

## Soil properties and distribution of heavy metals and boron within three Greek *Histosols*

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Three Greek soil profiles originating mostly from lacustrine deposits in the district of Filippii (Northern Greece), were studied. These soils have been formed both from organic and inorganic materials that were deposited by precipitation and developed through the action of aquatic organisms. According to Soil Taxonomy (1992), they are classified as *Histosols* and belong to the suborder of *Saprists*. The pH of the soil horizons ranged among soil horizons from 6.2 to 7.8. The total soil nitrogen content ranged between 7.5 and 17.0 g kg<sup>-1</sup> and the soil organic matter was between 108.7 and 206.4 g kg<sup>-1</sup>. Calcium carbonate was detected into ten horizons and ranged between 1.4 and 27.8%, whilst it was not found in five of the examined soil layers. This is suggested to reflect the presence or absence of aquatic organisms, the shells of which contain CaCO<sub>3</sub> and enrich soil by means of weathering. Heavy metals extracted by 4 M HNO<sub>3</sub> were in the following order Fe>Mn>Zn>Pb>Ni>Cu>Cd, and their average concentrations were 7190, 294, 72.3, 58.2, 33.3, 17.3 and 5.1 µg g<sup>-1</sup>, respectively. The distribution of trace elements greatly differs amongst the examined samples and the range of the pseudototal form of Fe was 1873–18550 µg g<sup>-1</sup>, of Mn 54.7–585, of Cu 4.5–40, of Zn 22.0–185, of Pb 20.5–143, of Ni 15–64.7 and Cd 3.3–6.9 µg g<sup>-1</sup>. The sequentially extracted by Na<sub>2</sub>-EDTA, HNO<sub>3</sub> and NaOH were found to be the prevailing metal forms. Iron deficiency symptoms have been observed in certain crops, and manganese deficiency was also detected in some maize crops cultivated in slightly alkaline soils. Furthermore, the plant available boron concentration was determined, as deficiency symptoms were observed in some districts cultivated with sugar beets. The distribution was generally not influenced by soil properties, although a weak relationship between organic carbon and boron was found. Measures such as rational water management, tillage practices, and fertilization could be applied towards minimization of soil degradation, micronutrient disorders and optimization of crop productivity.

Key words: heavy metals, boron, histosols, sequential extraction, soil subsidence

## INTRODUCTION

Chemical fractionation of soil Fe, Mn, Cu, Zn, Pb, Ni and Cd is often conducted, in order the distribution of these elements amongst different fractions to be investigated in certain soil horizons. The ability of the organic soil constituents to bind metals such as Cu and Zn, is well recognized, whilst Ni distribution is related either to organic matter or to amorphous oxides and clay fractions (Kabata-Pendias and Pendias 1984). Severe Cu deficiencies have appeared in places when new areas of acid *Histosols* were drained and developed, whilst Mn deficiencies is most often observed on naturally wet fields rich in organic matter that have been drained and put into crop production (Kubota and Allaway 1972). The natural Pb content of soil is inherited from parent material, whilst the greatest concentration is often found in the organically rich surface horizons of the uncultivated soils (Fleming et al. 1968). It has been pointed out (Cottenie et al. 1979) that sequential extractions of soils may yield more information than single extractions. Knowledge of the trace metal forms can be used as a basis that provides reproducible results by a given chemical extractant and may contribute to fertilization practices.

In soils, boron the only nonmetal among the studied trace elements, is considered to be very mobile element among the micronutrients. Thus, the B movement in soils follows the water flux, and in cool-zone soils is leached downward in soil profiles, whereas in soils of arid or semiarid regions is likely concentrate in surface horizons.

Organic soils cover less than 5% of the cultivated area in Greece (Yassoglou 1995) and are cultivated mainly with maize, sugar beets, cotton, tomatoes and wheat. With over 30% of the originally wetland area in Greece now drained for agricultural use, much attention needs to be focused on managing the remaining natural wetlands, for their ecological importance under natural vegetation. In some cases, these should be returned to previous natural undrained conditions.

Attempts are made to prepare maps showing the distribution of trace elements in various parts of Greece, where organic soils or soils rich in organic matter have been recorded. This kind of study is essential in establishing field experiments aiming to the investigation of problems relevant

to deficiency, toxicity or interactions among trace elements that may affect the nutrient availability to plants.

## MATERIALS AND METHODS

### Study area

The studied soils are located in the district of Filippi (Fig. 1). They have been formed mainly from organic materials deposited by precipitation and have been developed through the action of aquatic organisms. They have been classified as *Histosols* (Soil Taxonomy 1992) and belong to the suborder of *Sapristis*. In general, the majority of Greek arable soils are characterized by the presence of organic matter at concentrations lower than 20–30 mg g<sup>-1</sup> (Yassoglou 1995).

### Soil Sampling — Analytical procedure

Soil samples were collected from cultivated fields, in order to include representative soil types of the district. Fifteen composite samples were taken from each soil horizon or layer in the three studied *Histosols*. The main macroscopic differences can easily be distinguished and consist of geomorphology, soil color, drainage, soil texture and structure. Profile P<sub>1</sub> is located on the depression of the studied area, whilst P<sub>2</sub> lays about 2 km far from P<sub>1</sub> and P<sub>3</sub> is located on the P<sub>1</sub>–P<sub>2</sub>, at a distance of less than 3 km from P<sub>2</sub>. The “pseudototal” content of iron, manganese, lead, cadmium, nickel, copper and zinc in the soil samples was determined in extracts obtained from 2 g samples which were digested by 12.5 ml 4M HNO<sub>3</sub>. The filtered extracts were placed on a hot plate at 80 °C for 16 h. All samples were sequentially extracted in order to determine the various forms in which the metals were associated. The following extractants were used (Sposito et al. 1982):

0.5 M KNO<sub>3</sub>, (16 h)

Deionized water, (2 h, extraction three times)

0.5 M NaOH, (16 h)

0.05 M Na<sub>2</sub>-EDTA, (6 h)

4 M HNO<sub>3</sub>, for sulfide forms (16 h)

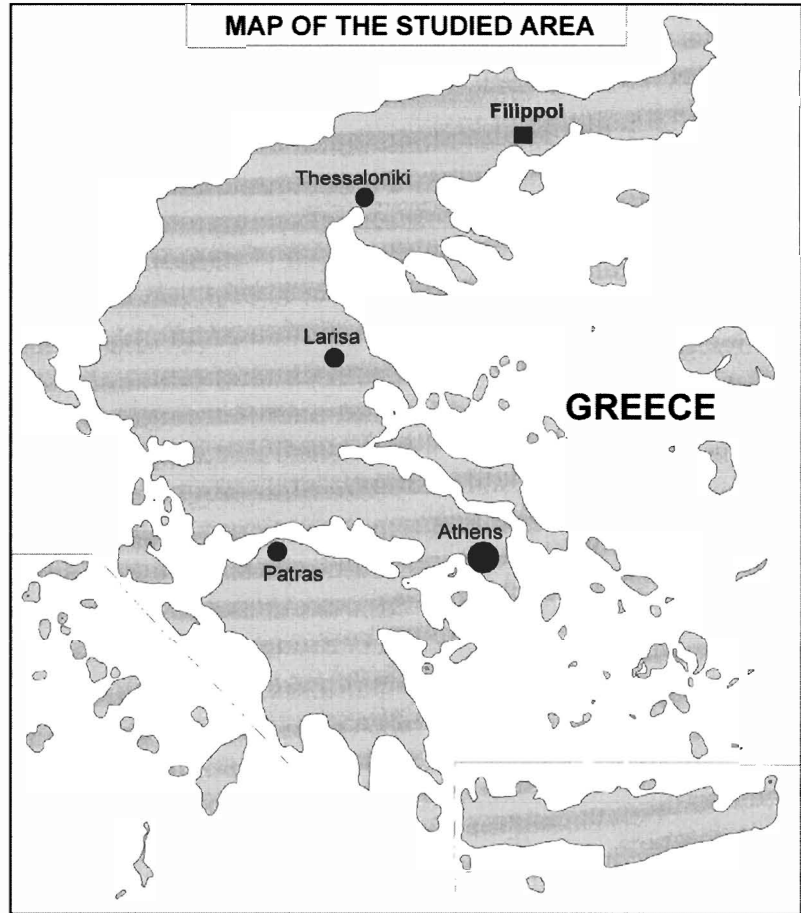


Fig. 1. Map of the studied area.

After extraction, the suspension was centrifuged and the resulting supernatant solution was decanted and filtered. The content of metals in the solution was determined by atomic absorption spectrophotometry. The instrument employed was a Varian Spectr. 400AA -Plus. All results given are averages of triplicate independent samples. Checking of procedure was conducted by using BCR 141 as a reference material at the Soil Institute of Athens. The content of metal extracted by a given extracting reagent was calculated according to the following equation:

$$\mu\text{g extracted} = C \times 25 \text{ g} - C' \times M,$$

where  $C$  is the concentration of the metal in the solution ( $\mu\text{g g}^{-1}$ ),  $C'$  is the concentration of the metal in the solution extracted in the previous step of the sequence  $\mu\text{g g}^{-1}$  and  $M$  is the mass of solution (g) carried over to the present extraction from the previous one.

A modified wet digestion, Walkley and Black method (Allison 1965), was used for the organic matter determination and the pH was measured in a 1:1 soil- $\text{H}_2\text{O}$  suspension (McLean 1982), whilst total soil nitrogen was determined by salicylic-sulfuric acid digestion (Bremner 1996). The azomethine-hydrogen method (Keren 1996) was used for determining the plant available boron and  $\text{CaCO}_3$  was measured by using a Bernard apparatus (Duchafour 1965).

## RESULTS AND DISCUSSION

In most of the studied soils material was mineral matter, organic matter being only approximately 18–35% of soil mass. The pH ranges between 6.2 to 7.8. Total soil nitrogen ranges between 7.5–17.0  $\text{g kg}^{-1}$  (Table 1) which is much higher than

the mean content usually observed in Greek soils (Yassoglou 1995).

The sum of the sequentially extracted heavy metals of 15 soil samples was linearly correlated to the respective total amounts of the elements extracted with concentrated HNO<sub>3</sub>. The correlation coefficient for iron was  $r=0.996$ , for manganese  $r=0.987$ , lead  $r=0.996$ , for cadmium  $0.857$ , for nickel  $0.954$ , for copper  $0.999$  and for zinc

$0.998$ . Based on average concentrations, metals extracted by 4 M HNO<sub>3</sub>, the following rank was determined: Fe>Mn>Zn>Pb>Ni>Cu>Cd.

The observed irregularities and discontinuities can be attributed to soil horizons stratification by means of soil formation process.

Mean iron and manganese content was 7190  $\mu\text{g g}^{-1}$  and 294  $\mu\text{g g}^{-1}$ , respectively (Table 2 and Table 3). The level of concentration may be at-

Table 1. Concentration and distribution of boron and certain soil properties of the studied profiles.

Profile	Depth (cm)	Horizons	pH (1:1)	CaCO <sub>3</sub> %	Total Nitrogen g kg <sup>-1</sup>	Organic Carbon g kg <sup>-1</sup>	C:N	B $\mu\text{g g}^{-1}$
P1	0-38	O <sub>Ap</sub>	7.7	20.2	8.1	118	14.6	0.7
	38-62	O <sub>a2</sub>	7.7	21.0	7.5	117	15.6	1.2
	62-93	O <sub>a3</sub>	7.8	19.4	8.8	116	13.5	1.2
	93-134	O <sub>e4</sub>	6.8	n.d.	17.0	125	7.4	1.0
	134-160	O <sub>e5</sub>	7.7	27.8	9.4	134	14.3	0.9
P2	0-28	O <sub>Ap</sub>	7.6	19.4	16.9	206	12.2	2.3
	28-52	O <sub>a2</sub>	6.6	n.d.	14.8	137	9.3	1.1
	52-75	O <sub>a3</sub>	6.3	n.d.	16.8	137	8.1	1.0
	75-107	O <sub>i4</sub>	6.2	n.d.	15.9	132	8.3	2.1
	107-135	O <sub>i5</sub>	6.4	n.d.	15.7	109	6.9	1.3
P3	0-35	O <sub>Ap</sub>	7.8	5.0	11.5	124	10.6	0.7
	35-62	O <sub>a2</sub>	7.7	5.0	11.6	124	10.7	0.6
	62-95	O <sub>i3</sub>	7.2	2.7	16.1	118	7.3	1.8
	95-114	O <sub>i4</sub>	7.2	2.3	12.8	131	10.3	1.0
	114-150	O <sub>i5</sub>	7.0	1.4	14.0	115	8.2	0.9

Table 2. Concentration and distribution of iron within soil horizons.

Profile	Depth (cm)	Fe <sub>pseudot.</sub> $\mu\text{g g}^{-1}$	Sequential extraction					SUM $\mu\text{g g}^{-1}$
			Fe <sub>KNO3</sub>	Fe <sub>H2O</sub>	Fe <sub>NaOH</sub> $\mu\text{g g}^{-1}$	Fe <sub>EDTA</sub>	Fe <sub>HNO3</sub>	
P1	0-38	10967	3.0	205.6	765	1967	6213	9154
	38-62	10710	3.0	225.4	836	2413	5994	9471
	62-93	9883	3.1	213.2	861	1976	5419	8472
	93-134	4033	2.6	11.8	527	1017	2375	3933
	134-160	1873	2.4	15.8	73	224	1319	1634
P2	0-28	9693	6.0	32.4	1325	2329	5450	9142
	28-52	4562	5.1	14.1	1269	1495	1631	4414
	52-75	6446	3.4	24.9	2063	2090	2194	6375
	75-107	2412	2.4	11.3	462	787	1119	2382
	107-135	2400	2.3	5.4	167	293	1863	2331
P3	0-35	18550	2.8	143.1	1372	3167	12338	17023
	35-62	17077	2.7	147.8	1575	2875	11906	16507
	62-95	3975	2.6	35.1	1556	993	1281	3868
	95-114	2970	2.1	13.1	211	653	1975	2854
	114-150	2297	1.9	6.2	87	237	1669	2001

tributed to parent material heredity and processes through soil genesis. Other authors (Levesque and Mathur 1996) have also found similar trends for these metals in cultivated organic soils. Prevailing forms of Fe and Mn were those extracted by HNO<sub>3</sub>, Na<sub>2</sub>-EDTA and NaOH (sulfide and carbonate associated with and organically bound form, respectively). Iron deficiency symptoms have been observed in certain crops of the studied area, especially in slightly alkaline soils with high calcium carbonate content. According to Greek experience, a range between 25 to 50 µg g<sup>-1</sup> for soil available iron is considered adequate for main arable crops demand. Hence, the observed iron deficiency symptoms in certain soil spots can be attributed mainly to the presence of calcium carbonate and partially to micronutrient disorders.

Manganese deficiency was also observed in some maize crops cultivated in slightly alkaline soils due to oxidation of this element during the dry and warm growing period. Calcareous peat soils are frequently low in available Mn and it is on these soils that Mn deficiency often occurs in crops. Soil analysis is not very reliable in diagnosing available soil Mn status in relation to crop response and is assumed that ammonium acetate extractable Mn correlates best with Mn deficiency (Mengel and Kirkby 1979). The following regressions were found between pseudototal Fe and

pseudototal Mn:

$$Y_{\text{Fepseudotot}} = 712.9 + 22.0X_{\text{Mnpseudotot}} ;$$

(n=15, r<sup>2</sup>=64.77\*\*\*, p<0.001)

The mean content was 17.3 µg g<sup>-1</sup> for copper (Table 4) and 72.3 µg g<sup>-1</sup> for zinc (Table 5), whilst the dominant forms in both elements were sulfide, carbonate associated and organically bound form. The mean content for copper that was found in Canadian organic soils was about eight times higher (Levesque and Mathur 1986) and was not attributed only to parent material differences, but also to applications of Cu to organic soils. In general, the copper content in the studied soils is assumed to be in normal levels, which can be ascribed mainly to the origin and weathering of parent material during soil genesis. A strong relation was found between the organically bound form and Cu extracted by 4M HNO<sub>3</sub>:

$$Y_{\text{Cu(NaOH)}} = -0.33 + 0.40X_{\text{Cusum}} ;$$

(n=15, r<sup>2</sup>=94.3\*\*\*, p<0.001)

In practice, high available phosphate levels in soil are well known to reduce Zn availability and can resulting Zn deficiency. It was formerly held that this occurred because the formation of zinc phosphate in the soil reduced the Zn concentration in the soil solution to deficiency levels (Mengel and Kirkby 1979). Although in the examined

Table 3. Concentration and distribution of manganese within soil horizons.

Profile	Depth (cm)	Mn <sub>pseudot.</sub> µg g <sup>-1</sup>	Sequential extraction					SUM µg g <sup>-1</sup>
			Mn <sub>KNO3</sub>	Mn <sub>H2O</sub>	Mn <sub>NaOH</sub> µg g <sup>-1</sup>	Mn <sub>EDTA</sub>	Mn <sub>HNO3</sub>	
P1	0-38	582	1.3	4.1	14.9	192	218	430
	38-62	475	1.2	4.0	15.1	217	202	439
	62-93	455	1.2	4.8	18.3	202	190	416
	93-134	55	1.3	0.2	5.5	25	17	49
	134-160	370	2.8	8.3	20.8	153	167	352
P2	0-28	312	1.6	1.0	19.2	126	143	291
	28-52	102	1.9	0.2	15.7	45	28	91
	52-75	140	2.1	0.3	21.0	57	47	127
	75-107	129	2.6	0.6	17.9	65	28	114
	107-135	84	4.1	1.1	6.2	39	23	73
P3	0-35	585	0.9	6.6	22.3	333	196	559
	35-62	550	0.9	6.6	23.4	315	178	524
	62-95	123	1.0	0.6	20.1	61	32	115
	95-114	327	4.8	4.8	19.7	152	120	301
	114-150	120	5.1	1.7	5.7	65	36	114

soils farmers add appreciable amounts of phosphate fertilizers, zinc deficiency was not recorded.

Lead content ranges between 20.5–143  $\mu\text{g g}^{-1}$  and the mean lead concentration (Table 6) was Pb 58.2  $\mu\text{g g}^{-1}$ , whilst the main forms were found to be sulfide and carbonate associated. In general, the surface or upper subsurface layers have a higher Pb content, but discontinuities in this ele-

ment may be attributed to stratified deposits, which differ in organic matter content and decomposition degree. This explanation is in accordance with other authors (Kabata-Pendias and Pendias 1984) who reported that the greatest Pb concentrations are often exhibited in the organic rich horizons. The accumulation of lead in soil surface horizons is of great ecological importance

Table 4. Concentration and distribution of copper within soil horizons.

Profile	Depth (cm)	$\text{Cu}_{\text{pseudot.}}$ $\mu\text{g g}^{-1}$	Sequential extraction					SUM $\mu\text{g g}^{-1}$
			$\text{Cu}_{\text{KNO}_3}$	$\text{Cu}_{\text{H}_2\text{O}}$	$\text{Cu}_{\text{NaOH}}$ $\mu\text{g g}^{-1}$	$\text{Cu}_{\text{EDTA}}$	$\text{Cu}_{\text{HNO}_3}$	
P1	0-38	40.0	1.4	2.2	14.0	9.1	12.4	39.1
	38-62	39.5	1.3	1.9	14.1	9.9	11.6	38.8
	62-93	33.4	1.4	1.9	12.0	7.9	9.8	33.0
	93-134	8.4	1.3	0.8	2.2	1.9	2.1	8.3
	134-160	9.5	1.2	0.5	1.7	2.0	3.5	8.9
P2	0-28	15.5	1.3	1.0	6.2	3.7	3.1	15.3
	28-52	7.8	1.4	0.5	3.2	1.7	0.8	7.6
	52-75	11.1	1.6	1.1	5.1	2.1	1.1	11.0
	75-107	8.6	1.1	0.7	2.4	2.0	2.1	8.3
	107-135	6.5	1.1	0.9	1.5	1.6	1.3	6.4
P3	0-35	26.9	1.1	1.2	12.2	7.9	3.3	25.7
	35-62	25.9	1.0	1.1	11.1	7.0	4.0	24.2
	62-95	13.9	1.1	0.7	6.6	3.2	2.2	13.8
	95-114	7.9	1.1	0.6	1.8	2.1	1.5	7.1
	114-150	4.5	0.9	0.7	1.0	1.1	0.7	4.4

Table 5. Concentration and distribution of zinc within soil horizons.

Profile	Depth (cm)	$\text{Zn}_{\text{pseudot.}}$ $\mu\text{g g}^{-1}$	Sequential extraction					SUM $\mu\text{g g}^{-1}$
			$\text{Zn}_{\text{KNO}_3}$	$\text{Zn}_{\text{H}_2\text{O}}$	$\text{Zn}_{\text{NaOH}}$ $\mu\text{g g}^{-1}$	$\text{Zn}_{\text{EDTA}}$	$\text{Zn}_{\text{HNO}_3}$	
P1	0-38	107	1.2	3.9	9.3	22.0	61.0	97.4
	38-62	105	1.3	4.1	10.5	21.1	58.9	95.9
	62-93	98	1.1	3.9	9.7	24.7	55.9	95.3
	93-134	43	1.3	2.5	6.3	15.2	11.3	36.6
	134-160	42	1.0	1.5	5.7	16.4	14.8	39.4
P2	0-28	37	0.9	1.2	5.3	9.8	15.3	32.5
	28-52	22	1.3	1.2	4.2	6.0	5.0	17.7
	52-75	29	1.1	1.0	7.9	12.3	5.6	27.9
	75-107	56	1.2	1.7	10.6	22.1	15.6	51.2
	107-135	185	1.7	2.4	26.3	73.8	78.4	182.6
P3	0-35	82	0.8	2.2	8.2	16.8	47.4	75.4
	35-62	77	0.8	2.0	7.7	16.7	45.8	73.0
	62-95	47	0.9	1.1	13.8	14.4	12.8	43.0
	95-114	60	0.9	1.8	12.2	14.5	29.4	58.8
	114-150	94	0.9	2.0	12.1	24.1	48.6	87.7

because it restricts the potential of biological activities and consequently leads to soil organic matter increase due to uncompleted decomposition (Tyler 1976).

Mean nickel concentration (Table 7) was  $33.3 \mu\text{g g}^{-1}$ , about four times higher than other organic soils (Levesque and Mathur, 1986) and ranged between  $15.0\text{--}64.7 \mu\text{g g}^{-1}$ . It was reported that in

Danish *Histosols* the content ranges between  $1.9\text{--}5.0 \mu\text{g g}^{-1}$  whilst in Polish *Histosols* it ranges between  $0.2\text{--}50.0 \mu\text{g g}^{-1}$  (Kabata-Pendias and Pendias 1984). Nickel distribution in soil profiles is related either to organic matter or to amorphous oxides and clay fractions, depending on soil types. However, the Ni concentration in surface soils also reflects soil forming processes and pollution

Table 6. Concentration and distribution of lead within soil horizons.

Profile	Depth (cm)	$\text{Pb}_{\text{pseudot.}}$ $\mu\text{g g}^{-1}$	Sequential extraction					SUM $\mu\text{g g}^{-1}$
			$\text{Pb}_{\text{KNO}_3}$	$\text{Pb}_{\text{H}_2\text{O}}$	$\text{Pb}_{\text{NaOH}}$ $\mu\text{g g}^{-1}$	$\text{Pb}_{\text{EDTA}}$	$\text{Pb}_{\text{HNO}_3}$	
P1	0-38	110.6	0.5	4.9	9.8	44.7	48.2	108.1
	38-62	142.9	0.6	5.6	17.4	59.1	50.8	133.5
	62-93	114.8	0.8	5.1	10.2	41.5	43.4	101.0
	93-134	24.3	1.3	5.4	0.3	8.7	7.8	23.5
	134-160	35.6	0.3	2.8	0.4	8.7	20.5	32.7
P2	0-28	70.6	1.9	1.0	5.4	22.1	32.0	62.4
	28-52	30.0	1.9	4.9	1.3	9.9	5.6	23.6
	52-75	30.7	0.9	3.2	2.8	9.6	5.6	22.1
	75-107	20.5	0.3	3.6	0.4	8.4	6.8	19.5
	107-135	22.3	0.4	2.8	n.d.	7.6	8.1	18.9
P3	0-35	94.2	0.3	3.4	7.1	37.2	43.0	91.0
	35-62	84.0	0.5	3.8	7.4	34.5	35.1	81.3
	62-95	33.5	1.4	3.8	3.2	12.6	8.9	29.9
	95-114	36.7	0.4	5.1	n.d.	8.5	13.1	27.1
	114-150	23.1	0.4	4.5	n.d.	8.1	7.5	20.5

Table 7. Concentration and distribution of nickel within soil horizons.

Profile	Depth (cm)	$\text{Ni}_{\text{pseudot.}}$ $\mu\text{g g}^{-1}$	Sequential extraction					SUM $\mu\text{g g}^{-1}$
			$\text{Ni}_{\text{KNO}_3}$	$\text{Ni}_{\text{H}_2\text{O}}$	$\text{Ni}_{\text{NaOH}}$ $\mu\text{g g}^{-1}$	$\text{Ni}_{\text{EDTA}}$	$\text{Ni}_{\text{HNO}_3}$	
P1	0-38	60.3	5.0	1.3	11.2	9.6	29.5	56.6
	38-62	61.6	4.9	2.3	12.0	10.9	27.5	57.6
	62-93	64.7	4.8	2.6	10.5	8.7	24.1	50.7
	93-134	20.0	4.7	0.6	4.4	3.8	3.3	16.8
	134-160	23.9	4.5	1.0	4.1	3.9	9.8	23.3
P2	0-28	34.6	4.5	0.5	6.6	5.6	9.3	26.5
	28-52	20.7	5.0	0.7	4.9	4.1	2.2	16.9
	52-75	21.1	4.7	1.8	6.0	4.6	2.6	19.7
	75-107	19.8	4.3	1.6	3.5	4.1	2.9	16.4
	107-135	15.0	4.3	1.5	2.1	3.9	2.5	14.3
P3	0-35	36.3	4.1	1.2	5.4	7.3	11.7	29.7
	35-62	37.3	3.8	0.6	5.3	6.4	14.0	30.1
	62-95	28.0	3.8	0.5	5.9	5.5	5.9	21.6
	95-114	33.2	3.5	0.8	3.6	3.6	6.2	27.7
	114-150	22.4	3.6	0.4	3.0	3.3	5.2	15.5

(Kabata-Pendias and Pendias 1984). It was found that the dominant forms were sulfide, carbonate associated and organically bound form.

The mean cadmium content (Table 8) was Cd 5.1  $\mu\text{g g}^{-1}$  and the prevailing forms were sulfide and carbonate associated. This concentration is relatively high and may reflect the phosphate fertilization in combination with the chemical composition of the parent material. Phosphate fertilizers are also known as important sources of Cd and this has been found in Greek soils cultivated with asparagus (Karyotis et al. 1995).

The distribution of trace elements greatly differs amongst the examined samples and the range of the pseudototal form of Fe was 1873–18550  $\mu\text{g g}^{-1}$ , of Mn 54.7–585, of Cu 4.5–40, of Zn 22.0–185, of Pb 20.5–143, of Ni 15–64.7 and Cd 3.3–6.9  $\mu\text{g g}^{-1}$ . The sum of Fe ranged 83.5–98.9% of the pseudototal form, of Mn 74.0–95.5%, of Cu 89.9–99.3%, of Zn 80.5–97.5%, of Pb 72.0–97.7%, of Ni 69.2–97.5% and Cd 65.6–98.2% (Table 9).

The sequentially extracted by  $\text{HNO}_3$ ,  $\text{Na}_2\text{EDTA}$ , and  $\text{NaOH}$  were found to be the prevailing metal forms and represent a significant percentage of the sum.

Pronounced differences of heavy metals among soil profiles were recorded (Table 10). Mean content of pseudototal form was higher in

the P1 except for iron in which P3 was richest. Boron concentration was found equal in both profiles P1 and P3 and higher in P2.

Average content of the plant available boron in the fifteen samples was 1.19  $\mu\text{g g}^{-1}$ , whilst the range was between 0.6–2.3  $\mu\text{g g}^{-1}$  (SD 0.5). Deficiency symptoms were observed in certain areas cultivated with sugar beets. This phenomenon is restricted in sandy soils where the infiltration rate is very high. A weak relationship between organic carbon and boron was found, indicating that an amount of boron is bound to soil organic matter:

$$Y_{\text{boron}} = -0.42 + 0.01X_{\text{org. carbon}} ; \\ (n=15, r^2= 31.6^*, p<0.05)$$

The pH ranged between 6.2–7.8 (Table 1) and it should be stressed that six subsurface soil samples were acid. Slightly alkaline soils containing  $\text{CaCO}_3$  are located on depressions and the calcium carbonate originates from decomposed microorganisms' cells that lived in the soil.

It can be argued that these soils are very vulnerable and management strongly affects physical, chemical as well as biological properties. A soil surface subsidence of about 1–3.5 meters, has been estimated to have occurred over the last fifty years. Rational water management, tillage practices, avoidance of heavy machinery and proper fertilization could contribute to the soil and water

Table 8. Concentration and distribution of cadmium within soil horizons

Profile	Depth (cm)	$\text{Cd}_{\text{pseudototal}}$ $\mu\text{g g}^{-1}$	Sequential extraction					SUM $\mu\text{g g}^{-1}$
			$\text{Cd}_{\text{KNO}_3}$	$\text{Cd}_{\text{H}_2\text{O}}$	$\text{Cd}_{\text{NaOH}}$ $\mu\text{g g}^{-1}$	$\text{Cd}_{\text{EDTA}}$	$\text{Cd}_{\text{HNO}_3}$	
P1	0-38	5.7	0.2	n.d.	0.7	2.1	2.6	5.6
	38-62	6.4	0.2	n.d.	0.7	2.0	2.5	5.4
	62-93	5.9	0.2	n.d.	0.7	2.0	2.6	5.5
	93-134	3.8	0.2	n.d.	n.d.	1.4	1.1	2.7
	134-160	6.1	0.2	n.d.	n.d.	1.5	3.7	5.4
P2	0-28	6.9	0.2	n.d.	0.6	1.8	2.7	5.3
	28-52	4.7	0.5	0.5	0.5	1.5	0.5	3.5
	52-75	4.9	0.4	0.3	0.8	1.5	0.5	3.5
	75-107	3.8	0.2	0.4	0.3	1.6	0.8	3.3
	107-135	3.6	0.2	0.8	0.3	1.4	0.8	3.5
P3	0-35	5.3	0.2	0.4	0.7	2.1	1.5	4.9
	35-62	5.7	0.2	0.3	0.7	1.9	1.2	4.3
	62-95	3.6	0.2	0.3	0.5	1.7	0.8	3.5
	95-114	6.4	0.2	0.6	0.2	1.5	1.7	4.2
	114-150	3.3	0.2	0.2	n.d.	1.3	0.8	2.5



quality, without any yield reduction.

Among the public works, care can be taken in drainage and groundwater level maintainance at the proper depth in which oxidation of organic matter and soil subsidence risk are minimized. The productivity depends very much on proper management and degradation of peat soils can be ameliorated by application of practices, such as: nutrient management, maintenance of soil fertility and protection of soil and water resources, drainage and groundwater surface preservation at the highest possible level in order to reduce organic matter oxidation rate and the associated soil subsidence. Overliming of acid *Histosols* should be avoided because at high pH values organic colloids bind micronutrients such as Zn, Cu and Mn, leading to deficiency symptoms.

#### 4. CONCLUSIONS

Most of the material of the studied soils was mineral matter, organic matter and total soil nitrogen

contents were higher than the mean contents usually observed in Greek soils and irregularities could be attributed to deposition of organic layers during soil formation. The pH values vary within horizons, and in one of the profiles all soil layers were found either neutral or alkaline. Average content of the elements extracted by 4M HNO<sub>3</sub> was higher for Fe and Mn, whilst low content was determined for Cu and Cd. The exhibited content discontinuities can be attributed to stratification of soil horizons by means of soil forming processes.

The distribution of trace elements greatly varies amongst the examined samples, and so does the sum of metals to the pseudototal form. The sequentially extracted by HNO<sub>3</sub>, Na<sub>2</sub>-EDTA, and NaOH were found to be the main forms for Fe, Mn, Cu, Zn and Ni. It is obvious that the sequentially extracted by HNO<sub>3</sub> and Na<sub>2</sub>-EDTA were found to be the dominant forms which represent a significant percentage of the sum.

Pronounced differences of trace elements between the examined soil profiles were recorded.

Table 9. Ratio of sum of the sequentially extracted metals to pseudototal form (%).

Profile	Depth (cm)	Fe <sub>sum</sub> /Fe <sub>pseud</sub>	Mn <sub>sum</sub> /Mn <sub>pseud</sub>	Cu <sub>sum</sub> /Cu <sub>pseud</sub>	Zn <sub>sum</sub> /Zn <sub>pseud</sub>	Pb <sub>sum</sub> /Pb <sub>pseud</sub>	Ni <sub>sum</sub> /Ni <sub>pseud</sub>	Cd <sub>sum</sub> /Cd <sub>pseud</sub>
P1	0-38	83.5	74.0	97.8	90.8	97.7	93.9	98.2
	38-62	88.4	92.5	98.2	91.3	93.4	93.5	84.4
	62-93	85.7	91.6	98.8	97.2	88.0	78.4	93.2
	93-134	97.5	90.1	98.8	84.7	96.7	84.0	71.0
	134-160	87.3	95.1	93.7	93.8	91.8	97.5	88.5
P2	0-28	94.3	93.2	98.7	87.1	88.4	76.6	76.8
	28-52	96.8	89.3	97.4	80.5	78.7	81.6	74.5
	52-75	98.9	91.5	99.1	97.2	72.0	93.4	71.4
	75-107	98.7	89.1	96.5	91.3	95.1	82.8	86.8
	107-135	97.1	87.5	98.5	98.5	84.7	95.3	97.2
P3	0-35	91.8	95.5	95.5	91.7	96.6	81.8	92.4
	35-62	96.7	95.1	93.4	95.2	96.8	80.7	75.4
	62-95	97.3	93.1	99.3	90.7	89.2	77.1	97.2
	95-114	96.1	91.9	89.9	97.5	73.8	83.4	65.6
	114-150	87.1	94.8	97.8	93.7	88.7	69.2	75.8

Table 10. Mean content of trace elements among soil profiles (4 M HNO<sub>3</sub>)

Profile	Fe <sub>pseudot.</sub>	Mn <sub>pseudot.</sub>	Cu <sub>pseudot.</sub> µg g <sup>-1</sup>	Zn <sub>pseudot.</sub>	Pb <sub>pseudot.</sub>	Ni <sub>pseudot.</sub>	Cd <sub>pseudot.</sub>	boron
P1	7493	387	26.2	79	86	46	5.6	1.0
P2	5103	153	9.9	66	35	22	4.8	1.6
P3	8974	341	15.8	72	54	31	4.9	1.0

Mean content of pseudototal form was higher in the P<sub>1</sub> except for iron in which P<sub>3</sub> was richest. Boron concentration was found equal in both profiles P<sub>1</sub> and P<sub>3</sub> and higher in P<sub>2</sub>.

The Cd content was found relatively high and may originate both from parent material and phosphate fertilization. The distribution of trace elements greatly differs amongst the examined samples, and the sum of the sequentially extracted elements also varies.

Relationship between pseudototal Fe and pseudototal Mn, as well as between Cu extracted by NaOH and Cu extracted by 4M HNO<sub>3</sub>, were revealed. The weak relationship between organic carbon and boron ( $p < 0.05$ ) indicates that boron is bound to soil organic matter.

More research should be carried out mainly on tillage practices, irrigation schedules and application of fertilizers. Furthermore, studies regarding micronutrient uptake are going to be conducted in certain crops in combination with study of micronutrients mineralization.

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