ECOLOGICAL RISKS FROM TRACE ELEMENTS IN QUATERNARY AGRICULTURAL SOILS OF LEBANON-EAST MEDITERRANEAN

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ABSTRACT

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Soil contamination by trace elements (TE) causes health and environmental risks. This work focused on arable lands of Central Bekaa of Lebanon, East Mediterranean. The spatial distribution of TEs in the cultivated soils was mapped. Results showed accumulation of Cr and Ni, in the soil-plant interface layer, exceeding the multifunctional land use (soil threshold I <50 and <40 mg kg^{-1}, respectively) and controlled land use (soil threshold II-100 mg kg^{-1}). The index of geoaccumulation (Igeo) showed no hazards from Zn with moderate to strong contamination from Pb and moderate hazard from Ni, Cu, Cd and Cr. A cross sectional soil sampling from the Litani river to the eastern hill of Terbol showed accumulation of TEs at foot slopes and at river's banks. Human activities within the plain contribute to further soil contamination with risk of pollutants transfer to food chain. Additional sampling of plant and corresponding soil in hot spots showed TE content in the plant leaves to be mostly within or slightly above the permissible values in wheat and potato. Considering the soil quality regarding chemical pollution is a necessary factor in land use planning for the elaboration of adapted to local soil conditions thresholds of TEs content in the soil for suitable land use, either in agriculture or alternative uses.

Keywords: Sources of trace elements, agriculture, soil quality, land use, food safety

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INTRODUCTION

Soil contamination by trace elements (TEs) is one of the emerging public health and environmental hazards. Assessing the natural abundance and accumulation of TEs in agricultural soils are the first steps for soil contamination assessment and land use control (Rodriguez-Eugenio et al., 2018). The available Lebanese soil data points to the absence of local standards and norms related to soil pollution with TEs. Despite the efforts to complement national soil information by establishing a georeferenced soil database in the country (Darwish et al. 2006), the use of geomorphological, physical and physico-chemical soil characteristics is restricted to the erosion, desertification, land capability and partially land suitability assessment.

With increasing human pressure, the status of TEs in the dryland soils is of paramount importance for land quality assessment. It is served as basic information to evaluate the impact of land use on soil pollution and to assess the applicability of the European standards to local soil conditions. While the European thresholds are listed in function of content of hazardous elements in the soil (Eikmann and Kloke, 2000), building the criteria of soil contamination, i.e., level of TEs for suitable land uses, must be based not only on TE concentration in the soil matrix, but also on soil characteristics and TEs bioavailability and mobility (Kassir et al., 2012; Abou Jaoude et al., 2019). Determining the threshold and intervention levels in the soils of arid and semi-arid regions is crucial for decision makers and land users to decide on appropriate agricultural and non-agricultural land uses with minimum public health and environmental threats.

TEs in the soil have a geogenic and human origin caused by the lithology and land use history (Möller et al., 2005). Many industrial processes involve solubility or leaching of TE ions to aqueous solutions which then are released into the environment via wastewater (Nestle, 2002). Upstream and downstream mismanagement of water and fertilizer inputs are impacting the limited natural resources of East Mediterranean (Muller and Darwish, 2004). This is particularly observed in pollution problems due to excessive use of fertilizers and pesticides, dumping of industrial and domestic wastes and discharge into rivers, dry wadi beds, sand pits and quarries (Darwish et al., 2011). Farmers, therefore, irrigate with water of low quality exerting cumulative effect on land quality and sustainable use. In the absence of active extension service, nutrient build up in the soils is observed, especially in semi-arid Lebanese areas, due to low fertilizers use efficiency (Darwish *et al.* 2005). Byproducts in fertilizers, emissions from industry, transport and energy sectors have also contributed to the soil and groundwater contamination with TEs (Kassir et al., 2012).

Recent studies on the soil-plant-TEs interaction from Kazakhstan urban soils, located near a Zn-Pb smelter, and from the Lebanese coastal area with organic production, showed the direct effect of land use history on soil quality and human health risks (Woszczyk et al. 2018; Fadel et al. 2016). The first study revealed the soils displayed high contamination with Cd and moderate to strong contamination with Pb and Zn, with increased public health risks from high Cd and Pb bioavailability. The second work showed no TE contamination in the soil with absence of significant correlation between TE content in soils and plants, indicating complex soil, soil solution, element behavior and plant type mechanisms controlling TEs uptake and their transfer from the soils to plants.

Because the public health and agro biodiversity are affected, monitoring the origin, state and development of soil and groundwater pollution with TEs is of extreme importance. Until now, 6% of the Lebanese lands were tested for TE composition and pollution. Therefore, the need arises for national assessment of soil quality to meet the challenges of SDGs and locally adapt soil TEs thresholds for suitable land use and implement policy for proper and sustainable land management and protection. The purpose of this study was to assess the state of contamination of the main agricultural soils with TEs and assess the potential human health exposure, eco-toxicity level and ecological risk from TEs in the central Bekaa plain, the main food producing area of Lebanon.

MATERIALS AND METHODS

Description of the study sites

The study area is located in the Central Bekaa plain, totaling about 12,753 ha. It extends from Mount Lebanon eastward through the Litani River towards the eastern mountain chain (Figure 1). The climatic conditions of the area are characterized by 600-700 mm of precipitation and a mean annual temperature of 15 degrees C. The mean potential ET reaches about 1500 mm/year, while the seasonal ET is 1200-1400 mm/year (Nimah, 1992). The Bekaa plain consists of fan deposits and a mixture of colluvial and alluvial material representing mainly deep, non-calcareous Fluvisols and Cambisols with some inclusions of Vertisols and

Regosols (Darwish *et al* 2006). The soils of the area are mainly saturated with exchangeable calcium, with total CaCO3 content between 15% and pH value ranging between 7.8 and 8.0. The soils are clay with a clay content between 45 and 60% and relatively poor in organic matter (1.0-1.5%). Agriculture in the area is practiced mainly with field crops, fruit trees and vegetables.

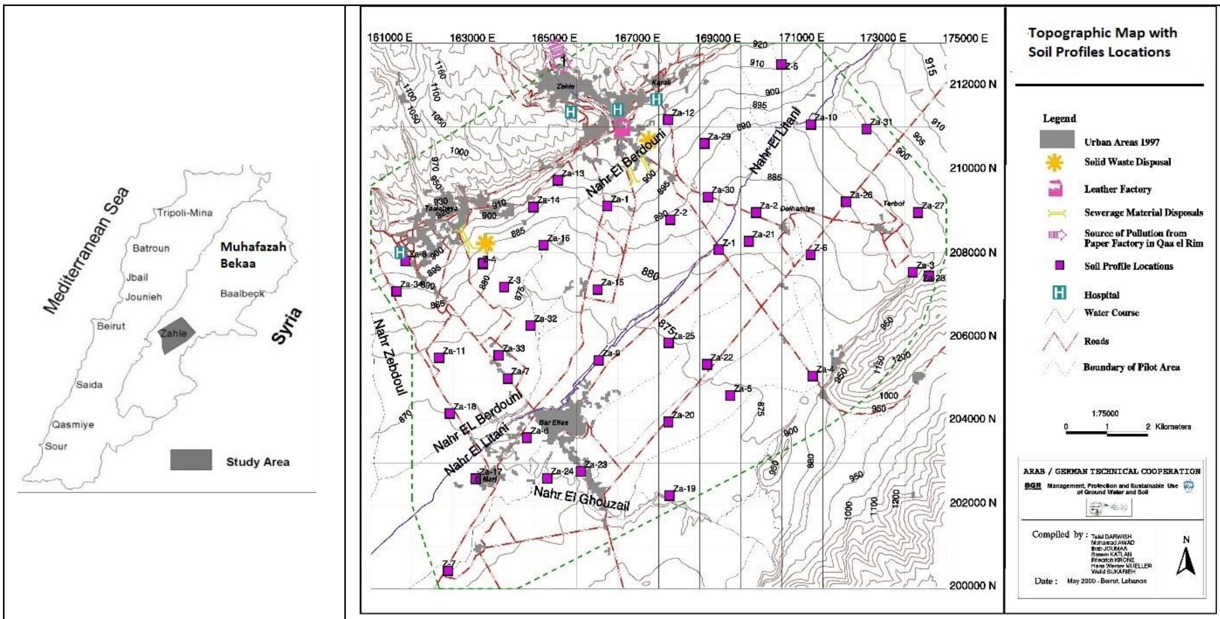


Figure 1. Topographic map of the Central Bekaa area with soil profile locations (red squares) and main sources of TE contamination (solid waste disposal, hospitals, wastewater canals, transport).

ISO 10381-1 to 5 was used for the assessment of soil contamination with TEs. Soil profiles were excavated in a grid system (1x1 km^2) with due consideration of agricultural land use in the plain (Figure 1) and sampled horizon wise up to the depth of 200 cm or to the water table depth whenever its level was shallower. Soil sampling was done in reverse order (from the bottom to the surface) to avoid cross contamination. In this study, the georeferenced soil samples locations were used for TEs spatial mapping (Figure 2). Samples from a transect from the Litani River toward the eastern hill and randomly selected profiles were used to assess accumulation risk index. Circular grid sampling around the hot spot was followed to estimate the TEs bioavailability risk through plant uptake.

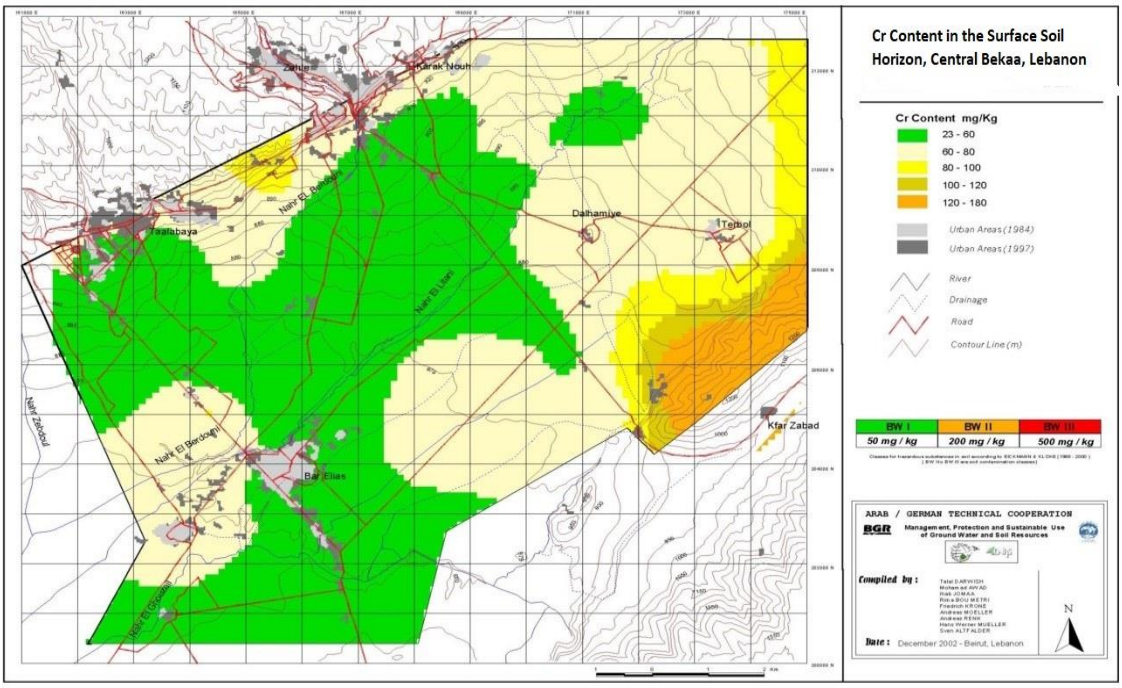


Figure 2. Spatial distribution of Cr in topsoil of Central Bekaa Plain, Lebanon (Reference?)

Field sampling and preparation

Soil samples from the excavated soil profiles were collected horizon wise starting from the bottom of the pit upwards, in order to avoid cross contamination. Whenever a hot spot or diffuse contamination of TEs was discovered, a secondary soil sampling from topsoil (0-20 cm) and plant sampling was carried to assess the extent of pollution and risk of transfer to the plants. Because Cr and Ni were the most abundant TEs in the soils of the area, the region was divided into three zones with Cr ranges of <50, 50-100 and >100 $mg.kg^{-1}$ with the aim to check the variability of soil TEs content as affected by fragmented land tenure and diverse land use.

To check the origin of TEs in the soil, notably at foot slopes, soil sampling was undertaken in altitudinal sequence within a distance of 7.5 km, starting from the Litani River banks (elevation of 750m) up to the summit of nesting eastern Terbol hill (elevation of 1050m) with eroded shallow Leptosols. Therefore, to check the geogenic origin of the increased Cr and Ni values near Terbol in the Bekaa plain (Lebanon), three profiles (0-50 cm) along a Catena above the area were collected.

To assess the extension of the Pb contamination around the contaminated hot spot near El Marj, a circular grid (ISO 10381-1) was chosen up to 500 m around the original soil profile

(Figure 3). Only topsoil was sampled (0-20 cm) and analyzed to check the spatial Pb distribution risk.

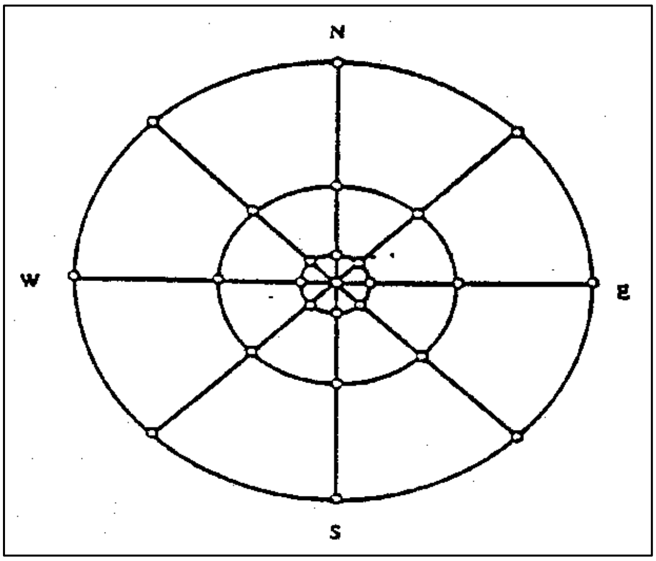


Figure 3. Scheme of a circular grid sampling around the hot spot showing high level of Pb in Central Bekaa, Lebanon (o- sampling point).

Soil and plant analysis

Eventually, plant samples (wheat, potato, lettuce and alfalfa) were collected to estimate the risks from direct consumption of edible part and risks from indirect pathways (products from animal consuming the shoots) of assessed TEs, notably Cr and Pb transfer to human body. The edible plant samples were cleaned from soil and dust, air dried then grinded and dried at the oven at 70° C until constant dry weight, acid digested then analyzed for TE content using atomic adsorption. The soil samples were cleaned from roots and gravels, disintegrated, air dried, ground and sieved through 2 mm sieve and stored in clean place for further analyses.

The soil physical and chemical characteristics were analyzed by methods adopted for the Middle East region (Ryan *et al.*, 2001). Following the ISO 11466, Aqua Regia was used for the digestion of the soil samples for the determination of the TEs total content in the soil of Bekaa Plain. The exchangeable portion of TEs was not conducted for two reasons: First, the Eikman and Kloke classification of land use suitability is based on total TE content in the soil. Second, we collected also the plant samples from the control sites and hot spots and analyzed them for TEs content. This is the end picture of TEs accumulation in different plant parts.

Although the exchangeable form of TEs is the mobile fraction that is supposed to be removed by the plants, the element transfer from the soil to the plant is subject to different factors like the plant behavior, soil texture, cation exchange capacity, moisture conditions, oxidation-reduction potential and elements behavior under different soil pH values. Soil and plant analyzes were carried out in the BGR-soil-laboratory, Hannover, Germany. The procedures were done after relevant ISO 11466 and quality control.

The level of soil pollution by TEs was evaluated using the criteria of Eikman and Kloke (2000). This concept considers three levels of soil contamination with TEs (Table 1): I. Non polluted soils with multifunctional land use, II. Slightly contaminated soils with restriction to soil use for leaf vegetables and, with increasing TEs content, controlled suitability for technical crops, fruit trees and agroforestry, III Contaminated soils that need restoration.

Table 1. Use and "Site and Protection Group Specific Land Use Options" oriented values for hazardous TEs in soils* (mg kg^{-1})

Land Use	Soil Value	As	Cd	Cr	Ni	Cu	Zn	Hg	Pb
Multifunctional land use	I	20	1	50	40	50	150	0.5	100
Agricultural Crops- Fruits and Vegetables	II	40	2	200	100	50	300	10	500
Technical crops	III	50	5	500	200	200	600	50	1000
Non Agrarian Ecosystems	IV	60	10	500	200	200	600	50	2000

** Source: Eikman and Kloke (2000).*

Quality control and statistical analysis

The applied methodology was quality-controlled, with reproducible results by means of reference samples from "The International Soil-Analytical Exchange Program" of the University of Wageningen, the Netherlands. Cd and Pb were analyzed by means of ETA-AAS, As by means of Hydride formation, AAS ($NaBH_4$), Cu, Cr, Co, Ni by means of Flame-AAS. The ratio of TEs determination in aqua regia in measured soil samples to the expected (standard) was 0.9913-1.0206 for Ni and Pb, 1.004 for Cd, 1.065-1.076 for Cr and 1.044-1.055 for Cu. The spatial analysis and TE mapping were done using the universal kriging method with a matrix pixel of 5 m x 5 m resolution. Analysis of variances (ANOVA) and Tukey post hoc test were performed using R.

Assessment of the potential risk and toxicity from trace elements

Exposure from dietary intake was assessed using the natural range of TE values in plants reported by Scheffer and Schachtschabel, 1992. To distinguish the origin of TEs, the index of geoaccumulation (I_{geo}) was calculated using the equation (1) implemented by Mediolla et al., 2008 and Okedeyi et al., 2014:

$$I_{geo} = \log_2 (Cn/1.5\ Bn) \qquad \text{Equation (1)}$$

Where Cn is the concentration of the TE in the soil; Bn is the geochemical background concentration of the same metal. The pollution index (C^i_f), the potential ecological risk index (E^i_f) from a TE and the potential toxicity response index (*RI*) from various TEs were assessed following the recommendation of Guo et al. (2010), using the equation (2):

$$C^i_f = C^i s / C^i\ reference \qquad \text{Equation (2)}$$

Where C^i_f is the pollution index, $C^i s$ is the measured content of given TE in the soil sample. C^i *reference* is the background value of the same TEs. The TEs background values used in this paper are derived from the analyzed Lebanese soil samples determined from the German-Arab Technical Cooperation Project (2000) for Lebanese soils of Central Bekaa derived from quaternary sediments, which are 11.4, 1, 12, 64, 0.1 and 12.1 mg.kg^{-1} for Ni, Pb, Cu, Zn, Cd and Cr respectively. The potential ecological risk was calculated using equation (3):

$$E^i_f = C^i f * T^i f \qquad \text{Equation (3)}$$

Where E^i_f is the potential ecological risk index, $C^i f$ is the pollution index and $T^i f$ is the response coefficient for the toxicity of the single TE. The thresholds of the potential ecological risk index E^i_f (Zhao et al. (2005) are: low <40, moderate 40-80, high 80-160, very high 160-320 and Severe >320. The corresponding toxicity coefficients, as evaluation criterion based on toxicity (Zhao et al. (2005), are 5 for Ni, Pb and Cu, 1 for Zn, 30 for Cd and 2 for Cr. The potential toxicity response index was calculated using equation (4):

$$RI = \Sigma E^i_f \qquad \text{Equation (4)}$$

Where *RI* is the potential toxicity response index. The potential toxicity response index adapted from Zhao et al. (2005) is <150 low, 150-300 moderate, very high 300-600 and serious >600. ΣE^i_f is the sum of potential ecological risk indices for a given TE.

RESULTS AND DISCUSSION

TEs in the Quaternary arable soil

Results showed similar distribution pattern of Cr and Ni in the surface Ap horizon of the soils of Central Bekaa Plain of Lebanon with relative accumulation of Cr and Ni in some areas, notably at foot slopes, exceeding the soil contamination value II (Figure 2). It is considered that the geology of the study area does not have lithologies that host mineralization that could have supplied those TEs (Khawlie, 1983). Thus, the main sources of soil pollution with TEs in Bekaa Plain is probably manmade. Fortunately, excluding other potential sources of organic pollution, the soil in a large part of the Central Bekaa plain is still pristinely clean regarding the TE contamination and thus, it can be considered convenient to the cropping of sensitive to contamination crops, like the leafy vegetables.

Some areas of the Bekaa plain showed TEs content increase on the soil surface, compared to subsoil, by more than 50% for Co, Cr, Ni, Cu, Zn and by more than 100% for Pb (Table 2). Earlier studies from Nijeria reported that Pb levels generally decreased with distance from the vicinity of a ceramic industrial site (Lyaka and Kakulu, 2012). Other locations from the area of study showed increased TE content in the subsoil (160-180 cm), posing the question of origin and causes of accumulation in the subsoil. In this area, water table level was observed at 180 cm with sign of mottling throughout the lower soil layers, implying higher mobility of hydrated forms of TEs during the winter season. Although the calculation of I_{geo} showed no strong concerns from Ni accumulation in the soil, a concentration of this metal at foot slope raises some concerns as this area is usually under irrigated horticulture and green vegetable production.

Table 2. Accumulation of TEs in the soil of selected sites of Bekaa Plain, Lebanon

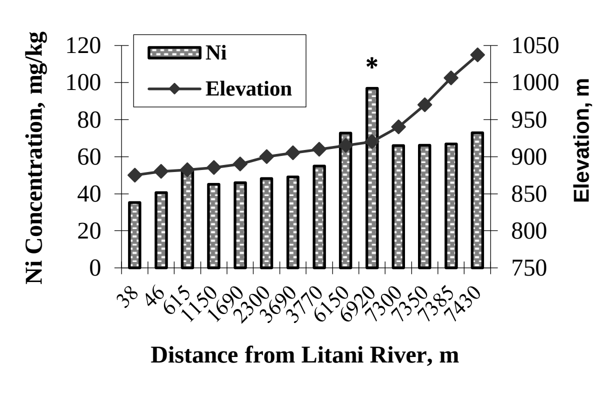
Location	Soil Depth cm	Pb	Cd	Ni	Cr	Zn	Cu	Water Table Depth cm
		mg/kg						
Saadnaeal	0-3*	21°°°	0.28°°	29.7°	40.0°°	147.0°°	30.7°°	180
	0-40	10.0°°	<0.2°	33.7°	43.3°°	62.0°	17.0°	
	40-85	9.7°°	<0.2°	31.7°	41.7°°	62.3°	16.3°	
	120-160	7.3°°	<0.2°	34.7°°	43.0°°	51.0°	15.0°	
	160-180	14.0°°°	<0.2°	53.0°°	79.1°°°	84.0°	26.0°°	
Taalabaya	0-10	14.7°°°	0.41°°	59.7°°	70.3°°	77.3°	35.3°°	800
	10-70	16.7°°°	0.41°°	60.7°°	71.3°°	79.7°	35.7°°	
	70-92	8.3°°	0.48°°	46.3°°	57.7°°	63.3°	24.3°°	
	92-150	7.0°°	0.39°°	39.7°°	48.3°°	51.3°	20.3°°	
	150-200	5.3°°	0.32°°	30.7°	35.7°°	41.0°	15.3°	

** Superficial sediment on soil surface after irrigation with non-treated sewage water; I_{geo} °Unpolluted; °°Moderately polluted; °°° Strongly polluted. Thresholds for I_{geo} are: 0 unpolluted, <1 unpolluted to moderately polluted, 1-2 moderately polluted, 2-3 moderately to strongly polluted, 3-4 strongly polluted, 4-5 strongly to very strongly polluted, >5 very strongly polluted.*

The absence of systematic difference in the distribution of zinc background level and highest values suggest a possible dependence on application of fertilizers and pesticides as well as possible use of sewage sludge on arable lands. Indication on higher Zn and Cu accumulation in arable lands was associated with the application of animal manure, fungicides and fertilizers (Kabata-Pendias and Adriano 1995). These two TEs show very high correlation exceeding 0.83 ($P<0.01$) while Cr and Ni present highly significant correlation $r^2=0.93$ ($P<0.01$). A high correlation among TEs in the soil might suggest similar processes that control the element associations in parent materials or common anthropic source. The release of Cr and Ni has been related to the energy use in urban and industrial activities that consume fossil fuels.

Catenary search for the source of TEs

Monitoring of soil quality from the river to the water divide line of surrounding eastern Terbol hill, through a catenary soil sampling across the plain, showed a steady increase of TE with some variability from the plain towards the summit with significant difference between the plain-foot slopes and foreslope (Figure 4). If we exclude a recent erosion-deposition process from the hills, such spatial distribution of TEs in the agricultural plain is associated with human activities including fertilization, irrigation with contaminated waters and emission from heavy traffic. The high Pb content in the soil of the plain notably near the river banks with relatively high geoaccumulation index points to human impact, as human activities and traffic have been the densest along the river's stream.



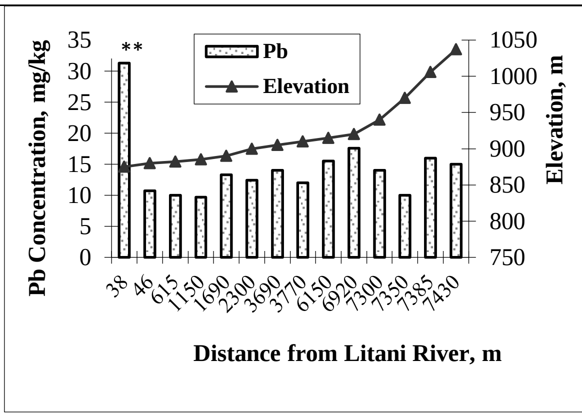


Figure 4. Spatial Distribution of Ni (left) and Pb (right) in the soils of Central Bekaa, Lebanon along a transect from the Litani River to the foreslope of eastern Terbol hill. *Significantly different at P<0.05; **Significantly different at P<0.01.

The results of Ni content showed that Ni I_{geo}>0.21 indicating moderate contamination at foot slope. For Pb, the I_{geo} was equivalent to 4.4, i.e., strongly contaminated along the river bank. For the rest of the plain I_{geo} varied between 2-3 and was moderately contaminated. Compared to the area under study, both Quaternary arable lands and soils developed from hard limestone in North Lebanon showed no harmful Pb accumulation (Nsouli et al., 2004). This and the relatively low content of Pb in Central Bekaa, except the river banks, supports the version of anthropogenic emissions as the primary source of lead input to the soil.

Similar results were reported by Husein et al. (2019), who related the increased levels of TEs in the topsoil surrounding the Orontes River in the district of Hamas, Syria, to intensive agricultural practices, agrochemical application and irrigation with untreated sewage water, beside the impact of urban and industrial expansion.

Some trace elements, like Ni, Cd, Pb and Cr, were reported to deposit on the soil surface from vehicle's exhausts and surface road degradation by traffic (Gupta, 2020). These TEs accumulate within the environment, which can affect humans and livestock health over time. Similarly, the absence of the metalloid As in the Bekaa plain and its main occurrence as scattered point source of contamination in the vicinity of chicken farms in Terbol supports the hypothesis of the application of poultry manures in agriculture or its sedimentation with surface runoff. It is reported that Arsanilic acid is used as growth promoter in broilers beside the possible risk of using organoarsenical herbicides which degrade into inorganic As (Chen et al. 2014).

A high enrichment with TEs is observed with the sediments imported with irrigation by raw sewage water, which brings significant amount of Pb, Cd, Cr, Zn and Cu. Surprisingly, Pb was found in high geoaccumulation indices in the area of study, not only on the topsoil but also in the subsoil, at the proximity of water table. This situation indicates high impact from the current soil hydrological regime beside human intervention and deep plowing to restore the fertility of emerged lands, which used to be wetland or bushland. Actually, during the sampling campaign, remains of bamboos were discovered at 100-150cm.

The accumulation of Pb in the entire soil profile can harm the biological activity. An increase of total earthworms mortality was observed in Libyan soils, with a simultaneous decline in the number of cocoons, affecting soil biological activity and productivity (Haeba *et al.*, 2013). Similar ecological risks were reported from Nile Delta, Egypt, due to increased content beyond background values of Zn, Cr and Pb, with evident translocation to deep soil layers (Khalifa and Gad, 2018). Also, this can be probably caused by more recent soil pedoturbation due to shrink swell clay properties in the area and mixing the topsoil into deeper horizons with time.

The seasonal fluctuation of water table, notably in locations with shallow water table, like the Fayda area near Zahle, can increase the mobility of these TEs and put under risk the soil-groundwater ecosystem functions. Water table depth multiplies its vulnerability in case of uncontrolled use. The deterioration of groundwater quality of the Gaza Strip was attributed to unrestrained solid waste disposal, overuse of fertilizers, pesticides and soil amendments in agricultural production, and the uncontrolled discharge of the wastewater over the soil surface (Alfarra and Hamada, 2019). Thus, the need to control human activities in sensitive areas, to monitor land use change and check the TEs load to the soil depending on different land use and agricultural practices. Moreover, this issue should be related to soil properties, soil-TEs-plant interaction and soil suitability to specific land uses.

The pH of the soils of the study area is neutral and the temporary anaerobic conditions can affect TEs mobility. The concentration of As, Cd, Hg, Pb and Zn in the surface horizons was explained by the rotation of vegetation, atmospheric deposition and their adsorption by the soil organic matter (Duchaufour, 1977). However, the elements found concentrated in the lower horizons of the soil profile, under positive water balance and seasonal, downward, percolation regime, tend to be associated with accumulations of the leached clays and hydrous oxides in the subsoil. Some soil types of the Bekaa Plain show uneven distribution of TEs with depth, probably due to the origin of the alluvial-colluvial material forming the studied Fluvisols and Regosols. The relative increase of Cr and Ni, detected by Oulabi *et al* (1999) in some Lebanese mountain springs could support the natural enrichment of water bearing rocks and sediments with these TEs although an illegally buried source of imported toxic wastes cannot be excluded.

To check the accuracy of the mapping process used in a the mapping of Cr spatial distribution in the surface soil layer of Central Bekaa, using the kriging method after a grid (1x1 km^2) within the German-Arab Technical Cooperation Project (2000), the area was divided into three zones (<50, 50-100 and >100 mg kg^{-1}). Soil and plant samples were collected from each of these zones to compare the matching between the predicted and measured Cr values and assess the associated risks to local population from the consumption of locally produced crops. Results showed high matching between the predicted and diagnosed soil TEs values in the recent soil sampling (Figure 5). However, the standard deviation of Cr content in the root zone varied between 13 and 19% in the two lower soil value groups (50 and 50-100 mg.kg^{-1}) and reached 40% in the highest Cr concentration zone (>100 mg.kg^{-1}) indicating diverse sources of contamination from geogenic and anthropologic sources under different land use policy with intensive agriculture, use of fertilizers and manure and local use, along water channels, of non-treated wastewater in irrigation. This output indicates sufficient density of soil sampling with the need to undertake more dense sampling for the mapping and characterization of human and environmental exposure to soil contamination with TEs.

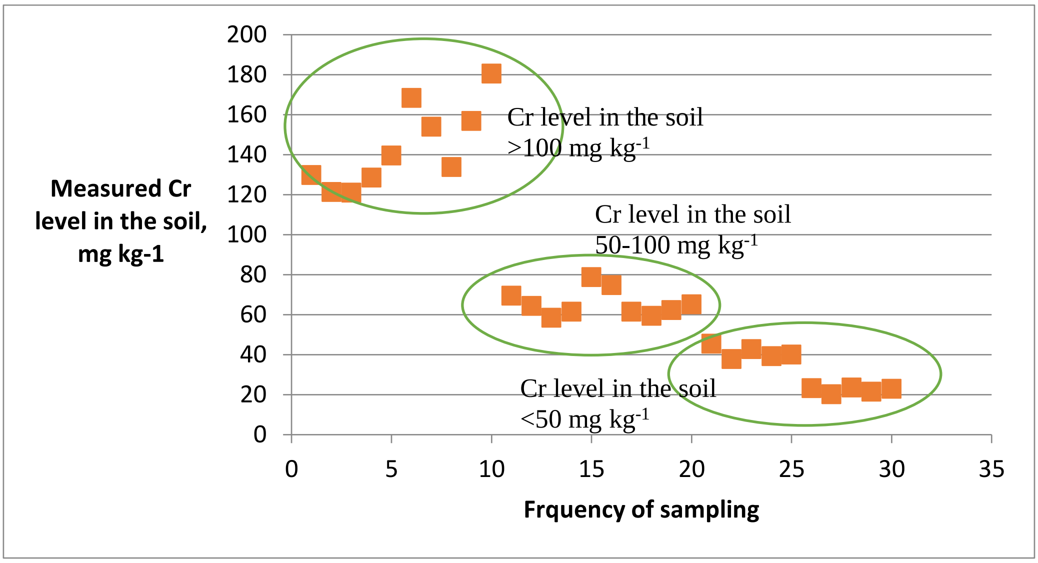


Figure 5: Distribution of Cr content in the soil samples for the evaluation of Cr bioavailability using an early produced map showing the spatial distribution of Cr in the upper soil layer with three categories of Cr content (<50, 50-100, >100 mg/kg), classified following Eikman and Kloke, 2020.

Potential risk and toxicity assessment

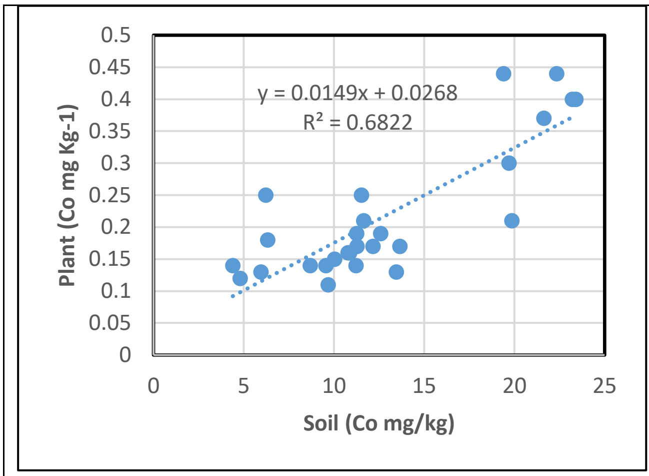
The ecological risk from the concentration of one or several TEs can be summarized in toxic effect on soil biological activity, soil quality and water quality. Assessing the potential ecological risk based on the equations 1-4, revealed high to moderate risk from Cd and Pb and low risks from Cr, Ni, Cu and Zn (Table 3). The overall cumulative potential toxicity response index for the six studied TEs revealed moderate level in 60% and low level in 40% of analyzed soil samples, which indicate the necessity for differential approach to suitable land use, cropping system and agricultural practices depending on soil quality and crop behavior. One of the main potential risks is related to food safety with increasing reports on cancer diseases from the villages of the middle Upper Litani basin equal four times the national average (The Beirut Report, 2019). Similar results were obtained from Northern Egypt, where TEs found in the blood of liver cancer affected patients, consuming agricultural products from Pb, Cd and As polluted sites, showed much higher levels than in control subjects (Elwakil *et al.*, 2017).

Table 3: Ecological toxicity index of representative soils from Central Bekaa, Lebanon

Location	Soil Depth	Pb	Cd	Ni	Cr	Zn	Cu	Potential toxicity response index
	cm	mg kg^{-1}						
Saadnaeal	0-3*	105	84	8.68	6.61	2.30	12.79	219.38
	0-40	50	60	9.85	7.16	0.97	7.08	135.06
	40-85	48.5	60	9.27	6.89	0.97	6.79	132.43
	120-160	36.5	60	10.15	7.11	0.80	6.25	120.80
	160-180	70	60	15.50	13.07	1.31	10.83	170.72
Taalabaya	0-10	73.5	123	17.46	11.62	1.21	14.71	241.49
	70-92	83.5	123	17.75	11.79	1.25	14.88	252.15
	92-150	41.5	144	13.54	9.54	0.99	10.13	219.69
	150-200	35	117	11.61	7.98	0.80	8.46	180.85
		26.5	96	8.98	5.90	0.64	6.38	144.39

Accumulation of TEs in plants and agricultural products

Our results on human exposure to Cd and Pb showed that Lettuce contains significantly lower content (0.06 and 0.91 mg kg^{-1}) than alfalfa 0.82 and 2.34 mg kg^{-1}, respectively). With regards to the total data set, only the Co content in the soil and plant samples correlated fairly well with each other ($r=0.493$, $p=0.01$). The other TEs (Cr, Cu, Ni, Pb) showed no or very week correlations (Cd $r=0.317$; Zn=0.377) between the content in the soils and nested plants. However, considering Alfalfa and Lettuce separately, a strong correlation could be found for Co and Ni ($r=0.825$ and $r=0.77$, respectively) correlating Alfalfa and lettuce plant samples with the corresponding values in the soil samples. Based on the linearity of the function, the best fit regression function was an exponential function with $r^2= 0.68$ and $r^2=0.59$, respectively (Figure 6).



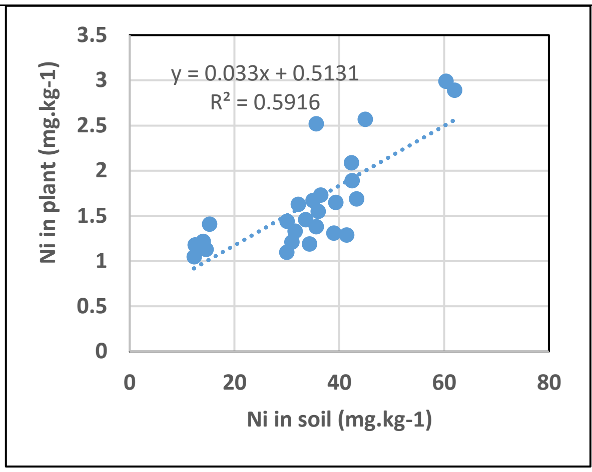


Figure 6. Content of cobalt (left) and nickel (right) in alfalfa grown in Central Bekaa Plain of Lebanon

Significant correlations between TEs content in soil and plants could also be found in alfalfa for Cd, Cr, Zn (r=0.543, r=0.605, r=0.483, respectively). For Lettuce, only Zn showed a significant correlation between the TE content in the soil and plant samples (r=0.608). This exhibits that the TEs uptake by leaf succulent plant can partly be conditioned by the total TE content in the soils. Although, the assessment of exchangeable form of TEs can provide preliminary feedback on elements mobility, other factors can trigger or limit TE uptake like plant species, redox conditions, soil pH, or the TE source and form, which can control the TE bioavailability and accumulation in consumable plants. In this regard, the Bioconcentration factor was used to characterize bioavailability and identify the potential risks from the consumption of crops cultivated on contaminated sites, based on the ratio of the element in the plant leaves to the content of the element in the soil (Mishra and Pandey, 2019).

Risks from point source pollution

A second hot spot area with high Pb concentrations in the topsoil was found near El Marj, East of the Litani River (circled in red in Figure 7). Soil and plant samples collected from the area surrounding the Pb contaminated site showed normal Pb values in the collected soil samples (Figure 7). This investigation indicated local soil pollution with Pb and the absence of any risk of diffuse Pb contamination of agricultural products from the area surrounding the hot spot. Indeed, the level of Pb in the alfalfa samples did not exceed the natural range, even in the contaminated site.

However, the input of some toxic trace elements with dust generated by vehicles was reported as the main source of some TEs transfer in the region (Gupta, 2020). This pathway can be responsible for the accumulation of Cr and even Cd in the five analyzed samples of the leafy succulent lettuce, cultivated on multi-functional soil with close to background level of Cr (Figure 8, Table 4). These results indicate the difficulty to control food safety even at local level, where different sources of pollution exist and several factors of TEs transport and availability interfere.

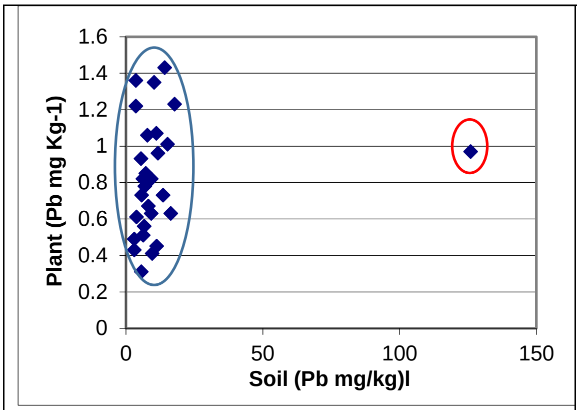


Figure 7. Level of Pb in alfalfa cultivated on a soil from Central Bekaa contaminated with a Pb point source. The outlier, circled in red, point indicates the center of the hot spot. The blue circle indicates the low level of Pb in plant samples collected circular wise around the hot spot.

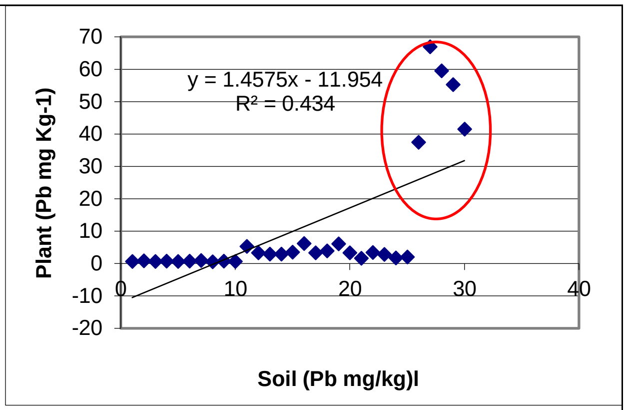


Figure 8. Accumulation of Pb in some Lettuce samples planted on non-contaminated soil (Al Kasr area, Central Bekaa). The points within the red circle indicate possible contamination of plant samples from non-soil sources.

Table 4. Concentration of some trace elements in soil and lettuce collected from sites with different level of soil Cr content in the Bekaa valley, Lebanon

Location	Cr range mg/kg	Soil Samples				Plant Samples (Lettuce)			
		Cd	Cr	Ni	Pb	Cd	Cr	Ni	Pb
		mg/kg				mg/kg			
Terbol	80-100	**2.0**	**130**	**77**	9	**0.62**	0.52	1.17	0.64
		1.9	**121**	**72**	4	0.47	0.46	1.07	0.79
		1.9	**121**	**71**	3	0.43	0.52	0.77	0.56
		2.0	**129**	**71**	4	**0.62**	0.49	0.96	0.70
		1.9	**140**	**78**	5	**0.62**	0.57	0.79	0.56
	60-80	0.3	**70**	**49**	7	**0.57**	0.96	1.82	0.69
		0.3	**65**	**46**	3	**0.63**	**1.21**	1.88	0.89
		0.4	**59**	**41**	6	0.3	0.74	1.27	0.48
		0.4	**62**	**42**	7	**0.54**	1.03	1.39	0.75
		0.3	**79**	**54**	3	0.47	1.00	2.16	0.65
Zahle	< 50	0.3	46	30	6	**0.62**	**1.53**	1.22	1.56
		0.2	38	26	3	**0.71**	**1.69**	1.72	3.34
		0.3	43	29	10	**0.78**	**1.78**	1.62	2.80
		<0.2	39	28	9	**0.7**	**1.45**	1.24	1.72
		<0.2	40	28	7	**0.75**	**1.56**	1.16	1.97
Natural range		1.0	50	40	100	< 0,5	0,1-1	< 3	< 10

It is interesting to note that assessing TEs accumulation in different plants parts, according to Scheffer and Schachtschabel (1992), showed non-hazardous levels in the edible part of largest two strategic crops cultivated in the country: wheat and potato (Table 5). However, TE accumulation was significant in the green vegetative parts (shoots of wheat and potato) that are usually plowed in (potato shoots) and undergo mineralization. In this case, TEs are either released back to the soil probably under more available form or provided to animal as fodder stuff (wheat shoots). This exposure through indirect pathway can undermine food safety for local population if not properly controlled.

Table 5 :TEs distribution in different crop parts (mg.kg^{-1}) collected from Central Bekaa Plain, Lebanon

CROP	Plant part	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Wheat	shoot	0.033	0.051	**3.36***	1.76	0.47	0.47	6.9
	grain	0.026	0.017	0.18	4.21	0.23	0.02	27.4
	shoot	0.049	0.29	**4.24**	3.12	1.71	0.75	13.8
	grain	0.040	0.009	0.44	5.22	0.36	0.05	37.4
	shoot	0.028	0.079	**3.21**	5.15	0.76	0.48	5.2
	grain	0.012	0.019	0.81	4.06	0.45	0.09	23.5
	shoot	0.063	0.088	**6.36**	3.50	0.96	0.62	17.1
	grain	0.037	0.014	0.68	6.15	0.23	0.05	33.7
	shoot	0.041	0.086	**6.68**	3.05	0.89	0.61	12.8
	grain	0.021	0.010	0.54	5.14	0.23	0.02	27.6
Potato	shoot	**1.52**	**2.55**	**4.42**	21.2	**13.8**	1.16	51.6
	shoot	**1.68**	**2.64**	**6.16**	18.7	**11.8**	1.72	54.9
	tuber	0.084	0.36	0.32	9.05	1.18	0.09	19.4
Natural range		< 0,5	<0,5	0,1-1	2-20	< 3	< 10	5-100

** Numbers in bold exceed the natural range set by Scheffer and Schachtschabel 1992*

Assessing the state of TEs in cultivated soils of the drylands areas showed that they are derived from different sources like rock weathering and accumulation caused by pedogenic processes. Additional sources of TEs in the soils are attributed to intensive fertilizer application and the use in irrigation of non-treated sewage water, containing industrial waste. These sources are determining both the background values and thresholds detected in the Quaternary, alluvial, soils of Lebanon.

The raised concerns on food safety are justified by the calculated pollution index, ecological risks index and potential pollution response index which revealed 60% of analyzed soil samples in the Central Bekaa plain located along a transect from the river to the hill summit representing moderate and high ecological risks, notably from Cd and Pb. Linking soil quality with soil physico-chemical properties suggests the creation of local, adapted to soil conditions, thresholds for TEs pollution in the arid and semiarid Mediterranean zones. This also suggests defining the suitable agricultural or nonagricultural land uses.

CONCLUSION

Human activities are the main factors contributing to additional soil contamination and probable pollutants transfer to soil-plant and water ecosystems, notably in plant accumulators like lettuce. The TEs content on the soil surface of the Central Bekaa plain increased by more than 50% for Co, Cr, Ni, Cu, Zn and by more than 100% for Pb. A highly significant correlation between Cu and Zn and between Cr and Ni indicating similar origin and behavior was found. Up to 60% of analyzed soil samples have moderate and high risks pollution index, ecological risks index and potential pollution response index. A low ecological risk from soil Cr was detected. The increased content of Cr in wheat and potato shoots points to indirect risk of TEs transfer with consumed animal products. On the contrary, the riskiest element in this study (Cd) showed levels exceeding the natural range only in potato shoots. Although grown on multifunctional soil, some accumulation of Cr and Cd was found in the lettuce. These conditions suggest the necessity to consider not only the form of TEs in Quaternay dryland soils but also other soil-TE-plant interactions to assess the potential and actual ecological risk. A differential approach based on the integrated consideration of soil conditions and quality as well as crop response can provide relevant information for decision makers and landowners for suitable and sustainable land use to reduce and stop TEs associated public health risks and environmental hazards.

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