American-Eurasian J. Agric. & Environ. Sci., 1 (3): 282-287, 2006
ISSN 1818-6769

Heavy Metal Distribution: A Survey from Ordu Province in the Black Sea Region

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Abstract: Heavy metals may be important trace elements in the nutrition of plants, animals and humans, while others are not known to have positive effects on nutrition status. However, all of these may have toxic effects if they occur excessively. Actually Ordu province, near the Black Sea and part of the eastern Turkey, is the center of hazelnut production. The objective of the present investigation was to evaluate some total heavy metal contents such as Cd, Pb, Ni, Cu and Zn in soils of agricultural ecosystems in Ordu province from Black Sea region in Turkey. It has been determined total heavy metal contents of soils were 0.3-5.1 μg Cd g^{-1}, 39.7-245.6 μg Pb g^{-1}, 16.7-270.0 μg Ni g^{-1}, 57.5-316.6 μg Cu g^{-1} and 35.5-582.5 μg Zn g^{-1}. Relationships between total heavy metal contents and some soil properties were investigated in forty disturbed soil samples. Also, significant relations between total heavy metal contents and some soil properties, especially clay content, were determined at $p<0.01$.

Key words: Agricultural ecosystems · heavy metals · copper · cadmium · nickel · lead

INTRODUCTION

It is well known that micronutrients such as iron (Fe), manganese (Mn), copper (Cu) and zinc (Zn) are essential metals for plant growth and yield. However, plants may accumulate heavy metals existing in soils, such as cadmium (Cd), nickel (Ni), chromium (Cr) and lead (Pb), they are not essential for plant growth also may cause serious problems to the environment [1, 2]. The concentration of heavy metals in soil solution plays a critical role in controlling the availability of ions to plants [3]. The solubility and, therefore, the bioavailability of heavy metal ions vary widely because many factors influence their concentration in soil solution. The most important factors affecting metal solubility or availability are soil pH [4], clay content [5] and organic matter content [2, 6].

Soil heavy metal contamination, mainly comes from industrial activity, atmospheric deposition, field application of sewage sludge and the other agricultural practices (fertilizers, pesticides etc.) is one of the major environmental risks in agricultural ecosystems and industrial region of Turkey. This contamination has received much attention in recent years. In the last decades, human activities have continuously increased the levels of heavy metals circulating in the environment [7]. Heavy metals can be also found in the parent rock from which soils have developed. The anthropogenic heavy metals are believed to be easily accumulated in the topsoil [8, 9], causes in potential problems such as toxicity to plants and animals [10, 11], accumulation in food chain, perturbation of the ecosystem and adverse health effects [12, 13]. Much research has been conducted on heavy metal contamination in soils from various anthropogenic sources such as industrial wastes [14] automobile emissions [15], mining activity [16] and agricultural applications of sewage sludge, fertilizers and pesticides [17-19].

Total heavy metal analysis may give information on possible enrichment of the soil by heavy metals, but generally and for most elements, there is a not sufficient criterion for estimating their biological effect, availability of the metals for plants [20].

Ordu province is an area with intensive agricultural and horticultural production surrounds in the Black Sea. It is one of the major hazelnut growing areas of Turkey. The objective of this study was to determine background levels of heavy metals in agricultural soils of Ordu province and to assess the relationships between total heavy metal concentrations and some soil properties.

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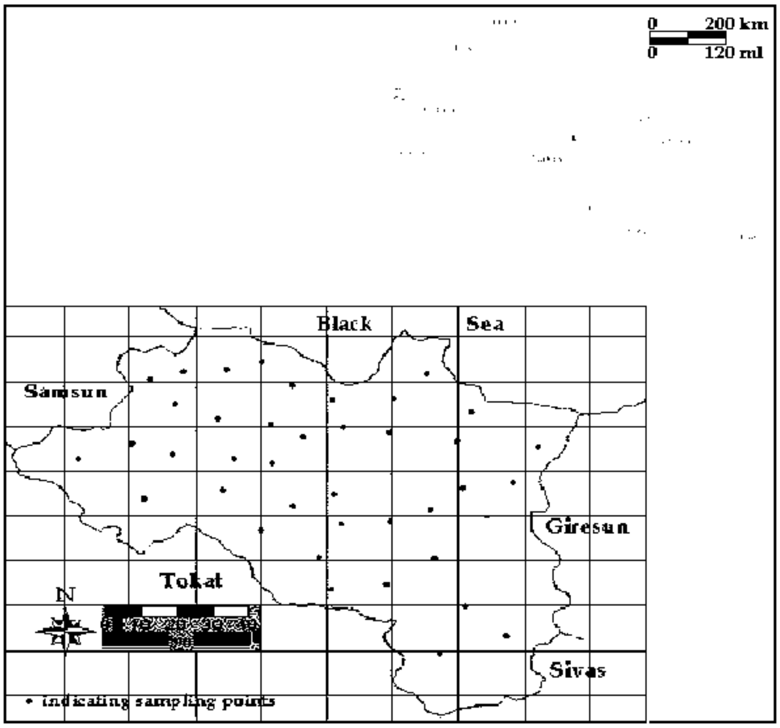

Fig. 1: Location of the sampling sites

MATERIALS AND METHODS

Study site: The study area is entitled as Ordu province (Fig. 1) and is located in the Black Sea region of the northern Turkey (40°18'N, 38°40'E) and has semi-humid climate with temperatures ranging from -7.2°C in January to 33°C in June. The annual mean temperature is 13.9°C and the annual mean precipitation is 1103 mm based on a 25-year period [21].

Soil sampling and preparation for analysis: Soil samples of field-moist weight were collected from the 0-20 cm in depth at forty sampling points using a soil sampler. Plant residues and roots were removed by hand and soils were sieved through a 2-mm grid and transferred to laboratory cool boxes. Samples were kept at room temperature and then analyzed. All data reported are means of three replicates and are expressed on a moisture-free basis. Moisture content was determined by drying the soil samples at 105°C for 24 h [22].

Soil characterization: The following basic soil characteristics were determined: pH in 1:2.5 (w/v) soil:water suspension by pH-meter [23]; $CaCO_3$ content by Scheibler Calcimeter [22]; particle size distribution by the hydrometer method [24]; organic carbon content by the modified Walkley-Black method [25].

Determinations of heavy metals: The soil samples were dried at 110°C for a total period of one day. Soil samples were sieved using 0.074 mm sieves for the sake of homogeneity. Weighted samples were transferred into acid baths. The acids volumes used were 15 ml HCl (12 M) and 5 ml HNO_3 (14 M) for each sample (10:1 extractant to soil ratio). On a hot plate, the samples were heated at 120°C. After observing reddish gas exit from the heated samples and making sure that the prepared samples are almost dry, the samples were removed from the hot plate. A 10 ml HCl and HNO_3 mixture (both were of 1% v/v) was added to each sample. Whatman papers were used to filter the prepared samples into the test tubes. Another blank sample was prepared without soil samples. For each heavy metal of concern, three standards were used for completing the analyses using a Perkin Elmer 2280 model atomic absorption spectrophotometer with flame or graphite furnace [26]. All data reported are means of three replicates and are expressed on a moisture-free basis.

Statistical analysis: Statistical analyses were performed using the Statistical Package for Social Science (version 10.0; SPSS Inc., Chicago, IL, USA) program. Pearson's correlation coefficients and P-values were calculated for all possible variable pairs.

RESULTS AND DISCUSSION

Soil properties: Some physico-chemical properties of soil samples obtained from 40 sampling points at 0-20 cm depths in the total of 6000.52 km^2 study area are presented in Table 1.

Soil texture was not similar for all samples and also clay, silt and sand contents of the forty samples were 8-53, 13-34 and 23-79%, respectively. The mean value of soil pH was 6.38 which have slightly below the well established values (6.7-7.3) in cultivated soils The high $CaCO_3$ in few soils (2 soil samples have >25% $CaCO_3$) probably may be due to their origin from lime parent material. Twenty-nine soil samples were non calcareous. The organic matter content ranged from low to high (Table 1).

Heavy metal concentrations: The descriptive statistics on the heavy metal concentrations of the soils are presented in Table 2.

The total heavy metals of soils were 0.25-5.13 μg g^{-1} Cd, 39.69-245.61 μg g^{-1} Pb, 16.69-269.91 μg g^{-1} Ni, 57.53-316.64 μg g^{-1} Cu and 35.47-582.55 μg g^{-1} Zn, respectively. Some individual values of these heavy metals exceeded the upper limit considered toxic for corn plants; 3 to 8 μg g^{-1} for Cd; 60 to 125 μg g^{-1} for Cu; 100 to 400 μg g^{-1} for Pb and generally the range of excessive or toxic amounts of Ni in most plant species varies from 10 to 100 μg g^{-1} [27]. Background levels of the studied elements are presented Table 3.

In certified values, background levels of the studied heavy metals are generally low in content comparing the found values. Also heavy metal concentrations are very close to the worldwide average value in soil.

Table 1: Descriptive statistics on selected soil physical and chemical properties (n = 40)

Soil property	Range	Arithmetic mean	Geometric mean
Sand %	23-79	49.78	47.77
Silt %	13-34	24.83	24.17
Clay %	8-53	25.40	22.84
Organic carbon %	0.49-3.17	1.64	1.48
$CaCO_3$ %	0.01-49.81	4.50	0.46
pH, (1:2.5 v/w soil:water)	3.90-8.50	6.38	6.23

Table 2: Heavy metal concentrations of soil samples (μg g^{-1})

Heavy metal	Range	Arithmetic mean	Geometric mean
Cd	0.25-5.13	1.70	1.50
Pb	39.69-245.61	74.58	68.90
Ni	16.69-269.91	69.99	58.01
Cu	57.53-316.64	126.33	118.22
Zn	35.47-582.55	243.31	190.95

Total Cd contents ranged from 0.25 to 5.13 μg g^{-1} (Table 3). The total Cd contents of soils are generally within the range of 0.1 to 1.0 μg g^{-1} found in soils by Kloke [28]. The mean value of total concentration of Cd (as arithmetic mean 1.70 μg g^{-1}) was much higher than background level of the soil [29].

Total Pb contents in soil samples ranged between 39.69 to 245.61 μg g^{-1} (Table 3), total Pb contents of soils are within the range of 0.1 to 20 μg g^{-1} found in soils respectively [28]. Mean value of total concentration of Pb (74.58 μg g^{-1}) was much higher than background value of the soil [29].

Total Ni contents of soil samples varied between 16.69 to 269.91 μg g^{-1} (Table 3), total Ni contents of soils are with in the range of 2 to 50 μg g^{-1} found in soils generally [28]. Mean value of total concentration of Ni (69.99 μg g^{-1}) was much higher than background value of the soil for Ni [29]. In general, in crop plants there is much more concern about nickel toxicity, for example, in relation to application of sewage sludge which is often high in nickel content [30].

Table 3: Heavy metal concentrations of soil samples (μg g^{-1})

	Certified values				
Heavy metal	GAP region	Karadeniz region	Bafra plain	USA	Found values
Cd	1.17-2.57	1.81	1.8-2.7	0.18	0.25-5.13
Pb	13.75-34.57	36.01	46.79-144.15	10.4	39.69-245.61
Ni	60.23-111.37	112.95	n.a	16.5	16.69-269.91
Cu	18.34-36.5	67.22	25.5-58.5	15.6	57.53-316.64
Zn	81.2-650	279.43	n.a	41.4	35.47-582.55

na: no available, [1]Hakerlerler *et al.* [31], [2]Kızılkaya *et al.* [32], [3]Aşkın *et al.* [33], and [4]Holmgren *et al.* [34]

Table 4: Heavy metal contents of agricultural areas and tolerable levels [28]

	(µg g^{-1})	
Heavy metal	Range	Tolerable level by soil
Cd	0.1-1	3
Pb	0.1-20	100
Ni	2.0-50	50
Cu	1.0-20	100
Zn	3.0-50	300

Total Cu contents of soil samples varied from 57.53 to 316.64 µg g^{-1} (Table 2). Total Cu contents of soils are generally within the range of 1 to 20 µg g^{-1} by Kloke [28]. The mean value of total concentration of Cu (126.33 µg g^{-1}) was much higher than background value of the soil [29]. In the study of GAP Region soils by Hakerlerler *et al.* [31], also found 18.34 to 36.50 µg g^{-1} Cu. Similar findings were reported by Kızılgöz *et al.* [35].

Total Zn contents in soil samples ranged between 35.47 to 582.55 µg g^{-1} (Table 3), total Zn contents of soils are within the range of 3 to 50 µg g^{-1} found in soils respectively [28]. Mean value of total concentration of Zn (243.31 µg g^{-1}) was much higher than background value of the soil [29].

Heavy metal contents of agricultural areas and tolerable levels are presented Table 4.

On average the heavy metal contents of the soils were normal, but many of the soils showed an increased content compared to the normal range. This confirmed the findings of Hakerlerler *et al.* [31], Kızılkaya [36], Kızılkaya and Aşkın [37] and in some cases there was also a clear enrichment, which could be due to air pollution and to the application of fertilizer. In general, the heavy metal contents in arable soils were rather slightly increased levels and were rarely above the tolerable value. This is rather surprising because most of the present and historical agricultural practices releasing heavy metals are located in those areas. Apparently there was not much long-term accumulation in soils. From the frequency distribution, however, it appears that there were a number of soils clearly enriched with heavy metal, as there was no normal distribution. In Ordu province, where unknown industrial sources of heavy metal occur, the contents no showed a normal distribution with an average and median value. From those results it is obvious that other sources (fertilizers and manure) have clear impact on the heavy metal contents of arable soils. Additionally, Pb was poorly correlated with most of the other elements in spite of the occurrence of some common industrial sources and agricultural practices except for vehicle traffic in land. The use of Pb in fuel has made it the most widespread pollutant. Consequently, this could be due to a midrange transport of heavy metal containing dust particles originating from human activities and agricultural practices (fertilizers and pesticides) in the soils around Ordu province.

The relationships between soil heavy metal concentration and some soil properties: Correlation analysis was used to establish relationships between total concentrations of heavy metals and soil physicochemical parameters. Table 5 shows the correlation coefficients have relations between Cd, Pb, Ni, Cu and Zn concentrations of soils and some soil properties.

Total Cd, Ni, Pb, Cu and Zn contents were positively correlated with the soil clay content. Organic carbon content was not correlated with the total heavy metal concentrations, because of large soil clay contents of the samples and these metals probably adsorbed on the clay fraction. Shuman [38] also found that heavy metals in soil were associated primarily with the clay fraction. Similarly, Lee *et al.* [39] found that positive correlations between total heavy metal contents and clay content of soils in Oklahoma Benchmark soils. Contents of Cd, Ni, Pb and Cu

Table 5: Correlation coefficients between soil parameters and total concentration of heavy metals

	Heavy metal concentration (µg g^{-1})				
Soil properties	Cd	Ni	Pb	Cu	Zn
Sand %	-0.425***	-0.508***	-0.294	-0.576***	-0.367*
Silt %	-0.011	0.085	-0.096	0.357*	0.137
Clay %	0.516***	0.582***	0.407**	0.535***	0.384*
Organic carbon %	0.141	0.145	0.202	0.034	0.172
$CaCO_3$ %	0.504***	0.721***	0.505***	0.510***	0.202
pH	0.471***	0.423**	0.235	0.331*	0.141

***p<0.001, **p<0.01, *p<0.05

positively correlated ($p<0.01$) with $CaCO_3$ content. This observation concurs with the findings in other studies [40, 41]. Although soil pH gave positive correlations with total Cd, Ni and Cu contents, the values of soil pH did not affect the total concentration of the other metals (Table 5).

CONCLUSIONS

Actually the anthropogenic contribution of heavy metals into the environment far exceeds natural inputs. Sources of heavy metals include river inputs, local runoff and atmospheric deposition, agricultural practices etc. The arable soils that were not in the vicinity of sources of heavy metal containing dust, showed rather normal values of heavy metal contents. However for most of the elements there was some slight increase above the background values and in a very few cases the soils can be considered as slightly contaminated. The influence of human activities on the soil heavy metal contents was clearly presented. In the past, the Cu and Zn contents were slightly raised, possibly due to excessive fertilization with animal manure. However, none of these soils can be considered as really contaminated. In spite of the very long history of pollution Ordu province, the increase in the soil concentration was rather limited for heavy metals. Apparently, the well-drained acidic soils do not allow much accumulation of these elements.

In the area where these soils were sampled there are only a few minor industrial sources and also less manure was used in the past. The territories affected the agricultural practices and the environmental factors.

It is important to observe contamination levels with heavy metals in agricultural soils and monitor soil contamination status by regular soil samplings several means of heavy metals mitigation effect could be applied in the agricultural area such as addition of adsorbent materials-clay and zeolith to soils, phytoremediation and bioremediation. Geochemical investigations of agricultural soils in the Ordu province could help to estimate background concentrations of Cu, Cd, Pb, Ni and Zinc.

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