

THE BACKGROUND LEVELS OF HEAVY METALS IN VERTISOLS UNDER MEDITERRANEAN TYPE OF CLIMATE IN THE REGION OF TURKEY

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ABSTRACT

Vertisols are important agricultural soils in the region. These soils are under various vegetables, sunflower and wheat cultivation. Fifteen soil sites were selected in this research. This research was carried out to determine background levels of total and DTPA extractable Fe, Mn, Zn, Cu, Ni, Cr, Pb, Co, and Cd with some important soil properties.

KEYWORDS: Vertisols, heavy metals, pollution

DETAILED ABSTRACT

This region is important for agricultural production. Vertisols are non irrigated agricultural lands. These soils were well developed in the region. This research was provided useful information for their proper land management. The soils had high clay contents and values increased with depth in all the studied sites. pH of the soils is alkaline due to calcareous parent material. These soils had high CEC with the high clay content. The obtained results were indicated that total and DTPA extractable of Fe, Mn, Zn, Cu, Ni, Cr, Pb, Co, and Cd concentrations were varied from low to moderate levels for these agricultural lands.

INTRODUCTION

Many researchers have extensively studied the relationship of trace elements to problems of soil fertility and plant nutrient. However, the focus has been on their potential toxicity, as a result of an increase of industrial activity, the excessive use of fertilizers and pesticides, the application of sewage sludge, and waste disposal on land and mining in the last decade [13].

The distribution of heavy metals in soil profiles, as well as their availability, is controlled by parameters such as the intrinsic properties of the metal and soil's characteristics [10]. The quantity and quality of adsorption sites, concentration and type of organic and inorganic complexes, cationic and ionic composition of the soil, hydraulic conductivity, and microbial activity are factors that affect the behaviour of the metals.

The accumulation and persistence of many trace elements creates an important environmental problem [3]. An increase in the contents of heavy metals could produce potentially serious hazards in the soil-plant-animal system [7]. These concerns make it necessary to know their levels in soils, and to do this sensitive, precise, accurate and easy to use analytical methods must be developed. The aim of this research was to determine background levels of total and DTPA extractable Fe, Mn, Zn, Cu, Ni, Cr, Pb, Co, and Cd with some important properties of agricultural soils from the campus area of Uludag University in the Bursa province, Turkey.

MATERIALS AND METHODS

The research area is located in the Bursa plain of northwestern Turkey between 40° 13' - 40° 14' N latitudes and 28° 50' - 28° 51' E longitudes ranging from 100 m to 160 m above mean sea level. The mean annual precipitation and temperature are 713.1 mm and 14.4 °C in the region. The soil temperature and moisture regimes are thermic and xeric respectively. Fifteen Vertisol soil sites were selected for the present study. These soils were formed on marl parent material. The research area is slowly drained and cultivated for various vegetables, sunflower (*Helianthus annuus L.*) and wheat (*Triticum aestivum L.*).

The soil samples were analyzed for particle-size distribution [12], pH in a 1:2 soil:water ratio [18], organic carbon [21], total nitrogen [9], calcium

carbonate [20], electrical conductivity [25], available phosphorus [22], CEC [24], exchangeable cations [26] and DTPA extractable Fe, Mn, Zn, Cu, Cd, Co, Cr, Ni and Pb [16]. 1 g soil samples were digested in a mixture of concentrated HNO₃ and HCl (3:1 ratio) and analyzed for total concentrations of Fe, Mn, Zn, Cu, Ni, Cr, Pb, Co, and Cd by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer).

RESULTS AND DISCUSSION

Some physical and chemical properties of the studied soils were given in Table 1. The soils showed similar physical and chemical properties. The texture is clay all the studied soils. Clay content of soils ranged from 45.1 to 62.3% and increased with depth. The pH values varied from 7.6 to 8.2. The high pH values were due to calcareous parent material. Electrical conductivity values ranged from 0.39 to 0.84 dS m⁻¹. The results indicated that these soils are not saline. The organic C and total N values varied from 0.67 to 1.29% and from 0.07 to 0.12% respectively, and both decreased consistently with depth. C/N ratios ranged from 9.0 to 13.4. The low organic carbon and total nitrogen values were due to rapid decomposition of organic matter under Mediterranean climate in the northwestern Turkey. The CaCO₃ content of the soils increased with depth and values varied from 1.5 to 6.9%. The highest values were shown at the lowest horizons due to calcareous parent material. Available P values ranged from 10.17 to 24.79 mg kg⁻¹ and decreased with depth. These values were in sufficient levels to support the growth of most arable plants [17, 19]. CEC values were highest in the subsurface horizons and the similar trend was observed in the clay contents of the soils. CEC values varied from 37.7 to 47.5 cmol (+) kg⁻¹. Exchangeable Ca and Mg ranged from 31.8 to 41.4 cmol (+) kg⁻¹ and from 3.1 to 3.9 cmol (+) kg⁻¹, respectively. Exchangeable K varied from 1.6 to 2.5 cmol (+) kg⁻¹ and decreased with depth. Exchangeable Na ranged from 1.0 to 1.8 cmol (+) kg⁻¹ and increased with depth. Base saturation was 100% in all the profiles due to the presence of free CaCO₃. Aydinalp [4, 6] stated that some similar soil properties were determined for Vertisols in the region. The main differences occurred organic carbon and total nitrogen values. The investigated soils had lower organic carbon and total nitrogen values than the other soils of the region.

The other physical and chemical properties showed minor differences in both studied areas. This is probably due to formation of soils where the soils developed under similar parent material, topography and climate.

The total metal concentrations of the soils are presented in Table 2. The values of Fe, Mn, Zn and Cu varied from 25,993.000 to 54,187.000 mg kg⁻¹, 805 to 1772 mg kg⁻¹, 56.50 to 105.03 mg kg⁻¹ and 33.54 to 73.40 mg kg⁻¹ respectively. Cd ranged from 0.23 to 0.51 mg kg⁻¹, Co from 32.10 to 46.20 mg kg⁻¹ and Cr from 24.07 to 72.78 mg kg⁻¹. The values of Ni varied from 21.27 to 43.68 mg kg⁻¹ and Pb from 19.14 to 30.56 mg kg⁻¹. Apparently, the total heavy metal concentrations were highest in the surface

horizon and lowest in the lower horizon. The total metal concentrations had the following order:

Fe>Mn>Cu>Zn>Cr>Co>Ni>Pb>Cd. This trend was also observed for the DTPA extractable metals. In general, the total heavy metal concentrations were very low than found in some agricultural soils of the plain [5]. Pollution in examined soils does not exceed the allowed limits [2]. The different degree of mobility of the metals in the soil profile is attributed to organic transport or to the presence of cracks and channels in the soil [10]. The mobility of heavy metals is an important factor, because it determines their availability for plants and microorganisms that take up the dissolved elements in the soil solution [14].

Table 1. Some physical and chemical properties of the soils

Profile No	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Texture	pH 1:2 soil:water	EC (dS m ⁻¹)	Org. C (%)	Total N (%)	C/N	CaCO ₃ (%)	Available P, mg kg ⁻¹	CEC	Exchangeable cations				BS (%)
														Ca	Mg	K	Na	
1	0-20	16.6	30.2	52.3	C	7.7	0.55	1.14	0.09	12.7	2.0	18.15	43.1	37.1	3.3	2.2	1.4	100
	20-40	16.9	28.4	54.1	C	7.8	0.50	0.90	0.08	11.2	3.2	16.07	45.2	39.0	3.5	2.0	1.5	100
2	0-20	16.4	33.7	48.9	C	7.7	0.61	1.18	0.09	13.1	2.5	15.38	40.4	34.5	3.2	2.0	1.3	100
	20-40	16.0	30.5	53.0	C	7.9	0.47	0.97	0.08	12.1	3.8	11.29	42.1	36.1	3.6	1.7	1.6	100
3	0-20	8.4	35.6	55.2	C	7.8	0.50	1.16	0.10	11.6	1.9	17.83	45.5	39.5	3.3	2.1	1.5	100
	20-40	9.0	33.1	57.5	C	7.9	0.42	0.91	0.09	10.1	2.7	15.04	46.0	39.7	3.4	2.0	1.7	100
4	0-20	16.6	32.0	50.4	C	7.6	0.54	1.10	0.11	10.0	2.6	14.30	40.3	34.3	3.1	2.3	1.3	100
	20-40	16.8	30.2	52.3	C	7.8	0.51	0.95	0.10	9.5	3.0	10.17	41.5	35.2	3.3	2.0	1.5	100
5	0-20	21.8	30.1	47.2	C	7.9	0.72	1.03	0.11	9.4	3.4	21.35	39.2	33.9	3.4	2.3	1.1	100
	20-40	22.4	27.5	49.5	C	8.0	0.65	0.81	0.09	9.0	4.7	17.68	41.0	35.0	3.6	1.9	1.3	100
6	0-20	25.5	28.4	45.1	C	7.8	0.78	1.07	0.08	13.4	3.6	23.04	37.7	31.8	3.5	2.0	1.2	100
	20-40	24.7	25.9	48.7	C	8.0	0.60	0.75	0.07	10.7	4.9	20.17	39.6	33.7	3.7	1.7	1.4	100
7	0-20	19.5	26.7	53.0	C	7.9	0.70	1.10	0.09	12.2	3.8	21.35	40.8	35.2	3.3	2.1	1.0	100
	20-40	19.7	24.5	55.3	C	8.1	0.51	0.84	0.08	10.5	5.4	19.48	42.2	36.7	3.6	1.6	1.2	100
8	0-20	19.5	29.1	50.7	C	7.8	0.77	1.21	0.10	12.1	3.2	24.57	41.7	35.0	3.5	2.4	1.1	100
	20-40	19.9	27.8	51.9	C	7.9	0.65	0.72	0.08	9.0	4.7	20.61	43.8	37.4	3.8	2.0	1.4	100
9	0-20	15.5	28.0	55.8	C	8.0	0.80	1.25	0.11	11.4	3.9	21.78	42.0	35.3	3.7	2.5	1.3	100
	20-40	15.1	26.5	57.9	C	8.1	0.71	0.83	0.09	9.2	5.8	17.52	44.2	37.6	3.9	2.1	1.5	100
10	0-20	12.7	27.4	59.0	C	8.0	0.74	1.29	0.10	12.9	4.5	23.03	45.3	39.3	3.4	2.4	1.0	100
	20-40	11.3	25.8	62.3	C	8.2	0.62	0.67	0.07	9.6	6.9	18.44	47.5	41.4	3.6	2.2	1.2	100
11	0-20	7.7	35.2	56.1	C	7.9	0.79	1.32	0.12	11.0	4.0	24.79	44.9	38.8	3.5	2.3	1.1	100
	20-40	6.3	33.9	59.2	C	8.2	0.65	0.77	0.08	9.6	5.7	20.08	46.3	40.0	3.7	2.0	1.4	100
12	0-20	2.8	37.8	58.7	C	7.9	0.84	1.20	0.10	12.0	4.4	21.88	43.6	37.7	3.4	2.4	1.0	100
	20-40	2.7	36.1	60.8	C	8.0	0.58	0.88	0.08	11.0	5.0	17.64	45.2	39.1	3.5	2.2	1.2	100
13	0-20	10.1	38.7	50.4	C	8.0	0.77	1.17	0.09	13.0	3.8	23.50	41.5	35.9	3.3	2.1	1.1	100
	20-40	9.7	37.5	52.3	C	8.1	0.63	0.92	0.08	11.5	4.6	19.27	43.1	37.6	3.4	1.8	1.2	100
14	0-20	6.8	37.9	54.6	C	7.6	0.58	1.10	0.10	11.0	1.7	18.04	42.7	36.3	3.5	1.8	1.4	100
	20-40	6.5	36.1	56.9	C	7.7	0.41	0.83	0.09	9.2	2.0	15.22	44.5	38.2	3.7	1.6	1.5	100
15	0-20	8.4	39.4	51.4	C	7.8	0.55	1.15	0.10	11.5	1.5	16.34	40.3	33.8	3.7	1.9	1.6	100
	20-40	7.9	38.0	53.7	C	7.9	0.39	0.94	0.09	10.4	2.6	13.17	42.1	35.7	3.8	1.7	1.8	100

Table 2. Total metal concentrations of the soils at two sampling depths.

Profile No	Depth (cm)	metal concentration, mg kg ⁻¹								
		Fe	Mn	Zn	Cu	Cd	Co	Cr	Ni	Pb
1	0-20	39,430.000	1207	96.88	64.92	0.50	35.77	40.25	30.25	25.32
	20-40	29,968.000	1065	71.23	59.10	0.31	32.10	32.14	24.07	22.45
2	0-20	35,972.000	1303	90.91	72.93	0.43	38.26	40.78	36.98	28.26
	20-40	27,445.000	918	82.48	54.36	0.25	35.17	24.46	27.30	21.30
3	0-20	32,078.000	1366	104.41	65.82	0.34	34.73	56.24	30.92	25.34
	20-40	25,993.000	1244	87.12	41.63	0.26	33.10	48.36	27.45	22.07
4	0-20	41,405.000	1537	84.17	73.24	0.44	37.72	40.35	40.43	20.95
	20-40	31,179.000	1372	78.84	52.18	0.37	34.96	24.07	30.78	19.14
5	0-20	43,147.000	1057	105.03	49.57	0.38	40.82	64.60	31.15	25.29
	20-40	36,248.000	805	93.42	35.61	0.25	37.18	56.49	24.63	22.50
6	0-20	46,605.000	1262	77.58	50.24	0.50	43.12	72.78	36.94	27.12
	20-40	33,705.000	923	58.93	41.77	0.38	39.87	48.45	27.30	25.47
7	0-20	48,054.000	1347	80.75	56.52	0.49	43.05	64.58	30.52	30.56
	20-40	35,702.000	1073	67.44	36.49	0.24	40.14	56.43	21.27	26.63
8	0-20	44,743.000	1418	69.10	66.15	0.45	40.85	72.70	40.83	33.47
	20-40	40,086.000	1187	61.35	47.07	0.23	37.26	64.29	34.47	30.12
9	0-20	49,208.000	1299	67.63	55.32	0.37	41.33	65.03	43.68	28.25
	20-40	34,425.000	970	56.50	33.54	0.35	38.75	56.82	37.14	22.86
10	0-20	54,187.000	1315	74.32	58.43	0.43	46.20	65.04	37.69	25.45
	20-40	43,736.000	1152	62.17	54.27	0.35	41.96	48.93	28.08	21.97
11	0-20	47,793.000	1603	75.08	48.90	0.44	40.47	56.32	31.47	24.90
	20-40	44,958.000	1342	64.96	41.63	0.24	37.89	41.25	24.82	21.38
12	0-20	46,212.000	1772	102.80	64.35	0.51	41.14	56.21	37.44	24.14
	20-40	29,751.000	1618	83.71	51.87	0.39	38.02	32.07	31.56	19.57
13	0-20	44,683.000	1660	97.24	63.17	0.50	43.26	64.48	30.75	24.36
	20-40	35,054.000	1375	89.50	41.94	0.36	39.34	55.95	24.59	19.83
14	0-20	47,721.000	1672	103.29	73.40	0.51	40.73	48.24	33.47	25.80
	20-40	41,898.000	1430	88.31	58.12	0.44	36.02	32.12	27.16	22.56
15	0-20	44,675.000	1713	96.24	73.03	0.38	40.92	56.07	40.69	23.51
	20-40	30,591.000	1428	77.56	42.60	0.24	37.84	48.12	31.73	22.42

In addition, the retention and loss of heavy metals is influenced by precipitation, saturation, water's displacement speed, complexation, interaction with other soil constituents, adsorption, and oxide-reduction process [11]. It has also been shown that exchange sites are important in reducing the movement of these metals in the soil.

The DTPA extractable metal concentrations of the soils are presented in Table 3. The values of heavy metals are found in higher concentrations in the surface horizon and decreased with depth. The values of Fe ranged from 6.07 to 12.66, Mn from 6.24 to 13.31, Zn from 1.10 to 1.97 and Cu from 4.14 to 8.93 mg kg⁻¹. Cd varied from 0.04 to 0.08, Co from 0.49 to 0.67 and Cr from 0.03 to 0.09 mg kg⁻¹. The

values of Ni varied from 0.08 to 0.14 and Pb from 0.87 to 1.20 mg kg⁻¹. The values of extractable Fe, Mn, Zn, Cu, Ni, Cr, Pb, Co, and Cd are lower than those obtained by several authors [1, 8, 15]. However, DTPA extractable microelements are in sufficient levels for plant growth [17, 19].

Exchangeable heavy metals quantified in the examined soils had low concentration because of the nature of the exchange sites and its alkaline pH. The advantage of a pH above 6.0 and a high content of clay is that heavy metal ion activity is kept low in the solution. Besides, with a high pH, there will be no problems of toxicity derived of an increase in the availability of metals, since these ions are almost totally absorbed, fixed or precipitated. pH changes

affect the formation of different chemical species of the metals and can lead to the formation of complexes of hydroxides and carbonates [23].

Table 3. DTPA-extractable metal concentrations of the soils at two sampling depths.

Profile No	Depth (cm)	Metal concentration, mg kg ⁻¹								
		Fe	Mn	Zn	Cu	Cd	Co	Cr	Ni	Pb
1	0-20	9.17	9.20	1.88	8.01	0.08	0.55	0.05	0.10	1.15
	20-40	7.03	8.14	1.40	7.25	0.05	0.50	0.04	0.08	1.00
2	0-20	8.25	9.83	1.73	8.47	0.07	0.58	0.05	0.12	1.10
	20-40	6.38	7.05	1.61	6.63	0.04	0.54	0.03	0.09	0.95
3	0-20	7.49	10.27	1.97	7.81	0.05	0.52	0.07	0.10	1.18
	20-40	6.07	9.49	1.72	5.14	0.04	0.49	0.06	0.09	1.02
4	0-20	9.55	11.55	1.65	8.72	0.07	0.55	0.05	0.13	1.04
	20-40	7.23	10.38	1.52	6.49	0.06	0.52	0.03	0.10	0.95
5	0-20	9.91	8.13	1.97	5.90	0.06	0.60	0.08	0.10	1.12
	20-40	8.46	6.24	1.78	4.17	0.04	0.57	0.07	0.08	1.03
6	0-20	10.72	9.56	1.43	6.08	0.08	0.62	0.09	0.12	1.15
	20-40	7.80	7.03	1.10	5.22	0.06	0.59	0.06	0.09	1.08
7	0-20	11.04	10.45	1.52	6.81	0.08	0.65	0.08	0.10	1.18
	20-40	8.26	8.38	1.31	4.45	0.04	0.60	0.07	0.07	1.07
8	0-20	10.43	10.71	1.27	7.97	0.07	0.62	0.09	0.13	1.20
	20-40	9.37	9.22	1.15	5.62	0.04	0.58	0.08	0.11	1.12
9	0-20	11.49	9.83	1.32	6.83	0.06	0.64	0.08	0.14	1.15
	20-40	8.02	7.40	1.13	4.14	0.05	0.60	0.07	0.12	0.97
10	0-20	12.66	9.98	1.45	7.23	0.07	0.67	0.08	0.12	1.07
	20-40	10.30	8.71	1.24	6.70	0.05	0.64	0.06	0.09	0.93
11	0-20	11.24	12.04	1.48	6.03	0.07	0.62	0.07	0.10	1.03
	20-40	10.58	10.15	1.31	5.12	0.04	0.58	0.05	0.08	0.87
12	0-20	10.92	13.31	1.97	7.92	0.08	0.60	0.07	0.12	1.09
	20-40	7.05	12.40	1.65	6.30	0.06	0.56	0.04	0.10	0.92
13	0-20	10.46	12.82	1.88	7.67	0.08	0.62	0.08	0.10	1.13
	20-40	8.23	10.74	1.74	5.02	0.05	0.58	0.07	0.08	0.95
14	0-20	11.17	13.09	1.93	8.93	0.08	0.60	0.06	0.11	1.20
	20-40	9.84	11.27	1.69	7.04	0.07	0.55	0.04	0.09	1.12
15	0-20	10.36	12.93	1.85	8.85	0.06	0.61	0.07	0.13	1.17
	20-40	7.11	11.07	1.50	5.14	0.04	0.57	0.06	0.10	1.09

Biological activity can also alter the solubility of the metals in soil for reasons that directly or indirectly change the state of oxidation of the metals. The concentration of dissolved complexing bonders, especially fulvic acids, controls the mobility of the metals in the soil. These compounds contain a large proportion of aromatic nuclei with –OH and –COOH and other oxygen-rich groups that are bonded to them [23]. Thus, fine-textured soils or those with horizons with high contents of organic matter, have a

greater capacity to adsorb metals than soils with a sandy texture or low content of organic matter.

CONCLUSION

The heavy metals are found adsorbed and fixed in the soils. This is due to the alkaline pH, which causes the metals to precipitate as hydroxides, carbonates, sulphates or phosphates. The obtained results indicated that the total and DTPA extractable metals ranged from low to moderate levels in the research area.

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