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Trace and rare earth element (REE) status of Çarsamba fan soils in the Ancient Konya lake region, Turkey

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Agricultural practices and long-term application of phosphate and nitrogen fertilizers causes the accumulation of U and some heavy metals in the surface soil of agricultural fields. We investigated the soil constituents that contribute to the accumulation of U and some trace heavy metals. For this purpose, the concentrations of some rare earth element (REE) and trace elements collected from 17 sampling sites in the Çumra Basin were determined. The mean concentrations of La and Ce in surface soils was 33.8 and 65.4 mg/kg, respectively; in sediment, they were 32.7 and 61.8 mg/kg, respectively. The mean values of Mo, Cu, Pb, Zn, Co, Ni, Mn, As, Cd, U and Th were 0.69, 24.2, 19.4, 64.6, 16.2, 76.9, 593, 11.4, 0.24, 11.0 and 0.19 mg/kg, respectively, all of which were within the permitted levels according to national Soil Pollution Control Regulation. High concentrations of Pb and Ni were observed in the soil compared to these sediments. The intensive N fertilization and agriculture activities have caused enrichment and slight environmental pollution for Ni (76.9 mg/kg) and Pb (19.4 mg/kg) in Çarsamba fan soils. Cultivated topsoil showed the same contents of U (2.0 mg/kg) and Cd (0.24 mg/kg) as in sediments. The results showed that successive application of phosphate fertilizer did not increase the concentrations of U and Cd in topsoil.

Key words: Çumra soil, enrichment/depletion, heavy metal, pollution, rare earth element.

INTRODUCTION

Human activities, particularly in the industrial period, have brought numerous potentially hazardous trace elements to the environment (Nriagu, 1996). These anthropogenically derived elements can be transported through the atmosphere to locations that are remote from emission sources. Lake sediments provide an archive of environmental change both within the lake ecosystem and region and, therefore, have been used around the world in order to study natural environmental change or human impacts. Many studies have clearly shown that lake ecosystems have been contaminated by trace elements from anthropogenic sources for at least the last

150 years (Renberg, 1986; Williams, 1991; Heyvaert et al., 2000; Patrick et al., 1995; Farmer et al., 1996; Yang et al., 2002). However, the distribution of trace elements in lake sediments not only reflects pollution from atmospheric deposition but also reveals the past drainage basin or land-use histories (Oldfield et al., 2003; Yang et al., 2003). The REEs, which are also known as lanthanides, comprise 15 elements with atomic numbers ranging between 57 and 71, that is, from La to Lu. Typically, the low-atomic number members of the series are called light rare earth elements (LREE: 57 to 62), while those with higher atomic numbers are termed heavy (HREE: 63 to 71). They are fractionated during the crystallization of minerals from magma and during the regional metamorphism of volcano-sedimentary rocks (McLennan, 1989). REEs have very similar chemical properties and tend to be present naturally as a group

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rather than alone, which makes them very useful tracers in geochemical studies (Henderson, 1984). REE data, however, might also be useful in the provenance determination of coarse and fine-grained sedimentary rocks or even in soil genesis (Cullers et al., 1987; Egashira et al., 1997; Yoshida et al., 1998). Yoshida et al. (1998) found that REEs were rather resistant during soil-formation processes because their concentrations and the chondrite normalized patterns are not so far from those of the possible parent material. Therefore, knowledge of REE concentrations in soils is required as background data for estimating soil contamination due to anthropogenic sources.

Elevated concentrations of some REEs, such as La, Ce, Sm, Eu and Tb have been found in industrial and urban environments (Yoshida et al., 1998). These elements are likely to be released into the environment, mainly from coal-burning and nuclear energy material processing (Kabata and Pendias, 2001) and agricultural uses (Xu et al., 2002, 2003). Intensive use of phosphate and nitrogen fertilizers has been a distinctive feature of Turkish agriculture. Phosphatic fertilizers added to agricultural soils can also be sources of REEs (Tsumura and Yamasaki, 1993). Brown et al. (1990) demonstrated that the REEs could stimulate the growth of cereals, vegetables, fruits and tea. Inorganic compounds of REEs such as REE (NO₃)₂ which act as microelement fertilizers have entered the environment and accumulated in the ecosystem (Xu et al., 2002; Ding et al., 2006). Phosphate fertilizers contain appreciable amounts of U as an impurity (Mortvedt and Beaton, 1995; Raven and Loeppert, 1997; McBride and Spiers, 2001). On the basis of the U concentration in phosphate fertilizers, McBride and Spiers (2001) estimated that 50 years of the application of a specific phosphate fertilizer (for example, 100 kg ha⁻¹ year⁻¹ as P₂O₅) would lead to the addition of 2.4 kg of U per hectare to the topsoil corresponding to an increase of about 1 mg/kg in the soil U. In a paddy field in Japan, the increase in soil U due to the application of calcium superphosphate fertilizer (600 kg ha⁻¹ year⁻¹ as mixed fertilizer) for 10 years was estimated to be 5.3% of the total U in the soil (Tsumura and Yamasaki, 1993). The Çarşamba fan soils in the Çumra Basin are located 50 km south of the Konya province in central Anatolia. This is one of Turkey's most advanced agricultural areas. The fast development of rural-industry has not only increased farmers' income but also has caused some serious environmental problems. The discharges of untreated industrial and domestic solids, wastewater, and agricultural practices have caused chronic heavy metal and organic contamination. It often has been reported that agricultural soil is polluted with heavy metals and/or organic pollutants (Cao, 1998; Cao and Hu, 2000).

The aim of this paper is to investigate the status and distribution patterns of some trace and REE elements in Çumra basin soils and related sediments to assess the

effect of agricultural practices and application of fertilizers on heavy metal contamination as an environmental issue.

MATERIALS AND METHODS

Study area

The region is a part of the Great Konya Basin in the Konya Province, located in the Central Anatolian Plateau at latitude 37 to 38°N and longitude 32 to 35°E at an altitude of about 1000 m and distance of 50 km from the city of Konya, Turkey. It is situated on the Çarşamba River fan sediments. Its average length is 35 km and its width is about 5 km. The Çumra Basin is located in the southwest Great Konya Basin and is bordered by the Toros Mountains in the south, the Anatolides in the west and north, and other high plateaus in the north. Several rivers flow into the Great Konya Basin, mainly from the south and the west. The physicochemical and mineralogical properties of soils and sediments and the formation and diagenesis of carbonates under the lacustrine environment in the Great Konya Basin have been extensively studied by many researchers (Driessen and de Meester 1969; Driessen, 1970; de Meester 1970a, b, 1971; Muller et al., 1972; Vergouwen, 1981). The geological maps of the Konya Basin, Turkey are shown in Figure 1. The Great Konya Basin itself is filled by quaternary sediments (de Meester, 1970b). During some periods of the Late Pleistocene epoch, most of the Great Konya Basin was covered by a shallow lake with a fairly constant water level (12 to 20 m), leaving a number of sandy beach ridges and sand plains located roughly at the 1010 m contour. Soft-lime lake bottom were covered by variety sediments resulting from different physiographic units.

The alluvial fans or inland deltas consist of sediments ranging from coarse sand to heavy clay. The region was the first open field for irrigation, beginning in 1912. The plant pattern includes cereals, beans, sugar beets, vegetables. In the region, excessive chemicals were used such as nitrogen, phosphate fertilizers and pesticides for decade years.

Soil sampling, analysis and calculation of the enrichment factor (EF)

The field sampling programme was performed in 2009 to study the characterization of the trace elements and REEs in the soil of the Çumra Basin. For this purpose, soil and sediment samples were collected at 17 locations. Soil for this investigation was collected from the agricultural field in the alluvial fan soils of Çarşamba Basin. The soils classified according to FAO taxonomy as a Fluvisol. Main physical and chemical properties of the soils are listed in Table 1. Locations were selected around the Çarşamba River which is the near-surface soils (0 to 20 cm in depth) and sediments (70 to 120 cm) were sampled using a plastic spade to avoid any heavy-metal contamination. Each surface soil sample comprised a composite of 5 subsamples taken within a 1 × 1 m². The soil and sediment samples were air-dried at 20°C for one week and sieved through a 2 mm polyethylene sieve to remove the plant debris, pebbles and stones. They were ground in a mechanical agate grinder to a fine powder for subsequent geochemical analysis. Chemical determination of selected trace and rare earth elements were performed by Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Samples were taken in to solution by alkaline fusion using a mixture of 0.25 g soil or sediment powder and 0.75 g flux (lithium tetra and metaborate). 0.2 N HNO₃ solutions diluted to 1:1000. An aliquot of the sample solution was analyzed for the trace element and REE, on

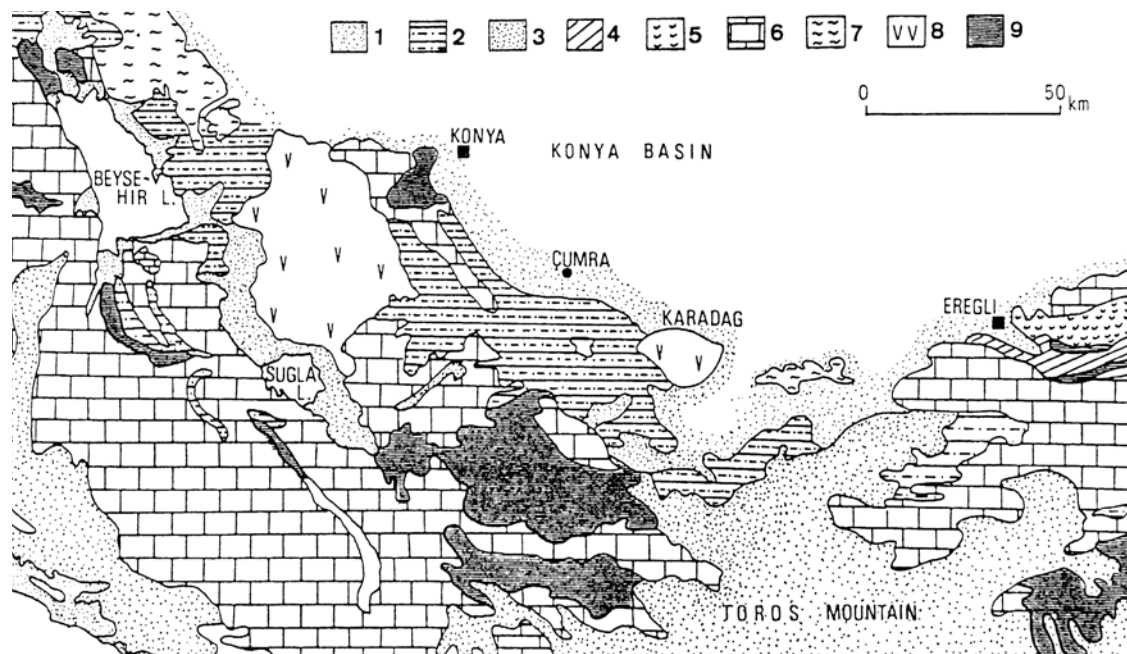


Figure 1. Geological map in the Konya Basin. 1: alluvium, 2: limestone (Neogene), 3: limestone, marly sandstone (Miocene), 4: flysch, 5: gypsum, marly limestone (Oligocene), 6: limestone (Mesozoic), 7: schist (Paleozoic), 8: andesitic basalt and 9: ultrabasic mass (Inoue et al., 1998).

Table 1. Main physical and chemical properties and coordinates of the soil studied.

Site	Coordinates		pH _(H₂O) (1/2.5)	EC (µS.cm ⁻¹) (1/2.5)	CaCO ₃ (%)	Organic matter (%)
	Latitude	Longitude				
1	37° 34' 05"	32° 47' 45"	7.75	172	18.29	1.28
2	37° 34' 39"	32° 47' 38"	7.81	162	18.29	1.31
3	37° 34' 59"	32° 47' 30"	7.89	238	13.52	1.21
4	37° 35'20"	32° 47' 16"	8.01	138	11.14	0.9
5	37° 35'34"	32° 47' 20"	7.95	152	13.52	0.78
6	37° 35'55"	32° 47' 27"	7.96	188	11.93	0.98
7	37° 36'21"	32° 47' 45"	7.91	203	11.93	1.16
8	37° 36'55"	32° 47' 19"	8.21	103	13.52	0.52
9	37° 36'57"	32° 46' 49"	8.23	178	15.11	0.98
10	37° 36'58"	32° 44' 58"	8.07	127	15.11	0.53
11	37° 35'01"	32° 45' 43"	7.81	233	13.52	1.1
12	37° 34'37"	32° 45' 07"	7.98	285	11.93	1.59
13	37° 34'18"	32° 45' 07"	8.07	163	12.73	0.88
14	37° 33'52"	32° 45' 06"	8.09	157	16.70	1.45
15	37° 33'38"	32° 46' 04 "	7.99	159	19.09	1.17
16	37° 33'36"	32° 46' 40"	8.06	152	17.50	1.34
17	37° 33'28"	32° 46' 46"	7.84	258	20.68	1.4

a combination simultaneous/Sequential (ICP-MS). Detection limits were 0.1 -1 ppm for all trace elements and 0.1 to 0.5 2ppm for REE. The instrument was calibrated using certified standard reference materials (OREAS24P and G1). To better evaluate the nature of soils and sediments and the effect of weathering and possible

recycling on trace and rare earth elements of sediments under semiarid conditions, reference sediment was chosen for comparison in the study, that is, North American Shale Composite (NASC) from Taylor and McLennan (1985). All procedures were replicated three times for each soil and the means were reported

(Chao and Sanzalone, 1992). Soil pH was measured potentiometrically both in a 1: 2.5 soil / water (w / v) suspension with a glass electrode (Soil Survey Laboratory Methods Manual, 2004). Electrical conductivity (EC) was determined potentiometrically in 1: 2.5 soil / water suspension (Soil Survey Laboratory Methods Manual, 2004). Organic matter in the soils was determined using the Walkley and Black wet digestion method (Van Lagen, 1993). The amount of carbonate in the soil was measured by Scheibler calcimeters (Soil Survey Laboratory Methods Manual 2004). The ratio between the contents of an element in any given horizon to those of its parent materials or sediments can be used to assess its relative mobility in the soil profile. This element ratio refers to the relative enrichment or depletion of the element, that is, >1 indicates enrichment, <1 indicates depletion and = 1 indicates no change in the relative abundance of element (Singh et al., 2005). Trace elements and the REE enrichment factor (EF) were calculated for each site and for each element. The EF ratio is a concentration of a given trace element or REE in the surface layer (0 to 20 cm interval) to the concentration in deep sediments (70 to 120 cm interval).

$$EF = \frac{[REE \text{ or Trace metal}]_{(0-20 \text{ cm})}}{[REE \text{ or Trace metal}]_{(70-120 \text{ cm})}}$$

Besides Europium anomalies are estimated to determine the weathering intensity by comparing the measured concentration of Eu with an expected concentration of Eu* obtained by interpolation between the normalized values of Sm and Gd, as proposed by Taylor and McLennan (1985):

$$Eu/Eu^* = Eu/N / \sqrt{(Sm/N) \times (Gd/N)}$$

RESULTS

Some trace element and REE content of studied soils and sediment were documented in Table 2. The mean concentrations of La and Ce were 33.8 and 65.3 in soil and 32.7 and 61.8 in sediment. The highest La and Ce contents of soils were found in sites 14 and 13, respectively. Site 9 has the highest content of La and Ce in sediments. However compared to the NASC (North American Shale Composite) values (39 mg La /kg, and 76 mg Ce/kg) (Hasking and Frey, 1966), all results for REE contents of the soils and sediments in the Çumra region are within the normal range. La/Yb)N in the soils and sediment ranged from 0.81 to 1.5 and ranged from 1.48 to 3.40 respectively. (Eu/Eu*)N value show negative anomalies in all sites (Table 3). The mean contents of U and Th were 2, and, 11.0 mg.kg⁻¹ respectively. U concentration of soil is very close to that of sediment. The mean U/Th ratio was 0.19. The U/Th ratio did not show a significant difference between soil and sediment at all sites. In addition, the U/Th ratio decreased from sediment to soil. The U content in the soils (with phosphate fertilization) and sediment ranged from 1.5 to 2.5 mg kg⁻¹ and from 1.5 to 2.7 mg kg⁻¹, respectively.

Trace Elements the distribution of metal among soils of different kinds depends on the combination of soil

properties, including soil type, texture, pH, redox condition, organic matter content, and mineral composition (Ngujen-Trung et al., 1992). According to results, all element contents of the soils studied are in the range of mean values in surface soils worldwide (Kabata-Pendias and Pendias, 2001). The mean contents of Mo, Cu, Pb, Zn, Co, Ni, Mn, As, Cd, U and Th were 0.69, 24.2, 19.4, 64.6, 16.2, 76.9, 593, 11.4, 0.24, mg.kg⁻¹ respectively. Trace elements show a general depletion or slight enrichment. Cd, Cu, Mo, Zn, Co, Pb As and Th show a significant enrichment only at sites 6, 10, and 17. However the Ni showed strong an enrichment tendency. Ni concentration increases in the soils at more sites. Pb concentration ranged from 13.6 to 24.0 mg.kg⁻¹ in surface soils and this value ranged from 10.7 to 20.7 mg.kg⁻¹ in sediments. The concentrations of selected elements in surface soil were higher than those in sediments. Pb had a slight enrichment. Cd content displayed the depletion in sites 1, 2, 5, 11, 13, and 14. Otherwise, it showed slight or strong enrichment at other sites. Slight or strong depletion were found at all sites for Mn, Mo, Co. On the other hand Zn shown enrichment tendency.

DISCUSSION

The trace metal and REEs concentrations of soils depend on parent material, weathering processes and climate, human activity also seems to be involved. Because of geochemical composition of the surface layers is similar to that of the parent material or the deepest sediments, the different sediments have a profound effect on the soils physical and chemical properties. REEs can also be enriched during the soil-formation processes, even if the source material is not granitic rock (Yoshida et al., 1998). In addition, REEs are added to fertilizers that stimulate the growth of cereals, vegetables, fruits and tea (Brown et al., 1990; Yuan et al., 2001).

In general, all measurement values are considered to be normal for continental crust and REE content of lake sediment and soil in Çumra is consistent with the values of other lake sediments. The ratio between the contents of an element in any given horizon and those of its parent material or sediment can be used to assess its relative mobility in the soil profile.

Fertilizers containing rare earth elements La and Ce are widely used to increase rice production in China. Some fertilizers contain 14.7% Ce and 9.7 % La in China (Xiong, 1994). A lot of fertilizer raw material which is exported from China was used to produce fertilizer in Turkey. So soils could be contaminated and for some soils the La and Ce contents could be higher than sediments and parent material due to fertilization containing REE. In Table 4 we present enrichment factor of trace elements and REE of the studied soils and sediments. As indicated in Table 4, La and Ce are only slightly enriched

Table 2. Some trace and REE concentrations of studied soils and sediments (mg/kg).

Site	Element													
	La	Ce	Mo	Cu	Pb	Zn	Co	Ni	Mn	As	Cd	U	Th	U/Th
Soil														
1	29.9	58.9	0.73	28.8	18.7	66.4	17.5	84.3	640	13.9	0.30	1.9	9.4	0.20
2	30.5	60.6	0.67	24.3	18.3	64.3	17.2	90.4	580	12.1	0.24	1.9	9.8	0.19
3	33.0	60.7	0.56	25.0	18.6	62.8	15.5	70.4	561	11.2	0.22	1.9	10.5	0.18
4	31.8	58.3	0.57	15.9	20.3	51.0	11.9	43.7	410	7.9	0.18	2.2	9.4	0.23
5	34.6	65.0	0.69	21.7	15.5	58.4	15.9	84.7	554	10.8	0.16	2.0	10.9	0.18
6	36.3	73.9	1.31	27.2	23.6	77.1	17.8	91.6	695	11.6	0.31	2.3	14.0	0.16
7	36.3	68.9	0.58	21.9	20.7	65.4	15.6	67.9	603	13.5	0.20	2.2	12.2	0.18
8	33.9	60.2	0.44	14.1	13.6	42.5	11.5	34.3	411	6.4	0.14	1.5	8.7	0.17
9	33.4	60.1	0.66	16.5	15.3	48.8	11.0	46.6	460	6.4	0.12	1.6	8.9	0.18
10	31.0	58.7	0.40	12.0	15.0	39.4	10.8	40.8	409	6.5	0.13	1.6	9.4	0.17
11	35.2	70.6	0.67	25.7	21.6	71.8	18.4	94.3	664	12.3	0.24	2.0	12.4	0.16
12	37.4	75.3	0.72	30.1	24.0	79.8	19.2	100.7	721	11.8	0.39	2.3	14.0	0.16
13	38.6	76.1	0.68	26.7	22.3	72.8	18.3	87.6	633	11.6	0.21	2.5	13.6	0.18
14	39.0	75.2	0.67	33.3	23.1	86.4	20.1	108.9	768	15.2	0.31	2.1	13.4	0.16
15	34.4	70.2	0.80	31.7	21.1	79.7	19.1	95.6	703	15.9	0.36	2.1	11.3	0.19
16	28.3	55.4	0.79	27.5	18.0	65.0	17.1	81.2	593	13.8	0.29	2.1	8.9	0.24
17	31.0	62.6	0.80	29.2	19.9	66.9	18.6	84.6	672	13.6	0.33	1.9	9.5	0.20
Mean	33.8	65.3	0.69	24.2	19.4	64.6	16.2	76.9	593	11.4	0.24	2.0	11.0	0.19
Sediment														
1	32.2	63.8	0.86	36.7	16.8	70.8	23.9	94.1	807	12.9	0.36	1.7	8.5	0.20
2	34.1	64.7	0.69	29.1	18.0	65.1	18.8	102.8	671	12.7	0.27	1.8	9.8	0.18
3	31.6	57.1	0.39	15.2	14.2	42.6	14.8	47.7	432	8.6	0.19	1.9	8.4	0.23
4	31.0	53.1	0.56	11.0	14.6	35.0	12.0	33.7	343	12.6	0.15	2.3	8.1	0.28
5	33.4	62.4	1.70	27.6	16.8	60.1	20.8	129.2	773	13.9	0.4	2.2	9.8	0.22
6	37.7	70.7	1.57	27.8	19.4	69.3	20.4	86.3	765	12.7	0.14	2.7	11.5	0.23
7	31.9	62.9	0.54	16.4	16.7	52.1	14.4	19.0	480	33.6	0.17	2.3	9.9	0.23
8	26.1	50.9	0.7	8.1	12.7	31.1	12.5	38.6	404	5.7	0.11	1.8	8.0	0.23
9	46.8	85.7	0.61	10.6	11.8	51.6	12.3	26.1	479	6.2	0.08	1.6	10.4	0.15
10	24.3	44.1	0.22	6.0	10.7	23.0	8.3	24.0	270	4.8	0.08	1.5	6.3	0.24
11	34.5	69.2	1.06	27.5	19.6	64.5	19.2	81.3	1034	13.9	0.28	2.5	11.0	0.23
12	36.7	68.4	1.24	25.2	19.8	73.2	16.3	80.0	730	11.2	0.26	2.6	12.6	0.21
13	33.1	66.9	0.80	20.5	18.2	59.9	15.4	70.7	590	12.1	0.23	2.2	10.5	0.21
14	35.3	66.4	0.90	31.0	20.7	71.7	19.6	107.5	797	14.3	0.36	2.3	12.3	0.19
15	31.0	59.3	0.98	29.0	16.9	69.3	19.0	90.2	768	14.0	0.34	1.9	9.2	0.21
16	30.1	56.5	0.53	24.2	17.1	60.8	17.0	83.3	588	12.2	0.28	1.9	9.6	0.20
17	26.3	49.0	0.47	18.3	13.9	43.6	12.0	54.1	585	10.1	0.23	1.9	7.4	0.26
Mean	32.7	61.8	0.81	21.4	16.3	55.5	16.3	68.7	619	12.4	0.23	2.1	9.6	0.22

at sites 3, 4, 5, 7, 8, 10, 11, 12, 13, 14, 15, and 17 (EF higher than 1) whereas at sites 1, 2, 5, and 16 they are not enriched (Cortizas et al., 2003; Singh et al., 2005; Sterckman et al., 2006). The normalized values of La and Ce and the EF values showed that the REE values of soils and sediments are within the range of mean values in surface soils worldwide and not strongly enriched (Kabata-Pendias and Pendias, 2001). Eu anomalies,

indicators of weathering and oxidation conditions in soils, showed a homogenous distribution, and no any significant differentiations were found between values (La/Yb)_{CN} and Eu anomalies of studied soils and sediments were shown in Table 3. In all sites, Eu anomalies were negative and very close to each other. The similarity of the negative Eu anomalies indicates the existence of low and similar weathering conditions. Due

Table 3. (La/Yb)CN and Eu anomalies of studied soils and sediments.

	Site																
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Soil																	
(La/Yb)CN	1.30	1.56	1.92	1.98	20.1	1.58	1.86	2.96	2.24	2.25	0.81	1.81	1.77	1.70	1.50	1.30	1.35
Eu/Eu*	0.82	0.81	1.04	0.95	0.85	0.80	1.04	0.93	1.02	0.96	0.88	0.82	0.68	0.72	0.66	0.82	0.75
Sediment																	
(La/Yb)CN	1.48	1.75	2.12	2.25	1.82	1.73	2.14	2.07	3.40	2.65	1.77	1.78	1.80	1.71	1.59	1.64	1.91
Eu/Eu*	0.69	0.79	0.85	0.91	0.81	0.72	0.82	0.92	0.95	1.01	0.77	0.81	0.78	0.70	0.77	0.70	0.75

Table 4. Enrichment factor of trace elements and REE.

Site	Element													
	La	Ce	Mo	Cu	Pb	Zn	Co	Ni	Mn	As	U	Th	Cd	
1	0.93	0.92	0.85	0.78	1.11	0.94	0.73	0.90	0.79	1.08	1.12	1.11	0.83	
2	0.89	0.94	0.97	0.84	1.02	0.99	0.91	0.88	0.86	0.95	1.06	1.00	0.89	
3	1.04	1.06	1.44	1.64	1.31	1.47	1.05	1.48	1.30	1.30	1.00	1.25	1.16	
4	1.03	1.10	1.02	1.45	1.39	1.46	0.99	1.30	1.20	0.63	0.96	1.16	1.20	
5	1.04	1.04	0.41	0.79	0.92	0.97	0.76	0.66	0.72	0.78	0.91	1.11	0.40	
6	0.96	1.05	0.83	0.98	1.22	1.11	0.87	1.06	0.91	0.91	0.85	1.22	2.21	
7	1.14	1.10	1.07	1.34	1.24	1.26	1.08	3.57	1.26	0.40	0.96	1.23	1.18	
8	1.30	1.18	0.63	1.74	1.07	1.37	0.92	0.89	1.02	1.12	0.83	1.09	1.27	
9	0.71	0.70	1.08	1.56	1.30	0.95	0.89	1.79	0.96	1.03	1.00	0.86	1.50	
10	1.28	1.33	1.82	2.00	1.40	1.71	1.30	1.70	1.51	1.35	1.07	1.49	1.63	
11	1.02	1.02	0.63	0.93	1.10	1.11	0.96	1.16	0.64	0.88	0.80	1.13	0.86	
12	1.02	1.10	0.58	1.19	1.21	1.09	1.18	1.26	0.99	1.05	0.88	1.11	1.50	
13	1.17	1.14	0.85	1.30	1.23	1.22	1.19	1.24	1.07	0.96	1.14	1.30	0.91	
14	1.10	1.13	0.74	1.07	1.12	1.21	1.03	1.01	0.96	1.06	0.91	1.09	0.86	
15	1.11	1.18	0.82	1.09	1.25	1.15	1.01	1.06	0.92	1.14	1.11	1.23	1.06	
16	0.94	0.98	1.49	1.14	1.05	1.07	1.01	0.97	1.01	1.13	1.11	0.93	1.04	
17	1.18	1.28	1.70	1.60	1.43	1.53	1.55	1.56	1.15	1.35	1.00	1.28	1.43	
Mean	1.05	1.07	0.85	1.13	1.19	1.16	1.00	1.12	0.96	0.92	0.97	1.14	1.05	

to (La/Yb)N not increases significantly from sediment to topsoil and negative (Eu/Eu*)N anomalies, LREE is not enriched profoundly during weathering). The content of total REE in sediment close to total REE of soils indicates that only a small amount of REE can be released and leached away during weathering and not increased by fertilization. The result indicates that the application of fertilizer has not caused a REE pollution problem and should not significantly affect food safety and human health. But Xu et al. (2002) found that accumulation of most light earths (e.g. La, Ce, Pr and Nd) and Gd in plant tops at the level of 2 kg rare earths ha⁻¹ and concentrations of REE in a field grown maize decreased in order of root>>stem>grain after application of rare earths. The Same researchers report that the dosage < 0.23 kg ha⁻¹ year⁻¹ currently applied in China, can hardly affect the safety of maize grains in arable soils

even over along period. In this study plant were not used. For this reason, further examination need to determine accumulation of REE in plants in the studied area.

The amounts of trace elements in soils generally are similar to amounts in sediments except for Ni and Pb. Some trace elements show depletion at some sites or slight enrichment at the other sites. All values are under the limit values according to Soil Pollution Control Regulation of Turkey (Minister of Environment and Forest, 2005). There was no source for Pb around the region (without traffic around the region). However the enrichment of Pb should be related to atmospheric deposition or agricultural traffic.

In the studied soils, the surface/sediment ratios for Zn exceeded 1.0, indicating the accumulation of these elements in surface soils not only from agricultural activity but also from other causes such as plant uptake and

perhaps atmospheric deposition. According to Kabata-Pendias and Pendias (2001) the average Zn content is 67 mg Zn/kg. It shows that the Zn content in the soils did not decline due to crop harvest.

Ni, Cu, U are known to be present in considerable amounts in phosphate fertilizers (Mermut et al., 1996) and it is highly probable that their presence in the soil stemmed from phosphate fertilizer application. In addition, sludge and compost for (Ni and Cu) and pesticide (for Cu) could be the main source of these elements in agricultural soils if these materials have been applied for a long time. Nickel (Ni) concentration was found higher in soils than sediments in 12 of sites. Ni is a heavy metal that exists as an ion at a very low level (6 - 92 mg kg⁻¹). It is a micronutrient for some crops but may become toxic to plants, animals and human if normal levels are exceeded. Complex formation of metal ions at binding and active sites are necessary for the catalytic activity of some enzymes. Urease is a common soil enzyme that may require Ni for activity. In recent years, some fertilizer manufacturers in Turkey have added bioavailable Ni to fertilizers to restore and increase the level of urease activity. Ni contents of the soils were found to be above the limits set out by the Soil Pollution Control Regulation of Turkey (Minister of Environment and Forest 2005). High Ni concentration should be related with N fertilizers containing Ni in studied soil. The results indicate that application of fertilizer has not caused a trace strong metal pollution except Ni. High Ni content shows Ni pollution, which was probably related to cultivation and soil management (that is N fertilizing). High Cu content at some sites could be due to pesticide use. However the changes in amounts of Ni, Zn and Cu in the topsoils from the application of fertilizer were not clear. The interpretation of our result therefore needs further examination. Concentrations of Mo Co, As and Mn in the soils were not significantly higher than those in sediments, which suggests that the contents of these elements in the soils are not increased by agricultural activities.

The accumulation of U in agricultural soil is important from the viewpoint of radiation protection. The concentration and chemical speciation of U in agricultural soil will provide important information when considering the potential threat of agricultural food-derived U to human health. Phosphatic fertilizer using for agricultural soils could be a source of REE as well as U and Th. Long-term application of phosphate fertilizers increases the concentration of U in agricultural soil, as reported previously (Tsumura and Yamasaki, 1993; Yoshida et al., 1998; Rothbaum et al., 1979; Takeda et al., 2006; Stojanović et al., 2006; Taylor, 2007). In the soils studied the concentrations of U in the soil obtained from soils with a long-term application of NPK were close to those in sediments (1.5 to 2.7 mgkg⁻¹). To investigate U accumulation in agricultural soils in more detail, the concentration

of U/Th in soils was examined because the increasing tendency for U to accumulate in agricultural soils become clear when U/Th ratio is used rather than the U content alone. The reason of this is phosphate fertilizers contain 10 to 200 times more U than do soils but the Th content is lower than that in soils (Yoshida et al., 1998; Takeda et al., 2004). In this study, we compared the U/Th ratio in different types of soil and operationally defined U speciation in the soil collected from study area, and sediments with and without the application of phosphate fertilizers respectively. The U/Th ratio and the concentration of U in surface layer of agricultural soils did not show a significant differentiation from the sediments. Our result showed that successive applications of phosphate fertilizer did not increase the concentrations of U and Cd in the topsoil. Cd concentrations are increased only at site 6. Our results suggested that the U is not as an impurity from the phosphate fertilizer left in the surface soil of the investigated fields. This observation supports the concept that the U/Th ratio can be a useful indicator of U accumulation of anthro-pogenic origin in the soil.

Conclusion

A dataset for the concentrations of some REEs in 17 soil and 17 sediment samples collected from Çarsamba fan soils (Çumra Basin) was analyzed from the viewpoint of soil pollution in relation to agricultural use. In the Çumra Basin, there is not a significant effect of REE accumulation due to fertilizer application on the soil environment quality. The concentration of La and Ce in the soils was in the range of the background values for world soils.

The concentration of Pb, Cu, and Ni in surface soils showed a tendency to increase with agricultural activities. The N fertilization caused the accumulation of Ni in the soil surface. The nickel concentrations of the soils studied were found to be above the limits set by the Soil Pollution Control Regulation. The high Ni concentration should be related with intensive use of N fertilizer in the area. Changes in concentration of Ni in the topsoils from the application of fertilizer were still not clear. Our results, therefore, need further examination. The U concentration in soil has not been increased by the long-term application of phosphate fertilizer. The U/Th ratio was a useful indicator of the U accumulation of anthropogenic origin in the soil in Turkey.

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