DISTRIBUTION AND AVAILABILITY OF ZINC AND IRON AS INFLUENCED BY DIFFERENT LAND USE SYSTEM

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ABSTRACT

Land use has a strong influence on soil. This paper is based on a research that was conducted to study the effects of different land use patterns in heavy metal accumulation and to measure the bio-availability of heavy metals. Significant difference was found in soils undergoing different land use systems, as well as among different heavy metals. The results showed that there was a large difference in effects of accumulation of Iron (Fe) and Zinc (Zn) in soils under different land use patterns. Based on the assessments of heavy metal concentrations in soil of maize field or wheat cultivated land, the higher accumulation of heavy metals was found in fallow land as compared to pasture lands. While minimum concentration was found in forest land (both thick and thin). The concentration of metals considerably varied in order of $HClO_4 + HNO_3 > Na_2EDTA > NaOH > KNO_3 > H_20$ for Zn and other metals. Results from the study showed that land use effects soil depth and the concentration of heavy metals decreases with soil depth.

Keywords: *Crops, Heavy metals, Land use system, soil.*

1. INTRODUCTION

Land utilization has significant implications for heavy metal concentration in the soil. Change in land use usually leads to a change in cultivation management, which may deeply influence the soil quality [20]. As heavy metals in soils have direct influence on human health through food intake, the content of heavy metals is becoming one of the most important evaluation indices for soil quality. The effects of land use patterns on heavy metal accumulation have been investigated that mainly focused on farmland, uncovered vegetable land, forest land and orchards [43].

Mo¨ller, A., et al. (2005) assessed the extent and severity of heavy metal contamination of arable soils of Ghouta, Damascus – an area of intensive agricultural production [1]. The group examined the present degree and spatial distribution of heavy metal concentrations in 51 soil profiles and in 22 topsoil samples in the Ghouta area. The soils were digested with aqua regia for heavy metal analysis. Lead (Pb), Copper (Cu), and Zinc (Zn) concentrations in the topsoils exhibited increased values due to anthropogenic impact. The major sources for heavy metal contamination in Damascus city are most possibly emissions from vehicles. These emissions transported by air and sewage water together with household and industrial sewage effluents have been considered to be responsible for the increased heavy metal concentrations found in the soils of the central Barada area. However, the values in most of the cases were below tolerable limits for agricultural use. Chromium concentrations up to 1800 mg kg^{-1} were found near a tannery industrial estate. Concerning the health risk to the population, bioavailability and mobility of heavy metals seems to be of minor importance in view of the soil properties of the study area. However, direct ingestion of soil, e.g., by children and inhalation of dust may contribute largely to the accumulation of heavy metals in human and livestock.

Land use has always had a strong influence on soils. In most areas it is the main factor in determining soil quality [25]. Threats to soils, such as erosion, contamination, humus reduction, sealing and excavation can be linked to land use [8]. It is important to gain sufficient knowledge about the effects of different types of land use on soil properties and on the capacity of the soil to fulfil certain functions. Urban environments are the areas where soils most directly interact with humans [38]. Many researchers have highlighted the need for a better understanding of urban soils, focusing on the information needed for soil management [37]. The prolonged presence of the contaminants in urban soils and their proximity to people are increasing the exposure of the urban population to heavy metals. Information on the mobilization, dispersion, deposition and distribution of potentially toxic metals in urban ecosystems plays an important role in the assessment of trace metal contamination and in the evaluation of potential environmental and health implications [7].

Although greenhouse vegetable fields are an important land use pattern that developed very rapidly in recent years and contributed largely to the supply of agricultural products, especially vegetables. There are some cultivation practices, such as excessive and inappropriate use of chemical and organic fertilizers, that when applied for vulnerability management practices, caused soil quality to degrade in greenhouse vegetable fields. A few studies concerning the accumulation of heavy metals in soils have also been made [29]. Therefore, research on heavy metal accumulation and the rules of variation on land-use patterns has important theoretical and

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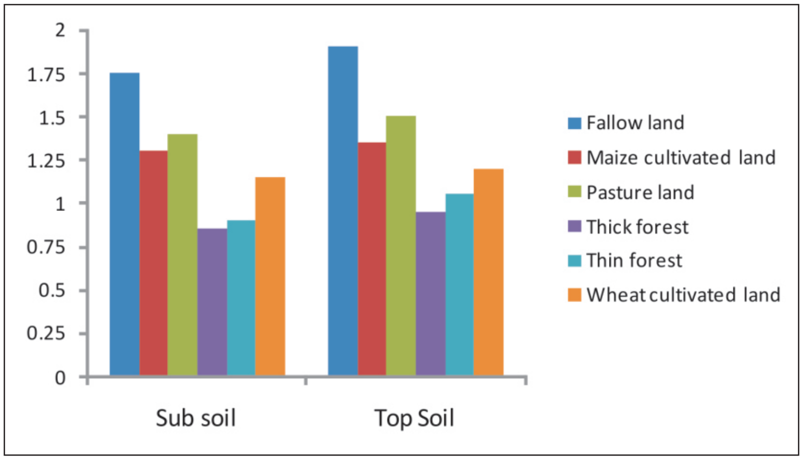

Figure-1a: KNO_3 Fe mg kg^{-1}
Fe content in top and sub profiles of different land use systems

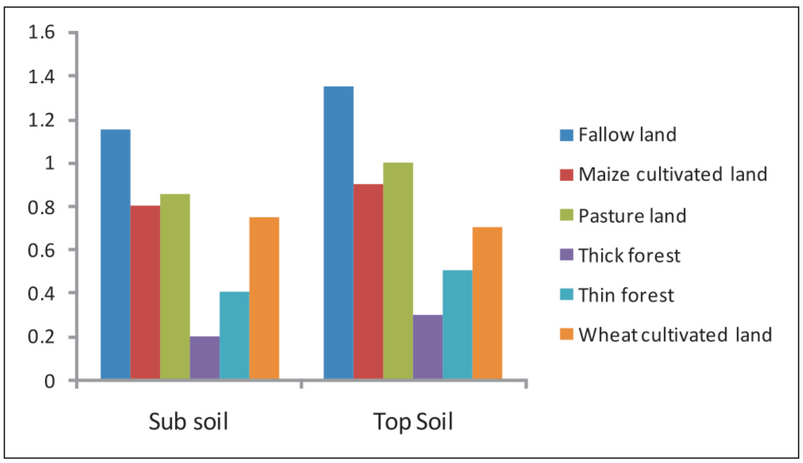

Figure-1b: H_2O Fe mg kg^{-1}
Fe content in top and sub profiles of different land use systems

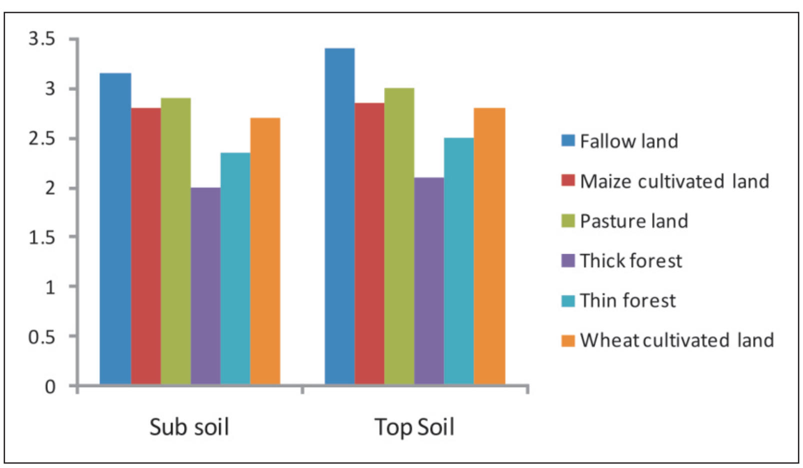

Figure-1c: NaOH Fe mg kg^{-1}
Fe content in top and sub profiles of different land use systems

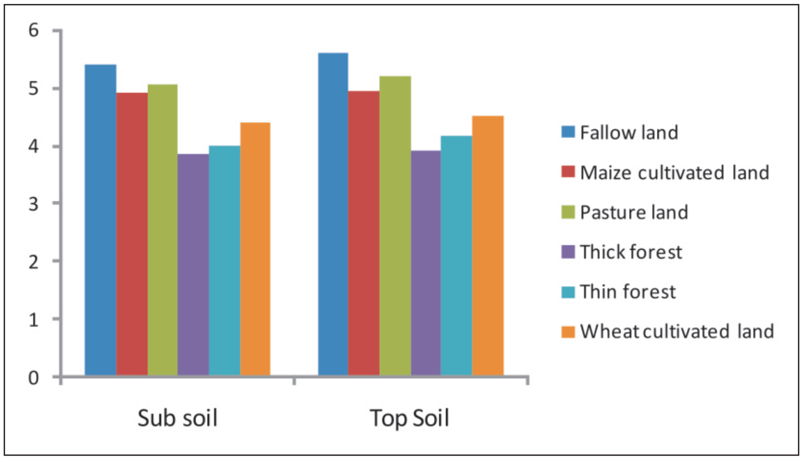

Figure-1d: EDTA Fe mg kg^{-1}
Fe content in top and sub profiles of different land use systems

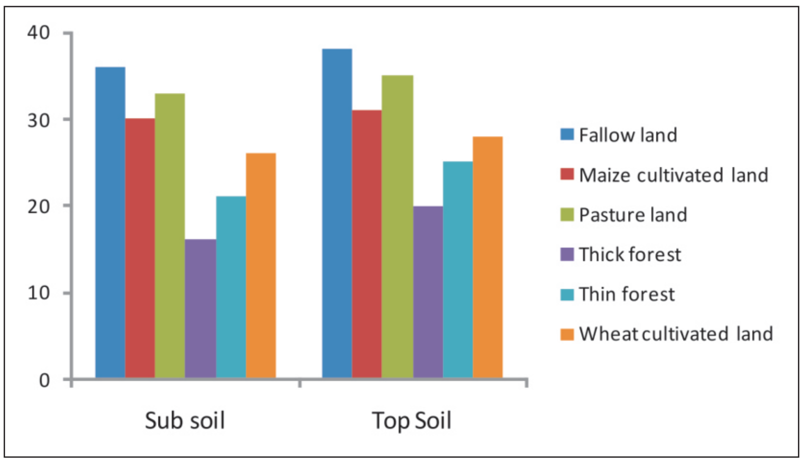

Figure-1e: HNO_3 Fe mg kg^{-1}
Fe content in top and sub profiles of different land use systems

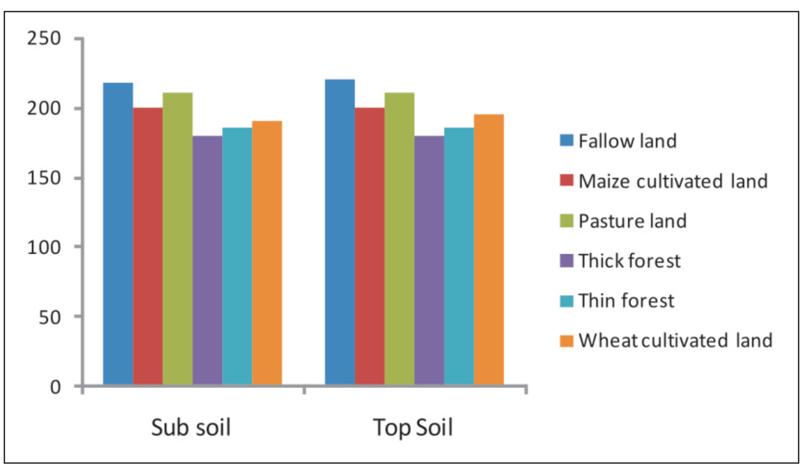

Figure-1f: Soil (Total) Fe mg kg^{-1}
Fe content in top and sub profiles of different land use systems

practical value not only on the optimum utilization of land, but also on preventing excessive accumulation of heavy metals which leads to degradation of soil quality [30]. The research focused on the impacts of different land use patterns on heavy metal accumulation in soils. It aimed to provide a reasonable theoretical basis for ecological risk assessment, forecasting of heavy metal accumulation in soils and sustainable use of soil resource under highly intensive farming.

Bai, L.Y., et al. (2010) studied heavy metal accumulation in soils of different land patterns, and its influencing factors, which would provide a theoretical basis for controlling the content of heavy metals in soils [4]. To identify the effects of land use on the accumulation of heavy metals in soils, 148 soil samples were collected from four land use patterns, including greenhouse field, uncovered vegetable field, maize field and forest field in China. Cr, Ni, Cu, As, Cd, Pb, and Zn contents of those samples were determined with Inductively Coupled Plasma (ICP) and ICP-Mass. The result showed that there was rather a large difference in effects of the accumulation of Cr, Ni, Cu, As, Cd, and Zn in soils under different land use patterns except for Pb. Based on the assessment that compared with background concentrations in soil, a higher accumulation of heavy metals was found, in greenhouse and uncovered vegetable fields, and much less in maize field and forest area. The mean contents of heavy metals in soils from high to low were arranged in order of greenhouse field, uncovered vegetable field, maize field, and forest field. Cd and Cu had relatively serious accumulation in soils compared to Cr, Ni, As, and Zn. The accumulation of heavy metals, such as Cr, Ni, Cu, As, Cd, and Zn in soils was significantly affected by land use patterns. It was suggested that the application of chemical fertilizers, organic fertilizers and pesticides with high contents of heavy metals should be avoided to prevent the accumulation of heavy metals and keep high quality soils for sustainable use.

Essentially, the heavy metals have only become a focus of public interest since analytical techniques have made it possible to detect them even in very small traces or amounts. The relatively careless handling of heavy metals and their compounds in former times can partly be explained by the fact that their effects were unknown. Today analytical detection is possible down to a thousandth of a mg kg^{-1} for certain matrixes. This has made it possible for toxicologists in animal experiments to follow up the effects of individual substances down to the smallest concentrations. Their warnings particularly with regard to the effects on health of chronic consumption and the accumulations to which this leads have startled the public and at times mostly as a result of the activities of so-called pressure groups have generated genuine hysteria [2]. All this has taken place in the context of a steady increase in the processing of all types of heavy metals in industry and the household. Therefore, proper disposal, recycling and the regulation of the application of sewage to agricultural land, have assumed great importance [16].

Hovmand, M.F., et al. (2008) analyzed atmospheric heavy metal (HM) deposition (bulk precipitation) in Denmark, combined with European emission inventories, that form the basis for calculating accumulated atmospheric input to a remote forest plantation on the island of Laesoe [34]. Soil samples were taken in two depths that is from 0-10 cm and 10-20 cm from eight forest sites at the island to determine the increase in heavy metal content in the eolian deposited top soils of the plantation. Concentrations of lead, cadmium, copper, zinc, vanadium, nickel, and arsenic were determined in atmospheric deposition and in soils. The accumulated atmospheric deposition is of the same magnitude as the increase of these metals in the top soil.

Although soil heavy metal pollution is often mentioned, little recent information is available on heavy metal transfer from soil to vegetables [42]. Some studies reported that the bioavailability of soil metal to vegetable is controlled by soil properties, soil metal speciation and plant species [13]. In addition, foliar uptake of atmospheric heavy metal emissions have also been identified as an important pathway of heavy metal contamination in vegetable crops [35].

Hao, et al. (2009) conducted study on vegetable fields in peri-urban areas, from where they received large amounts of extraneous heavy metals because of rapid urbanization and industrialization in China [22]. The concentrations of Cu, Zn, and Pb in 30 soil samples and 32 vegetable samples collected from 30 different sites in Southern Jiangsu Province of China were measured and their transfer from soil to vegetable was determined. The results showed that the soil samples had wide ranges of pH (4.25–7.85) and electrical conductivity (EC) (0.24–3.42 dS m^{-1}). Among the soil samples there were four soil samples containing higher Cu and two soil samples containing higher Zn concentrations than those specified in the Chinese Soil Environmental Quality Standard. However no vegetable sample was found to contain a high level of Cu or Zn. In contrast one vegetable sample contained 0.243 mg Pb kg^{-1} FW that was above the Chinese Food Hygiene Standards whereas the corresponding soil Pb concentration was lower than the Chinese Soil Environmental Quality Standard.

Vegetable crop plants have high ability to accumulate metals from the environment, and may pose risks to human health when they are grown on or near contaminated lands, and consumed. Metal accumulation in plant depends on plant species, growth stages, types of soil and metals, soil conditions, weather and environment [3]. Thus, accumulation of heavy metals in the edible parts of vegetables represent a direct pathway for their incorporation into the human food chain [19]. The health risk will depend upon the land use systems, its physical characteristics, types of vegetables cultivated and the consumption rate [12].

2. MATERIALS AND METHODS

The soil samples were collected from six different land systems. These samples were taken from Thick forest (THF), Thin forest (TNF), Pasture land (PSL), Fallow land (FWL), Wheat cultivated land (WCL) and Maize cultivated land (MCL). From each land system, two soil samples were taken, i.e., one from top soil profile (0-20 cm) and one from sub-soil profile (20-100 cm), and each sample was replicated three times. Heavy metal fractions were determined by sequential extraction procedure. For determination of total metal concentration, samples were digested with HNO_3^- $HClO_4$ (1:5) on hot plate and then brought to a volume of 50 ml with distilled water. Polarized Zeeman atomic absorption spectrophotometer was used in order to determine the concentration of metals.

Modified version of sequential extraction procedure was used in order to fractionate different forms of metals (Pb, Cd, Zn, Ni, Cu, Fe). Sequential extraction was carried out for each soil sample of six different land systems by using 5 g of soil sample in 50 ml centrifuge tube. The trace elements were fractionated into exchangeable, adsorbed, organically bound, carbonate precipitated and residual forms by sequential extraction with 25 ml of KNO_3, de-ionized with water H_2O, 0.5M NaOH, 0.005M Na_2EDTA, 4M HNO_3. All these chemicals were added step by step and after the addition of each chemical, samples were shaken for 16 hrs in a shaker and then centrifuged for 10 min at 2500 rpm. The resulting supernatant solution was filtered by a 0.22 µm filter. The metal content in all these samples were determined by using Polarized Zeeman atomic absorption spectrophotometer using different standards.

3. RESULTS AND DISCUSSION

Heavy metals fractionation through different land systems: Thick forest (THF), Thin forest (TNF), Pasture land (PSL), Fallow land (FWL), Wheat cultivated land (WCL) and Maize cultivated land (MCL)], showed significant difference in all land systems. The concentration of heavy metals considerably varied in order of $HClO_4$ + HNO_3 > Na_2EDTA > NaOH > KNO_3 > H_20 for metals, such as Zinc (Zn), Copper (Cu), Lead (Pb), Cadmium (Cd), and Iron (Fe). However the concentration of heavy metal for Ni was in the order of $HClO_4$ + HNO_3 > NaOH > Na_2EDTA > KNO_3 > H_2O (Table-1). There was a significant difference in the accumulation of different concentrations of heavy metals in different land systems. Bai, Ling-yu, et al (2010) showed highly significant difference in the accumulation of Cr, Ni, Cu, As, Cd, and Zn in soils under different land use patterns.

The Fe content in different land use systems were greater in top soil profiles than the sub-soil profiles (Figure-1). The total iron content in the fallow land having highest amounts of total, water soluble, exchangeable, carbonate precipitated, residual and organically bound forms were present in top profiles as compared to sub profiles (Figure-1). Greater Fe concentration was observed in top soil profile than in sub soils. In the surface soil horizon micronutrient distribution was controlled by soil pH and cation exchange capacity and so on [26]. The natural and human disturbance was greater in the surface horizon than in the deeper layers. Zn content in different fractions depended on respective total metal concentrations in different land system soils, showed that the metal extractability is higher in the contaminated soils as compared to non-contaminated soils irrespective of the extractant used, indicating greater potential bio-availability of metals in the contaminated soils [32].

Since heavy metals can naturally occur within some P fertilizers, and relatively high contents of Cu, Zn, and other heavy metals occur in organic manures, continuous and combined use of these nutrient sources at high application rates can lead to the accumulation of heavy metals in agricultural soils [35]. The total concentration of Zn in different land use systems was found to be the highest in fallow land soil

Table-1: Zn concentrations (mg kg^{-1}) in different Land Use Systems

Profiles	Lands	KNO_3	H_2O	NaOH	EDTA	HNO_3	Total Soil	Plant
Top-Soil	FWL	0.38	0.18	0.56	1.92	36.65	123.25	5.15
	MCL	0.27	0.13	0.38	1.42	32.45	101.75	4.45
	PSL	0.29	0.17	0.43	1.60	34.87	110.15	4.91
	THF	0.21	0.05	0.21	0.32	25.11	71.23	3.05
	TNF	0.23	0.07	0.25	0.51	25.02	77.92	3.92
	WCS	0.24	0.10	0.30	0.82	30.67	89.25	4.23
Sub-Soil	FWL	0.33	0.17	0.52	1.70	35.05	113.65	5.12
	MCL	0.25	0.10	0.31	1.25	31.15	95.15	4.32
	PSL	0.27	0.15	0.40	1.59	33.25	103.15	4.65
	THF	0.18	0.03	0.19	0.25	21.77	62.33	2.85
	TNF	0.21	0.05	0.22	0.42	22.55	65.12	3.65
	WCS	0.23	0.07	0.27	0.68	29.22	82.15	4.05
	LSD	0.005	0.007	0.006	0.032	0.317	0.068	0.089

with 123.25 mg kg^{-1} and lowest in thick forest (71.23 mg kg^{-1}) (Table-1). Zinc is a necessary element for humans, animals and plants and is often found in the limestone soils. Chemical fertilizers, pesticides and pigments add in zinc to the environment, which is also used in a variety of alloys, such as bronze and brass [36].The extractable zinc content using different extractants was noticed in the following order HNO_3 > Na_2EDTA > NaOH > KNO_3 (Table-1). Zinc was mostly concentrated in the residual fraction, although it was also present in other fractions [5]. The greater percentage of Zn in the residual fraction probably reflects the greater tendency for Zn to become unavailable [5]. A significant amount of Zn was associated with the non residual fractions in soils studied, indicating that this metal was potentially bioavailable. The exchangeable fraction is generally considered immediate nutrient reservoir for plants [13]. The greater concentration of Zn was in residual form but its content was also significant in carbonate, precipitated and organically bound form. Water and soils in the suburbs have suffered from heavy metal pollution to some extent, which might lead to excessive accumulation of one or several heavy metals, such as Cd, Hg, Cr, As, and Pb in vegetables [25]. Metals associated with carbonates would be susceptible to pH changes, and may be regarded as potentially phytoavailable.

4. CONCLUSIONS

A study was conducted to compare changes in heavy metals fractions through different land systems, which were thick forest (THF), thin forest (TNF), pasture land (PSL), fallow land (FWL), wheat cultivated land (WCL) and maize cultivated land (MCL). The research focused on the impacts of different land use patterns on heavy metal accumulation in soils. It aimed to provide a reasonable theoretical basis for ecological risk assessment, forecasting of heavy metal accumulation in soils and sustainable use of soil resource. The study showed significant difference in all land systems. Heavy metals were observed highest in fallow land, and lowest in thick forest land. The concentrations varied in order of FWL > PL > MCL > WCL > TNF > TFS. The concentrations of heavy metals considerably varied in order of $HClO_4$ + HNO_3 > Na_2EDTA > NaOH > KNO_3 > H_20 for Zn, Cu, Pb, Cd, Fe. However, the concentration of nickel was in the order of $HClO_4$ + HNO_3 > NaOH > Na_2EDTA > KNO_3 > H_2O. Results showed that land use affects soil depth and concentration of heavy metals decreased with soil depth. This research carried on heavy metal accumulation under different land use systems has important theoretical and practical value, not only on the optimization of land use but also on preventing excessive accumulation of heavy metals that leads to degradation of soil quality.

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