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ARASTIRMA MAKALESİ /RESEARCH ARTICLE

COPPER, LEAD, CADMIUM AND NICKEL FRACTIONS IN AGRICULTURAL SOILS: A STUDY IN BAFRA PLAIN Tayfun AŞKIN¹, Rıdvan KIZILKAYA², Coşkun GÜLSER³

ABSTRACT

The objective of the present investigation was to evaluate some total heavy metal contents (Cu, Cd, Ni and Pb) and their fractions, such as exchangeable (EX-), organic (OM-), Mn oxide (MnO-), amorphous Fe oxide (AFeO-), crystalline Fe oxide (CFeO-) and residual (R-) fractions in soils of agricultural ecosystem soils in Bafra Plain in Turkey. Total heavy metal contents and their fractions with some soil properties were investigated in twenty disturbed soil samples. It has been determined that the total heavy metal contents of soils were 25.5-58.5 μ g Cu g⁻¹, 1.8-2.7 μ g Cd g⁻¹, 76.1-210.4 μ g Ni g⁻¹, and 46.8-144.2 μ g Pb g⁻¹. On the other hand, the significant relations (p<0.01) were determined between total heavy metal contents and soil clay contents.

A sequential fractionation showed that 1.39-13.04 % total heavy metals were EX- (1.39 % Cu, 13.04% Cd, 2.88% Ni, 2.76% Pb), 1.85-4.35 % were OM- (1.85 % Cu, 4.35% Cd, 2.46% Ni, 1.88% Pb), 2.54-13.43 % were MnO- (2.54 % Cu, 8.70% Cd, 5.34% Ni, 13.43% Pb), 8.70-27.25% were AFeO- (19.63 % Cu, 8.70% Cd, 27.25% Ni, 23.99% Pb), 4.35-24.58 % were CFeO- (21.48 % Cu, 4.35% Cd, 24.58% Ni, 22.41% Pb) and 24.19-52.17 % R-(37.18 % Cu, 52.17% Cd, 31.74% Ni, 24.19% Pb). The positive correlations were obtained between the heavy metal fractions, OM-, EX- and Sum-, and some soil properties such as, organic carbon and clay content.

Key Words: Agricultural soils, Heavy metal fractions, Copper, Cadmium, Nickel, Lead

TARIM TOPRAKLARINDA BAKIR, KURŞUN, KADMİYUM VE NİKEL FONKSİYONLARI: BAFRA OVASINDA BİR ÇALIŞMA

ÖZ

Bu araştırmanın amacı; Bafra ovası tarımsal ekosistem topraklarında, bazı toplam ağır metalleri (Cu, Cd, Ni ve Pb) ve bunların değişebilir (EX-), organik bağlı (OM-), Mn okside bağlı (MnO-), amorf Fe okside bağlı (AFeO-), kristalin Fe okside bağlı (CFeO-) ve artık (R-) fraksiyonlarını araştırmaktır. Toplam ağır metal içerikleri ve fraksiyonlarının bazı toprak özellikleriyle olan ilişkileri yirmi adet bozulmuş toprak örneği kullanılarak araştırılmıştır. Toprakların toplam ağır metal içerikleri; 25,5-58,5 μg Cu g⁻¹, 1,8-2,7 μg Cd g⁻¹, 76,1-210,4 μg Ni g⁻¹ ve 46,8-144,2 μg Pb g⁻¹ olarak belirlenmiştir. Diğer taraftan toprakların toplam ağır metal içerikleriyle kil kapsamları arasında önemli ilişkiler (p<0.01) elde edilmiştir.

Ağır metal fraksiyonlarından değişebilir fraksiyonu (EX -) 1,39-13,04 % (1,39 % Cu; 13,04% Cd; 2,88% Ni; 2,76% Pb), organik bağlı fraksiyonu (OM-) 1,85-4,35 % (1,85 % Cu; 4,35% Cd; 2,46% Ni; 1,88% Pb), mangan okside bağlı fraksiyonu (MnO-) 2,54-13,43 % (2,54 % Cu; 8,70% Cd; 5,34% Ni; 13,43% Pb), amorf demir oksitlere bağlı fraksiyonu (AFeO-) 8,70-27,25% (19,63 % Cu; 8,70% Cd; 27,25% Ni; 23,99% Pb), kristalin demir oksitlere bağlı fraksiyonu (CFeO-) 4,35-24,58 % (21,48% Cu; 4,35% Cd; 24,58% Ni; 22,41% Pb) ve artık (R-) fraksiyonu 24,19-52,17% (37,18% Cu; 52,17% Cd; 31,74% Ni; 24,19% Pb) arasında değişmiştir. Toprakların organik karbon içeriği ve kil kapsamları ile ağır metallerin organik bağlı, değişebilir ve toplam fraksiyonları arasında pozitif önemli ilişkiler de saptanmıştır.

Anahtar Kelimeler: Tarım toprakları, Ağır metal fraksiyonları, Bakır, Kadmiyum, Nikel, Kurşun

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1. INTRODUCTION

Soil contamination is one of the major environmental risks in Turkey. Soil heavy metals contamination mainly comes from industrial activity, atmospheric deposition and field application of sewage sludge, has received much attention in recent years. 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 (Baker, 1990; Samsoe-Petersen et al., 2002), causes in potential problems such as toxicity to plants and animals (Ma et al., 2002; Berti and Jacobs, 1996), accumulation in food chain, perturbation of the ecosystem and adverse health effects (Forstner, 1985; Stalikas et al., 1997). In the last decades, human activities have continuously increased the levels of heavy metals circulating in the environment (Ma and Rao, 1997). Contamination of heavy metals in soil is of major concern because of their toxicity and threat to human life and the environment (Purves, 1985). Much research has been conducted on heavy metal contamination in soils from various anthropogenic sources such as industrial wastes (Parry et al., 1981) automobile emissions (Langerwerff and Specht, 1970), mining activity (Dudka and Adriano, 1997), and agricultural applications of sewage sludge, fertilizers and pesticides (Adriano, 1986; Tiller, 1989; Jensen and Bro-Rasmussen, 1992).

Soil pollution of agricultural areas surrounding big plains is a major environmental problem. The Bafra Plain is an area with intensive agricultural and horticultural production surrounds Samsun province in the Black Sea. It is one of the major agricultural areas of Turkey.

Heavy metal enrichment of agricultural soils may increase plant availability and movement of heavy metals through the food chain (Chaney et al., 1987). The problem of heavy metal toxicity is enhanced by the fact that seemingly healthy plants may accumulate them in concentrations that might endanger human health (Harris et al., 1996). Total heavy metal analysis may give information concerning possible enrichment of the soil with 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 (Ramos et al., 1994). The chemical form of a metal in the soil determines its mobilization capacity and behavior in the environment.

Several systems of heavy metal fractionation have been proposed. Heavy metals in soils may be (i) in soil solution as ionic or organically complexed (ii) on exchange sites of relative soil components; (iii) complexed with organic matter; (iv) included in oxides and hydroxides of Al, Fe and Mn; and (v) entrapped in primary and secondary minerals (Hodgson, 1963; Jenne, 1977; Viets, 1962). Heavy metals present in these categories have different remobilization behaviors under changing environmental conditions (Forstner, 1985). Geochemical forms of heavy metals in soil affect their solubility, which directly influence

their bioavailability (Xian, 1987). Several soil selective sequential extraction schemes have been described in the literature (Tessier et al., 1979; Shuman, 1979, 1985; Rauret et al., 1989).

The objective of the present study was to determine background levels of heavy metals in agricultural soils of Bafra plain in Turkey and to evaluate total heavy metal concentrations among different fractionations.

2. MATERIALS AND METHODS

2.1 Study Sites

The study areas were located in the Black Sea region, of northern Turkey (Latitude, 41°21'N; longitude, 36°15'W). The sampling areas (Figure 1) have the typical Black Sea climate (semi humid, $R_{\rm f}=47.21$), with temperatures ranging from 6.6 °C in February to 23.0 °C in August. The annual mean temperature was about 14.2 °C, and the annual precipitation was 670.4 mm (Anon, 2002).

The irrigated 20 sites were sampled from alluvial soils. These sites included intensively cultivated vegetable fields and wheat and corn fields. All sites have a history of chemical fertilizer use (e.g., diammonium phosphate, triple super phosphate and calcium ammonium nitrate) and pesticide (e.g., herbicide, insecticide) applications for 35-40 years. In addition, sewage sludge is used into soil as fertilizer on the study area (Ceyhan et al., 2002).

2.2 Soil Collection and Characterization

Twenty bulk surface (0-20 cm depth) soil samples were collected from different agricultural lands in Bafra plain. The soil samples were air dried at room temperature and passed through a sieve with 2 mm openings.

The following basic soil characteristics were determined: pH in 1:2.5 (w/v) soil:water suspension by pH-meter (Jackson, 1962); cation exchange capacity (CEC) according to Bower method (US Salinity Lab. Staff., 1954); CaCO₃ content by Scheibler Calcimeter (Soil Survey Staff, 1993); particle size distribution by the hydrometer method (Bouyoucos, 1951); organic carbon content by the modified Walkey – Black method (Jackson, 1962). Total soil heavy metal contents were determined using Aqua Regia – HF – HNO₃ and HCl solutions and Cu, Pb, Cd, Ni concentrations were determined by atomic absorption spectrophotometer (Kacar, 1995).

2.3 Fractionation Procedures of Heavy Metals

Copper, lead, cadmium and nickel distribution in the exchangeable, organically complexed, Mn oxide, amorphous Fe oxide, Crystalline Fe oxide and residual fractions were determined (Table 1) (Shuman 1979, 1983, 1985, and 1988).

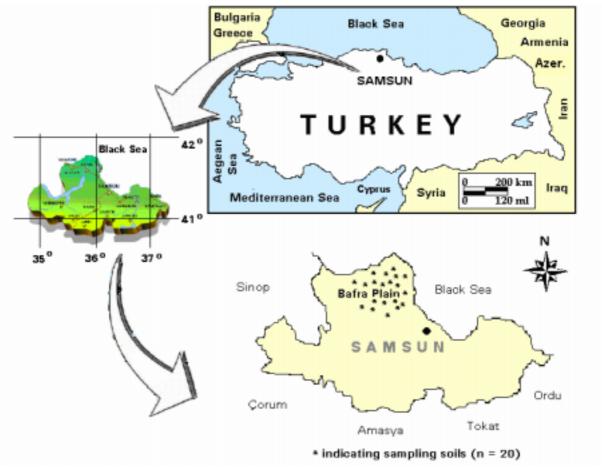


Figure 1. Location of the sampling sites

Table 1. Heavy metal fractionation procedure

Fraction	Solution	Soil, g	Solution, ml	Conditions
Exchangeable	1 M Mg(NO ₃) ₂	10	40	Shake 2 h.
(EX-)	(pH 7.0)			
Organically complexed	0.7 M NaOCl	10	20	30 min in boiling water
(OM-)	(pH 8.5)			bath. Stir occasionally.
				Repeat extraction.
Manganese oxide bound	0.1 M NH ₂ OH.HCl	1	50	Shake 30 min.
(MnO-)	(pH 2.0)			
Amorphous iron oxide	$0.2 \text{ M} (NH_4)_2 C_2 O_4 \text{ in}$	1	50	Shake 4 h in the dark.
bound (AFeO-)	0.2 M H ₂ C ₂ O ₂ (pH 3.0)			
Crystalline iron oxide	0.1 M ascorbic acid in the	1	50	30 min boiling water bath.
bound (CFeO-)	above oxalate solution			Stir occasionally.
Residual (R-)	Conc. HF, conc.HNO ₃			
	and conc. HCl in sequence			

Specific details of the fractionation procedure are given below:

Exchangeable (EX-): Ten grams of air dried, 2-mm sieved soil, and 40 ml 1 M Mg(NO₃)₂ were shaken for 2 h in a 100 ml centrifuge tube. The sample was centrifuged for 10 min., the supernatant decanted, and 40 ml of deionized water added. The sample was then shaken for 3 min., centrifuged as before use and two centrifugates combined for analysis.

Organically complexed (OM-): Twenty milliliters of 0.7 M NaOCl, pH 8.5, was added to the soil in the centrifuge tube. The sample was heated in a water bath at 100 °C for 30 min., centrifuged, and the supernatant decanted and filtered using no.42 Whatman paper. This step was repeated, and the filtrates combined. After addition of 20 ml of deionized water, the sample in the centrifuge tube was shaken for 3 min., centrifuged, filtered, and the filtrate combined with the NaOCl extract.

For the following steps, the soil from the centrifuge tube was air dried and ground to pass a 0.5 mm stainless steel sieve.

Manganese oxide bound (MnO-): Five grams of soil and 50 ml of 0.1 M NH₂OH.HCl, pH 2.0, were shaken for 30 min. in a 100 ml centrifuge tube. The sample were then centrifuged and filtered as above. Fifty milliliters of deionized water was added, shaken with the soil for 3 min., and discarded.

Amorphous iron oxide bound (AFeO-): Fifty milliliters of 0.25 M NH₂OH.HCl + 0.25 M HCl were added to the soil in the centrifuge tube, followed by shaking for 30 min. at 50 $^{\circ}$ C in a water bath. The samples were centrifuged, filtered, and washed as in the previous step.

Crystalline iron oxide bound (CFeO-): Fifty milliliters of 0.2 M (NH₄)₂C₂O₄ + 0.2 M H2 C₂O₄, pH 3.0, were added to the soil in the centrifuge tube and heated for 30 min at 100° C in a water bath, swirling occasionally, The samples were then centrifuged and filtered as above.

Residual (R-): The soil samples were transferred into acid baths. The acids and their spent volumes were 6 ml conc. HCl, 2 ml conc. HF and 2 ml conc. HNO₃ for 2.5 g soil sample. 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 6 ml conc. HCl, 2 ml conc. HF and 2 ml conc. HNO₃ were added to soil sample. Whatman filter papers were used to filter the prepared samples into the test tubes.

Cu, Pb, Cd and Ni in all extracts were determined by flame atomic absorption spectrophotometer

(Perkin Elmer 2280) using and air-acetylene-flame device.

Statistical analyses were performed using the SPSS computer program-

3. RESULTS AND DISCUSSION

Some soil properties are given in Table 2. Typical alluvial soils vary from moderate to fine in texture, low in organic carbon content and alkaline in reaction. The lime (CaCO₃) contents showed high variability and were comparable with the other soil properties

Descriptive statistics of heavy metal fractions are given in Table 3. The sum of all the fractions for each heavy metal is also shown in Figure 2.

The values between the total analyses and sums of fractions are very close. This situation indicates that the procedure for heavy metal fractionation was adequate. The sum over total ratio values for Cu, Cd, Pb and Ni were 0.84, 0.91, 0.89 and 0.94 respectively. Generally, the sums of heavy metal contents were lower than the total heavy metal contents in uncontaminated or less polluted soils

Some individual values of these heavy metals exceeded the upper limit considered toxic for corn plants; Cd from 3 up to 8 $\mu g.g^{-1}$; Cu from 60 up to 125 $\mu g.g^{-1}$; Pb from 100 up to 400 $\mu g.g^{-1}$ and generally the range of excessive or toxic amounts of Ni in most plant species varies from 10 up to100 $\mu g.g^{-1}$ (Kabata-Pendias and Pendias, 2001).

3.1 Copper

Total Cu contents of soil samples varied from 25.5 to 58.5 μ g.g⁻¹ (Table 3). Generally total Cu contents of soils are within the range of 1 to 20 μ g.g⁻¹ by Kloke (1980). Mean value of total concentration of Cu was much higher than background value of the soil (43.3 μ g.g⁻¹) (Cabrera et al., 1999).

The Cu contents of soils in EX-, OM-, MnO-, AFeO- and CFeO- fractions were 1.39, 1.85, 2.54, 19.63 and 21.48 % of the total Cu, respectively. Most Cu content among the fractions was obtained in the residual fraction as 37.18 % (Fig. 2). Generally, the association with different fractions was ordered as follow: R-> CFeO-> AFeO-> MnO-> OM-> EX-.

3.2 Cadmium

Total Cd contents in soil samples ranged from 1.83 to 2.73 $\mu g.g^{-1}$ (Table 3). Generally total Cd contents of soils are within the range of 0.1 to 1.0 $\mu g.g^{-1}$ found in soils by Kloke (1980). Mean value of total concentration of Cd was much higher than background level of the soil (2.3 $\mu g.g^{-1}$) (Cabrera et al., 1999).

Table 2. Selected soil properties (n=20)

Soil properties	Observed range	Mean ± Std. Dev.	
рН	7.85 – 8.45	8.15 ± 0.16	
Organic C, %	0.86 - 2.31	1.40 ± 0.44	
CaCO ₃ , %	0.37 - 13.37	4.56 ± 3.81	
CEC, me.100g ⁻¹	11.42 – 36.18	22.33 ± 7.35	
Clay, %	28.82 - 59.48	40.83 ± 8.71	

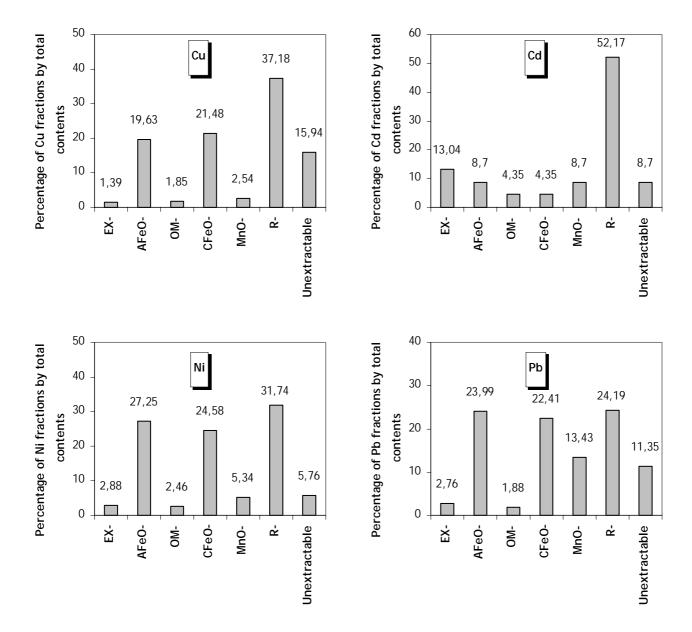


Figure 2. Percentage of heavy metal fractions by total contents

Table 3. Descriptive statistics for heavy metal fractions (n=20)

Total heavy		Heavy metal fractions						
metal		OM -	MnO -	AFeO -	CFeO -	R -		
	Cu, μg g ⁻¹							
25.5	< 0.1	< 0.1	<0.1	5.3	4.6	5.7		
58.5	1.4	1.6	2.3	14.0	13.4	20.6		
43.3	0.6	0.8	1.1	8.5	9.3	16.1		
9.5	0.3	0.4	0.9	2.7	2.5	7.3		
	Cd, µg g ⁻¹							
1.8	0.2	< 0.1	< 0.1	< 0.1	< 0.1	0.9		
2.7	0.5	0.2	0.2	0.2	0.2	1.5		
2.3	0.3	< 0.1	0.2	0.2	< 0.1	1.2		
0.2	< 0.1	0.0	0.0	0.0	0.0	0.2		
			Ni, μg g	1				
76.1	3.0	2.7	5.9	20.8	19.4	21.3		
210.4	5.8	4.2	9.0	59.6	53.4	70.6		
142.4	4.1	3.5	7.6	38.8	35.0	45.2		
37.9	0.8	0.5	0.9	11.2	10.4	15.0		
	Pb, μg g ⁻¹							
46.8	0.8	0.8	5.2	10.3	11.8	9.3		
144.2	7.2	5.1	22.1	35.1	33.0	42.7		
101.3	2.8	1.9	13.6	24.3	22.7	24.5		
30.7	2.2	1.4	5.4	7.6	6.4	8.7		
	25.5 58.5 43.3 9.5 1.8 2.7 2.3 0.2 76.1 210.4 142.4 37.9 46.8 144.2 101.3	25.5 < 0.1 58.5	EX - OM - 25.5	EX - OM - MnO - Cu, μg g 25.5 < 0.1 < 0.1 < 0.1 58.5	EX - OM - MnO - AFeO - Cu, μg g ⁻¹ 25.5 < 0.1 < 0.1 < 0.1 5.3 58.5 1.4 1.6 2.3 14.0 43.3 0.6 0.8 1.1 8.5 9.5 0.3 0.4 0.9 2.7 Cd, μg g ⁻¹ 1.8 0.2 < 0.1 < 0.1 < 0.1 < 0.1 2.7 0.5 0.2 0.2 0.2 2.3 0.3 < 0.1 0.2 0.2 2.3 0.3 < 0.1 0.2 0.2 0.2 < 0.1 0.0 0.0 0.0 Ni, μg g ⁻¹ 76.1 3.0 2.7 5.9 20.8 210.4 5.8 4.2 9.0 59.6 142.4 4.1 3.5 7.6 38.8 37.9 0.8 0.5 0.9 11.2 Pb, μg g ⁻¹ 46.8 0.8 0.8 5.2 10.3 144.2 7.2 5.1 22.1 35.1 101.3 2.8 1.9 13.6 24.3	etal EX - OM - MnO - AFeO - CFeO - Cu, μg g ⁻¹ 25.5 < 0.1		

The amounts of Cd fractions in EX-, OM-, MnO-, AFeO- and CFeO- fractions were 13.04, 4.35, 8.70, 8.70 and 4.35 % of total Cd, respectively. Most Cd (52.17 %) was present in the residual fraction (Fig. 2). Generally, the association of Cd with different fractions was ordered as follow; R->EX->AFeO-=MnO->CFeO-=OM-. Most Cd was extracted in the residual fraction, which was in agreement with the other studies (Ramos et al., 1994; Ma and Rao, 1997; Kızılkaya and Aşkın, 2002).

3.3 Nickel

Total Ni contents of soil samples varied between 76.10 to 210.43 $\mu g.g^{-1}$ (Table 3), total Ni contents of soils are with in the range of 2 to 50 $\mu g.g^{-1}$ found in soils generally (Kloke, 1980). Mean value of total concentration of Ni was much higher than background value of the soil for Ni (142.4 $\mu g.g^{-1}$) (Cabrera et al., 1999). 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 (Marschner, 1995).

The amounts of Ni fractions, EX-, OM-, MnO-, AFeO- and CFeO- fractions, were 2.88, 2.46, 5.34, 27.25 and 24.58 % of total Ni, respectively in soils. The highest in content of Ni (31.74 %) was found in the residual fraction (Fig. 2). The association of Ni with different fractions followed as; R-> AFeO- > CFeO- > MnO- > EX- > OM- . This order was consistent with the results by Hickey and Kittrick (1984). The highest Ni content, found in the residual fraction, might be sourced from because Ni2+ which has the highest crystal field stabilization energy of the common divalent metals, and thus has a high potential to be enriched in clay minerals (Wang et al., 1997).

3.4 Lead

Total Pb contents in soil samples ranged between 46.79 to 144.15 $\mu g.g^{-1}$ (Table 3), total Pb contents of soils are within the range of 0.1 to 20 $\mu g.g^{-1}$ found in soils respectively (Kloke, 1980). Mean value of total concentration of Pb was much higher than background value of the soil (101.3 $\mu g.g^{-1}$) (Cabrera et al., 1999).

The amounts of Pb in EX-, OM-, MnO-, AFeO- and CFeO- fractions were 2.76, 1.88, 13.43, 23.99 and 22.41 % of the total Pb, respectively. The highest Pb content (24.19 %) was also obtained in the residual fraction (Fig. 2). The association of Pb with different fractions was found in the following order; R- > AFeO- > CFeO- > MnO- > EX- > OM-. In the study of contaminated Southwest Poland soils by Chlopecka et al. (1996), also found that amounts of the highest Pb was associated with the oxide fraction and only very low amounts of Pb was in the exchangeable fractions. Similar findings were reported by Ramos et al.(1994) and Chlopecka (1993).

3.5 The Relationships between Soil Heavy Metal Fractions and Some Soil Properties

The relationships between Cu, Cd, Ni and Pb fractions of soils and some soil properties are given in Table 4.

Total Cu, Cd, Ni and Pb contents were positively correlated with clay content. Organic C content was not correlated with total heavy metal distributions, because of large soil clay contents of the samples and these metals probably adsorbed on the clay fraction. Similarly, Lee et al. (1997) found that positive correlations between total heavy metal contents and clay content of soils in Oklahoma Benchmark soils.

The mean Cu, Cd, Ni and Pb contents in the organically complexed fraction (OM-) were relatively low (Table 3) and about 1.85, 4.35, 2.46 and 1.88 % of the total heavy metal contents respectively. The fractions of OM-, are readily available

for plant uptake, occur in soil organic matter and soil solutions. The amount of Cu, Ni and Pb contents positively correlated (p<0.01) with soil organic carbon content in OM- fractions. This relationship is in agreement with the known fact that soil organic carbon is most important single factor controlling the metal mobility in OM- fraction (Adriano, 1986; Kabata-Pendias and Pendias, 1992). Organic matter may act as a strong absorbent for heavy metals and could complex as humicmetal complex. Copper often forms more stable complexes with organic components than the other metals. The preference of Cu for organic matter is supported by the high stability constant of Cu complexes with organic matter (Irving and Williams, 1953). Other studies have pointed to Cu as being associated with the organic fraction (Pardo et al., 1990).

Exchangeable metals (EX-) are held by an electrostatic attraction on the exchange sites the surface and interface of negatively charged inorganic and organic particles of the soils. EX- forms are the first to be brought into solution and considered to be easily available for plant (Dudka et al., 1996). Cadmium contents in soil EX- fraction were higher than the other metal levels (Figure 1). Copper, Cd, Pb and Ni contents positively correlated (p<0.01) with CEC and clay content in EX- fractions. Soil pH gave positive correlations with exchangeable Ni and Cd contents. This observation concurs with the findings in other studies (Dudka et al., 1996).

Copper, Pb and Ni were mainly associated with the Fe (amorphous and crystalline) – Mn oxide fractions. These metal oxides have stability constants high in enough to be concentrated in these fractions. Several other workers have found Cu, Cd, Pb and Ni as to be highly associated with Fe and Mn oxides (Ramos et al., 1994; Kuo et al., 1983). Heavy metals may co precipitate with salts of oxygen acids both inorganically and biogenetically and are susceptible to pH changes (Dudka et al., 1996).

The final fraction is the residual that was the solid remaining after the extractant fractions. More than 20 % of the total Cu, Cd, Pb and Ni were extracted in the residual fraction (Figure 1), which was in agreement with the other fractionation studies (Hickey and Kittrick, 1984; Ramos et al., 1996; Dudka et al., 1996). The variation in amount of residual Cu and Pb with clay content was consistent with the findings of Chlopecka et al., (1996). Shuman (1979) also found that trace metals in the residual fraction was associated primarily with the clay fraction.

Table 4. Correlation coefficients for relationships between Cu, Cd, Pb and Ni fractions and soil properties (*p<0.05; **p<0.01;***p<0.001)

Total and Fractions of Heavy metals, μg.g ⁻¹		Soil Properties						
		рН	Organic C, %	CaCO ₃ , %	CEC, me.100g ⁻¹	Clay, %		
Cu	Total	0.307	- 0.127	- 0.030	0.506	0.701 **		
	EX -	0.429	- 0.414	0.256	0.667 **	0.559 *		
	OM -	- 0.271	0.707 **	0.183	- 0.204	- 0.214		
	MnO -	0.337	- 0.165	- 0.453 *	0.523 *	0.306		
	AFeO -	0.293	- 0.158	0.023	- 0.014	- 0.173		
	CFeO -	- 0.086	0.125	0.314	- 0.043	0.244		
	R -	0.045	- 0.251	- 0.103	0.316	0.596 **		
	Sum -	0.156	- 0.247	- 0.022	0.348	0.610 **		
Cd	Total	0.311	- 0.055	0.098	0.205	0.546 **		
	EX -	0.555 **	- 0.626 **	- 0.015	0.643 **	0.565 **		
	OM -	0.208	- 0.250	0.045	0.296	0.208		
	MnO -	0.413	- 0.093	0.065	0.194	0.495 *		
	AFeO -	0.448 *	- 0.480 *	0.139	0.242	0.567 **		
	CFeO -	0.264	- 0.253	0.067	0.181	0.570 **		
	R -	0.149	- 0.023	- 0.326	0.260	0.406		
	Sum -	0.411	- 0.325	- 0.212	0.500 *	0.644 **		
	Total	0.359	- 0.268	- 0.207	0.693 **	0.669 **		
	EX -	0.281	- 0.161	- 0.242	0.640 **	0.607 **		
	OM -	- 0.054	0.832 ***	- 0.120	- 0.214	- 0.132		
Pb	MnO -	0.071	- 0.276	- 0.439	0.541 *	0.488 *		
	AfeO -	0.202	- 0.345	- 0.343	0.564 *	0.594 **		
	CfeO -	0.151	- 0.270	- 0.353	0.479 *	0.565 **		
	R -	0.621 **	- 0.300	0.255	0.587 **	0.527 *		
	Sum -	0.342	- 0.295	- 0.221	0.637 **	0.638 **		
Ni	Total	0.388	- 0.240	- 0.241	0.699 **	0.598 **		
	EX -	0.517 *	- 0.273	0.025	0.817 **	0.855 **		
	OM -	- 0.167	0.785 **	- 0.093	- 0.223	- 0.042		
	MnO -	0.095	- 0.425	- 0.516 *	0.457 *	0.444		
	AFeO -	0.201	- 0.253	- 0.346	0.560	0.432		
	CFeO -	0.216	- 0.247	- 0.374	0.574 **	0.441		
	R -	0.459 *	0.010	0.041	0.475 *	0.361		
	Sum -	0.346	- 0.162	- 0.224	0.597 **	0.458 *		

4. CONCLUSION

Heavy metal contents and their fractions were presented from the total and sequential extraction procedures in soil samples obtained from the Bafra plain. The results indicated that heavy metal enrichment was in the surface soil (0-20 cm) than the range of excessive or toxic suggested by literature. The territories affected by the some agricultural practices and environmental factors. The possible reasons of these conditions are following:

- Soil has a role not only in the agricultural production media but also in the maintenance of environmental quality,
- Increasing of the soil heavy metal contaminations may be sourced from the application of sewage sludge and agricultural chemicals such as fertilizers, pesticides etc. into agricultural area. These inputs may cause heavy metal enrichment of soils,
- The distribution of heavy metals due to muffler emissions on the roads and agricultural activities, the existence of no restrictions for no-lead benzine usage in the vehicles, in the environment,
- Not only to observe contamination levels with heavy metals in agricultural soils but also monitoring soil contamination status by means of soil samplings is very important periodically. Soil heavy metal status should use to provide some initial data on the identification of contamination sources and the degree of soil pollution by heavy metals.

Also, the application of reclamation methods, such as the addition of adsorbent materials - clay and zeolit to soils, or phytoremediation, or bioremediation are required in the study area or in similar agricultural area. Geochemical investigations of agricultural soils in the Bafra Plain are made it possible to estimate background concentrations of Cu, Cd, Pb and Ni.

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