CHARACTERIZATION OF GARDEN SOIL POLLUTION IN THE MINING VILLAGE OF STRATONI, N. GREECE

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Abstract

Complete characterization of soil pollution in sulphide ore mining areas can assist risk assessment because the potential risk of chemical species is related not only to the total content of elements in soil but also to the type of bounding of elements to solid phases and their solubility. The methodology of this study included a combination of chemical analysis and mineralogical determination of surface soil samples from house gardens and communal country spaces in a mining village of north Greece. The content of soil Pb, Zn, Cu, Cd, Fe and Mn was determined by sequential extraction with 5 operational stages and subsequent measurement by AAS. The produced chemical data were coupled by XRD and SEM-EDS mineralogical analysis. Results show variety of solid phases withholding the metals, thus differentiation of metal mobility/ availability in the environment. Lead has high mean concentration of 1090 μg g^{-1} but is fractioned mostly (53%) in the residual phase of less soluble soil components limiting its potential bioavailability. Zinc, Cd and Mn with means of 878 μg g^{-1}, 6 μg g^{-1} and 4465 μg g^{-1} respectively, participate in appreciable proportion (5-25%) in easily extractable phases indicating easy mobilization and greater potential bioavailability.

Key words: *heavy metals, geochemistry, sequential extraction, soil mineralogy.*

Περίληψη

Ο πλήρης χαρακτηρισμός της ρύπανσης του εδάφους από βαρέα μέταλλα σε περιοχές εξόρυξης και εκμετάλλευσης θειούχων κοιτασμάτων δίνει πολύτιμες πληροφορίες σχετικά με τον τρόπο συγκράτησης των μετάλλων στο έδαφος και την ευκολία αποδέσμευσής τους από τη στερεά φάση, οπότε και τη δυνητική επικινδυνότητα για τον έμβιο κόσμο. Η μεθοδολογία της εργασίας αυτής περιλαμβάνει συνδυασμό χημικών αναλύσεων και ορυκτολογικού προσδιορισμού δειγμάτων επιφανειακού εδάφους από κήπους σπιτιών ενός μεταλλευτικού χωριού της βόρειας Ελλάδας. Οι συγκεντρώσεις των στοιχείων μετρήθηκαν στο έδαφος ακολουθώντας μια μέθοδο διαδοχικών εκχυλίσεων σε 5 στάδια με χρήση Φασματομετρίας Ατομικής Απορρόφησης. Τα αποτελέσματα διασταυρώθηκαν με ορυκτολογικά δεδομένα Περιθλασιμετρίας Ακτίνων X, παρατηρήσεις ηλεκτρονικής μικροσκοπία και μικροανάλυση. Τα βαρέα μέταλλα στην περιοχή μελέτης παρουσιάζουν ποικιλία ως προς τις μορφές εμφάνισης στο έδαφος και την κινητικότητά τους. Ο μόλυβδος με ολική συγκέντρωση 1090 μg g^{-1} κατανέμεται κατά 53% στην υπολειμματική, δυσδιάλυτη φάση του εδάφους σε αντίθεση με τα στοιχεία Zn, Cd

*και Mn τα οποία έχουν ολικές συγκεντρώσεις 878 μg g⁻¹, 6 μg g⁻¹ και 4465 μg g⁻¹ αν-
τίστοιχα, και συμμετέχουν με υψηλότερα ποσοστά στις πιο διαλυτές - κινητικές φάσεις
του εδάφους αποτελώντας πιθανά μεγαλύτερη απειλή για τον έμβιο κόσμο στην περιο-
χή.*

1. Introduction

The surface earth environment is characterized by redistribution of chemical elements and
significant interactions within the system rock-soil-water-air-life. In sulphide mining industrial
areas, soil is usually enriched in heavy metals due to both natural erosion of metalliferous minerals
and anthropogenic influences. The latter, through mining and associated mineral processing
activities, may cause increased dispersion and exposure of contaminants derived from natural
sources with health implications to humans and animals. However, the occurrence alone of
elevated concentrations of heavy metals in the environment does not indicate there is a significant
risk as this will depend on a number of factors including their chemical form, concentration,
bioavailability, the size of the mineral particles in which the elements occur, the extend of
exposure and the dose received (Appleton, 1995). Thus, very high concentrations may not pose a
health risk as the element may be in a mineral or chemical form that is relatively immobile,
insoluble in water and not taken up by plants or by humans and animals if ingested. Conversely,
some elements become more available in acid waters and soils and may therefore be taken up by
plants or mobilized and transported in surface and groundwater.

Soil has a central role as a sink and an exposure pathway of pollution to humans and animals in
heavy metal contaminated sites (Thornton, 1993; Abrahams and Steigmajer, 2003). Surface soil
may receive heavy metals through the processes of fluvial, gravitational and atmospheric
dispersion. Significant pollution pathways include inhalation of wind-blown dust and ingestion of
contaminated food and water. In entering the food chain, soil characteristics such as organic matter
content, pH, Eh, clay and iron content, affect mobility of heavy metals and hence their availability
to growing plants and crops (Appleton, 1995; Kabata –Pendias and Pendias, 1984). Also, direct
ingestion of contaminated soil and dust is believed to be a major way of transfer of potentially
harmful elements into humans. Several scientific studies worldwide have provided strong evidence
that especially young children are prone to ingest relatively large amounts of contaminated dust or
dirt indirectly from contamination on their hands (Clausing et al., 1987; Watt et al., 1993).

It follows that detailed characterization of surface soil in metal mining areas can give invaluable
information in the study of the potential risk for humans and animals. Specifically, the portion of
chemical elements' total content in an earth material that can be liberated to the surface environ-
ment and the biosphere through mechanical, chemical or biological processes, i.e. their geoavaila-
bility, is related to the susceptibility and availability of their resident mineral phases to alteration
and weathering reactions (Smith and Huyck, 1999). Geochemical studies based on bulk analysis
and sequential extraction tests have been used in several occasions in relevant sediment and soil
pollution studies (Tessier et al., 1979; Pickering, 1998; Li and Thornton, 2001). Mineralogical
studies utilising XRD and SEM is another approach for polluted soil characterisation (Davis et al.,
1993; Camm et al., 2003). However a combined geochemical and mineralogical approach in the
study of the resident phases in soil and sulphide mine tailings is addressed by only few authors in
the literature (Adamo et al., 1996; Adamo et al., 2002; Boulet and Larocque, 1998). This paper
presents the findings of research on geochemical and mineralogical characterization of garden soil,
with the aim to contribute further to the understanding of processes controlling elemental release
within a mining village surface environment in north Greece.

2. Materials and Methods

2.1. Soil Sampling and Sample Preparation

Thirty eight surface soil samples were collected from a total area of 0.7 km^2 within an industrial area, the mining village of Stratoni in Chalkidiki peninsula, North Greece. Following a stratified random sampling design, the total residential area was divided into strata based on building blocks. One house was randomly selected inside each stratum and one soil sample was collected from the garden (Figure 1). Samples were also collected from communal, recreational areas within the settlement as well as from the primary school and the kindergarten playgrounds. The average distance between sampling sites was 150 m and the selected sampling depth was 0-5 cm in order to avoid mixing of material from deeper soil horizons that might reflect different sources of pollution. A hand auger was used to collect a 4-fold composite sample from an area of 1 m^2 at each sampling location after removing surface vegetation, making up a field sample of 500 g after mixing. Nine duplicate samples were collected at random locations, 10 m away from the original site for estimating sampling uncertainty of the measurements (Ramsey and Argyraki, 1997). This distance represented the locational accuracy provided by the GPS instrument that was used.
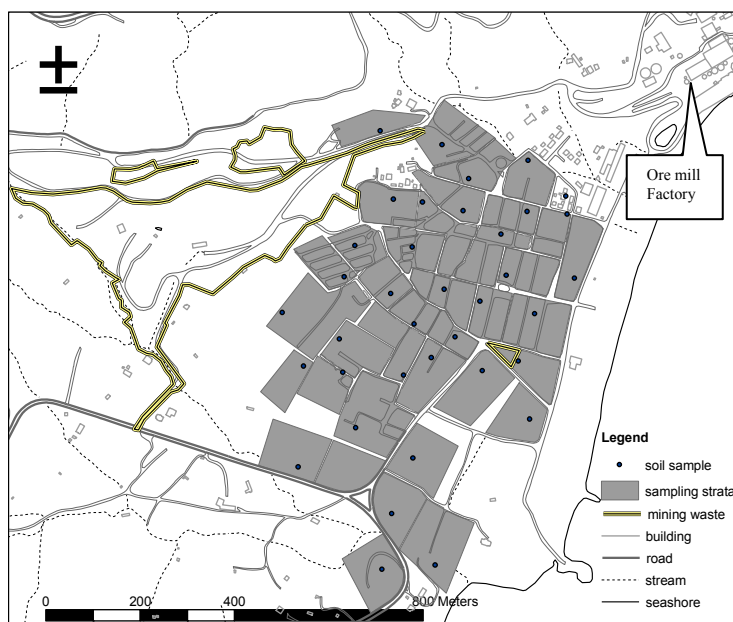

Figure 1 – Map of Stratoni village in north Greece, showing the soil sample collection points.

Field soil samples were carried to the laboratory in plastic bags and were prepared for chemical analysis by drying at a temperature of 40°C, disaggregating, sieving by a 2mm plastic sieve, grinding with automatic mill in an agate mortar and final sieving to pass through a 100μm sieve, thus producing the laboratory sample. All utensils that were used were thoroughly cleaned between the samples in order to avoid cross contamination.

2.2. Analytical Procedures

2.2.1. Chemical Analysis

Concentrations of Pb, Zn, Cu, Cd, Mn and Fe in soil samples were measured by Perkin Elmer 1100B AAS at the laboratory of Economic Geology and Geochemistry, University of Athens after total dissolution of 500mg soil with a mixture of HF, HClO$_4$ and HNO$_3$ acids.

After determining the total content of metals, a sequential extraction with 5 steps (Tessier et al., 1979; Li et al., 2001) was carried out on 10 samples selected on a basis of total metal content and sample location. The method examines the possible "operationally defined" geochemical phases of metals in overburden materials including metallurgical processing wastes and residual or alluvial contaminated soil. Extraction was carried out progressively on an initial weight of 1g of test material. The chemicals used and operationally defined chemical fractions are outlined below:

- Fraction 1: exchangeable (exchangeable phase) – sample extracted with magnesium chloride at pH 7.

- Fraction 2: bound to carbonate and specifically adsorbed (carbonate phase) – residue extracted with sodium acetate at pH 5.

- Fraction 3: bound to Fe-Mn oxides (reducible phase) - residue extracted with hydroxylammonium hydrochloride.

- Fraction 4: bound to organic matter and sulphide (oxidisable phase) – residue extracted with nitric acid, hydrogen peroxide and ammonium acetate.

- Fraction 5: residual phase – residue digested with concentrated nitric, perchloric and hydrofluoric acids.

Analar® – grade chemicals and deionised water were used throughout the analysis. All glass laboratory utensils were washed with a detergent, then soaked for 24 hours in 5% HNO_3 acid solution and rinsed repeatedly with deionised water. Reference materials, duplicates and reagent blanks were distributed at random throughout the whole extraction procedures to make the most realistic assessments of data quality. Three international certified reference materials by NIST (SRM2709, SRM2710 and SRM2711) were used for estimating analytical bias and 18 analytical duplicates were used for estimating analytical precision.

The significant parameter of soil pH was determined after mixing soil with deionised water and organic carbon content was determined by titration with $K_2Cr_2O_7$ in an acid environment.

2.2.2. Mineralogical Analysis and Microanalytical Method

Mineralogical determination was performed on the high density (SG> 2.96) fraction of selected soil samples, after gravity separation in tetrabromoethane. A Siemens D-500 instrument was used for XRD analysis. Scanning Electron Microscopy and EDS analysis were carried out on resin impregnated/ carbon coated samples, using a Jeol JSM 5600 SEM instrument, equipped with an Oxford ISIS 300 micro analytical device. Examination in the backscattered electron (BSE) mode permitted the localisation of areas where heavy metals were concentrated. All analysis was performed in the facilities of Faculty of Geology and Geoenvironment, University of Athens.

3. Results and Discussion

3.1. Total Concentration of Heavy Metals in Soil

Quality control on measurements of total concentrations yielded acceptable results for most studied heavy metals. Analytical bias was estimated within ±10% of the certified value, and analytical precision was better than ±5% of mean value for a 2s interval. In exception to the above, analytical precision for Fe reached ±14% probably due to volumetric errors and precision of Cd was ±30% probably due to low concentration readings near the detection limit of the method.

The descriptive statistics of total concentrations of the studied elements are presented in Table 2.

Table 2 - Descriptive statistics of total concentration of heavy metals in soil in μg g^{-1} (n = 38).

Element	Mean	Median	Standard deviation	Min	Max
Pb	1090	1071	390	124	2042
Zn	878	712	569	133	2520
Cu	184	184	50	45	285
Cd	6	6	3	2	15
Fe	45700	45103	9205	23786	73767
Mn	4465	2940	4368	394	19777

In Table 3 the measured concentrations are compared to the global soil mean (Levinson, 1980), estimated concentrations in soils of the wider area from a previous study (Kelepertsis et al., 2006) as well as selected international soil pollution guideline values for residential and industrial areas.

Table 3 – Comparison of measured concentrations of heavy metals in soil, with selected international guideline limits in μg g^{-1}.

Element	Mean	Global soil mean[1]	Wider area soil mean[2]	G. Britain (DOE-ICRCL)[3]		France[4]	Canada[5]	USA[6]
				Small garden	Open space	Clean-up	Industrial use limit	Clean -up
Pb	1090	17	895	550	1500	1000	1000	400
Zn	878	50	654	280	280-560	3000	1500	-
Cu	184	20	150	140	140-280	1000	500	600
Cd	6	1	3	5	12-15	20	20	39
Fe	45700	35000	61160	-	-	-	-	-
Mn	4465	530	3037	-	-	10000	-	-

[1] Levinson, 1980, [2] Kelepertsis et al., 2006, [3] ICRCL, 1990, [4] CCME, 1992, [5] ASTM, 1995, [6] New Jersey DOE, 1999.

The data show elevated concentrations of all studied elements, well above the global soil mean but also higher than the mean concentrations in soils from the wider area. Specifically, Pb with a mean value of 1090 μg g^{-1} is very close to the maximum concentration limit for industrial areas and exceeds the concentration limit for small gardens by a factor of 2. Average concentrations of Zn, Cu and Cd are 878 μg g^{-1}, 184 μg g^{-1} and 6 μg g^{-1} respectively, exceeding concentration limits for small gardens but conforming the limits for areas of industrial use according to Canadian standards. Iron and Mn are elements of less environmental concern in respect with health hazard, nevertheless they demonstrate mean concentrations of 5% and 4465 μg g^{-1} respectively, which are higher than the estimated means in the wider area.

Significantly high correlation coefficients were observed between Zn and Cd (>0.9), Mn and Pb>Cd (>0.7), Pb and Cd>Cu>Zn (>0.5), Cu and Fe>organic carbon (>0.6). The high correlation between the elements indicates common origin and can be attributed to presence of metallic minerals and their weathering products in surface soil. The high correlation between organic carbon and Cu shows the significant role of organic matter in the speciation of this element. Soil pH was measured between 3.9 and 8.0 with a mean value of 6.9, signifying environmental conditions that favour precipitation of metals in solid phases.

3.2. Partition of Heavy Metals in Operationally Defined Solid Phases

The analytical results of the sequential extraction procedure demonstrated precision between ±2% and 20% for all elements and all extraction steps. Analytical bias, estimated by analysis of the NIST certified reference materials was also found to be within acceptable limits except for Fe. The data were subsequently processed within their stated uncertainties.

Figure 4 presents the proportion (%) of each metal in each one of the 5 operationally defined phases. These phases differ in respect with potential availability of elements into the environment and include in order of decreasing availability (Tessier *et al.*, 1979): (a) the exchangeable phase, i.e. the fraction of metals adsorbed in exchange sites on surfaces of clays and colloids; (b) the carbonate phase, i.e. the metal fraction associated with carbonate minerals and metals specifically adsorbed on surfaces of amorphous precipitates of Fe, Al, Mn oxides/ hydroxides and phosphates; (c) the reducible phase comprising metals associated with Mn and Fe oxides through co-precipitation and binding within the oxide structure; (d) the oxidisable phase, i.e. the fraction of metals bound to soil organic matter and metals incorporated in the structure of sulphide minerals and (e) the residual phase including elements incorporated in the crystal lattice of silicate minerals and vitreous metallurgical phases such as slag.

The data of sequential extraction soil analysis in this study show that the fractionation of studied heavy metals varies. This observation has significant implications on the potential bioavailability of metals, thus their potential risk for human and animal health. Specifically, Pb is fractioned mainly (53%) in the residual phase of relatively insoluble soil components as well as the reducible phase of Fe-Mn oxides (40%) which also represent stable solid phases.
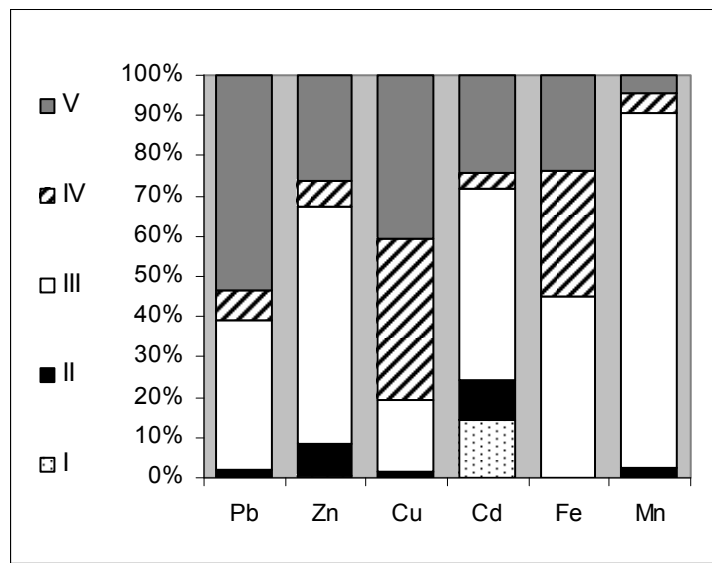

**Figure 4 – Partition (%) of heavy metals in 5 operationally defined soil phases (n = 10).
(I):exchangeable, (II): carbonate and specifically adsorbed, (III): reducible, (IV): oxidisable,
(V): residual.**

On the contrary, Zn, Cd and Mn appear in the residual phase in lower concentration, fractioned by 25%, 23% and 5% respectively. These elements have noticeable share in the first two easily extractable extraction steps (5- 25%). Manganese is extracted by 90% in the reducible phase, while Cu appears in great proportion (40%) in the oxidisable phase, probably indicating the significant role of organic matter as a bounding factor for this element. Iron is fractioned mainly in the reducible phase (45%) and in the oxidisable phase of sulphides and organic matter (30%).

Table 5- Significant correlation coefficients in the 5 steps of sequential extraction. (OC: organic carbon)

Parameter	Fraction I Exchangeable	Fraction II Specifically adsorbed	Fraction III Reducible	Fraction IV Oxidisable	Fraction V Residual
Cu/OC				0.74	0.61
Zn/OC				0.55	
Cd/OC				0.58	
Fe/OC	0.64			0.79	
Mn/OC		0.71			
Pb/Fe					0.60
Cu/Fe	0.83		0.65		
Cd/Fe				0.81	
Pb/Mn				0.77	0.56
Cu/Mn	0.52				
Zn/Mn	0.52	0.78	0.64	0.72	
Cd/Mn		0.64	0.86		
Fe/Mn	0.59				0.64
Zn/Cd	0.96	0.96	0.93	0.86	0.95

Table 5 presents the most significant correlation coefficients of the metals and organic carbon in the sequential extraction fractions. These coefficients provide evidence about the most significant factors affecting speciation of metals in soil. It is observed that organic carbon, which is a significant component of surface garden soil, correlates very well with most studied elements in the oxidisable phase. Zinc and Cd are highly correlated in all extraction stages indicating the common origin of these elements from sphalerite. Correlation of Zn, Cd and Mn in fractions I, II and III indicates the association of these elements with easily extractable phases, suggesting increased mobility in the environment. Lead is correlated with Fe in the residual phase possibly indicating the coexistence of the two elements in metallurgical slag grains in soil.

3.3. Mineralogical Data and Microanalysis

Identified minerals with XRD analysis comprise mainly (95%) common soil inorganic phases such as quartz, feldspar, mica and clay minerals. Sulphide minerals such as sphalerite and insoluble weathering products containing heavy metals such as alunite and tsumcorite were also recorded in the diffraction spectra. SEM-EDS observations and microanalysis results indicated that the studied material is rich in quartz> feldspar> Fe-Mn oxides> sulphide minerals.

Microanalysis of selected bright particles in back-scattered mode indicated presence of secondary minerals of very low solubility, enriched in heavy metals, particularly Pb (Figure 6). Specifically, the lead-phosphate mineral pyromorphite (logKsp= -84.4) has been identified in several grains. Also, the practically insoluble mineral corkite (logKsp= -112.6), which is a Pb-rich member of the alunite supergroup (Jambor, 2000) was identified. The exact chemical composition of identified corkite in the studied samples is presented on a phosphorus- sulfur- arsenic ternary diagram in Figure 7. Abundant Fe and Mn oxides and oxy-hydroxides, enriched in heavy metals were also found by SEM-EDS in agreement with the sequential extraction results. Sulphide grains corresponding to the primary mineralization of the wider area were also identified including galena, sphalerite, arsenopyrite and pyrite. The latter, often appears oxidised, forming pseudomorph crystals. Finally, anthropogenic grains of weathered metallurgical slag were observed. The composition of such grains is characterized by a Si-Fe- Ca vitreous phase, enriched in heavy metals. In many instances, slag grains appear weathered with pyromorphite precipitates on their periphery.
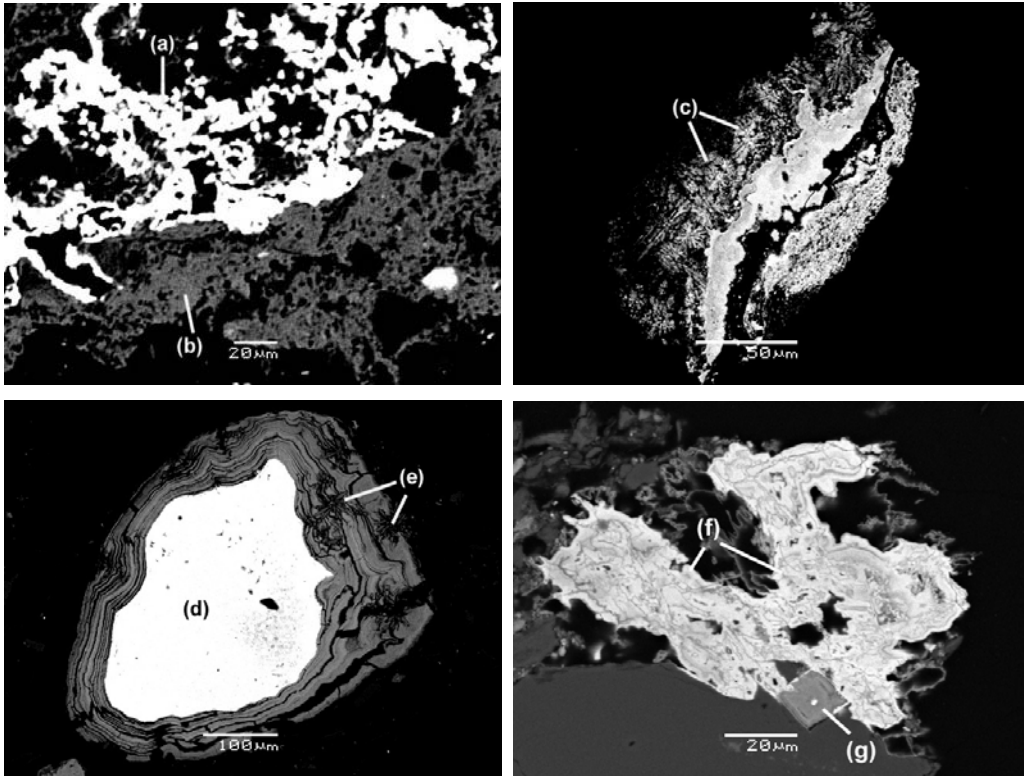
Figure 6- SEMs in back-scattered mode of selected bright particles: (a) Pb- alunite (corcite), (b) jarosite, (c) pyromorphite, (d) metallurgical slag containing Si, Fe, Pb, (e) pyromorphite, (f) Fe-Mn oxide enriched in heavy metals, (g) oxidised pyrite pseudomorph.
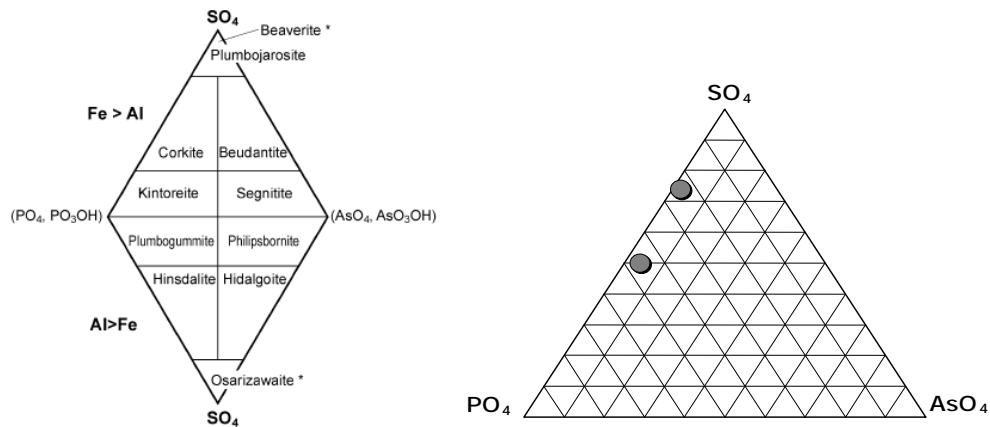

Figure 7 – Phosphorus- sulfur- arsenic double ternary diagram showing mineral species of the alunite supergroup (Jambor, 2000). Circles on ternary diagram on the right indicate microanalytical results of this study corresponding to corcite composition (log*Ksp* = -112.6).

3.4. Mobility of Heavy Metals in Surface Soil

The combined results of total chemical analysis, sequential extraction, mineralogical analysis and microanalysis were used to indirectly assess the potential mobility and bioavailability of metals in garden soil.

3.4.1. Lead

Lead has high mean total concentration of 1090 μg g^{-1} in soil. However, according to sequential extraction data, this element is fractioned mostly (53%) in the residual phase of less soluble soil components. Microanalytical SEM results indicate that Pb is abundant in anthropogenic phases (metallurgical slag) as well as natural phases of very low solubility (pyromorphite, alunite, tsumcorite). It seems that physicochemical conditions of soil in the study area, favour precipitation of such phases, thus limiting the potential mobility and bioavailability of Pb. The element is also associated with Fe-Mn oxide phases, which in the oxidizing surface environment are considered to be very stable, and to a lesser extent associated with sulphide phases, i.e. galena.

3.4.2. Zinc

Sequential extraction data indicate that Zn with a total concentration of 878 μg g^{-1} is primarily associated with Fe-Mn oxides (60%) in surface soil. Indeed, SEM-EDS observations confined Zn within Fe-Mn oxi-hydroxide phases together with other potentially toxic elements such as Pb and As. 25% of Zn was fractioned in the residual phase of the sequential extraction, probably reflecting the high content of this element in the metallurgical slag grains. Only 6.5% of the element was fractioned in the oxidisable phase of sulphides and organic matter, while 8% was determined as specifically adsorbed on surfaces of solid soil phases. In general, this element appears to be more mobile than Pb, however its total concentration combined with its fractionation data do not raise serious concerns about its potential threat for the living environment.

3.4.3. Copper

Copper was fractioned mainly in residual phase (40%) and oxidisable phase (40%) of the sequential extraction. In the studied samples it showed a strong correlation with Fe and organic carbon while SEM-EDS analysis indicated its association with Fe-Mn oxides. These observations as well as the fact that Cu is not a characteristic element of the primary mineralization of the area and its total concentration in soil is not extremely high (184 μg g^{-1}), provide no evidence of increased risk for the local environment. Anthropogenic sources of Cu are also expected to contribute to this element's distribution in surface garden soil through application of $CuSO_4$ as a pesticide.

3.4.4. Cadmium

The average concentration value of cadmium in soil was estimated at 6 μg g^{-1}, however poor analytical precision of ±30% contributes to increased uncertainty when interpreting the geochemical data for this element. The high correlation coefficient between Cd and Zn indicates common origin of the two elements from sphalerite, in spite the fact that no Cd was found by SEM-EDS microanalysis. The sequential extraction results indicated that Cd is associated with easily extractable phases of the 1st step, i.e. Cd ions are loosely adsorbed on surfaces of solid phases in soil. This observation signifies increased mobility and possible enhanced bioavailability of the specific element.

3.4.5. Iron

Volumetric errors possibly contributed to increased uncertainty on Fe concentrations in this research. Nevertheless, the results demonstrated the significant role of this element as a controlling factor for the distribution and mobility of the other studied elements, mainly through the scavenging properties of formed Fe-oxides in soil. Studied soils are rich in Fe (mean concentration of 4.6%). The element was fractioned in the reducible phase of sequential extraction procedure by 45%, the oxidisable phase by 30% and the residual phase by 25%.

3.4.6. Manganese

Manganese does not pose a great health threat however, like Fe has an important role in controlling the mobility of other elements. 90% of the total Mn soil content (4465 μg g^{-1}) in this study was fractioned in the reducible phase. This result agrees with SEM-EDS data where Fe-Mn oxides were observed as dominant soil phases, attracting heavy metals. Also the sequential extraction data indicated a good correlation between Mn- Zn-Cd in the 1st three extraction steps indicating that Mn is relatively mobile in this particular soil environment.

4. Conclusions

The combination of geochemical and mineralogical data has been applied successfully in the characterization of surface soil within the Stratoni mining village environment. The applied methodology gave useful information with respect to the potential risk for the environment imposed by heavy metals in soil, which would not be available if only the total concentrations of heavy metals were measured. Specifically, sequential extraction results coupled by SEM-EDS microanalysis data indicated variety of solid phases withholding the metals, thus differentiation of metal mobility/ availability in the study area. Lead has high mean concentration but is fractioned mostly in the residual phase of less soluble soil components limiting its potential bioavailability while Zn, Cd and Mn, participate in appreciable proportion in easily extractable phases indicating easy mobilization and greater potential bioavailability. The output of the research can be used in conjunction with other relevant information for risk assessment and for selecting appropriate remediation measurements in the area.

5. Acknowledgments

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