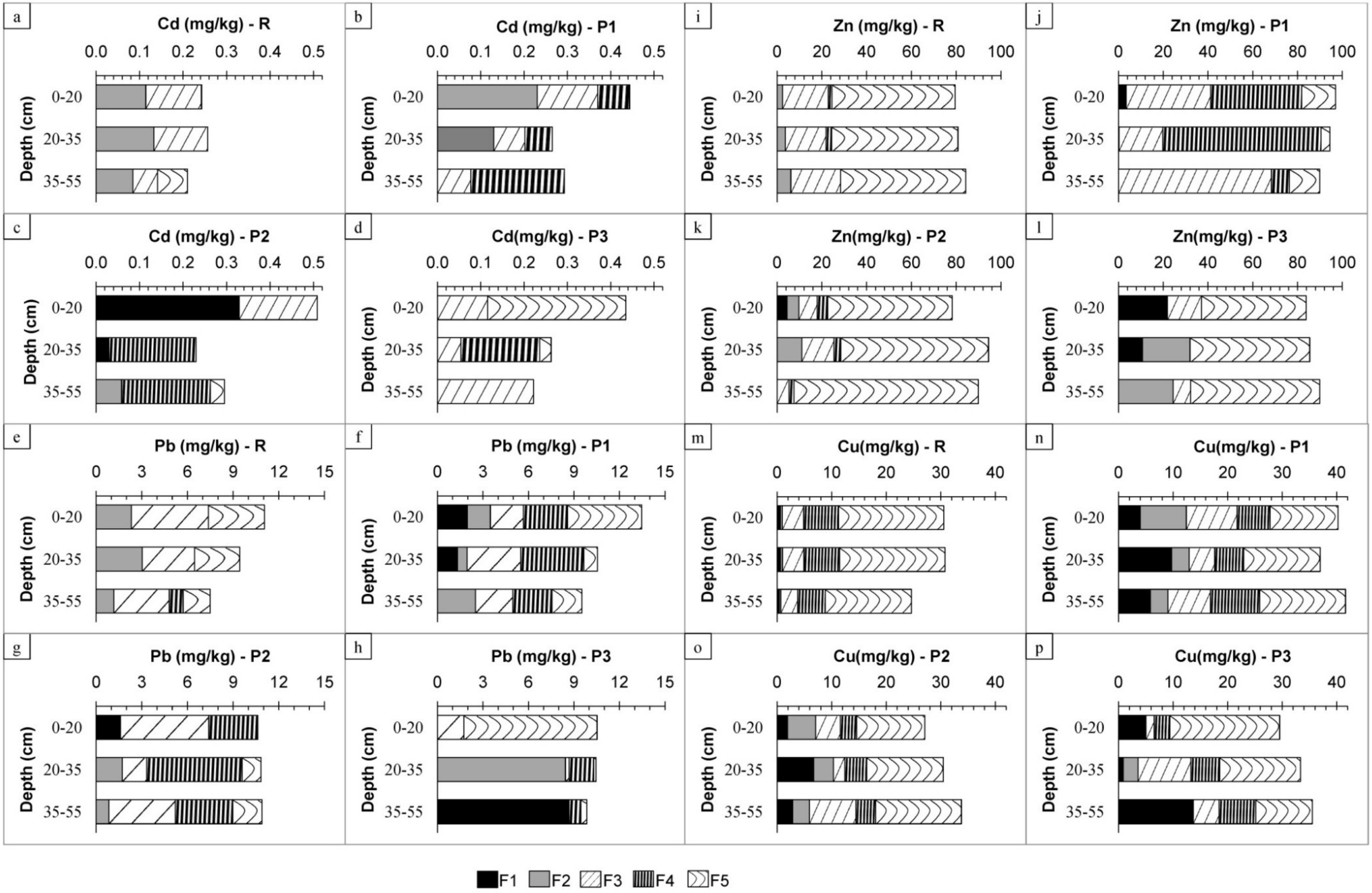


Figure 5. 3 Time-variation of TEs geochemical fractions concentrations in the soil profile – Reference parcel R (T=0); PF-amended parcels P1 (T1 = 4 months); P2 (T2 = 11 months); and P3 (T3 = 15 months). F1–Exchangeable; F2–Acid Soluble; F3–Reducible; F4–Oxidizable

At T1 (parcel P1), these two fractions (F1 and F2) held a larger quantity of copper at all depths (12.43, 12.97 and 9.06 mg kg^{-1} in 0-20 cm, 20-35cm, and 35-55cm respectively) (Figure 5. 3n). A mobilization of Cu in the soil profile of parcel P1 was therefore induced (3% to 32%, 3% to 35%, and 3% to 23 % increase in mobile fractions (F1 and F2) at 0-20, 20-35 and 35-55cm, respectively, comparing R to P1), with a decrease occurring mainly in the fraction associated with clays (F5) (63% to 32%; 63% to 35% ; 64% to 36% at 0-20, 20-35 and 35-55cm, respectively).

At T2 (P2), Cu quantities in fractions F1 and F2 decreased in the soil profile (12.43 mg kg^{-1}–31% to 7.05 mg kg^{-1}–26%, 12.95 mg kg^{-1}–35% to 10.33 mg kg^{-1}–34%, and 9.05 mg kg^{-1}–22% to 5.91 mg kg^{-1}–18%, in layers 0-20, 20-35, and 35-55, respectively (Figure 5. 3o).

At the end of the experiment in P3, Cu was partitioned in the reducible, oxidizable and alumino-silicate fractions of the soil (Figure 5. 3p). However, 17% and 39 % of Cu content was present in the exchangeable fraction (F1) in layers 0-20 and 35- 55cm.

The development of Cu exchangeable fraction F1 in the soil horizons was the immediate result of the application of PF carrying this Cu species in abundance (40.7%) relative to the background (~0%). Fraction F2 could be formed by the adsorption of Cu to soil carbonate (CaCO3) surfaces (Dudley et al. 1991). The general increase in the reducible fraction could be attributed to the binding of some Cu in soluble form to Fe–Mn oxides. Mclaren and Crawford (1973) reported that manganese oxides played a crucial role in binding copper in soil. Cu mobility in soils may be enhanced by forming complexes with soluble organic ligands (Jiries et al. 2001).

Cu, Pb & Zn versus Cd

Fe/Mn oxides and clays were the most susceptible to changes that resulted in an increase of Pb, Zn and Cu solubility in soil profile. The presence of soluble phosphates and sulfates in PF amendment (at least 85-90% of the total P in PF is water-soluble) (Chien et al. 2011) may have had a significant impact on Pb, Zn and Cu solubility. After fifteen months of amendment (parcel P3), comparing to the reference plot, the mobile fractions and mainly the exchangeable fraction (F1) showed increments in Cu, Pb and Zn amounts relative to the reference (14%, 7.7%, 35.5% for Cu; 23%, 32.9%, 20% for Zn at 0-20, 20-35 and 35-55 cm respectively; and 48%, 72.4% for Pb at 20-35 and 35-55cm respectively), which could mobilize these TEs in soil profile, imposing a threat to the ground water. On the contrary, Cd was sorbed in soil particles (clays and Fe/Mn oxides and hydroxides) over the study period. These results were opposite to those of phosphogypsum-amended soil where Cd, after the study period, was mostly in the exchangeable fraction, whereas Pb, Zn and Cu were sorbed in soil particles (Kassir et al. 2012).

5.3.5 *TEs concentration in plants*

Concentrations of the studied elements in the entire plant, *Cichorium Intybus* L, collected from reference and amended parcels were presented in Table 5. 4, along with the respective TE concentrations in the soil plant's roots zone (0-20 cm) and the resulting soil-plant transfer factors (concentration in plant/concentration in soil). Figure 5. 4 illustrates the transfer factor time-variation for the different TEs.

Table 5. 4 TE concentration in whole plants and soil root zone, and the respective transfer factor, for the different parcels

	Cu (mg/kg)	*±SD*	*Pb (mg/kg)*	*±SD*	*Zn (mg/kg)*	*±SD*	*Cd (mg/kg)*	*±SD*
Parcel	**Plants** **Soil (0-20 cm)** **Transfer Factor**		**Plants** **Soil (0-20 cm)** **Transfer Factor**		**Plants** **Soil (0-20 cm)** **Transfer Factor**		**Plants** **Soil (0-20 cm)** **Transfer Factor**	
R	6.07	0.15	1.33	0.10	8.73	0.09	0.09	0.01
	37.06	2.41	12.42	0.81	103.25	6.71	0.31	0.02
	0.16	0.01	0.11	0.02	0.08	0.01	0.29	0.05
P1	9.61	0.11	2.54	0.11	13.81	0.31	0.29	0.02
	41.29	2.68	15.20	0.99	119.50	7.77	0.67	0.04
	0.23	0.02	0.17	0.02	0.12	0.01	0.43	0.06
P2	5.08	0.14	1.04	0.08	9.89	0.24	0.37	0.02
	31.38	2.04	12.66	0.82	94.31	6.13	0.71	0.05
	0.16	0.02	0.08	0.01	0.10	0.01	0.52	0.05
P3	9.67	0.45	2.58	0.24	10.83	0.61	0.19	0.01
	35.37	2.30	12.61	0.82	102.87	6.69	0.59	0.04
	0.27	0.03	0.20	0.03	0.11	0.01	0.32	0.04

The TE transfer factor (TF) is a measure of its availability to plant uptake. There are many factors that can influence the TF, including soil properties and TE chemical phases. The exchangeable fraction (F1) is readily available and considered to be the primary nutrient source for plants (Narwal and Singh 1998). The fraction associated with carbonate (F2) is potentially available for plant uptake, depending on soil pH conditions, whereas TE in the other chemical fractions (oxides-F3, organic-F4 , and residual-F5) with minimal solubility and very low mobility are not involved with the plants biological activities (Xian 1989). Thus, during the experiment course, the main changing factors affecting TEs bioavailability, hence their TFs, are the soil moisture content (associated with rainfall), soil pH (influenced by PF acidity), and the respective TEs leaching and available fraction concentrations. Cd exhibited the highest TF (0.32±0.04—0.52±0.05) among the other TEs in all parcels, followed by Cu (0.16±0.02—0.27±0.03). Pb and Zn had comparable TFs (0.08±0.01—0.17±0.02) in all parcels, except in P3 where it increased to 0.20±0.03 for Pb, while remained in the same range for Zn (0.11±0.01) (Table 5. 4).

In comparison with the reference parcel, it can be seen from Figure 5. 4 that the TF of Cd, thus its bioavailability, increased in P1 and P2 by about 49% and 78% , respectively, while it dropped back to near its reference value in P3. This variation in Cd bioavailability is in line with its chemical fraction changes depicted in Figure 5. 3. In fact, in the root zone (0-20 cm), the Cd pH-susceptible mobile fraction F2 increased from 0.102 mg/kg in parcel R to 0.203 mg/kg in P1 (Figure 5. 3a & 3b), simultaneously with a drop in the layer average pH from 8.23±0.54 to 6.92±0.45 (Table 5. 2). This was followed by a phase transformation yielding 0.303 mg/kg of Cd exchangeable fraction (F1) in P2, and the depletion of the mobile fractions in P3 (Figure 5. 3c & 3d).

The copper TF went through an increase in P1 by about 44% relative to the reference, declined to the reference value in P2, then increased again by about 71% in P3 (Figure 5. 4). If we examine Figure 5. 3m-p for Cu fractions in layer 0-20 cm, we find a similar fluctuating pattern in the mobile fractions (F1 & F2) concentrations, with the pH factor favoring the availability of the carbonate fraction (F2) to plant uptake.

Similarly, the Pb TF went through an increase of nearly 52% from R to P1, a drop in P2, followed by an increase of about 86% in P3 (Figure 5. 4). However, this increase in bioavailability of Pb in P3 is contradicted with the prevailing insoluble and residual Pb fractions in layer 0-20 cm (Figure 5. 3h). This could be explained by the idea that some plant roots were extended to deeper layer (20-35 cm), where the Pb plant available fraction F2 prevailed in P3 (Figure 5. 3h).

As for Zn, plant available fractions (F1 & F2) barely existed in parcels R, P1 and P2, with bio-available fraction F1 appearing in parcel P3 with a concentration of about 20 mg/kg in layer 0-20 cm (Figure 5. 3i-l). Zn plant availability, however, remained the same in P3 as in the other parcels, with relatively low TF (0.11±0.01). This could possibly be due to the existence of competing available Cu (Tani and Barrington 2005; László Simon 2000) in P3 layer 0-20 cm (Figure 5. 3p).

There was little evidence of significant elevated uptake of TEs in soil extensively amended with PFs. Pb, Zn, Cu and Cd concentrations were within the normal levels reported by Chaney (1989) (2-5 mg kg^{-1} for Pb; 15-150 mg kg^{-1} for Zn; 3-20 mg kg^{-1} for Cu; 0.5-1 mg kg^{-1} for Cd) though they are considerably higher than the reference, particularly for Cd. This phenomenon could be attributed to the formation of TEs phosphate compounds which are non absorbable. In fact, it is recognized that high levels of phosphate fertilization decrease Zn concentrations in plant tissues (Lindsay 1972; Moraghan 1984; Loneragan and Webb 1993), which was attributed to the interaction of P with Zn in soil (McLaughlin et al. 1995; Grant and Bailey 1997)**.** Cd availability in plants from PFs depends on many factors such as soil texture, plant species, Cd concentration, and type of fertilizers used (Singh and Myhr, 1997).

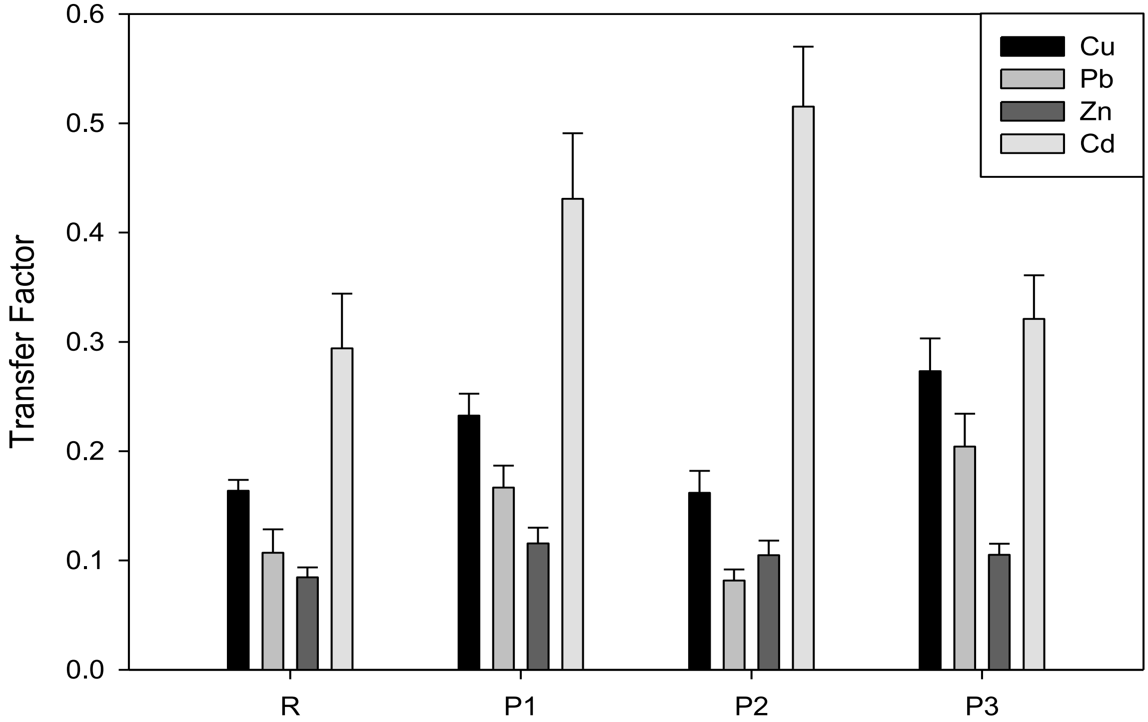


Figure 5. 4 Time-variation of the transfer factor of TEs in the plants – Reference parcel R (T=0); PF-amended parcels P1 (T1 = 4 months); P2 (T2 = 11 months); and P3 (T3 = 15 months)

5.3.6 *TEs Mobility comparison*

TE overall mobility during the study period could be compared by assessing the following mobility factor (MF), derived on the basis of the ratio of displaced (not retained) TE from a soil control volume—to its input to the control volume (Kassir et al. 2012):

$MF = 1 – (C_s – C_r)/C_{pf}$

Where,

C_s = TE average concentration in the control volume of studied soil profile (mg kg^{-1}) for all layers in parcels P1, P2 and P3

C_r = TE average concentration in reference soil for all layers (mg kg^{-1})

C_{pf} = TE concentration in PF (mg kg^{-1})

Comparing MF for the studied TEs, the order of their mobility was found to be: Zn (0.99) > Cd (0.98) > Cu (0.87) > Pb (0.42). This pattern is in accordance with data available in the literature of some mobility trends of TEs in soils (Carrillo-Gonzalez et al. 2006). It should be noted this assessment incorporates the transport of TEs in the soil by different mechanisms, including colloidal mobility that facilitates such transport (BIN et al. 2011).

5.3.7 *Mineral phases*

Samples of amended soil at different depths (from surface till 55 cm) and time (T1, T2 and T3) were examined by electron microscopy. Typical Electron micrographs and corresponding EDX spectra for different detected mineral phases were illustrated in Figure 5. 5. Particles of Gypsum in rectangular and rounded shape were associated with PFs having a molar ratio Ca/P = 0.5 or 1 (Figure 5. 5a). In parcel P2, this ratio (Ca/P) became 1.6 (Figure 5. 5b) suggesting a P transfer reaction occurred. Indeed, with heavy precipitations in parcel P1, P in the soil solution of parcel P2 can precipitate as Ca-P compounds (Chien et al. 2011). Furthermore, Fluor was found associated with these compounds leading to the formation of fluorine at depth 36-40 cm of parcel P2 (Figure 5. 5c). In fact, PFs manufactured from phosphate rocks may contain fluorine (Camelo et al. 1997; Mirlean et al. 2001) that can be responsible for polluting freshwater and groundwater (Mirlean et al. 2001). In fact, 1 g of fluorine may pollute 714 m^3 of water, with tolerable concentration being 1.4 mg L^{-1} (CONAMA 2005). Tubular forms of gypsum remained at depth

11-15cm of parcel P3 (fifteen months after amendment) (Figure 5. 5d), indicating that its threat to the soil and groundwater quality persisted after the study period.

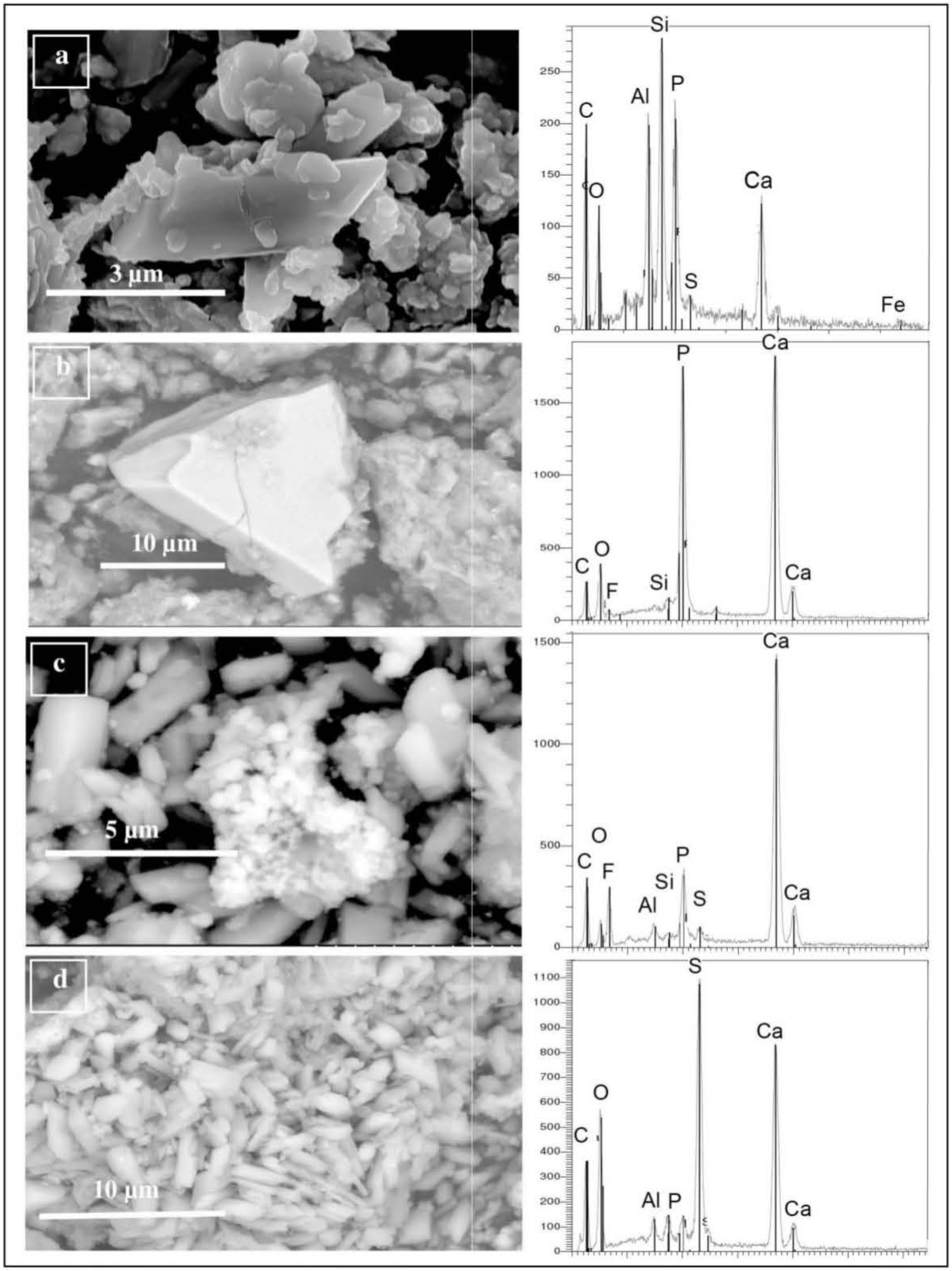


Figure 5. 5 Images of SEM and EDX microanalyses of parcels P1 and P3: (a) SSP; (b) tricalcic phosphate with fluorine (c) fluorine; (d) gypsum (CaSO4)

5.4 Conclusion

PF amendment increased the TEs concentration in the soil profile shortly (four months) after application, and caused a variation of the studied elements speciation through time. Precipitation, pH variation, and the drying-wetting cycle were the main factors controlling the accumulation and mobility of TEs in the soil profile.

The excessive addition of PFs (about forty times the locally used rate) increased TEs concentration in soil profile, but not to harmful levels. However, fluorine may be of major concern. Pb, Zn and Cu may as well reach the saturated zone, being steadily transferred to exchangeable fractions.

Since the studied TEs were found mainly in the exchangeable fraction of PF, they were transferred gradually to the soil matrix over the study period, except for Cd that appeared in its exchangeable fraction only after eleven months (in the 0-20 cm layer) following the amendment application, with an increment of 64% in percentage compared to the reference, to be finally adsorbed, four months later, by soil particles. Zn exchangeable fraction exhibited an increase of 26% and 13% in the 0-20 and 20-35cm layers, respectively, Pb of 84% in 35-55 cm, and Cu of 16% and 36% in 0-20 cm and 35-55 cm layers, indicating some risks to the food chain and groundwater ecology.

Soil-plant transfer factor was notably affected by PF application, with highest acquired values being for Cd, followed by Cu, Pb, and Zn. The TE transfer factor varied in accordance with the plant available fraction concentration alteration in the root layer. Although plants accumulated TEs in higher concentrations than the reference, they didn’t exceed the normal levels reported in the literature, which could be attributed to the formation of metal-phosphate in soil solution.

The current experimental study indicated that the risk of PFs amendment could be attributed to two reasons: (1) the presence of fluorine in the soil profile, imposing a threat to the saturated zone, and (2) the increment in mobile fractions of Pb, Zn and Cu in the deep soil profile layer, 35-55 cm, over a 15-months period may intrude as well a threat to the saturated zone, when long term soil exposures to PFs are considered.

To comprehensively evaluate the effects of PFs application, further investigations related to extended and seasonally repetitive use of PFs in the amendments of agricultural soils, with quantitative emphasis on soil contamination with fluorine, should be undertaken, based on similar analytical methodologies employed in this study.

Acknowledgements

This study was supported by (CSR-USEK). We wish to thank the staff of SARM (CRPG -UPR 80) where chemical analyses were carried out. Eng. R. Kassir is acknowledged for his valuable contribution in achieving this work.

6 Discussion Générale

L’objectif général de ce projet est d’évaluer le transfert et la mobilité des éléments traces métalliques dans les engrais chimiques et dans les déchets rejetés par les industries des engrais chimiques particulièrement le phosphogypse en collectant les résultats allant de l’industrie des fertilisants chimiques jusqu'à l’amendement des produits (phosphogypse et engrais phosphatés) dans un sol agricole. Ces résultats nous ont permis de répondre en partie à cet objectif. Un rappel des résultats obtenus avec une comparaison entre ceux de l’amendement du phosphogypse et les engrais phosphatés ainsi que des perspectives de ce travail sont présentées.

6.1 Rappel des principaux résultats de l’étude

Le travail s’est articulé autour de 3 sous-objectifs. Le sous –objectif 1 visant à évaluer la contamination du sol autour de l’industrie des fertilisants chimiques et les différentes sources responsables de cette contamination (chapitre 4). Le stockage des matières premières (roche phosphate), des sous-produits (phosphogypse), des produits obtenus (engrais phosphatés) en plein air et leur transport causent l’émission de la poussière riche en éléments traces métalliques. Cette poussière émise déposée sur le sol est la principale source de contamination de celui-ci autour de l’industrie. Un modèle d’estimation de dépôt atmosphérique est formulé et appliqué à l’industrie de Selaata. Les résultats montrent un flux important de Sr, Zn, Cr, U, Ni and Cd avec une corrélation significative avec les éléments traces métalliques mesurés dans les échantillons collectés. Même les résultats statistiques montrent une corrélation importante avec le phosphore qui représente le principal porteur de ces polluants, étant donné que celui-ci se concentre au Nord-Est de l’industrie principalement dû à la direction du vent. Les résultats de la spéciation de la roche phosphate, du phoshogypse et des engrais phosphatés ont montré que le Zn et le Cd sont majoritairement associés aux phases mobiles (échangeables et acido-solubles) et par suite constituent un danger potentiel pour l’environnement ainsi que pour les plantes cultivées dans cette région. Les résultats obtenus sur le site de Selaata ont débouché sur l’importance d’étudier la mobilité de ces éléments traces métalliques dans le profil du sol en relation avec le phosphogypse et les engrais phosphatés étant donné que ce sont les principales sources de contamination du sol autour de l’industrie. C’est pour cela que les sous-objectifs 2 et 3 visent à suivre l’évolution temporelle de la mobilité et du transfert de ces éléments dans un sol agricole épandu avec du phosphogypse et des engrais phosphatés.

Dans le premier cas où le sol est épandu avec du phosphogypse (chapitre 5), les métaux étudiés (Cd, Pb, Zn et Cu) sont transférés du phosphogypse au sol montrant ainsi une élévation de leur concentration pour atteindre un pic après 5 mois pour le Cd et 12 mois pour les autres (Pb, Zn et Cu) par comparaison au sol référence. Le phosphogypse épandu sur le sol a augmenté la solubilité des éléments étudiés étant donné qu'ils sont associés aux fractions échangeables et acido-solubles dans le phosphogypse alors que ces éléments étaient reliés dans la référence sol aux oxydes de fer et de manganèse et aux argiles. A la fin de notre étude et après 16 mois d'épandage, ces éléments sont sorbés dans les phases minérales du sol (phyllosilicates, oxydes de fer et de manganèse) alors que le Cd reste plutôt relié à la phase échangeable donc mobile. Il est important à mentionner l'apparition de la fraction oxydable F_4 où Pb et Cu y sont associés après 16 mois. La mobilité des éléments étudiés durant la période d'étude est dans l'ordre descendant Zn> Cd >Pb > Cu. Les plantes cultivées du type *Cichorium intybus*, utilisées dans la salade, ont montré une concentration élevée de Cd dans leurs feuilles (1-2,4 mg/kg) durant la période d'étude dépassant les valeurs normales (0,5 mg/kg). Par conséquent, l'utilisation du phosphogypse comme épandage sur le sol agricole doit se faire avec précaution.

Dans le deuxième cas où le sol est épandu avec des engrais phosphatés (chapitre 5), le pic des concentrations des éléments étudiés est atteint après 4 mois d'épandage. Un changement de la mobilité est détecté pour le Pb, Cu et Zn où ils sont principalement associés à la fraction échangeable au cours du temps alors qu'ils étaient dans la fraction réductible et résiduelle dans le sol référence. La mobilité de Cd décroît à la fin de cette étude où il se retrouve, comme dans la référence, dans les oxydes de fer et de manganèse et les argiles.

Les plantes cultivées ne montrent pas des concentrations de ces éléments dépassant les valeurs normales. Les résultats montrent que le danger relié à l'épandage des fertilisants phosphatés est la présence de la fluorine détectée par la microscopie électronique à balayage (MEB).

Les résultats montrent que la concentration totale moyenne de Pb, Zn et Cu augmente généralement durant les précipitations alors que celle de Cd diminue suite à l'épandage du phosphogypse (réalisé pendant une saison sèche). En effet, Jiries et al. (2001) ont trouvé que la concentration la plus élevée des éléments traces dans le sol est détectée lors des premières précipitations après une saison sèche. Cependant, il semble que la concentration de Cd a subi l'effet de la dilution avec l'eau de pluie.

Quant à l'épandage des fertilisants qui a été réalisé pendant la saison des précipitations, contrairement à celui du phosphogypse, une augmentation de la concentration moyenne de tous les éléments a été observée suivi d'une diminution pendant les saisons sèches à l'exception de Cd où sa concentration moyenne reste presque constante pendant la saison sèche.

Ce qui suggère que différents mécanismes interviennent dans le transport et la mobilité des éléments étudiés. Généralement, les éléments traces provenant du phosphogypse et des fertilisants phosphatés (métaux exogènes) peuvent être dissoutes et subissent les processus dans la rhizosphère pour être prélevés par les racines, ou bien ils passent dans la solution du sol où les mécanismes permettant leur mouvement dans le profil du sol peuvent se produire (Carrillo-Gonzalez et al., 2006) :

-La sorption de ces éléments dans les phases minérales comme les phyllosilicates et les oxydes et les hydroxydes de fer et de manganèse qui peuvent assurer leur transport dans le profil du sol sous forme de colloïdes-polluants. Un autre mécanisme peut avoir lieu après leur sorption est leur passage à travers les fissures durant le cycle des saisons sèches-humides.

- Les éléments présents dans la solution du sol peuvent être diffusés dans le profil du sol sous forme de complexes ou ions libre. La diffusion des éléments peut avoir lieu dans les aggrégats du sol dans lesquels ils sont adsorbés.
- Ces éléments peuvent être immobilisés ou stabilisés dans le sol.

On ne peut pas isoler un mécanisme de l'autre, souvent dans un système complexe comme le sol plusieurs mécanismes sont impliqués simultanément. Cependant, la contribution de chaque mécanisme depend des conditions du sol et des propriétés du métal. Sans oublier qu'une compétition de sorption peut avoir lieu entre les cations présents dans le système-sol et les cations exogènes provenant de l'amendement (Carrillo-Gonzalez et al., 2006).

Dans notre étude, les phyllosilicates et les oxydes de Fe et de Mn ont joué un rôle primordial dans la mobilité et le transport des éléments et plus particulièrement le mécanisme d'échange d'ions nécessitant ainsi des analyses plus approfondies et délicates.

Comparaison entre l'épandage du phosphogypse et des fertilisants phosphatés

L'amendement du phosphogypse et des fertilisants phosphatés sur le sol agricole a bien influencé la speciation des éléments étudiés. Cependant, la mobilité de ces éléments (Pb, Cu, Zn et Cd) diffère selon le sol est amendé par du phosphogypse ou des fertilisants phosphatés. En effet, à la fin de notre étude, Pb, Zn et Cu deviennent plus mobiles dans le sol épandu par les fertilisants phosphatés (associés à la fraction échangeable) que celui du phosphogypse alors que le Cd montre le contraire. En outre, le Cd absorbé par les plantes de type Chicorée dépasse les normes dans le sol épandu par le phosphogypse tandis que l'absorption des éléments étudiés par ces plantes ne montrent aucun danger sur la santé humaine dans le cas des fertilisants chimiques (au cours de notre étude). De ce fait, une augmentation du prélèvement de Cd est détectée en présence des sulfates (phosphogypse) suggérant la formation des complexes $CdSO_4$ absorbés alors que les complexes Cd-phosphates ne jouent pas ce rôle. Le risque lié à l'application des fertilisants phosphatés est la présence de la fluorine impliquant des analyses plus approfondies et à long terme.

Rôle des variations du pH

Le pH est un paramètre physico-chimique jouant un rôle sur la sorption/désorption des métaux. Dans notre étude le pH est variable ($6 < pH < 7$) avec une diminution plus accentuée dans le cas de l'épandage des fertilisants phosphatés pour atteindre à la fin de l'étude le pH du sol référence (pH=8) jouant ainsi le rôle du tampon. Cette variation du pH a impliqué une variation de la spéciation des métaux dans le sol. Des corrélations (positives ou négatives) entre le pH et la concentration des métaux (Cd, Cu et Zn) sont presentées dans cette étude. Cependant, la variation du pH ne semble pas être le facteur prédominant dans le prélèvement de Cd par les racines, du fait que la concentration de Cd dans les plantes est plus élevée dans le cas de l'application du phosphogypse que celle des fertilisants phosphatés. Par conséquent, d'autres paramètres physico-chimiques ont bien joué un rôle dans l'absorption de Cd par les racines comme la concentration en cations et anions majeurs.

6.2 Perspectives

Ce travail a mis en évidence l'impact de l'utilisation des engrais phosphatés depuis leur fabrication jusqu'à leur amendement sur le sol ainsi que sur l'homme. Il suggère que l'industrie des engrais chimiques est la source de pollution de l'atmosphère et du sol aux alentours et que l'amendement des sous-produits (phosphogypse) et des fertilisants phosphatés doit être realisé avec précaution. Une suite à donner à cette étude serait de faire un suivi temporal à long terme de l'amendement du phosphogypse et des fertilisants phosphatés.

Au niveau de l'industrie des fertilisants chimiques

Les échantillons étudiés aux alentours de l'industrie s'etendent à une distance de 1 Km montrant une contamination élevée du sol à cette distance dans la direction du vent. Il aurait particulièrement intéressant de faire une enquête d'évaluation de cette contamination à des distances plus grandes, ce qui nous permet de mettre en évidence la propagation de la contamination à travers l'atmosphère atteignant des régions agricoles ou urbaines.

Au niveau du transfert des éléments traces métalliques

Une part des éléments traces étudiés ont subi un transfert vertical vers des couches plus profondes stimulé par les fortes precipitations. Compte tenu que le sol etudié est du type Luvisol, propriétés de lessivage d'argile et des oxydes de Fe et de Mn, nous pouvions nous attendre à ce que les colloïdes jouent un rôle très important dans la migration de ces métaux dans le sol. Ces observations ont été confirmées par d'autres études (Citeau et al., 2003), cependant l'association entre les phases colloïdales et les métaux étudiés reste à confirmer.

Le transfert des éléments traces métalliques vers les Chicorées (transfert sol-plante) doit être plus approfondi pour mieux évaluer la contamination de la chaîne alimentaire et par suite le danger de la santé humaine. Par conséquent, on pourra travailler sur l'identification et la quantification des espèces chimiques des métaux absorbables par les racines plus particulièrement les ions libres en utilisant des méthodes électrochimiques ou des méthodes basées sur l'échange d'ion.

Au niveau de la mobilité des éléments traces métalliques

Un suivi de la mobilité des éléments traces métalliques dans le profil du sol à long terme (durant un temps plus long) et à une plus grande profondeur doit être accompli pour pouvoir mieux évaluer leur transfert dans les eaux souterraines. Les processus contrôlant la mobilité de ces éléments devraient être approfondis comme le pH, la capacité d'échange cationique (CEC), la matière organique…Un suivi parallèle de l'évolution temporelle des éléments radioactifs comme l'Uranium et le Polonium dans les parcelles épandues par du phosphogypse et des fertilisants phosphatés est d'une importance primordiale.

Références Bibliographiques

Abboud-Abi Saab, M., & Atallah, A. (1996). Impact of various sources of pollution on the populations of microplanctonic of the coastal waters of Batroun. Leb. Sci. Res. Rep., 11, 51-61.

Abboud-Abi Saab, M., & Dargham, L. (1998). Influence of winds on the dispersion of rejected chemicals of Ras-Koubba plant by the study of hydrological parameters and planctonic populations in marine environment. Ann. Rech. Scient., 1, 177-185.

Abi-Saleh, B. (1978). Etude phytosociologique, phytodynamique et écologique des peuplements sylvatiques du Liban. Aix-Marseille III,

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 theTotal Environment, 403, 80-88.

Adler (2001). Boues d'epuration et metaux lourds. Hexagone Environnement, 36, 27-29.

Adriano, D. C. (1986). Trace elements in the terrestrial environment. New York: Springer Verlag.

Adriano, D. C. (2001). Trace elements in terrestrial environments: Biochemistry, bioavailability and risks of metals (2nd ed.). New York: Springer-Verlag.

Aguilar-Carrillo, J., Barrios, L., Garrido., F., & Garcia- Gonzalez, M. T. (2007). Effects of industrial by-product amendments on As, Cd and Tl retention/release in an element-spiked acidic soil. Appl. Geochem., 22, 1515-1529.

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-Hajj, Z., & Muscat, C., From Europe to the Mediterranean. A Greenpeace report focusing on pollution by the fertilizer industry and the shift of such dirty technologies from Europe to developing countries in the Mediterranean, Tech. Rep., Greenpeace, 2000.

Al-Masri, M. S., Al-Kharfa, K., Khaleli, H., Al-Haleem, M. A., & Al-Hares, Z., Determination of natural radionuclides in air particulates and soil near phosphate mines and its port, Tech. Rep. AECS-PR/RSS 322, Atomic Energy Commission of Syria 2000.

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(5), 747-753.

Al-Masri, M. S., Ibrahim, S., & Al-Shamali, K., Tartous port pollution by trace metals resulting from phosphates loading activities., Tech. Rep. AECS-PR/ RRE 62, Atomic Energy Commission of Syria, 1999b.

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

Alcaraz Pelegrina, J., & Martinez-Aguirre, A. (2001). Natural radioactivity in ground waters around a fertilizer factory complex in South of Spain. Appl. Radiat. Isot., 55, 419-423.

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 Academic & Professional.

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., & M.J., D. (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., Case Study: Heavy metals and fluoride contents in the materials of Syrian phosphate industry and the vicinity of phosphogypsum piles, preprint (2011), to appear in Environ. Technol. Available at http://www.informaworld.com/10.1080/09593330.2011.552531.

Azouazi, M., Ouahidi, S., Fakhi, S., Andres, Y., Abbe, J. C., & Benmansour, M. (2001). Natural radioactivity in phosphates phosphogypsum and natural waters. J. Environ. Radioact.(54), 231-242.

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.

Baranowski, R., Rybak, A., & Baranowska, I. (2002). Speciation Analysis of Elements in Soil Samples by XRF. Polish J. Environ. Studies, 11(5), 473-482.

Barona, A., & Romero, F. (1996). Fractionation of lead in soil and its influence on the extractive cleaning with EDTA. Environ. Technol., 17(2), 63-70.

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.

Belzile, N., Lecomte, P., & Tessier, A. (1989). Testing readsorption of trace elements during partial chemical extractions of bottom sediments. Environ. Sci. Technol., 23, 1015-1020.

Benjamin, M. M., & Leckie, J. O. (1981). Multiple-site adsorption of Cd, Zn, and Pb on amorphous iron oxyhydroxide. J. Colloid Interface Sci., 79, 209-221.

BIN, G., CAO, X., DONG, Y., LUO, Y., & MA, L. Q. (2011). Colloid Deposition and Release in Soils and Their Association With Heavy Metals. Critical Reviews in Environmental Science and Technology 41, 41, 336-372.

Brigden, K., Stringer, R., & Santillo, D., Heavy metal and radionuclide contamination of fertilizer products and phosphogypsum waste produced by the Lebanese Chemical Company, Tech. Rep. 13/2002, Greenpeace Research Laboratories, 2002.

Brown, S., Christensen, B., Lombi, E., McLaughlin, M., McGrath, S., Colpaert, J., et al. (2005). An inter-laboratory study to test the ability of amendments to reduce the availability of Cd, Pb, and Zn in situ. Environmental Pollution., 138, 34-45.

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.

Camelo, L. G. L., Miguez, S. R., & Marban, L. (1997). Heavy metals inputs in phosphate fertilizers used in Argentina. Sci. Total Environ., 204, 245-250.

Campbell, C. G., Garrido., F., Illera, V., & Garcia- Gonzalez, M. T. (2006). Transport of Cd, Cu and Pb in an acid soil amended with phosphogypsum, sugar foam and phosphoric acid. Appl. Geochem., 21, 1030-1043.

Canete, S. J., Palad, L. J., Enriquez, E. B., Garcia, T. Y., & Yulo-Nazarea, T. (2008). Leachable 226Ra in Philippine phosphogypsum and its implication in groundwater contamination in Isabel, Leyte, Philippines. Environ. Monit. Assess., 142(1-3), 337-344, doi:10.1007/s10661-007-9933-6.

Cao, X. D., Ma, L. Q., Rhue, D. R., & Appel, C. S. (2004). Mechanisms of lead, copper and zinc retention by phosphate rock. Environ. Pollut., 131, 435-444.

Carrillo-Gonzalez, R., Simunek, J., Sauve, S., & Adriano, D. C. (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 Press.

Castillo-Carrion, M., Martin-Rubi, J. A., & Bernaldo de Quiros, E. O. (2007). The distribution and fixation of trace elements by the Vertisols of Malaga, southern Spain. Sci. Total Environ., 378, 28-35.

Canadian Council of Ministers of the Environment (CCME), Canadian Environmental Quality Guidelines, Canada, 1999. Available at http://ceqg-rcqe.ccme.ca/.

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-Verlag.

Chaney, R. L., Mielke, H. W., & Sterrett, S. B. (1988). Speciation, mobility and bioavailabity of soil lead. In B. E. Davies, & B. G. Wixson (Eds.), Lead in Soils: Issues and Guidelines (pp. 105–129). England: Science Reviews.

Chen, C., Xu, M., Ma, Y., & Yang, J. (2007). Evaluation of different phosphate amendments on availability of metals in contaminated soils. Ecotoxicol. Environ. Saf., 67, 278-285.

Chien, S. H., Prochnow, L. I., Tu, S., & Snyder, C. S. (2011). Agronomic and Environmental aspects of phosphate fertilizers varying in source and solubility: an update review Nutr. Cycl. Agroecosyst., 89, 229-255.

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. Watet Air Soil Pollution, 182, 245-261.

Chopin, E. I. B., Marin, B., Mkoungafoko, R., Rigaux, A., Hopgood, M. J., Delannoy, E., et al. (2008). Factors affecting distribution and mobility of trace elements (Cu, Pb, Zn) in a perennial grapevine (Vitis vinefera L.) in the Champagne region of France. Environmental Pollution, 156, 1092-1098.

Citeau, L., Lamy, I., Elsass, F., & Van Oort, F. (2003). Colloidal faciliated 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 possiblity of Using Crops as Metal Phytoremediants. Polish journal of Environmental studies, 14(1), 17-22.

CONAMA (2005). National Council for the Environment - Resolution nº 357 of March 17, 2005. Brasilia: CONAMA.

Conkline, C., 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, Tech. Rep. EPA 402-R 92-002, Washington, DC., 1992.

Countess, R. J., Barnard, W., Claiborn, C., Gillette, D., Latimer, D., Pace, T., et al., Methodology for estimating fugitive windblown and mechanically resuspended road dust emissions applicable for regional air quality modeling: Final report prepared for the Western Governors Association, Tech. Rep., Countess Environmental, Westlake Village, CA, 2001. Available at http://www.epa.gov/ttnchie1/conference/ei10/fugdust/countess.pdf.

Cowart, J., & Burnett, W. (1994). The Distribution of Uranium and Thorium Decay-Series Radionuclides in the environment a review. J. Env. Quality, 23(4), 651-662.

Darwish, T., Gradoussov, B., Sfeir, S., & Abdel Nour, L. (1988). The mineralogical and chemical composition of clay and the characteristics of mountain soils in Meten-Chimaly area, Lebanon. Soviet Soil Science, 20(6), 86-96.

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

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

De Conceicao, F. T., & Bonotto, D. M. (2006). Radionuclide, heavy metals and fluorine incidence at Tapira phosphate rocks, Brazil and their industrial (by) products. Environmental Pollution, 139, 232-243.

Degirmenci, N., Okucu, A., & Turabi, A. (2007). Application of phosphogypsum in soil stabilization. . Build.Enivon., 42, 3393-3398.

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.

Department of Meteorology (2010). Monthly Weather Data: 2005-2010. Unpublished Weather Reports. Lebanese Republic: General Direction of Civil Aviation, Ministry of Transports and Public Works.

DEQ, Emission Calculation, Fact Sheet #9843 Rev 11/05, 2005. Available at http://www.michigan.gov/documents/deq/deq-aqd-air-eval-era-EmissionCalculation-mineralproductprocesses_324070_7.pdf.

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.

Dubertret, L. (1953). Geological Map of Syria and Lebanon to 1/50000. In D. o. P. Works (Ed.), (pp. 21 sheets with instructions). Beirut: Catholic Printing.

Dudley, L. M., McLean, J. E., Furst, T. H., & Jurinak, J. J. (1991). Sorption of Cd and Cu from an acid mine waste extract by two calcareous soils: column studies. Soil Sci., 15, 121-135.

Duenas, C., Liger, E., Canete, S., Perez, M., & Bolivar, J. P. (2007). Exhalation of (222)Rn from phosphogypsum piles located at the Southwest of Spain. J. Environ. Radioact., 95(2-3), 63-74, doi:S0265-931X(07)00038-0 [pii] 10.1016/j.jenvrad.2007.01.012.

Elliott, H. A., Liberati, M. R., & Huang, C. P. (1986). Competitive adsorption of heavy metals by soils. J. Environ. Qual., 15, 214-219.

Enamorado, S., Abril, J. M., Mas, J. L., Perianez, R., Polvillo, O., Delgado, A., et al. (2009). Transfer of Cd, Pb, Ra and U from phosphogypsum amended soils to tomato plants. Water Air Soil Pollution, 203, 65-77.

Etyemezian, V., Gillies, J., Kuhns, H., Nikolic, D., Watson, J. G., Veranth, J., et al., Field Testing and Evaluation of Dust Deposition and Removal Mechanisms: Final Report. Prepared for The WESTAR Council, Lake Oswego, OR, Tech. Rep., Desert Research Institute, Reno, NV, the University of Utah, Salt Lake City, UT and NOAA, RTP, NC, 2003.

FAO, The European Soil Information System, Tech. Rep., Rome, 1999.

Farajalla, N., Marktanner, M., Dagher, L., & Zgheib, P., The National Economic, Environment and Development Studies (NEEDS) for Climate Change Project - Final Report, Tech. Rep., Issam Fares Institute for Public Policy and International Affairs - American University of Beirut, Beirut, 2010.

Farrah, H., & Pickering, W. F. (1993). Factors influencing the potential mobility and bioavailability of metals in dried lake sediments. Chem. Speciation Bioavailability, 5(3), 81-96.

Feix, I., & Wyart, J. (1998). Connaissance et maîtrise des aspects sanitaires de l'épandage des boues d'épuration des collectivités locales France: ADEME.

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 porfiles. European Journal of Soil Science, 58, 547-559.

Forbes, E. A., Posner, A. M., & Quick, J. P. (1976). The specific adsorption of divalent Cd, Co, Pb, and Zn on goethite. J. Soil Sci., 27, 154-166.

Garcia-Miragaya, J., Cardenas, R., & Page, A. L. (1986). Surface loading effect on Cd and Zn sorption by kaolinite and montmorillonite from low concentration solutions. Water Air Soil Pollution, 27, 181-190.

Garrido, F., Illera, V., & Garcia-Gonzalez, M. T. (2005). Effect of the addition of gypsum- and lime-rich industrial by-products on Cd, Cu and Pb availability and leachability in metal-spiked acid soils. Applied Geochemistry., 20, 397-408.

Geebelen, W., Adriano, D. C., van der Lelie, D., Mench, M., Carleer, R., Clijsters, H., et al. (2002). Selected bioavailability assays to test the efficacy of amendment-induced immobilisation of lead in soils. Plant and Soil, 249, 217-228.

Gleyzes, C., Tellier, S., Astruc, M., & (2002). Single and sequential extraction procedures for soil and sediment partitioning analysis. In P. Quevauviller (Ed.). RSC, Cambridge, UK. .

Grant, C. A., & Bailey, L. D. (1997). Interactions of zinc with banded and broadcast phosphorus fertilizer on the concentration and uptake P, Zn, Ca and Mg in plant tissues of oilseed flax. Can. J. Plant Sci., 73, 17-29.

Grant, C. A., Bailey, L. D., Harapiak, J. T., & Flore, N. A. (2002). Effect of phosphate source, rate and cadmium content and use of Penicillium bilaii on phopshorus, zinc and cadmium concentration in durum wheat grain. J. Sci. Food Agric., 82, 310-308.

Grodzinska, K., Godzik, K., & Szarek, G. (1987). Vegetables and soil contamination by heavy metals in allotment gardens in Cracow Agglomeration Bull. PAN Biol.Sci., 35, 111.

Guillaumaut, B., Mustapha, S. B., Moussa, H. B., Zaouali, J., Soussi, N., Mammou, A. B., et al. (1996). Pollution impact study in Gabes Gulf Tunisia using remote sensing data. J. Marine Technol. Society, 29, 246-258.

Gupta, S., Mehrotra, I., & Singh, O. V. (1990). Simultaneous extraction scheme: a method to characterize metal forms in sewage sludge Environ. Technol., 11(3), 229-238.

Guttormsen, G., Singh, B. R., & Jeng, A. S. (1995). Cadmium concentration in vegetable crops grown in a sandy soil as affected by Cd levels in fertilizer and soil pH. Fertilizer research., 41, 27-32.

Harrison, R. M., Laxen, D. P. H., & Wilson, S. J. (1981). Chemical associations of lead, cadmium, copper and zinc in street dusts and roadside soils. Environ. Sci. Technol. , 15, 1378–1383.

He, Z. L., Yang, X. E., & Stoffella, P. J. (2005). Trace elements in agroecosystems and impacts on the environment. J. Trace. Elem. Med. Biol., 19(2-3), 125-140, doi:S0946-672X(05)00096-9 [pii] 10.1016/j.jtemb.2005.02.010.

Hernandez, L., Probst, A., Probst, J. L., & Ulrich, E. (2003). Heavy metal distribution in some French forest soils: evidence of atmospheric contamination. Sci. Total Environ., 312, 195-219.

Hettiarachchi, G. M., Pierzynski, G. M., & Ransom, M. D. (2001). In situ stabilization of soil lead using phosphorus. J. Environ. Qual., 30, 1214-1221.

Huang, C. P., & Rhoads, A. (1989). The Adsorption of Zn(II) onto Hydrous Aluminosilicates. J.Colloid Interface Sci, 131(3), 289-306.

Hudson-Edwards, K. (1997). Contaminated Soils. Paper presented at the 3rd International Conference on the Biochemistry of Trace Elements,

IFA-UNDP, The fertilizer industry's manufacturing process and environmental issue, Tech. Rep. 28, UN Publications, Paris, 1998.

Jaradat, Q. M., Massadeh, A. M., M.A., Z., & Maitah, B. M. (2006). Fractionation and sequential extraction o fheavy metals in the soil of scrapyard of discarded vehicles. Environmental Monitoring and Assessment, 112, 197-210.

Jeng, A. S., & Singh, B. R. (1995). Cadmium status of soils and plants from a long time fertility experiment in southeast of Norway. Plant and Soil, 175, 67-74.

Jiries, A. G., Hussein, H. H., & Halaseh, Z. (2001). The quality of water and sediments of street run off in Amman. Jordan. Hydrol. Proc., 15, 815-824.

Juste (1988). Appréciation de la mobilité et de la biodisponibilité des éléments en trace du sol. Science du sol, 26/2, 103-112.

Kabala, C., & Singh, B. R. (2001). Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter. J.Environ.Qual., 30, 485-492.

Kabata-Pendias, A. (2004). Soil-plant transfer of trace elements-an environmental issue. Geoderma, 122, 143-149.

Kabata-Pendias, A., & Pendias, H. (1984). Trace elements in soils and plants. Boka Raton, Florida: CRC Press.

Kabata-Pendias, A., & Pendias, H. (2001). Trace Elements in Soils and Plants. Boca Raton: CRC Press.

Kacimi, L., Simon-Masseron, A., Ghomari, A., Derriche, Z., & Salem, S. (2006). Valorization of phosphogypsum by using it in cement manufactory. Paper presented at the COVAPHOS II,

Kassir, L. N., Darwish, T., Shaban, A., & Ouaini, N. (2012). Mobility of selected trace elements in Mediterranean red soil amended with phosphogypsum: Experimental study. Environmental Monitoring and Assessment, 184(7), 4397-4412, doi:10.1007/s10661-011-2272-7.

Kassir, L. N., Lartiges, B., & Ouaini, N. (2012). Effects of fertilizer industry emissions on local soil contamination: A case study of phosphate plant on the east Mediterranean coast. Environmental Technology, 33(8), 873-885, doi:10.1080/09593330.2011.601765.

Kheboian, C., & Bauer, C. F. (1987). Accuracy of selective extraction procedures for metal speciation in model aquatic sediments. Anal. Chem, 59, 1417-1423.

Kheboian, C., & Bauer, F. (1987). Accuracy of selective extraction procedures for metal speciation in model aquatic sediments. Anal. Chem., 59, 1417-1423.

Kim, N. D., & Fergusson, J. E. (1991). Effectiveness of a commonly used sequential extraction techniques in determining the speciation of cadmium in soils. Sci Total Environ, 105, 191-209.

Kirkham, M. B. (2006). Cadmium in plants on polluted soils: Effect of soil factors,hyperaccumualtion, and amendments. Geoderma, 137, 19-32.

Koo, B. J., Adriano, D. C., Bolan, N. S., & Barton, C. (2005). Plants roots exudates. In D.Hillel (Ed.), Encyclopedia of Soils in the Environment. Elsevier, Amsterdam, Netherlands.

Koss, V., & Kim, J. (1990). Modeling of strontium sorption and speciation in a natural sediment - groundwater system. J. Contam. Hydrol., 6, 267-280.

U. S. Environmental Protection Agency, 1988.

Kuboi, T., Noguchi, A., & Yazaki, J. (1986). Family-dependent cadmium accumulation characteristics in higher plants. Plant and Soil, 92, 405-415.

Kumpiene, J., Guerri, G., Landi, L., Pietramellara, G., Nannipieri, P., & Renella, G. (2009). Microbial biomass, respiration and enzyme activities after in situ aided phytostabilization of a Pb- and Cu-contaminated soil. Ecotoxicol. Environ. Saf., 72(1), 115-119, doi:S0147-6513(08)00182-6 [pii] 10.1016/j.ecoenv.2008.07.002.

Kuo, S., Huang, B., & Bembenek, R. (2004). The availability to lettuce of zinc and cadmium in a zinc fertilizer. Soil Science, 169, 363-373.

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.

Lambert, R., Grant C., & Sauve, S. (2007). Cadmium and zinc in soil extracts following the application of phosphate fertilizers. Science of the Total Environment, 378, 293-305.

Lamouroux, M., Paquet, H., Pinta, M., & Millot, G. (1968). Note preliminaire sur les mineraux argileux des alterations et des sols Mediterraneens du Liban. Servicio de Cartographia Geológica d'Alsace Lorraine 20(4), 277-292.

Lebourg, A., Sterckman, T., Ciesielski, H., & Proix, N. (1988). Trace element speciation in three unbuffered salt solutions used to assess their bioavailibility in soils. Environ.Qual. J., 27, 584-590.

Li, X., & Thornton, L. (2001). Chemical partitioning of trace and major elements in soils contaminated by mining and smelting activities. Appl. Geochem., 16, 1693-1706.

Lin, J. J., Noll, K. E., & Holson, T. M. (1994). Dry deposition velocities as a function of particle size in the ambient atmosphere. Aerosol Sci.Technol., 20, 239-252.

Lindsay, W. L. (1972). Zinc in soils and plant nutrition. Advances in Agronomy, 24, 147-186.

Lindsay, W. L. (1979). Chemical Equilibria in Soils. New York: Wiley.

Lock, K., & Janssen, C. R. (2003). Influence of aging on metal availability in soils. Review of Environmental Contamination and Toxicology., 178, 1-21.

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.

Loneragan, J. F., & Webb, M. J. (1993). Interactions between zinc and other nutrients affecting the growth of plants. In R. AD (Ed.), Zinc in soils and plants (pp. 119-134). Dordrecht: Kluwer Academic Publishers.

Lundgren, D., & Rangaraj, C., Fugitive dust control for phosphate fertilizer: Final report prepared for Florida Institute of Phosphate Research, Tech. Rep., University of Florida, Dept of Env Eng Sciences, Bartow, Fl, 1988. Available at http://fipr1.state.fl.us/fipr/fipr1.nsf/a1380a2dc3df745f85256b4b006398eb/36ff2d2e780c178f85256b2e005a4842/$FILE/01-015-069Final.pdf.

Luther, S. M., Dudas, M. J., & Rutherford, P. M. (1993). Radioactivity and chemical characteristics of Alberta phosphogypsum. Water, Air, & Soil Pollution, 69, 277-290.

Ma, Y. B., & Uren, N. C. (1995). Application of a new fractionation scheme for heavy metals in soils. Commun. Soil Sci. Plant Anal., 26, 3291-3303.

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.

Malan, J. J., Utilization of phosphogypsum: structure and achievements of the Second International Symposium on Phosphogypsum, Volume 1, Tech. Rep. Pub. No.01-037-055, Florida Institute of Phosphate Research (FIPR), Miami, FL, 1988.

Malavolta, E. (1994). Fertlilizantes e seu Impacto Ambiental. Produquimica, Sao Paulo.

Manceau, A., Schlegel, M. L., Musso, M., Sole, V. A., Gauthier, C., Petit, P. E., et al. (2000). Crystal chemistry of trace elements in natural and synthetic goethite. Geochim.Cosmochim.Acta, 64, 3643-3661.

May, A., & Sweeney, J. W. (1984). Assessment of environmental impacts associated with phosphogypsum in Florida. In R. A. E. Kuntze (Ed.), The Chemistry and Technology of Gypsum. (pp. 116-139): ASTM Special Technical Publication No. 861.

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

McBride, M. B. (1989). Reactions controlling heavy metal solubility in soils. In Advances in Soil Science (Springer-Verlag ed., pp. 1-56).

McBride, M. B. (1994). Environmental Chemistry of Soils. New York: Oxford University Press.

McLaren, R. G., & Crawford, D. V. (1973). Studies on soil copper: II. the specific adsorption of copper by soils. J. Soil Sci., 24, 443-452.

McLaughlin, M. J., Maier, N. A., Freeman, K., Tiller, K. G., Williams, C. M., & Smart, M. K. (1995). Effect of potassic and phosphatic fertilizer type, fertilizer Cd concentration and zinc rate on cadmium uptake by potatoes. Fertilizer research, 40, 63-70.

McLaughlin, M. J., Parker, D. R., & Clarke, J. M. (1999). Metals and micronutrients : Food safety issues. Fiels Crops Res, 60, 143-163.

McLaughlin, M. J., Tiller, K. G., Naidu, R., & Stevens, D. P. (1996). Review: the behavior and environmental impact of contaminants in fertilizers. Aust. J. Soil. Res., 34, 1-54.

Meguellati, N., Robbe, D., Marchandise, P., & Astruc, M. (1982). Etude des sites de fixation des metaux dans les sédiments. Journal Francais d'Hydrologie, 39(13 Fasc.3), 289-297.

Mehra, O., & Jackson, M. (1960). Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate Clays Clay Miner, 7, 317-327.

Menzies, N. W., Donn, M. J., & Kopittke, P. M. (2007). Evaluation of extractants for estimation of the phytoavailable trace metals in soils. . Environ. Poll., 145(121-130).

Mirlean, N., Rosienberg, A., Decker da Cruz, R., Casatelli, M. R., & Garcia, M. Avaliacao do fluor migravel das materias primas e dos fertilizantes fosfatados utilizados no Rio Grande do Sul. VIII In Congresso Brasileiro de Geoquimica and I Simposio de Geoquimica dos Paises do Mercosul. Resumos expandidos, 2001

Moraghan, J. T. (1984). Differential responses of five species to phosphorus and zinc fertilizers. Soil Sc. Plant Anal., 15, 437-447.

Mortvedt, J., & Beaton, J. (1995). Heavy Metal and Radionuclide Contaminants in Phosphate Fertilizers. In H. Tiessen (Ed.), Phosphorus in the global environement: transfer, cycles and management (pp. 93-106). New York: Wiley.

Mortvedt, J. J. (1991). Micronutrient fertilizer technology. In J. J. Mortvedt, F. R. Cox, L. M. Shuman, & R. M. Welch (Eds.), Micronutrients in Agriculture (2nd ed.). Madison, WI: Soil Science Society of America, Inc.

Morvedt, J. J. (2005). Heavy metals in fertilizers: their effects on soil and plant health. The International Fertilizer Society, Proceedings, no 575, York, UK.

Mullins, G. L., & Mitchell, C. C., Use of phosphogypsum to increase yield and quality of annual forages, Tech. Rep. Publ. No 01-048-084, Florida Institute of Phosphate, Bartow, 1990.

Nakhle, K., Le mercure, le cadmium et le plomb dans les eaux littorales libanaises: apports et suivi au moyen de bioindicateurs quantitatifs (éponges, bivalves et gasteropodes, preprint (2003), to appear in Available at.

Narwal, R. P., & Singh, B. R. (1998). Effect of organic materials on partitioning, extractability and plant uptake of metals in an alum shale soil. Water, Air and Soil Pollution, 103, 405–421.

Nasreddine, L., Nashalian, O., Naja, F., Itani, L., Parent-Massin, D., Nabhani-Zeidan, M., et al. (2010). Dietary exposure to essential and toxic trace elements from a Total diet study in an adult Lebanese urban population. Food and Chemical Toxicology, 48, 1262-1269.

Noll, K., & Aluko, O. (2006). Changes in large particle size distribution due to dry deposition processes. Aerosol Sci. , 37, 1797-1808.

Norge Geologiske Undersokelse (NGU) [Geological Survey of Norway]. ftp://ftp.ngu.no/A%20geochemical%20atlas/U_Uranium.pdf.

Nriagu, J., & Pacyna, J. (1988). Quantitative assessment of worldwide contamination of air water and soils by trace elements. Nature, 333, 134-139.

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.

Nziguheba, G., & Smolders, E. (2008). Inputs of trace elements in agricultural soils via phosphate fertilizers in European countries. Sci. Total. Environ., 390, 53-57.

Othman, I., & Al-Masri, M. (2007). Impact of phosphate industry on the environment: A case study. Appl. Radiat. Isot., 65, 131-141.

Pacyna, Emission factors of trace elements, Tech. Rep., University of London, Monitoring Assessment and Research Centre (MARC), London, 1984.

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 Jr., A. R. K., & 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.

Perez-Lopez R., Alvarez-Valero, & J.M., N. (2007). Changes in mobility of toxic elements during the production of phosphoric acid in the fertilizer industry of Huelva (SW Spain) and environmental impact of phosphogypsum wastes. Journal of Hazardous Materials, 148, 745-750.

Pfister, R. J., Philipp, G., & Pauly, H. (1976). Population dose from natural radionuclides in phosphate fertilizers. Rad. Environ. Biophysics 13, 247-261.

PNTTA (2000). Programme National de Transfert de Technologie en Agriculture. Bulletin N◦ 9. Rabbat: MADREF/DERD.

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,

Puls, R. W., & Bohn, H. L. (1988). Sorption of cadmium, nickel, and zinc by kaolinite and montmorillonite suspensions. Soil Sci. Soc. Am. J., 52, 1289-1292.

Puls, R. W., Powell, R. M., Clark, D., & Eldred, C. J. (1991). Effect of pH, solid/solution ratio, ionic strength, and organic acids on Pb and Cd sorption on kaolinite. Water, Air, and Soil Pollution, 57-58, 423-430.

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.

Raksasataya, M., Langdon, A. G., & Kim, N. D. (1996). Extractable trace elements in sediment following a sequential extraction procedure. Anal. Chim. Acta, 332, 1.

Ramos, L., Hernandez, L. M., & Gonzalez, M. J. (1994). Sequential fractionation of copper, lead, cadmium and zinc in soils from or near Donana National park. J. Environ. Qual., 23, 50-57.

Ribeiro, A., & Mexia, J. (1997). A dynamic model for the electrokinetic removal of copper from a polluted soil. J. Hazard. Mater., 56(257-271).

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: John Wiley.

Rouis, M. J., & Bensalah, A. (1990). Phosphogypsum management in Tunisia: environmental problems and required solutions. In Proceedings of the Third International Symposium on Phosphogypsum, Orlando, FL, FIPR (Vol. 1, pp. 87-105): Pub. No. 01-060-083.

Rutherford, P. M., Dudas, M. J., & Arocena, J. M. (1995). Trace Elements and Fluoride in Phosphogypsum Leachates. Environ.Technol., 16(4), 343-354.

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

Sadiq, M. (1991). Solubility and speciation of Zinc in calcareous soils. Water, Air, Soil Pollution, 57-58, 411-421.

Sayegh, A., Kazzakah, K., El-Khatib, A., Sfeir, S., & Khawlie, M., Soil mineralogy of Lebanon, Tech. Rep., SRLWDD-FAO, 1990.

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.

Sheppard, M. I., & Thibaut, D. H. (1992). Desorption and extraction of selected heavy metals from soils. Soil Sci Soc. Am.J., 56, 415-423.

Shuman, L. (1979). Zinc manganese and copper in soil fractions Soil Sci, 127, 10-17.

Simon, L. (2000). Effects of Natural Zeolite and Bentonite on the Phytoavailability of Heavy Metals in Chicory. In I. K. Iskandar (Ed.), Environmental Restoration of Metals-Contaminated Soils (pp. 261–271): CRC Press

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, Soil Pollution, 91, 351-362.

Singh, B. R., & Myhr, K. (1997). Cadmium uptake by barley as affected by Cd sources and pH levels. Geoderma, 84, 185-194.

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

Stahl, R. S., & James, B. R. (1991). Zinc sorption by manganese-oxide-coated sand as a function of pH. Soil Sci. Soc. Am.J., 55, 1291-1294.

Sterckman, T., Douay, F., Baize, D., Fourrier, H., Proix, N., & Schvartz, C. (2004). Factors affecting trace elements concentrations in soils developed on recent marine deposits from northern France. Appl. Geochem., 19, 89-103.

Tack, F. M., & Verloo, M. G. (1996). Chemical speciation and fractionation in soil and sediment heavy metal analysis. A review. Int. j. Environ. Chem., 59, 225-238.

Tani, F. H., & Barrington, S. (2005). Zinc and copper uptake by plants under two transpiration rates. Part II. Buckwheet (Fagopyrum esculentum L.). Environ. Pollut., 138(3), 548-558.

Tebodin, Dutch note on BAT for the phosphoric acid industry, Tech. Rep., RIZA, 2000.

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.

Tudoreanu, L., & Phillips, C. J. C. (2004). Modeling cadmium uptake and accumulation in plants. Advances in Agronomy, 84, 121-157.

Tuins, B. J. W., & Tels, M. (1990). Distribution of six heavy metals in contaminated clay soils before and after extractive cleaning. Environ.Technol., 11, 935-984.

UNEP/MAP, United Nations Environment Program, Mediterranean Action Plan, International Waters Tech. Rep. 9: Land and water, 2008.

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.

US EPA, Paper on radiation from phosphoric industry, Tech. Rep., US EPA, 2000.

U.S. Environmental Protection Agency, 1992.

Van Kauwenbergh, S. J. Cadmium content of phosphate rocks and fertilizers. In I. F. I. A. (IFA) (Ed.), Chennai, India, 2002

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.

Wang, Y.-F., Huang, K.-L., Li, C.-T., Mi, H.-H., Luo, J.-H., & Tsai, P.-J. (2003). Emissions of fuel metals content from a diesel vehicle engine Atmospheric Environment, 37(33), 4637-4643

Windfinder Website Beirut region wind & weather statistic. http://www.windfinder.com/windstats/windstatistic_beirut.htm Accessed 20 Mar 2011.

Xian, X. (1989). Effect of chemical forms of Cadmium, Zinc, and Lead in polluted soils on their uptake by cabbage plants. Plant and Soil 113, 257-264.

Yager, R., U.S. Geological Survey: The mineral industry of Lebanon, Tech. Rep., U.S. Department of the Interior 2005. Available at http://minerals.usgs.gov/minerals/pubs/country/2005/lemyb05.pdf.

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., & LD., N. (1998). Effects of surface treatment on surface sealing, runoff, and interril erosion. Transactions of the ASAE, 41(4), 989-994.

ANNEXE

Dry Deposition Calculation Methodology and Result Uncertainty Analysis

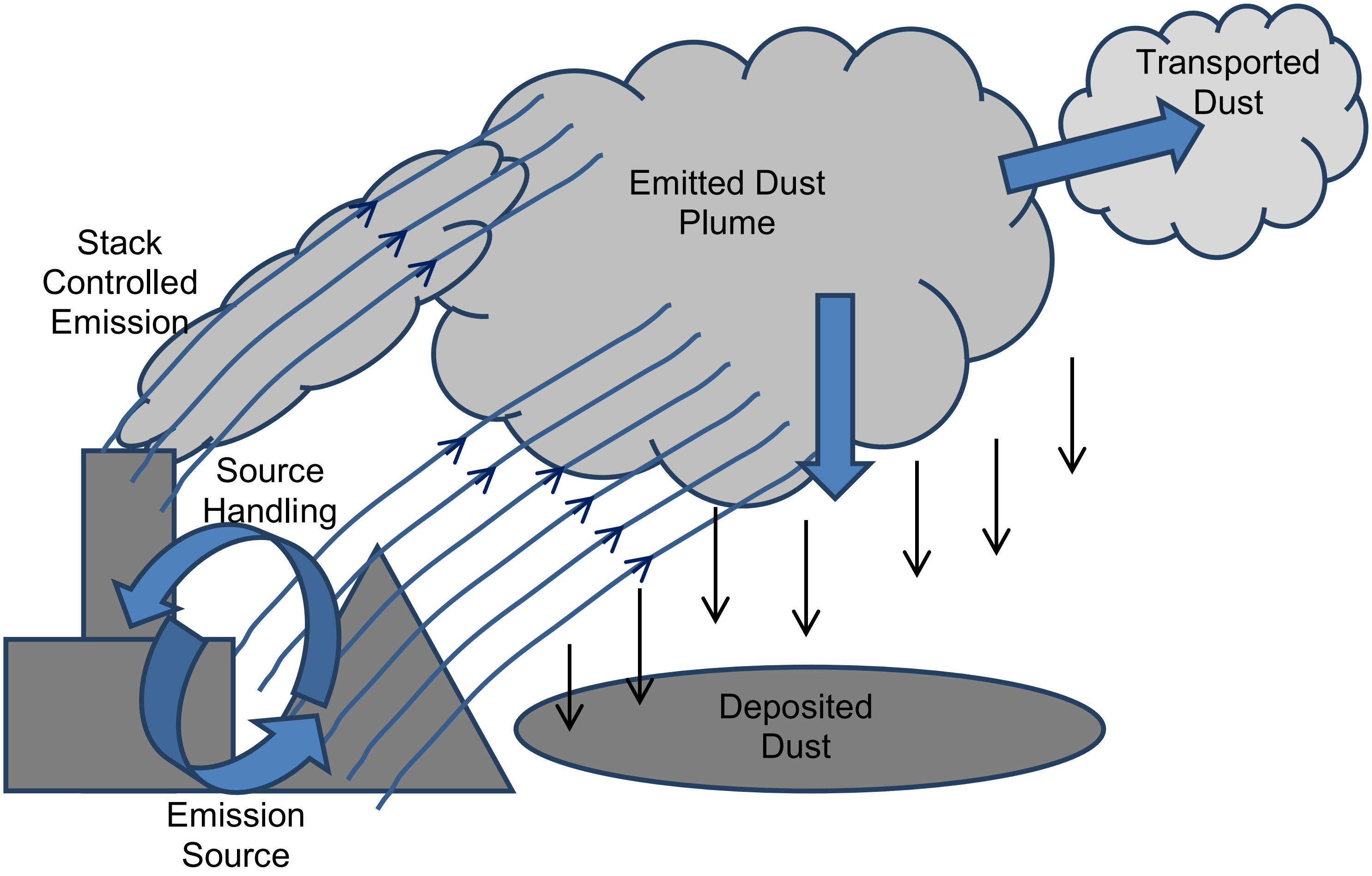
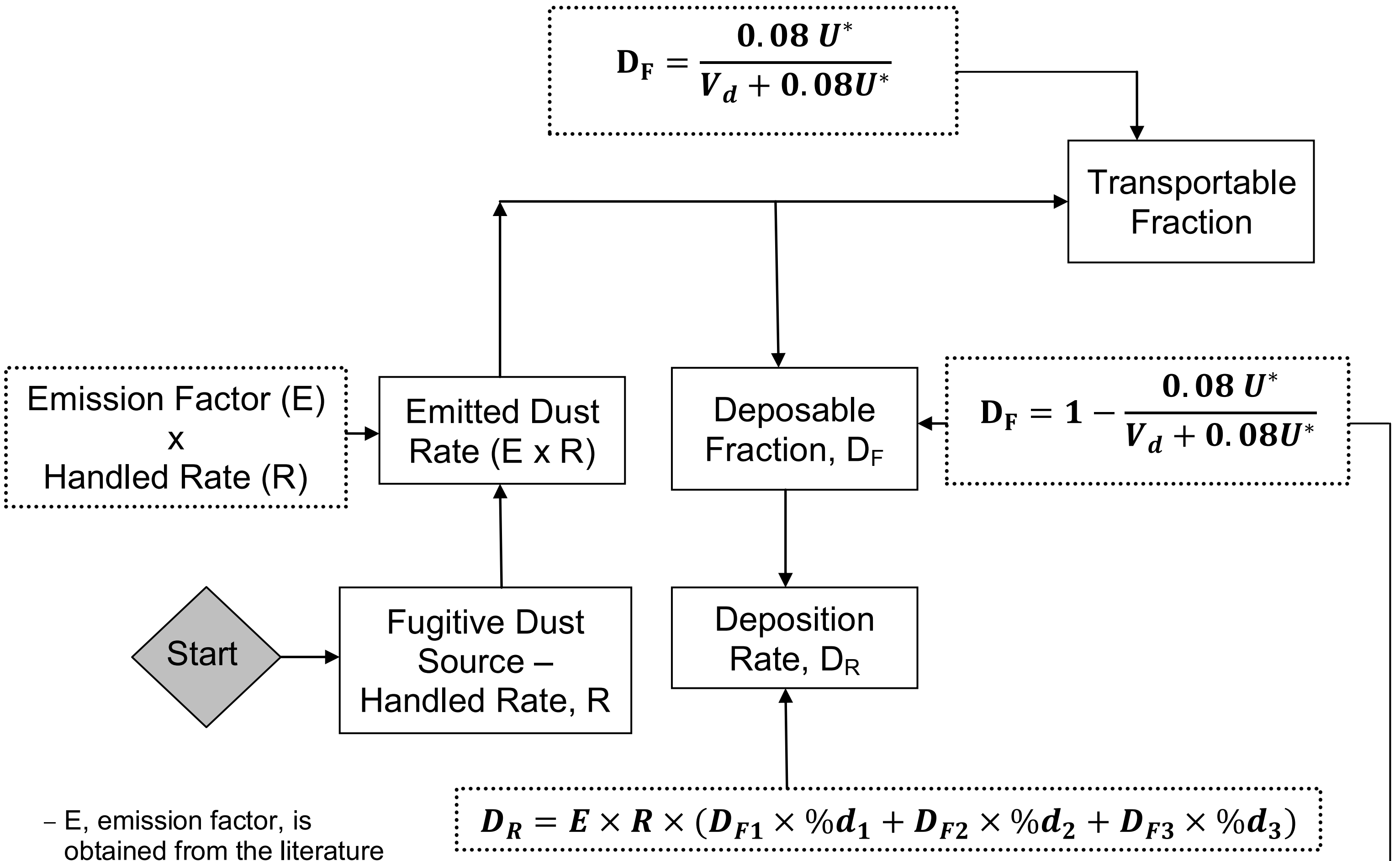


Figure A1 Dust emission and dry deposition schematic



- E, emission factor, is obtained from the literature for PF, PR, PG, and S.
- R, the production rate of the industry, for PF, PR, PG, and S.
- D_{F1} = Deposable fraction of particles $20<d_1<97$ µm
- D_{F2} = Deposable fraction of particles $10<d_2<20$
- D_{F3} = Deposable fraction of particle $d_3<10$ µm
- %d1, %d2 and %d3 (particulate size distribution) are obtained from the literature for PF, PR, and S (Lundgren and Rangaraj, 1988)
- D_R is then readily calculated from the above equation for PF, PR, PG, and S
- Trace element (TE) deposition rate = D_R (PF) x Concentration of TE in PF + D_R (PR) x Conc. of TE in PR + D_R (PG) x Conc. of TE in PG.

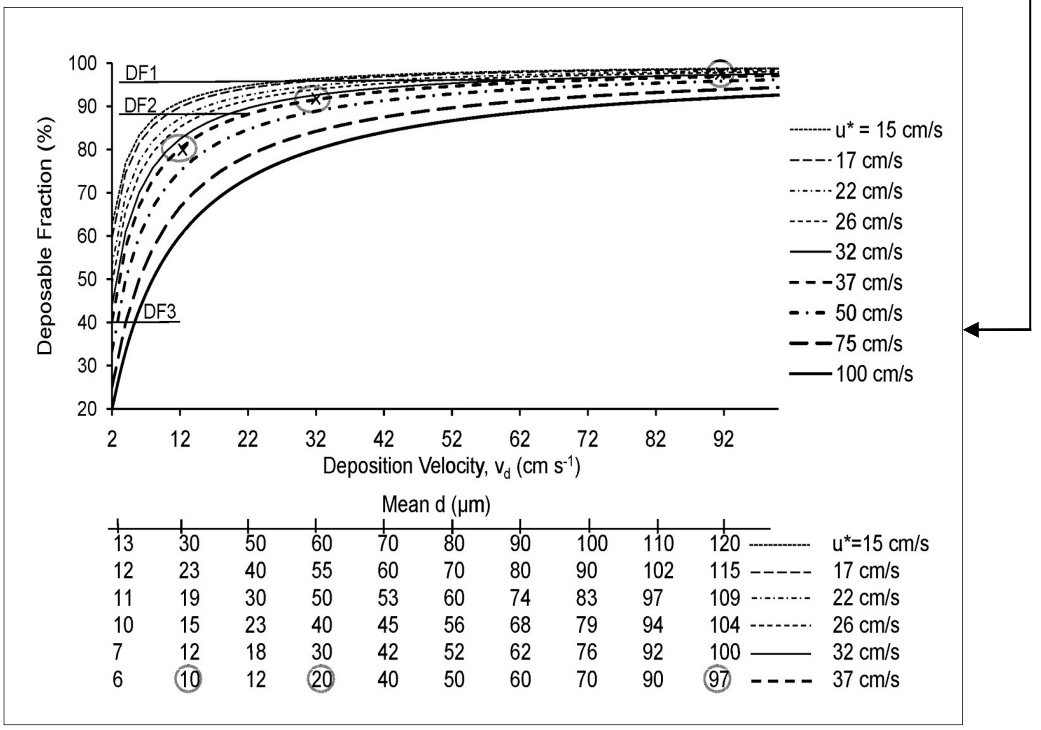


Figure A2 Dry deposition calculation scheme

Example–PR deposition rate and respective Cr flux:

Particulate size (μm)	**Average deposable fraction, D_F (figure above)**	**Dust PM mass size-distribution of PR[a]**
$20 < d_1 < 98$	0.95	60%
$10 < d_2 < 20$	0.88	30%
$d_3 < 1\ 0$	0.4	10%

Emission Factor, E ($g\ kg^{-1}$)	0.1362[a]
Handled product rate, R ($tons\ day^{-1}$)	840[c]
Fugitive dust emission, E x R ($kg\ day^{-1}$)	114
Deposition rate, D_R, (Equation) ($kg\ day^{-1}$)*	100
Dep. rate in major dep. area ($tons\ yr^{-1}$)[h]	22
Stack controlled emission ($kg\ day^{-1}$)[i]	0
Stack dust deposition ($tons\ yr^{-1}$)	-
Total dust deposition ($tons\ yr^{-1}$)	22
Major Deposition area (m^2)[j]	335000
Deposition average flux ($g.\ m^{-2}\ yr^{-1}$)	66
Cr deposition rate ($kg\ yr^{-1}$)[k]	3.5
Cr Average flux ($mg\ m^{-2}\ yr^{-1}$)	10

$$* \ \boldsymbol{D_R = E \times R \times (D_{F1} \times \%d_1 + D_{F2} \times \%d_2 + D_{F3} \times \%d_3)}$$

D_R = **0.1362**(g/kg)x10^{-3}(kg/g) x **840**(T/day)x10^{3}(kg/T) x (**0.95x0.6 + 0.88x0.3 + 0.4x0.1**) = 100 kg/day

Considering 220 dry days/yr in which the wind blows in the prevailing direction (Department of Meteorology, 2010; Windfinder Website), D_R becomes 100 x 220 = 22000 kg/yr = 22 T/yr

PR deposition average flux = 22(T/yr) x 10^6(g/T) / 335000 m^2 = 66 g/m^2/yr

Cr deposition flux = 157.10(mg/kg) x 66(g/m^2/yr) x 10^{-3}(kg/g) = 10.4 mg/m^2/yr

[a] (Lundgren and Rangaraj, 1988) reported dust particles mass size-distributions and average total plant-wide emission factors for PF, PR & sulphur

[c] (Abboud-Abi Saab and Dargham, 1998)

[h] Number of "dry" days with south-westerly wind is considered (i.e. 220 days/ year) (Windfinder Website ; Department of Meteorology 2010)

[j] Major deposition area was calculated from Figure 3. 3 (approximated by the area of a 60° arc with 800-m radius). Local dry deposition would take place mainly within a downwind distance of about 1 Km, since vertical mixing can reach high elevations (up to 30 m) at this distance for neutral to stable atmospheric conditions (Countess et al. 2001). In fact, this could be inferred from the distribution of the deposited phosphorus (Figure 3. 3), fading away beyond 800-meter downwind distance; a

major deposition area (Figure 3. 3) can be delimited according to this distribution pattern, and deposition fluxes can then be readily calculated.

[k] Using trace element concentrations given in Table 3. 1

Calculation Uncertainty

The accuracy of the calculation can be evaluated by analyzing the range of uncertainty of each term used in the basic deposition rate equation:

$D_R = E \times R \times (D_{F1} \times \%d_1 + D_{F2} \times \%d_2 + D_{F3} \times \%d_3)$

E, the site wide emission factor, obtained from accurate measurements (four decimal places) reported in the literature (Lundgren and Rangaraj 1988) can be assumed to be accurate to a good extent. However, an error factor may be introduced from the applicability of the obtained emission factor to the case study. Although the site wide emission factors were measured under similar circumstances as the present case study (similar type of fertilizer industry), an error range of ±10% could be introduced for a higher level of confidence in the calculation's range of accuracy.

R, the handled rate of the emission source, is assumed to be equal to the source input/ output rate, and is based on reported figures in the literature for the studied industry. This term is specific to the industry, and any associated uncertainty would be independent of the method accuracy.

D_{F1}, D_{F2}, and D_{F3}, the deposable fractions of the three particle size ranges, respectively, are based on a standard aerology equation of the transportable fraction of dust particles in terms of the friction velocity and deposition velocity. The uncertainty presented here is related to the used friction velocity curve (37 m/s) to conclude the deposition fractions. It can be seen from the deposition fraction curves (Fig. 3.2) that a range of friction velocity between 22 m/s and 50 m/s corresponds to a change to the deposable fraction associated with the friction velocity of 37 m/s by no more than ±5%. This range of friction velocity covers the local wind conditions with a great level of confidence. Hence, an uncertainty range of ±5 % for the deposable fractions should be applied.

%d1, %d2, and %d3 represent the particle size distribution based on reported measurements for similar emission source. Given the measurements were carried out on similar products/ raw materials, a ±10% applicability error is proposed for a higher level of confidence in the calculation's range of uncertainty.

Incorporating the above uncertainties in the basic equation:

$D_R = (E \pm 10\%) \times R \times [(D_{F1} \pm 5\%) \times (\%d_1 \pm 10\%) + (D_{F2} \pm 5\%) \times (\%d_2 \pm 10\%) + (D_{F3} \pm 5\%) \times (\%d_3 \pm 10\%)]$

Upper limit:

$D_{R,U} = 1.10\ E \times R \times (1.05\ D_{F1} \times 1.10\ \%d_1 + 1.05\ D_{F2} \times 1.10\ \%d_2 + 1.05\ D_{F3} \times 1.10\ \%d_3)$

$D_{R,U} = 1.10\ E \times R \times 1.05 \times 1.10 \times (D_{F1} \times \%d_1 + D_{F2} \times \%d_2 + D_{F3} \times \%d_3)$

$D_{R,U} = 1.27\ E \times R \times (D_{F1} \times \%d_1 + D_{F2} \times \%d_2 + D_{F3} \times \%d_3)$

$D_{R,U} = 1.27\ D_R$

Lower limit:

$D_{R,L} = 0.90\ E \times R \times (0.95\ D_{F1} \times 0.90\ \%d_1 + 0.95\ D_{F2} \times 0.90\ \%d_2 + 0.95\ D_{F3} \times 0.9\ \%d_3)$

$D_{R,L} = 0.90\ E \times R \times 0.95 \times 0.90 \times (D_{F1} \times \%d_1 + D_{F2} \times \%d_2 + D_{F3} \times \%d_3)$

$D_{R,L} = 0.77\ D_R$

Therefore, the deposition rate uncertainty range becomes: -23% to +27% of the calculated value.

TE deposition flux uncertainty:

The deposition area, A, has been estimated according to the ground phosphorus concentration pattern. An uncertainty of ±10% is assumed.

Upper value of flux range: $1.27\ D_R \times C/(0.9A) = 1.41\ \Phi$

Lower value of flux range: $0.77\ D_R \times C/(1.1A) = 0.7\ \Phi$

Where C is the concentration of TE in the source, and Φ is the TE deposition flux.

Therefore, the TE deposition flux uncertainty margin becomes: -30% to +41% of the calculated flux value.

Autorisation de Soutenance

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VU LES RAPPORTS ETABLIS PAR :

Monsieur LEGUBE Bernard, Professeur, ENSI Poitiers,

Madame MUNOZ Marguerite, Chargé de Recherches CNRS HDR, GET Observatoire Midi-Pyrénées.

Le Président de l'Université de Lorraine, autorise :

Madame NAFEH KASSIR Lina

à soutenir devant un jury de l'UNIVERSITE DE LORRAINE, une thèse intitulée :

"Les métaux lourds dans les engrais phosphatés et les sulfates rejetés par les industries des fertilisants : recherche sur leur transfert et leur mobilité dans les sols libanais"

en vue de l'obtention du titre de :

DOCTEUR DE l'UNIVERSITE DE LORRAINE

Intitulé du doctorat : **"Géosciences"**

Fait à Vandoeuvre, le **23 Novembre 2012**
Le Président de l'Université de Lorraine,
Pierre MUTZENHARDT
Par délégation
La Vice-Présidente du CS
Clotilde BOULANGER

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Résumé

Les métaux lourds dans les engrais phosphatés et les sulfates rejetés par les industries des fertilisants: Recherche sur leur transfert et leur mobilité dans les sols libanais

Résumé

Afin d'établir l'impact et le risque lié aux fertilisants chimiques depuis leur fabrication jusqu'à leur amendement sur la contamination des sols par les éléments traces métalliques, une étude de leur mobilité et leur transfert s'avère nécessaire.

L'objectif de ce travail de thèse était d'évaluer la source de contamination du sol par les éléments traces autour de l'industrie des fertilisants chimiques et suivre l'évolution temporelle de la mobilité et du transfert de ces éléments dans un profil du sol agricole amendé par des engrais phosphatés du type simple superphosphate (SSP) ou du phosphogypse. Pour cela nous avons utilisé des techniques permettant la caractérisation structurale et minéralogique des sols collectés comme la diffraction des rayons X et la microscopie électronique. Puis une caractérisation chimique des sols collectés concernant la concentration totale des éléments traces et des éléments majeurs a été établie. Comme la mobilité n'est pas stable au cours du temps dépendant de plusieurs paramètres physico-chimiques comme le pH, le potentiel redox, la teneur en matière organique, une extraction séquentielle a été adoptée le long de l'étude au cours du temps et dans le profil du sol amendé jusqu'à une profondeur de 55 cm. En outre, l'absorption des éléments traces par les plantes cultivées sur le terrain agricole amendé par les engrais ou le phosphogypse a été analysée au cours du temps afin d'évaluer le risque lié à la chaîne alimentaire et plus particulièrement la chaîne alimentaire humaine induisant des effets négatifs sur la santé. Une comparaison entre l'application du phosphogypse et celle des engrais a été mise en évidence à la finalité de ce travail.

***Mots-clés** : industrie des phosphates; la contamination des sols; les éléments traces; spéciation; phosphogypse; engrais phosphaté; amendement du sol; la mobilité; l'absorption des éléments traces*

Heavy metals in phosphate fertilizers and sulfates released by the fertilizer industries: Research on their transfer and mobility in Lebanese soils

Abstract

To determine the impact and risk of chemical fertilizers, from their manufacture to their amendment, on soil contamination by trace metals, the study of their mobility and transfer would be necessary.

The objective of this work was to evaluate the source of soil contamination by trace elements around the industry of chemical fertilizers, and to follow the temporal evolution of mobility and transfer of these elements in the profile of agricultural soil amended by superphosphate (SSP) fertilizers or phosphogypsum. To achieve our objective, we used techniques allowing the determination of structural and mineralogical characterization of collected soil samples, such as X-ray diffraction and electron microscopy. Chemical characterization related to the total concentration of trace and major elements of collected soils was established. As mobility was unstable over time, depending on several physico-chemical parameters such as pH, redox potential, and organic matter content, a sequential extraction was adopted throughout the study over time in the amended soil profile to a depth of 55 cm. In addition, the absorption of trace elements by agricultural crops cultivated over land amended with fertilizer or phosphogypsum was analyzed over time to assess the risk of their transfer to the food chain, especially the human food chain, imposing health hazards. A comparison between the effects of the application of phosphogypsum and phosphate fertilizer was carried out in concluding this work.

Keywords : *phosphate industry; soil contamination; trace elements; speciation*; *phosphogypsum; phosphate fertilizers; soil amendment; mobility; trace elements uptake*