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ORIGINAL ARTICLE

Trace element concentrations of soils, plants and waters caused by a copper smelting plant and other industries, Northeast Turkey

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Abstract The study area is situated in a large agricultural field which produces tobacco, maize, and other yearly cultivated vegetables in Tekkeköy, Samsun (NE-Turkey). In addition, a significant part of this area to the north along the Black Sea coast is occupied by several industrial plants such as a copper smelting plant (KBİ), a fertilizer plant (Tügsaş) and industrial park facilities (IPF). In order to reveal their environmental impacts, heavy metal analyses were conducted on soil, plant leaves and water samples collected within an area of approximately 30 km^2 around these plants. Soil samples within an area of 10 km^2 around these facilities are found to be highly polluted with Cu, Zn, Pb, Fe and Mn. Pollution occurs at surface and sharply dies out at 20 cm downwards in soil profile. Since the region is polluted mostly with base metals, the copper smelting factory appears to be the main source of pollution as it processes the massive sulfidic ores of the Black Sea area. Plants show Cu, Pb, Zn and Fe pollution around KBİ and Tügsaş and Cu and Pb around IPF. Pollutants observed in tobacco (Nicotiana tobacum) are Cu, Pb, Zn, Fe and S; in maize (Zea mays) Cu, Zn and Fe; and in cabbage (Brassica oleracea) Cu, Pb, Fe and S. The analyses of water samples collected from the study area reveal that Pb and, to a lesser degree, Cu and Fe pollution stem from KBİ; Cu, Fe and Mn pollution from Tügsaş; and Pb and minor amounts of Fe and Mn pollution from IPF. Factor analyses from analyzed metals and anionic complexes in water show three distinct groups: (a) an association of heavy metals with Na, K and Mg referring to pollution and acid leaching of soil, (b) an association of NH4, Fe, SO_4, Cl and Br indicating agricultural pollution and sea-water invasion in land near the shore line, and (c) HCO_3 behaving in a different manner in heavy metal precipitation.

Keywords Samsun · Tekkeköy · Karadeniz copper industries smelting plant · Fertilizer industry · The industrial park facilities · Pollution · Soil · Plants · Water

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Introduction

Organisms live in their specific habitats and that constitute their environment. At present, environment is defined as the physical place people live in. Industrial and mining activities have negative impacts on the ecological balance and particularly on flora and fauna. Therefore, people and their environments are being affected, strongly. Nowadays, environmental awareness and studies concerning environmental issues draw considerable attention in Turkey. From a sustainable development point of view, both the continuity of industrial and mining activities and the minimization of possible adverse effects of these activities are required. With this purpose, areas surrounding Karadeniz Copper Industries Smelting Plant (KBİ), Fertilizer Industry (Tügsaş) and Industrial Park Facilities (IPF) located in Tekkeköy, Samsun (NE/Turkey) are chosen as the study area (Fig. 1).

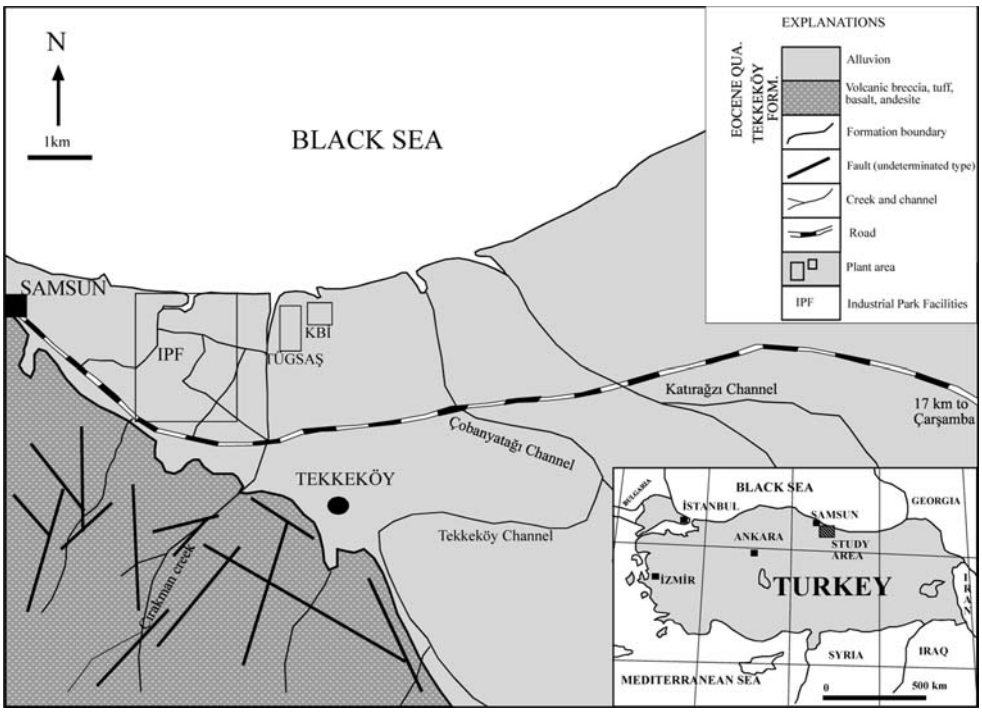


Fig. 1 Location and geologic map of the study area (revised from Yoldaş et al. 1985)

In previous studies performed in the study area, Müezzinoğlu (1973) had measured gaseous emissions of Fertilizer Industry (Tügsaş) before KBİ started its production. He had observed a release of 615 kg/h SO_2 from the Tügsaş chimney to the atmosphere. He stated that even if little amount of gaseous emissions release to atmosphere, because of rainy climate and high relative moisture observed in the region, these gaseous emissions have done acidic effects on soils and vegetation.

Çepel et al. (1980) examined the effects of SO_2 on some tree species of the Gelemen Forest Nursery. They found damages on coniferous trees and on tobacco leaves because of SO_2 release from KBİ and Tügsaş to the atmosphere.

Atamer (1985) studied the soils around KBİ and Tügsaş. He stated Tekkeköy and Çarşamba plains were highly polluted with heavy metals by these industries. He also expressed that heavy metal pollution resulted from undesirable raw materials during production stage and from the insufficiently operated instruments.

Kara et al. (1998) concluded that gaseous emissions released from chimneys of KBİ and Tügsaş to the atmosphere caused a great impact on some chemical characteristics, biological characteristics and microelements contents of agricultural soils the in region. They stated that these emissions have a polluting effect on the soils which had been limited to surface soil.

Although several environmental studies in this region had been carried out by some scientists (Çepel et al. 1980; Atamer 1985; Kara et al. 1998 etc.), none of these researchers examined environmental impacts on both soil, plant and water around KBİ, Tügsaş and IPF. Therefore this study aims to reveal the environmental impacts of these industries and to solve possible environmental problems that originated from KBİ, Tügsaş and IPF. The reason for choosing this area is that Çarşamba plain serves as a first-class cultivation field and hence meets a significant part of vegetable needs of the region. Moreover, since the study area is located at the seashore, facilities might have negative effects on sea.

Geology

The study area is situated in the East Pontides tectonic belt of Turkey. Eocene aged Tekkeköy Formation named by Yoldaş et al. (1985) and Quaternary alluvion are observed in the study area (Fig. 1). Volcano-sedimentary rocks dominate the basal part of Tekkeköy Formation and grade upwards into volcanites. Dark brown-colored volcanic breccia and green-white, cream-colored tuff are observed at the basement, whereas upper levels are represented by basalt and green, black-brown-colored andesite.

Volcanic breccia from place to place is loosely cemented and is fairly hard and solid in the study area. It contains few angular basalt and few gravels and blocks of andesite. It was observed that the tuff consists of

volcanic rock and crystal fragments. Groundmass is usually altered and likely to be carbonated and commonly clayed.

Materials and methods

Rock, soil, plant and water samples were collected from the vicinity of KBİ, Tügsaş and IPF in March 1999, August 2000, June 2001 and October 2001 (Fig. 2 a, b, c, d). In this sampling, water samples were collected from discharge water, sea, stream and groundwater. Soil and plant samples were collected from waste area and from surrounding soils (agricultural area). In addition, some more soil samples were collected from an area at a close proximity to KBİ both at surface (0–20 cm) and depth (20–50 cm) (Fig. 2a).

During August 2000 period, 9 soil, 14 plant and 10 water samples were collected from the study area (Fig. 2b). Two of water samples were tap water samples which are represented with (Ç). Water samples were filtered with porous unsized paper during collection and acidified by adding 2–3 ml of HNO_3 to 2 l polyethylene bottles to prevent the precipitation of metals and analyzed for heavy metals (SA: denotes water samples protected by HNO_3, analyzed for heavy metals).

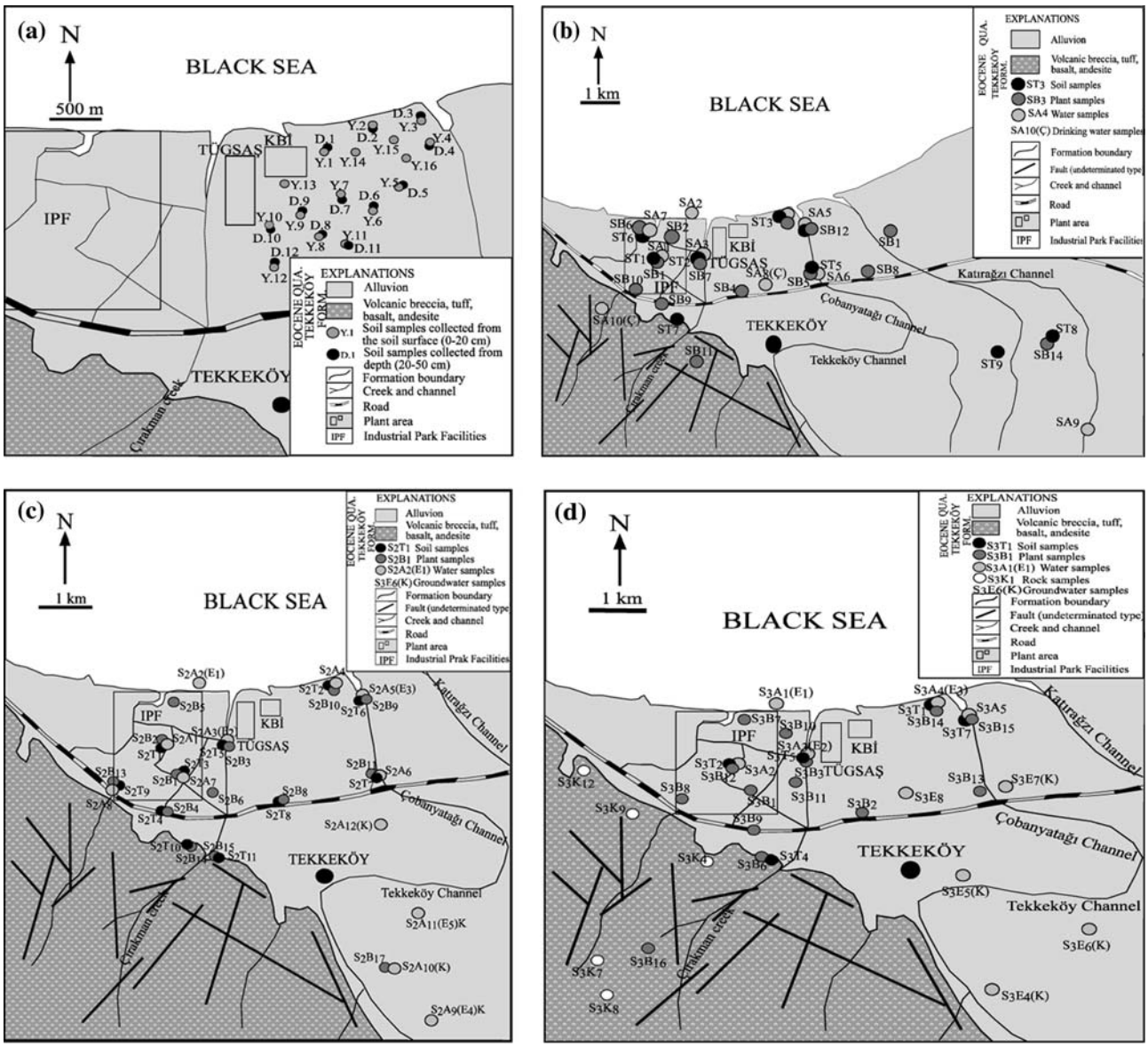


Fig. 2 **a** Maps showing sample locations in March 1999 **b** in August 2000 **c** in June 2001 and **d** in October 2001

In June 2001, 11 soil, 14 plant and 17 water samples were collected from the study area (Fig. 2c). Twelve of the water samples were analyzed for heavy metals and five others denoted as SE were analyzed for Na^+, K^+, Ca^{2+}, Cl^-, SO_4^{2-}, and F^-. Four of the analyzed water samples were groundwater samples and are represented with (K).

During the October 2001 period, 5 rock samples, 5 soil samples, 14 plant samples and 13 water samples were collected from the study area (Fig. 2d). Five of the water samples were analyzed for heavy metals, and eight others for some cations and anions.

Soil samples collected from the surface at 16 locations and depth 12 locations around KBİ in March 1999 period were analyzed for heavy metals by ICP-MS in the Acme Laboratory of Canada. Other soil, plant, water and rock samples collected from the study area were sent for analysis to the Geochemistry and Mineralogy Laboratories of the General Directorate of Mineral Research and Exploration (MTA). Soil samples were analyzed for heavy metals by ICP-AES using analysis method applied by Thompson and Walsh (1989). Plant samples were analyzed for heavy metals by ICP-AES using wet ashing technique applied by Kaçar (1972). Water samples were analyzed for heavy metals by ICP-AES and AAS using ASTM (1995) and standard methods (1980). Environmental impacts of KBİ, Tügsaş and IPF were determined depending on the results obtained from the above mentioned studies and possible sources and levels of pollution were tried to be determined.

Results and discussion

Soil pollution

Soils form as a result of chemical and mechanical weathering of rocks. Soil formation takes place under the influence of climatic and topographic controls, microbiological processes, the abundance of an element in the parent rock, the nature and duration of the weathering processes operating on the parent rock, gains and losses by physical processes, the solubility of the primary and secondary mineral phases present in the parent rock and in the soil, the type of vegetation and the type and amount of organic matter in the soil. As it is known, if element concentrations in the soils exceed critical levels (threshold value) defined for elements in soils, pollution occurs in soils. Critical levels described for some heavy metals in the soils are given in Table 1.

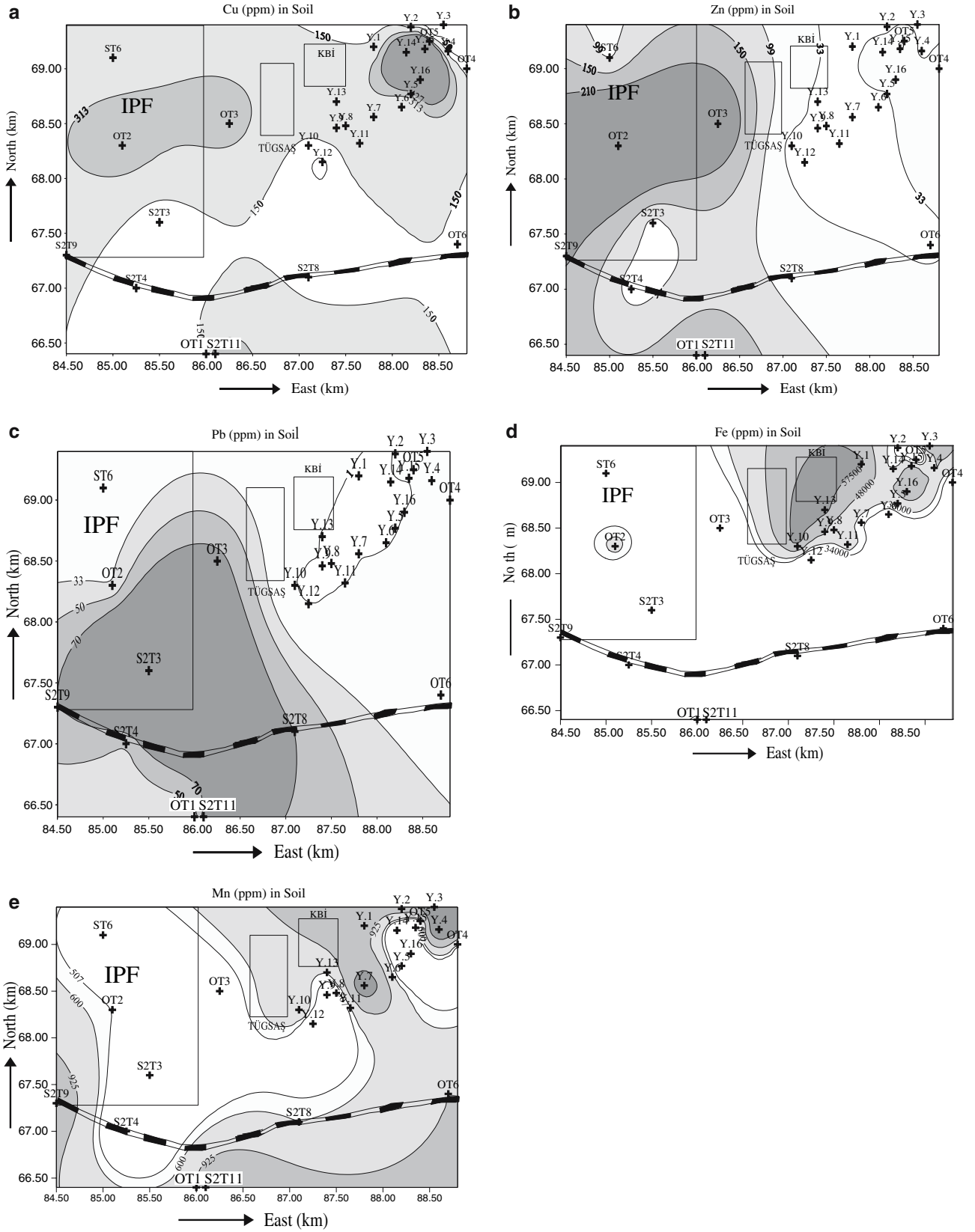
Element distributions

Distribution diagrams of element concentrations were examined for some elements (Cu, Pb, Zn, Fe and Mn) in all the soil samples collected from the study area. 50, 75 and 90th % values of concentrations of Cu, Pb, Zn, Fe and Mn were used to construct the equal concentration curves in distribution diagrams of element concentrations, by accepting threshold values the concentrations given in Table 1 (The critical values of heavy metals in Soil Pollution Control Regulation (Official Gazette, 2001) for Cu, Pb, Zn, Cd and according to the critical element values in soils described by Lindsay (1979) for Fe, Mn, and S). Kriging method was used to form distribution diagrams of element concentrations.

Cu values in soils of the study area are all over the critical value (>50 ppm) as defined by Soil Pollution Control Regulation of Turkey (Official Gazette 2001) (Fig. 3a). The highest concentrations of Cu were observed east of KBİ in the north-eastern part of the study area where Cu concentrations exceeded critical value 7–32 times. Similarly, Cu concentrations in samples numbered OT2 and OT3 west of Tügsaş (Fertilizer Industry) and near IPF were found to exceed the critical value (>50 ppm). Generally, an overall decrease in the Cu concentrations was observed further away from KBİ, Tügsaş and IPF. However, Cu concentrations were rather high in samples numbered S2T11 and OT1 collected from agricultural soils in the southern part of the study area. It is considered that high Cu concentrations probably originated from agricultural chemicals because there is not any ore related occurrence or any industries in this part of the study area. But, more data are needed to verify this

Table 1 Critical levels for some heavy metals in soils

Elements (ppm)	Critical levels	
	(Lindsay 1979)	Soil Quality Control Regulation of Turkey (Official Gazette 2001)
As	5	20
Cd	0.06	1
Co	8	20
Cr	100	100
Cu	30	50
Mo	2	10
Ni	40	30
Pb	10	50
Zn	50	150
Fe	38,000	
Mn	600	
S (%)	0.07	


a
Cu (ppm) in Soil
b
Zn (ppm) in Soil
c
Pb (ppm) in Soil
d
Fe (ppm) in Soil
e
Mn (ppm) in Soil
IPF
KBİ
TÜGSAŞ
ST6
OT1
OT2
OT3
OT4
OT5
OT6
S2T3
S2T4
S2T8
S2T9
S2T11
Y.1
Y.2
Y.3
Y.4
Y.5
Y.6
Y.7
Y.8
Y.10
Y.11
Y.12
Y.13
Y.14
Y.16
North (km)
East (km)
No th (m)

◀ **Fig. 3** **a** Distribution diagram of Cu concentrations in all soil surface samples collected from study area (Samples numbered Y are collected during March 1999, ST numbered samples are collected during August 2000 and June 2001; samples numbered OT are the average of the samples collected from the same locations that are collected during August 2000–June 2001–October 2001) **b** Distribution diagram of Zn concentrations in all soil surface samples collected from study area (Samples numbered Y are collected during March 1999, ST numbered samples are collected during August 2000 and June 2001; samples numbered OT are the average of the samples collected from the same locations that are collected during August 2000–June 2001–October 2001). **c** Distribution diagram of Pb concentrations in all soil surface samples collected from study area (Samples numbered Y are collected during March 1999, ST numbered samples are collected during August 2000 and June 2001; samples numbered OT are the average of the samples collected from the same locations that are collected during August 2000–June 2001–October 2001). **d** Distribution diagram of Fe concentrations in all soil surface samples collected from study area (Samples numbered Y are collected during March 1999, ST numbered samples are collected during August 2000 and June 2001; samples numbered OT are the average of the samples collected from the same locations that are collected during August 2000–June 2001–October 2001). **e** Distribution diagram of Mn concentrations in all soil surface samples collected from study area (Samples numbered Y are collected during March 1999, ST numbered samples are collected during August 2000 and June 2001; samples numbered OT are the average of the samples collected from the same locations that are collected during August 2000–June 2001–October 2001)

interpretation. If Cu concentrations observed in soils around these industries (KBİ, Tügsaş and IPF) were compared with similar industries operating metals in the world, Cu accumulation appeared fairly high in the surficial soils around KBİ, Tügsaş and IPF. Kabata-Pendias et al. (1981) expressed that soils contain 75–125 ppm Cu around a Cu smelter.

Zn concentrations in soils of the study area exceed critical value (>150 ppm) for Zn as described by Soil Pollution Control Regulation of Turkey (Official Gazette 2001) around Tügsaş and IPF (Şekil 3b). Zn concentrations observed around these industries are 2 to 3 times higher than the critical value, whereas Zn concentrations in all soil samples collected from KBİ are lower than the critical value. A gradual decrease in the concentrations of Zn was observed further away from Tügsaş and IPF. Therefore it is considered that Tügsaş and IPF are attributed to Zn pollution in soils. On the other hand, a reliable interpretation could not be made about high Zn concentrations observed in samples numbered S2T11 and OT1 collected from agricultural soils in the south of study area, as described for Cu distribution. In studies made around similar industries operating Zn-Pb, John et al. (1975) expressed that soils of Canada contain 185–1,397 ppm Zn; Harmsen (1977) stated that soils of Netherlands contain 915–3,626 ppm Zn; Johnson et al. (1975) expressed that soils of England contain 155–12,400 ppm Zn. Consequently, above stated Zn values are similar to Zn concentrations observed around Tügsaş and IPF.

Distribution diagram of Pb is similar to that of Zn. Pb concentrations are significantly higher around Tügsaş and IPF (Fig. 3c). Pb shows 2–4 times enrichment around Tügsaş and IPF according to critical value (>150 ppm) described by Soil Pollution Control Regulation of Turkey (Official Gazette 2001) for Pb. It is considered that Tügsaş and IPF caused Pb pollution in soils.

If Fe and Mn concentrations in soils of the study area are compared with critical levels (38,000 ppm for Fe and 600 ppm for Mn) in soils as described by Lindsay (1979) for Fe and Mn, they show significant enrichment around KBİ (Fig. 3d, e). Fe concentrations observed in soils around KBİ show two times enrichment relative to the critical value. Mn concentrations observed in soils around KBİ indicate 1.5–4.5 times enrichment with respect to the critical value. Fe concentration in sample numbered as OT2 collected from IPF exceeded the critical value. It is considered that KBİ attributed to Fe and Mn pollution in soils.

In order to see the downward variation of heavy metal concentration in soils, an area around KBİ was chosen to sample both at surface (0–20 cm) and depth (20–50 cm) in March 1999. Cu concentrations in soil samples collected from surface exceed the critical value (>50 ppm) described by Soil Pollution Control Regulation of Turkey (Official Gazette 2001) (Table 1 and Fig. 4a) and show significantly high values at northeastern part of the study area (>313 ppm) whereas Cu concentrations in soil samples collected from depth around KBİ waste area are much lower than Cu concentrations in soil samples collected from surface (Fig. 4b). The enhanced topsoil concentrations generally indicate a nonlithogenic source (anthropogenic) for the contamination.

Statistical analysis

Factor analysis Factor analysis (FA) is a receptor model technique that has been widely applied to the quantitative apportionment of large data set into several key components which may represent diverse source processes (Davis 1986). Factor analyses in this study were carried out by using SPSS 10 statistical program.

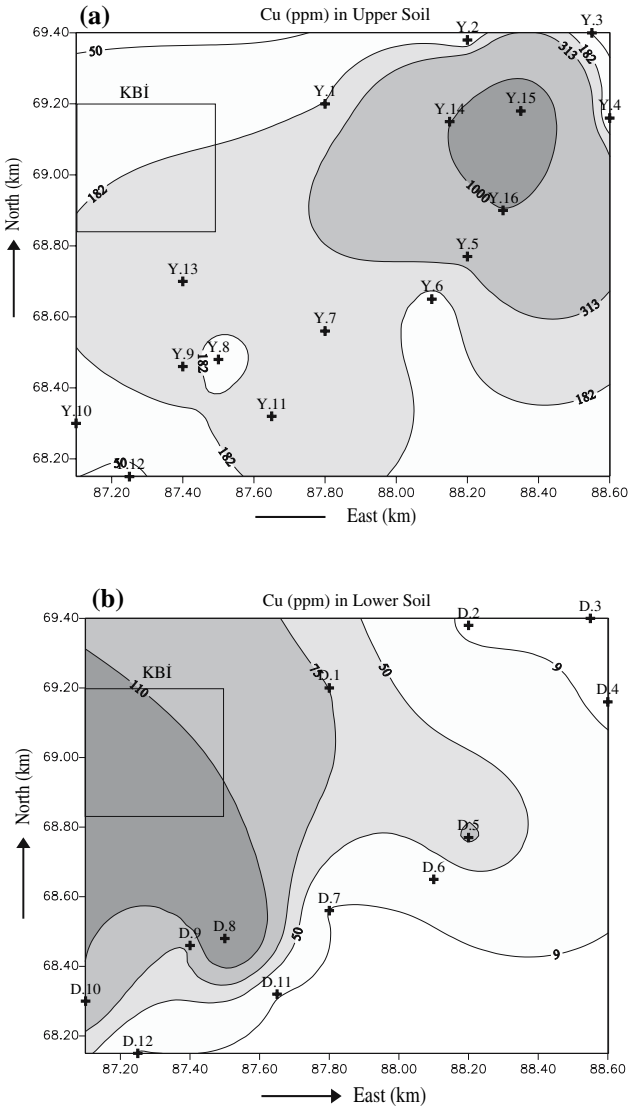


Fig. 4 Distribution diagram of Cu concentrations in the soil samples collected **a** from surface (0–20 cm) and **b** from depth from study area in March 1999

Table 2 Factor loading matrix for the metal concentration in the soil samples collected from study area

	Factors	
	Factor 1	Factor 2
Pb	–0.847	–0.100
Fe	0.851	0.202
Co	0.722	0.214
Zn	–0.569	0.442
Cr	–0.113	0.852
Cd	–0.387	–0.739
Mn	0.635	–0.665
S	0.392	0.362
Cu	0.256	0.872
% Variance	39.2	28.8
Eigenvalue	1.95	1.4

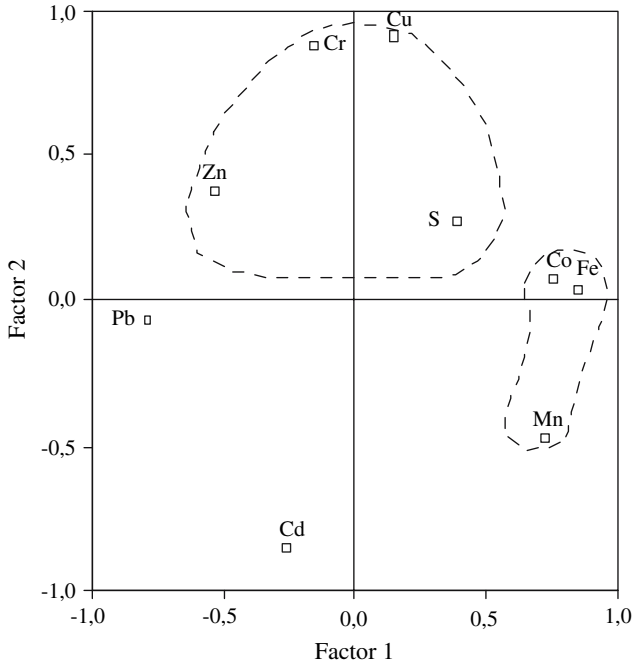


Fig. 5 Diagram of factor loading illustrating factor loading of metal concentration in the soil samples collected from study area

The input variables were the concentrations of nine trace elements in the soil samples collected from the study area. Based on factor analyses, it was revealed that 68% of total variance was explained by two factors (Table 2). According to calculated factor loading coefficients, factor 1 is represented by Fe, Mn, Co and –Pb, –Zn and factor 2 is by Cu, Zn, Cr and –Cd, –Mn (Fig. 5). It is hence concluded that factor 1 shows chemical composition of soils and factor 2, metal pollution. Pb is plotted negative sides of these factors. Different behavior of Pb might be due to the fact that ore processed in KBİ plant contains very little or almost no lead. Therefore, Pb pollution might be attributed to other sources such as traffic or other industries around.

Degree of contamination

In quantitative estimation of pollution, as a first step some element concentrations determined by the chemical analyses of the soil samples collected from the study area are normalized with respect to the element concentrations in Table 1 (The critical values of heavy metals in Soil Pollution Control Regulation (Official Gazette 2001 for Cu, Pb, Zn, Cd and according to critical element values in soils described by Lindsay (1979) for Fe, Mn, and S). The ratios obtained gave the degrees of enrichment or the degrees of pollution. As a second step by using metal ratios, the

average of the ratios is calculated and is called average enrichment factor. Consequently, average enrichment factors estimated for some elements (Cu, Pb, Zn, Fe, Mn, Cd and S) in the soil samples collected during August 2000, June 2001 and October 2001 periods are plotted such that the ratios greater than 1 imply element enrichment (Fig. 6).

If the average enrichment factors estimated for some elements in the soil samples collected in August 2000, June 2001 and October 2001 were compared with each other, the average enrichment factors estimated for Cu, Zn, and S were observed to be the highest in October 2001 and the average enrichment factors estimated for Cd were observed to be the highest in June 2001. Regarding seasonal pollution, the dominant pollutants in the soil samples are Cu, S, and Cd in August 2000; Cu, Pb, Mn, and Cd in June 2001; Cu, Zn, Fe, Mn, Cd and S in October 2001.

Pollution in plants

Plants uptake the elements into their bodies by cation exchange, diffusion in roots and absorption in leaves. Among these, cation exchange in roots is the most important one (Brooks 1983). The ability of plants to absorb trace elements is highly variable depending on the species, soil conditions, climate, and season. However, on average, this ability exhibits some general trends for particular elements (Kabata-Pendias and Pendias 1992; Pais and Jones 1997). In order to prove the probable toxicity in plants, some hazardous heavy metals and their critical levels in plant should be known. These levels were given in Tables 3 and 4.

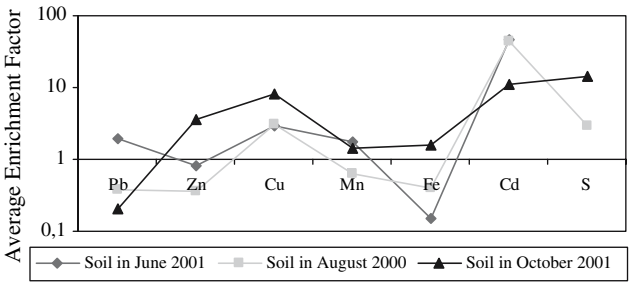


Fig. 6 Diagram of enrichment factors calculated for some elements in the soil samples collected from study area in August 2000–June 2001–October 2001 (The Cu, Pb, Zn and Cd elements are normalized based on the heavy metal critical values of Soil Pollution Control Regulation (Official Gazette 2001), given in Table 1; the Fe, Mn and S elements are normalized according to Lindsay's (1979) critical element values in soils)

Element distributions

Element contents of plants may not show element compositions of their surrounding soil and parent rock in the basement. While plants uptake some elements to their bodies without any limitation, some elements are not allowed to enter into plants bodies (Brooks 1983). So the element contents of each plant and tolerance to elements are different (Dudka et al. 1995). Consequently in order to interpret differences in the concentrations of elements of the various plant samples collected from the study area, some element (Cu, Pb, Zn, Fe and Mn) concentrations in plant samples were normalized as mentioned below (according to Jones et al. 1991 as described in Table 3 and according to low toxic levels as described by Pais and Jones 1997 given in Table 4).

The concentrations of Cu, Zn, Fe and Mn elements in the leaves of tobacco (*Nicotiana tabacum*; SB7, S2B3, S2B14, S3B3, S3B6, and S3B16), maize (*Zea mays*; SB1, S2B2, and S3B12), cabbage (*Brassica oleracea*; S2B5, and S3B7), lettuce (*Lactuca sativa*; S2B15) tomato (*Lycopersicum esculentum*; S2B6, and S3B11), apple (*Malus spp*; SB11, and S2B17) and walnut (*Juglans regia*; SB14) analyzed are normalized according to Jones et al. 1991 as described in Table 3. However, the concentrations of Pb in the leaves of the same plants and concentrations of Cu, Pb, Zn, Fe and Mn elements in the leaves of other plant samples such as reed (*Phragmites australis*; SB12, S2B1, S2B9, S3B1, S3B10, and S3B15), fig (*Ficus carica*; S2B13, and S3B8), poplar (*Populus gradentata*; SB4, S2B8, and S3B2), willow (*Salix sp.*; SB2, SB9, SB13, S2B4, and S3B9), oak (*Quercus spp.*; SB6), acacia (*Robinia pseudoacacia L.*; SB3, S2B10, and S3B14), pine (*Pinus spp.*; SB5, SB8, SB10, S2B11, and S3B13) analyzed are normalized according to low toxic levels as described by Pais and Jones (1997) given in Table 4. Averages of the concentrations of elements normalized in plant samples collected from the same sites in different seasons (August 2000, June 2001 and October 2001) were taken. Normalized values greater than 1 show the element toxicity.

The 50, 75 and 90th % values of concentrations of the normalized Cu, Pb, Zn, Fe and Mn were used to construct the equal concentration curves in distribution diagrams of element concentrations with respect to the critical value of 1. When distribution diagrams of concentration of elements were examined, Cu concentrations in plant samples were observed high in the study area (>1; Fig. 7a) and Cu concentrations reached fairly high degree around KBİ, Tügsaş and IPF (>6.2). Especially, Cu concentration in tobacco (OB3) col-

Table 3 Critical concentration levels of some elements in various plants (Jones et al. 1991)

Plant	Maize (Zea mays L.)			Plant	Tobacco (Nicotiana tabacum)		
Plant section Season	Leaf of stem –			Plant section Season	Young leaf Flowering		
Element (ppm)	Deficient	Sufficient	Excessive or toxic	Element (ppm)	Deficient	Sufficient	Excessive or toxic
Cu	<5	5–20	>20	Cu	<15	16–60	>60
Fe	<50	50–250	>250	Fe	<50	50–200	>200
Mn	<20	20–300	>300	Mn	<30	30–250	>250
Mo	<0.1	0.1–10	>10	Mo	<0.4	0.4–0.6	>0.6
Zn	<20	20–60	>60	Zn	<20	20–80	>80
S (%)	<0.15	0.15–0.5	>0.5	S (%)	<0.25	0.25–0.50	>0.50
Plant	Cabbage (Brassica olerace)			Plant	Lettuce (Lactuca sativa L.)		
Plant section Season	External leaf Maturation season			Plant section Season	External leaf Mature		
Element (ppm)	Deficient	Sufficient	Excessive or toxic	Element (ppm)	Deficient	Sufficient	Excessive or toxic
Cu	3–4	5–15	>15	Cu	5–7	8–25	>25
Fe	25–29	30–200	>200	Fe	40–49	50–100	>100
Mn	20–24	25–200	>200	Mn	10–14	15–250	>250
Mo	0.2–0.3	0.4–1	>1	Zn	20–24	25–250	>250
Zn	15–19	20–200	>200				
S (%)	0.25–0.29	0.30–0.75	>0.75				
Plant	Tomato (Lycopersicum esculentum L.)			Plant	Walnut (Juglans regin)		
Plant section Season	Leaf Flowering			Plant section Season	Leaf July-August		
Element (ppm)	Deficient	Sufficient	Excessive or toxic	Element (ppm)	Deficient	Sufficient	Excessive or toxic
Cu	3–4	5–50	>50	Cu	<4	4–20	>20
Fe	50–59	60–300	>300	Fe	<20	20–200	>200
Mn	40–49	50–250	>250	Mn	<30	30–300	>300
Zn	18–19	20–250	>250	Zn	<22	22–25	>25

Plant	Apple (Malus spp.)		
Plant section Season	leaf (young shoot) –		
Element (ppm)	Deficient	Sufficient	Excessive or toxic
Cu	4–5	6–50	50
Fe	40–49	50–300	300
Mn	20–24	25–200	201–300
Mo	0.05–0.1	>0.1	-
Zn	15–19	20–100	>100
S (%)	<0.2	0.2–0.4	>0.4

lected from the vicinity of Tügsaş was largely high (>8). This distribution pattern of Cu concentrations originated from soils polluted by KBİ, Tügsaş and IPF and from particle materials released from chimneys of these industries (KBİ, Tügsaş and IPF) to atmosphere. Cu concentrations in plants decreased further away from KBİ, Tügsaş and IPF. The observation of high Cu concentrations refers to Cu contamination in the plants

Table 4 Generalized critical concentration levels of some elements in plant leaves (Pais and Jones 1997)

Element (ppm)	Sufficient	Toxic
Cu	5–30	30–100
Pb	5–10	30–300
Zn	27–150	100–400
Mn	20–300	300–500
Fe	20–200	200–500
Cd	0.05–0.2	5–30
As	1–1.7	5–20
Ni	0.1–5	10–100
Cr	0.1–0.5	5–30
Co	0.02–1	15–50

around KBİ, Tügsaş and IPF. Zn was generally observed high in the study area (>1; Fig. 7b) and it was very high in approximately 5 km^2 area around KBİ and Tügsaş (>2). Consequently Zn concentrations were observed high near to KBİ and Tügsaş.

Pb concentrations were observed high in the north of the study area (>1). Pb concentrations were especially high in the plants around KBİ, Tügsaş and IPF (>5,6; Fig. 7c). Similar to previous elements, Pb pollution occurred near KBİ, Tügsaş and IPF. Fe was found generally high in the study area (>1; Fig. 7d). It showed elevated values around KBİ and Tügsaş (>15). Moreover high Fe concentrations were observed in the south of the study area (>25). This high Fe concentrations observed in the south of the study area were observed mostly in tobacco (Nicotiana tabacum; OB10) and lettuce (Lactuca sativa; S2B15) collected from agricultural area. It is considered that source of high Fe concentrations observed in tobacco (Nicotiana tabacum) and lettuce (Lactuca sativa) were to be agrochemicals. But this conclusion is still yet to be supported by more data.

Mn concentrations were observed high only in reed (Phragmites australis) samples (S3B10, OB11 and OB6) collected from the study area (>2; Fig. 7e). Mn concentrations did not exceed critical level in other plants (<1). Consequently Mn pollution was not observed in plants in the study area. It was considered that high Mn concentrations observed in reeds were caused by high affinity of Mn absorption as described by Groudev et al. 2001.

Statistical analysis

Factor analysis The input variables were the concentrations of 10 trace elements in the plant samples collected from the study area. In factor analyses, 57.2% of total variance was explained by two factors (Table 5). According to calculated factor loading coefficients, factor 1 refers to Cu, Pb, Zn, S and –Mn, –Cd, –Co and factor 2 to Fe and V (Fig. 8). In factor 1, Cu, Pb, Zn, S are strongly associated with each other and therefore it might be stated that this factor is a result of heavy metal pollution. Moreover, these toxic elements are frequently found in sites contaminated by KBİ, Tügsaş and IPF. In factor 2, Fe is toxic fairly and is commonly found in sites contaminated by KBİ and Tügsaş (Fig. 7d).

Degree of contamination

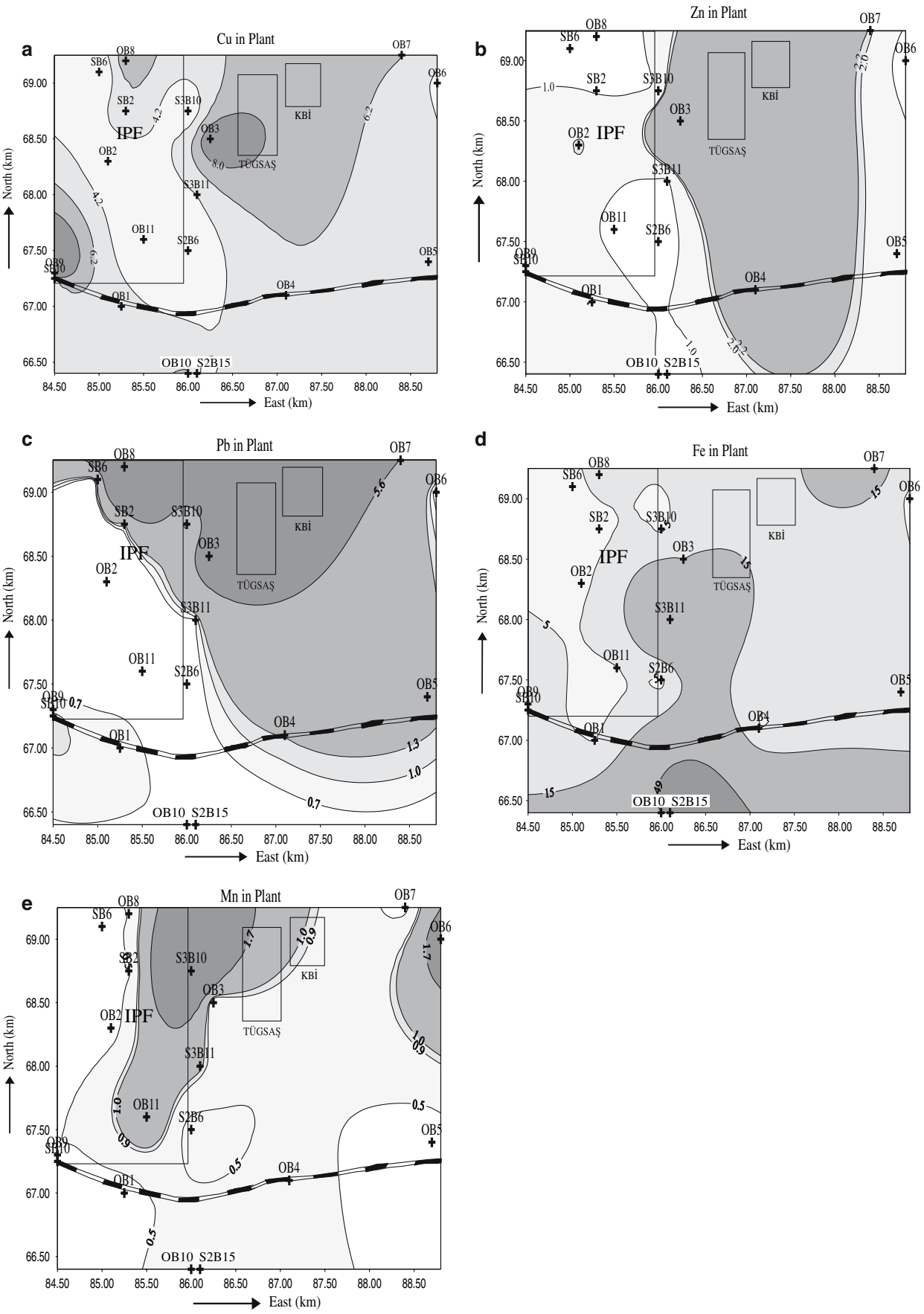
The average enrichment factors were calculated for some elements (Cu, Pb, Zn, Fe, Mn and S) in some plant samples such as tobacco (*Nicotiana tabacum*), maize (*Zea mays*) and cabbage (*Brassica oleracea*) collected in August 2000, June 2001 and October 2001. In this calculation, the concentrations of Cu, Zn, Fe, Mn and S in the leaves of tobacco (*Nicotiana tabacum*), maize (*Zea mays*) and cabbage (*Brassica oleracea*) analyzed are divided by the values given by Jones et al. 1991 as described in Table 3 and the concentrations of Pb in the leaves of same plants analyzed are divided by low toxic levels as described by Pais and Jones 1997, given in Table 4. A plot of the average enrichment factors is produced as a result (Fig. 9) and shows that pollutants in tobacco (Nicotiana tobacum) are Cu, Pb, Zn, Fe and S; in maize (Zea mays) are Cu, Zn and Fe; and in cabbage (Brassica oleracea) are Cu, Pb, Fe and S.

Water pollution

Factors affecting the chemical composition of most surface waters are climate (especially intensity and frequency of rainfall), lithology, geoavailability of elements, vegetation, topography, biological activity and time. However, the composition of water is most often controlled by interactions with earth materials through which the water flows (Smith and Huyck 1998). For surface waters, these interactions generally take place in the soil zone. The composition of uncontaminated surface waters varies depending on environmental conditions, analytical methods and possible contamination (Meybeck and Helmer 1989). Critical values at surface waters based on Water Quality Control Regulation (Official Gazette 1988) and the values obtained from the study are given in Table 6.

Element distributions

Distribution diagrams of concentrations for some elements (Cu, Pb, Zn, Fe and Mn) in the water samples


a
Cu in Plant
b
Zn in Plant
c
Pb in Plant
d
Fe in Plant
e
Mn in Plant
IPF
TÜGSAŞ
KBİ
OB1
OB2
OB3
OB4
OB5
OB6
OB7
OB8
OB9
OB10
OB11
SB2
SB6
S2B6
S3B10
S3B11
OB10 S2B15
North (km)
East (km)

◀ **Fig. 7** **a** Distribution diagram of Cu concentrations in the plant samples collected from study area (The values at the diagram are normalized according to the excess Cu concentration values determined at plant leafs by Jones et al. (1991) (indicated in Table 3) and according to the lowest toxicity values determined at plant leafs by Pais and Jones (1997) (indicated in Table 4). Samples numbered SB are collected during August 2000–June 2001–October 2001, OB numbered samples are the average of the samples collected during August 2000–June 2001–October 2001 from the same sampling locations). **b** Distribution diagram of Zn concentrations in the plant samples collected from study area (The values at the diagram are normalized according to the excess Zn concentration values determined at plant leafs by Jones et al. (1991) (indicated in Table 3) and according to the lowest toxicity values determined at plant leafs by Pais and Jones (1997) (indicated in Table 4). Samples numbered SB are collected during August 2000–June 2001–October 2001, OB numbered samples are the average of the samples collected during August 2000–June 2001–October 2001 from the same sampling locations). **c** Distribution diagram of Pb concentrations in the plant samples collected from study area (The values at the diagram are normalized according to the excess Pb concentration values determined at plant leafs by Jones et al. (1991) (indicated in Table 3) and according to the lowest toxicity values determined at plant leafs by Pais and Jones (1997) (indicated in Table 4). Samples numbered SB are collected during August 2000–June 2001–October 2001, OB numbered samples are the average of the samples collected during August 2000–June 2001–October 2001 from the same sampling locations). **d** Distribution diagram of Fe concentrations in the plant samples collected from study area (The values at the diagram are normalized according to the excess Fe concentration values determined at plant leafs by Jones et al. (1991) (indicated in Table 3) and according to the lowest toxicity values determined at plant leafs by Pais and Jones (1997) (indicated in Table 4). Samples numbered SB are collected during August 2000–June 2001–October 2001, OB numbered samples are the average of the samples collected during August 2000–June 2001–October 2001 from the same sampling locations). **e** Distribution diagram of Mn concentrations in the plant samples collected from study area (The values at the diagram are normalized according to the excess Mn concentration values determined at plant leafs by Jones et al. (1991) (indicated in Table 3) and according to the lowest toxicity values determined at plant leafs by Pais and Jones (1997) (indicated in Table 4). Samples numbered SB are collected during August 2000–June 2001–October 2001, OB numbered samples are the average of the samples collected during August 2000–June 2001–October 2001 from the same sampling locations)

collected from the study area were prepared. 50, 75 and 90th % values of concentrations of Cu, Pb, Zn, Fe and Mn were used to construct the equal concentration curves in distribution diagrams of element concentrations according to Class III (polluted water) criteria as described by Water Pollution Control Regulation (Official Gazette 1988) given in Table 6. Examination of the distribution diagrams of element concentrations reveals Cu concentrations lower than the critical value (<0.2 mg/l according to Class III (polluted water) criteria as described by Water Pollution Control Regulation (Official Gazette 1988)(Table 6 and Fig. 10a). However, Cu concentrations in water samples collected from KBİ and Tügsaş ranged from 0.06 to 0.18 mg/l were classed as slightly polluted water.

Table 5 Factor loading matrix for the metal concentration in the plant samples collected from study area

	Factors	
	Factor 1	Factor 2
Cd	**–0.77**	0.14
Cu	**0.83**	0.20
Zn	**0.66**	–0.29
Co	**–0.60**	0.16
Fe	–0.110	**0.94**
V	–0.25	**0.87**
Mn	**–0.56**	–0.24
S	0.29	–0.19
Pb	**0.58**	–0.05
Ni	0.15	0.16
% Variance	35.8	21.4
Eigenvalue	1.8	1.1

Zn concentrations are lower than the critical value (<2 mg/l; according to Class III (polluted water) criteria as described by Water Pollution Control Regulation (Official Gazette 1988) (Fig. 10b).

Pb concentrations were observed high around KBİ and IPF and in the north of KBİ and IPF (>0.05 mg/l; according to Class III (polluted water) criteria as described by Water Pollution Control Regulation (Official Gazette 1988) (Fig. 10c). Pb concentrations in water samples decreased further away from KBİ and IPF.

Fe concentrations were found lower than the critical value (<5 mg/l; according to Class III (polluted water) criteria as described by Water Pollution Control Regulation Official Gazette 1988) in water samples collected from the study area (Fig. 10d). However, around KBİ, Tügsaş and IPF Fe concentrations were observed 1.1–4.8 mg/l. According to these Fe concentrations, these waters were classed in slightly polluted water.

Mn concentrations were observed lower than the critical value (<3 mg/l; according to Class III (polluted water) criteria as described by Water Pollution Control Regulation Official Gazette 1988) in water samples collected from the study area (Fig. 10e). According to Mn concentrations (0.58–0.95) observed in water samples around Tügsaş and IPF, these waters were classed in slightly polluted water.

Statistical analysis

Factor analysis The input variables were the concentrations of 19 trace elements in the water samples;

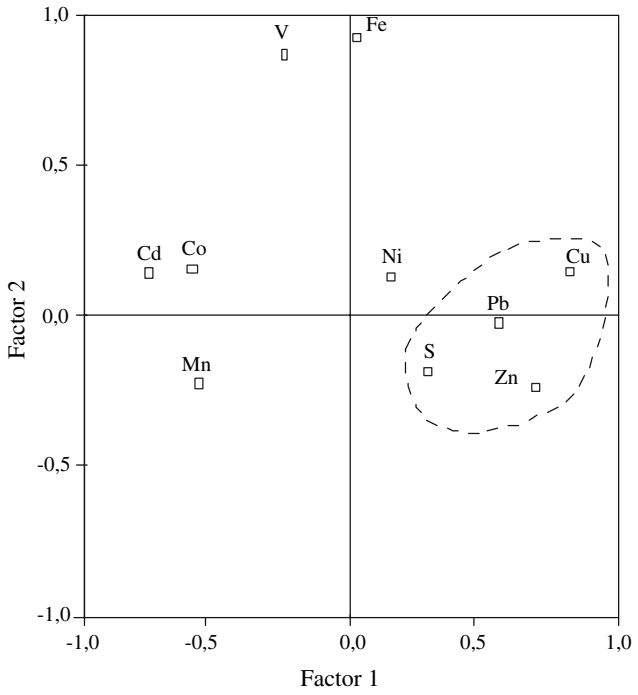


Fig. 8 Diagram of factor loading illustrating factor loading of metal concentration in the plant samples collected from study area

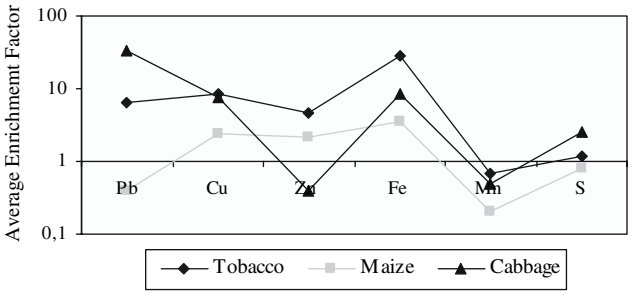


Fig. 9 Diagram of enrichment factors calculated for some elements in tobacco, in maize and in cabbage collected from study area (Cu, Zn, Fe, Mn and S are normalized according to the excess values determined for some elements by Jones et al. (1991) (see Table 3) for tobacco, maize and cabbage and the Pb is normalized according to generalized lowest toxicity values of plant leafs for some elements by Pais and Jones (1997) (see Table 4)

collected from the study area. In factor analyses, 89.1% of total variance was explained by two factors (Table 7). According to calculated factor loading coefficients, factor 1 refers to Na, Mg, K, Ca, F, NO_3, Pb Cu, Zn, Al and -HCO_3, –Ba and factor 2 to Fe, Mn, Br, Cl, SO_4 and –Cu, –Zn. In factor 1, these toxic elements (especially Pb, Cu, and Zn) are frequently found in sites contaminated by KBİ, Tügsaş and IPF. The high score of factor 1 corresponded to vicinity of these industries (Fig. 10a, b, c). HCO_3 indicates that wherever alkaline conditions occur, there no metal ever precipitated. Factor 2 shows precipitation of $FeSO_4$ and influence of seawater. Precipitation of $FeSO_4$ decrease while Cu, Pb, Zn concentrations are increasing in water. These element correlations were also indicated in the diagram of factor loadings (Fig. 11). In diagram, three different element groups are clearly separated as Cu–Pb–Zn, Fe–SO_4–Cl and HCO_3.

Degree of contamination

If the average enrichment factors calculated according to the Water Pollution Control Regulation (Official Journal 1988) Class I (high-quality waters) criteria for some elements in water samples collected during the August 2000, June 2001 and October 2001 periods were compared with each other, Cu, Pb, Fe and Mn were identified to be the pollutants in water samples (Fig. 12a) whereas, Pb is always the major pollutant in water samples based on Class III (polluted waters) criteria (Fig. 12b).

Conclusions

Cu, Zn, Pb, Fe and Mn pollution was determined in soil samples and the pollution appears to be limited to the soil surface. Most probable sources of Cu pollution are KBİ, Tügsaş and IPF; Zn and Pb pollution originates

Table 6 Critical values at surface waters based on Water Quality Control Regulation (Official Gazette 1988) and the values obtained from the study

Element	The values obtained from the study	Water Quality Control Regulation (Official Gazette 1988)			
		High Quality Water (I. Class Water) Mg/l	Slightly Polluted Water (II. Class Water) Mg/l	Polluted Water (III. Class Water) Mg/l	Heavily Polluted Water (IV. Class Water) Mg/l
Cu	0.02–0.45	**0.02**	0.05	**0.2**	>0.2
Pb	0.02–0.3	**0.01**	0.02	**0.05**	>0.05
Zn	0.05–1.2	**0.2**	0.5	**2**	>2
Fe	0.05–4.9	**0.3**	1	**5**	>5
Mn	0.03–2.1	**0.1**	0.5	**3**	>3
Cd	0.01–0.05	**0.003**	0.005	**0.01**	>0.01

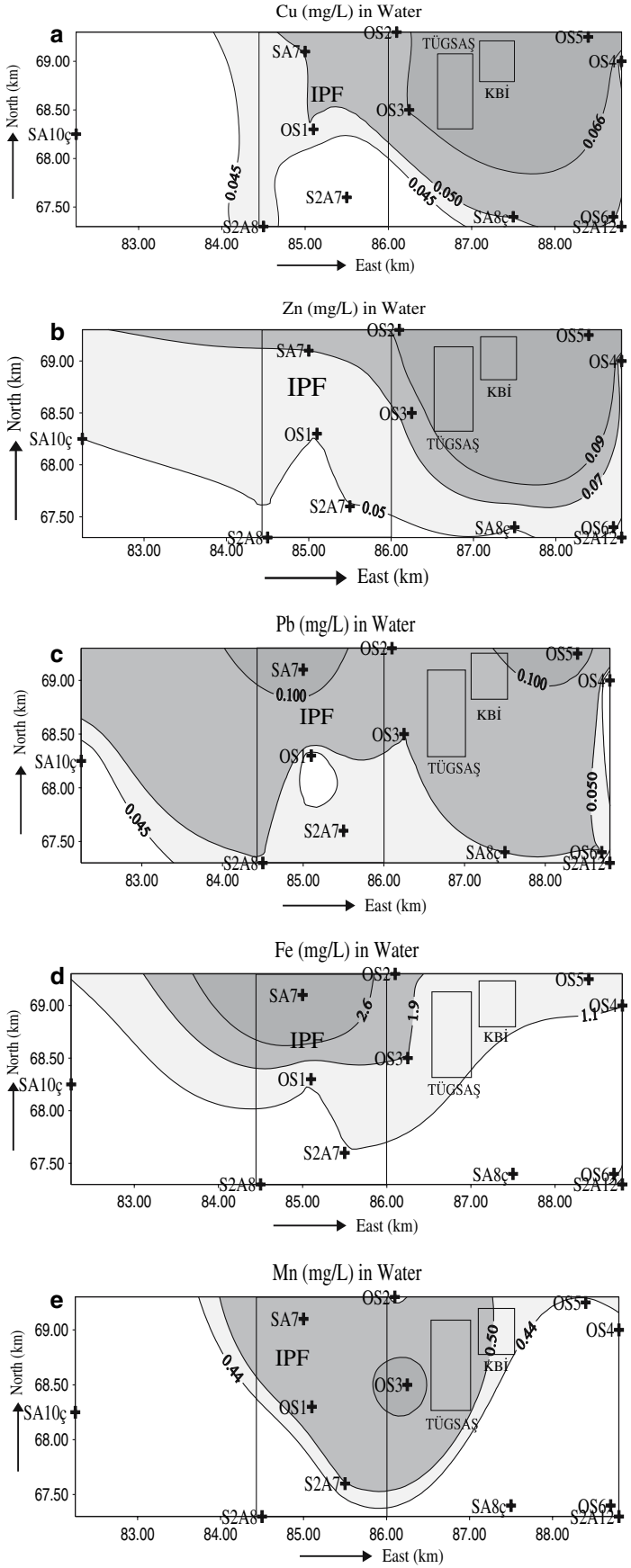


Fig. 10 **a** Distribution diagram of Cu concentrations in the water samples collected from study area (Samples numbered SA are collected during August 2000 and June 2001. Samples numbered OS are the average of the samples collected during August 2000–June 2001–October 2001 from the same sampling locations). **b** Distribution diagram of Zn concentrations in the water samples collected from study area (Samples numbered SA are collected during August 2000 and June 2001. Samples numbered OS are the average of the samples collected during August 2000–June 2001–October 2001 from the same sampling locations). **c** Distribution diagram of Pb concentrations in the water samples collected from study area (Samples numbered SA are collected during August 2000 and June 2001. Samples numbered OS are the average of the samples collected during August 2000–June 2001–October 2001 from the same sampling locations). **d** Distribution diagram of Fe concentrations in the water samples collected from study area (Samples numbered SA are collected during August 2000 and June 2001. Samples numbered OS are the average of the samples collected during August 2000–June 2001–October 2001 from the same sampling locations). **e** Distribution diagram of Mn concentrations in the water samples collected from study area (Samples numbered SA are collected during August 2000 and June 2001. Samples numbered OS are the average of the samples collected during August 2000–June 2001–October 2001 from the same sampling locations)

Table 7 Factor loading matrix for some elements and components in the water samples collected from study area

	Factors	
	Factor 1	Factor 2
Al	0.98	–4.29E–02
Na	0.958	–6.03E–04
Mg	0.957	–2.67E–02
K	0.897	–1.08E-02
HCO_3	–0.875	7.83E–02
F	0.814	–0.511
NO_3	0.747	–0.113
Ba	0.736	0.321
Ca	0.664	0.484
Pb	0.903	–0.015
Zn	0.832	–0.526
Cu	0.840	–0.484
SO_4	0.218	0.75
Br	0.533	0.741
Cl	0.502	0.725
Fe	0.593	0.759
NH_4	0.459	0.387
Mn	0.524	0.727
B	0.637	0.368
% Variance	56.8	32.3
Eigenvalue	2.8	1.6

from Tügsaş and IPF; Fe ve Mn pollution is attributed to KBİ. Regarding seasonal pollution, the dominant pollutants in soil samples are Cu, S, and Cd in August 2000; Cu, Zn, Mn, and Cd in June 2001; Cu, Zn, Fe, Mn, S and Cd in October 2001. The highest heavy metal pollution in soils is recorded to occur in October. The reason is that harvest in the region is almost completely made at the end of August. Therefore, the area has no vegetation cover at all and hence no metal uptake by plants. As a result all the metal stemmed from the industries is concentrated only in soils.

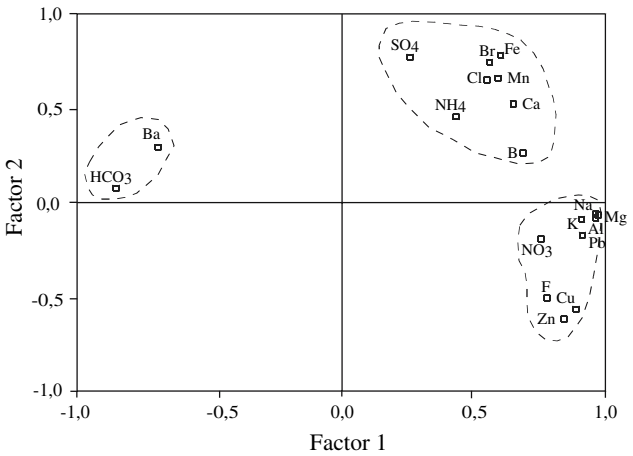


Fig. 11 Diagram of factor loading illustrating factor loading of some elements and components in the water samples collected from study area

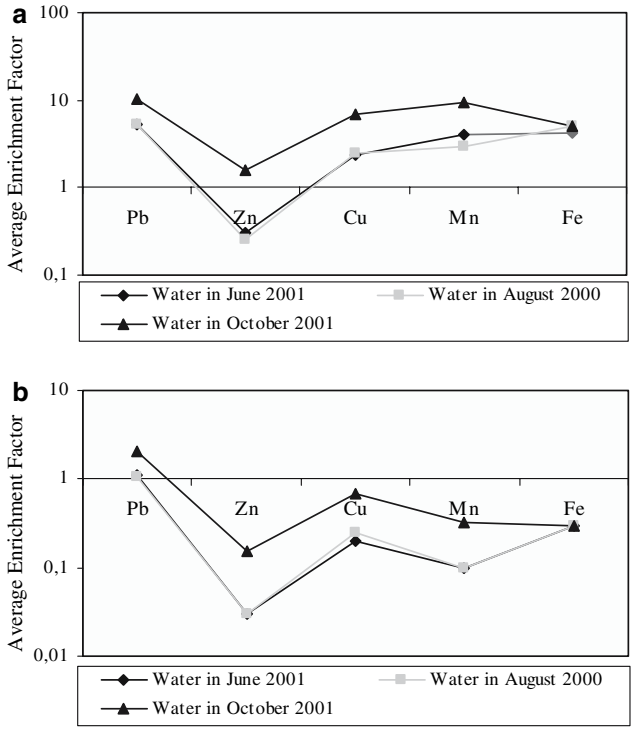


Fig. 12 **a** Diagram of enrichment factors calculated to Class I criteria (high quality waters) for some elements in the water samples collected from study area in August 2000–June 2001–October 2001 (Elements are normalized according to the values given in Table 6, values of the Water Quality Control Regulation 1st class water Official Gazette 1988). **b** Diagram of enrichment factors calculated to Class III criteria (polluted waters) for some elements in the water samples collected from study area in August 2000–June 2001–October 2001 (Elements are normalized according to the values given in Table 6, values of the Water Quality Control Regulation 3rd class water Official Gazette 1988)

In the plant samples collected from the study area, KBİ and Tügsaş appear to cause Cu, Pb, Zn and Fe pollution, and IPF appear to cause Cu and Pb pollution. Pollutants observed in tobacco (Nicotiana tobacum) are Cu, Pb, Zn, Fe and S; in maize (Zea mays) are Cu, Zn and Fe; and in cabbage (Brassica oleracea) are Cu, Pb, Fe and S. Of these plants, maize occurs to be less affected by metal pollution, due most probably to its longer roots penetrating deeper parts in relatively uncontaminated soils. Another factor might be narrower and less porous nature of its leaves restricting metal uptake during photosynthesis. The water samples collected from the study area revealed that KBİ has been the major agent causing Pb pollution and a relatively lower level of Cu and Fe pollution; Tügsaş is causing a lower level of Cu, Fe and Mn; and IPF are causing Pb pollution and a relatively lower level of Fe and Mn pollution. According to the

Water Pollution Control Regulation (Official Journal 1988) Class I (high-quality waters) criteria, Cu, Pb, Fe and Mn were determined to be the pollutants in water samples during the August 2000, June 2001 and October 2001 periods whereas, Pb is the major pollutant for all these time periods in water samples based on Class III (polluted waters) criteria. Factor analysis reveals three major groups of the analyzed elements: (a) an association of heavy metals with Na, K and Mg cations referring to pollution and acid leaching of soil, (b) an association of NH_4, Fe, SO_4, Cl and Br indicating agricultural pollution and seawater invasion in land near the shoreline, and (c) HCO_3 complex showing a reverse effect in heavy metal precipitation.

This study is a helping guideline to monitor the negative effects of a copper smelting plant and other industrial facilities over agricultural lands. The results obtained from plants revealed that tobacco and cabbage can be considered as good indicators of environmental parameters.

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