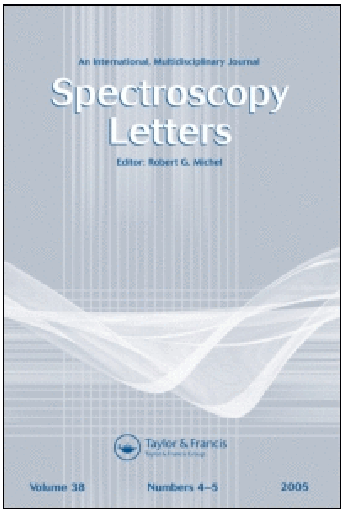

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Sources of Environmental Pollution in Ankara (Turkey): Geochemistry and Traffic Effects—PEDXRF Applications

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Online publication date: 05 April 2010

To cite this Article Kadıoğlu, Yusuf Kağan , Üstündağ, Zafer , Solak, Ali Osman and Karabıyıkoğlu, Gülseren(2010) 'Sources of Environmental Pollution in Ankara (Turkey): Geochemistry and Traffic Effects—PEDXRF Applications', Spectroscopy Letters, 43: 3, 247 — 257

To link to this Article: DOI: 10.1080/00387010903329391

URL: http://dx.doi.org/10.1080/00387010903329391

Spectroscopy Letters, 43:247–257, 2010

ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010903329391

Sources of Environmental Pollution in Ankara (Turkey): Geochemistry and Traffic Effects—PEDXRF Applications

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ABSTRACT Road dusts were collected from the main streets in the vicinity of Ankara, the capital city of Turkey, including exhaust dust samples from the different fuel-based motor vehicles and sample pieces of brake pads to characterize their metal compositions by polarized energy-dispersive X-ray fluorescence (PEDXRF) spectrometry. Road dust samples were gathered by a vacuum dust sweeper from nine different densely populated residential settlement regions of Ankara, far from large industrial plants. Heavy metal contents of the road dusts were analyzed during the summertime to determine the metal pollution due to the motor vehicle exhaust, abrasion of brake pads, and lithology, ignoring the industrial and heating sources of pollution. The results of the analysis showed that the elements of Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sn, Pb, and Th in road dust samples were not derived from the lithology and industrial plants but from the motor fuel exhausts and brake pad abrasion. Generally, urban environmental pollution due to the toxic trace metals from traffic is harmful for the human health as well as the ecosystems near Ankara.

KEYWORDS environmental pollution, heavy metal pollution, lithological pollution, road dust, XRF

INTRODUCTION

Ankara, Turkey's capital city, is the second major city in Turkey, with over 4 million people. It is located in the central Anatolia region of Turkey, north latitude 40°02′, north longitude 32°54′, and elevation of 850 m. The northern part of Ankara has a high topography forming volcanic outcrops, whereas, the central and southern parts of the city have low elevations in the form of clay-rich formation with low topography.

Motorized transportation and fossil fuel consumption in heating are generally regarded as the main two sources of urban air pollution.[1] In addition to the gaseous exhaust components from vehicles and the domestic and industrial chimney emission, the particulate pollutant has significant effects in urban environmental pollution.[2,3] Toxic trace metals are known to be harmful to human health as well as the ecosystems near densely populated

Received 14 August 2009; accepted 11 September 2009.

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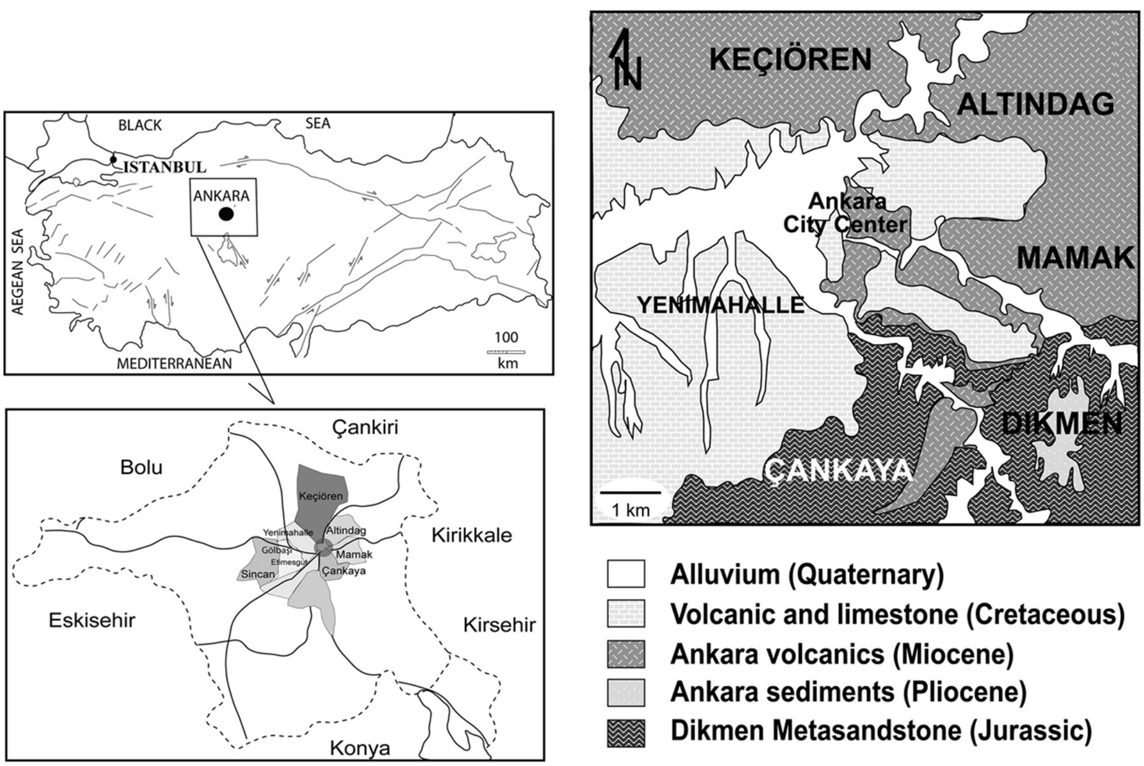
and industrial areas even at low concentrations when ingested and inhaled over a long period of time.[4–7]

Cardiovascular diseases and respiratory disorders are the main human health problems caused by long-term exposure to toxic trace metals present in air and in particulates in the street soil, especially near heavy traffic districts. Heavy metal particulate respiration has adverse effects, especially on sick and older people as well as children living in polluted areas. Some of the heavy metal contaminants may also act as immunotoxins, causing increased susceptibility to infectious diseases and parasites.[8] Generally, heavy metal toxicity is related to the oxidative damage induced in living systems, which can be promoted both by directly increasing the cellular concentration of reactive oxygen species and by reducing the cellular antioxidant capacity.[9]

Many reports are available on the measurement of heavy metal concentration in the environmental samples of the world's largest and heavily populated cities. Stikans et al. studied trace metals in background aerosols of urban and rural Kenya, Africa, by energy-dispersive X-ray fluorescence (EDXRF). They focused on determining the levels of trace metals in night aerosols of urban and rural Kenya.[10] Bandhu and coworkers analyzed aerosol samples from the industrial and commercial zones of Chandigarh, India, by EDXRF.[11] Manno et al. studied metal distribution in road dust samples collected in an urban area close to a petrochemical plant at Gela, Sicily, by inductively coupled plasma–mass spectroscopy (ICP-MS). They reported that the traffic appeared to be responsible for the high levels of Ba, Cu, Cr, Mo, Pb, Sb, and Zn.[12] Vedal and Dutton investigated wildfire pollution and daily mortality in a large urban area of metropolitan Denver, Colorado.[13] Soobader et al. studied levels of analysis for the study of environmental health disparities.[14] Hogervorst and coworkers studied the environmental effect of house dust in some heavy metal (cadmium and lead) and their effect in human population.[15] Meyer et al. studied factors affecting some lead and toxic metal (Pb, Cd, and As) levels in house dust in a smelter town in eastern Germany.[16] Dundar and Deryaoglu studied heavy metal determination in outdoor atmospheric dust depositions in Adapazarı City, Turkey. They determined Pb, Zn, Cd, Ni, Cr, and Cu concentrations of some



(a) (b)

FIGURE 1 **(a) Location of Ankara and city map showing the divisions. (b) Geological map of Ankara.**

dust deposition samples by atomic absorption spectrometry (AAS).[17] Burger and coworkers examined the levels of As, Cd, Cr, Pb, Mn, Hg, and Se in flathead sole and great sculpin from Adak Island in the Aleutians. They analyzed kidney, liver, and muscle of the region's fish species.[18]

EDXRF is a highly recommended and useful technique for the determination of heavy metals in various types of samples. This type of investigation is a nondestructive,[19] fast,[20] and easy[21–24] method for elemental analysis with relatively cheap instruments. In our laboratory, we studied multi-element analysis by polarized energy dispersive X-ray fluorescence (PEDXRF) in silver samples[24] and tincal ore waste.[25]

Mamak, Çankaya, Yenimahalle, Altındağ, Keçiören, Sincan, and Etimesgut are the main districts around the city center (Kızılay and Ulus) of Ankara (Fig. 1). Ankara was formerly the most polluted city in Turkey and the domestic and industrial use of fossil fuels (coal and fuel oils) has been banned since 1985. By the end of 2008, the total number of motor vehicles in Ankara was estimated to be above 1 million, showing very heavy traffic intensity and hence serious toxic metal pollution.

The present article is concerned with the chemical compositions of the collected dust from the roads in the vicinity of Ankara, analyzed by PEDXRF. A large set of road dust samples was collected in the city of Ankara during the summertime to analyze heavy metal pollution due to motor vehicle exhaust, abrasion of brake pads, and lithology, ignoring the industrial sources of pollution. There are no large-scale industrial plants in Ankara, except in the Ostim District, which is 20 km away from the city center and the dust sampling areas. Ankara is surrounded by mountains on four sides and therefore does not have a windy atmosphere, the chance of transportation of heavy metal–polluted dust and aerosols by air movement is very low.

GEOLOGY

Ankara is located to the north of central Anatolia and to the south of the İzmir–Ankara–Erzincan Suture zone. The basement of the region consists of Triassic metasandstone, which mainly crops out at the southern and southeastern parts of Ankara (Fig. 1). Allochthonous limestone and ophiolitic

TABLE 1 Content of the Elements Obtained from the Certified Material CRM 2126-81 Using PEDXRF Quantitative Method (with 95% Confidence)[a]

Elements or oxide	Certificate concentration	Measurement concentration
SiO_2	64.45 ± 0.09(%)	63.71 ± 0.07(%)
Al_2O_3	16.61 ± 0.13(%)	15.47 ± 0.04(%)
MgO	1.58 ± 0.04(%)	1.44 ± 0.04(%)
CaO	3.82 ± 0.05(%)	3.699 ± 0.007(%)
Na_2O	4.27 ± 0.08(%)	4.19 ± 0.14(%)
K_2O	3.12 ± 0.04(%)	3.502 ± 0.06(%)
TiO_2	6300 ± 200	5900 ± 200
P_2O_5	2290 ± 100	2076 ± 100
MnO	830 ± 50	974 ± 40
Fe_2O_3	4.64 ± 0.09(%)	4.48 ± 0.02(%)
Ba	970 ± 80	876 ± 5
Co	7.6 ± 0.7	7.2 ± 1.3
Cr	21 ± 2	20.2 ± 1.8
Cu	16 ± 2	15.4 ± 0.8
Ga	27 ± 2	26.4 ± 0.6
Ge	1.1 ± 0.2	ND
La	54 ± 7	52.6 ± 2.7
Mo	2.0 ± 0.3	1.98 ± 0.2
Nb	15 ± 3	14.3 ± 1.2
Ni	9.5 ± 0.9	9.4 ± 1.0
Pb	19 ± 2	18.4 ± 0.6
Rb	121 ± 8	120.9 ± 0.4
Sn	4.6 ± 0.5	4.4 ± 0.2
Sr	500 ± 50	491.1 ± 2
V	70 ± 6	65.4 ± 5.4
Y	25 ± 3	22.8 ± 0.3
Zn	69 ± 7	60.8 ± 1.2
Zr	230 ± 20	229.3 ± 1.0

[a]Concentrations of elements are given in μg/g except for those of major elements, which are in percentages. Precision is given as standard deviation in each case for three different measurements.

TABLE 2 Sample Names and Their Codes

Sample	Code	Sample	Code
Dust samples			
City center Ulus	CC-U	Keçiören	KO
Yeni Mahalle	YM	Sincan	SC
Altındağ	AD	Etimesgut	EM
Çankaya	CK	City center Kızılay	CC-K
Mamak	MM		
Exhaust and brake pad samples			
Exhaust unleaded gasoline	EG	Exhaust LPG	ELPG
Exhaust diesel	ED	Brake pad	BP
Volcanic (V) and clay-rich soil samples (CS)			
Clay-rich soil 1	CS-1	Volcanic 2	V-2
Clay-rich soil 2	CS-2	Volcanic 3	V-3
Clay-rich soil 3	CS-3	Volcanic 4	V-4
Volcanic 1	V-1	Volcanic 5	V-5

TABLE 3 **Chemical Compositions of Road Dust Samples Collected by a Sweeper Vehicle in Some Districts of Ankara**[a]

Element	CC-U	YM	AD	CK	MM	KO	SC	EM	CC-K
Mg	8130 ± 270	3230 ± 240	9020 ± 280	8460 ± 270	4790 ± 240	3430 ± 210	5000 ± 240	4710 ± 240	6570 ± 260
Al	2.814 ± 0.017%	1.442 ± 0.013%	2.586 ± 0.017%	2.795 ± 0.017%	2.339 ± 0.016%	2.308 ± 0.015%	2.072 ± 0.015%	2.174 ± 0.015%	2.096 ± 0.015%
Si	11.720 ± 0.030%	6.040 ± 0.017%	10.940 ± 0.030%	11.150 ± 0.030%	9.113 ± 0.022%	9.937 ± 0.022%	7.698 ± 0.020%	8.757 ± 0.021%	9.299 ± 0.023%
P	528 ± 16	193 ± 15	470 ± 17	419 ± 16	408 ± 16	299 ± 13	545 ± 17	318 ± 15	276 ± 17
S	1332 ± 11	1364 ± 11	1506 ± 12	1858 ± 14	1680 ± 12	983.1 ± 8.6	1376 ± 11	2219 ± 14	1377 ± 12
Cl	179.8 ± 2.9	175.3 ± 3.0	305.6 ± 3.9	209.0 ± 3.2	381.5 ± 4.2	235.1 ± 3.0	272.4 ± 3.6	182.5 ± 2.9	133.6 ± 2.6
K	7728 ± 70	4026 ± 55	7244 ± 69	8275 ± 72	7465 ± 66	7622 ± 62	6032 ± 62	6676 ± 62	5361 ± 63
Ca	14.28 ± 0.03%	23.48 ± 0.04%	17.93 ± 0.03%	17.46 ± 0.03%	16.40 ± 0.03%	11.07 ± 0.02%	21.07 ± 0.04%	14.53 ± 0.03%	22.41 ± 0.04%
Ti	3320 ± 28	1922 ± 24	3184 ± 29	2992 ± 28	2692 ± 25	2502 ± 21	2350 ± 26	2218 ± 22	2250 ± 27
V	96 ± 10	29.8 ± 8.0	83 ± 10	69 ± 10	61.9 ± 8.7	64.6 ± 7.2	58.8 ± 9.5	58.7 ± 7.9	48.7 ± 9.6
Cr	246.4 ± 9.9	97.0 ± 7.2	433 ± 13	257 ± 10	129.5 ± 7.5	114.2 ± 7.0	120.1 ± 7.5	97.5 ± 6.7	992 ± 18
Mn	720 ± 13	296.2 ± 9.4	606 ± 13	549 ± 12	591 ± 12	379.6 ± 9.4	417 ± 11	400.9 ± 9.8	411 ± 13
Fe	3.552 ± 0.008%	1.718 ± 0.005%	3.050 ± 0.007%	2.799 ± 0.007%	2.601 ± 0.007%	2.142 ± 0.006%	1.959 ± 0.006%	2.129 ± 0.006%	2.920 ± 0.007%
Co	27.4 ± 5.7	27.7 ± 6.1	27.5 ± 5.9	ND[b]	ND	29.2 ± 5.7	24.2 ± 5.7	19.5 ± 4.9	ND
Ni	51.1 ± 2.1	37.9 ± 1.9	92.0 ± 2.6	63.6 ± 2.2	45.5 ± 1.9	28.7 ± 1.4	42.0 ± 1.9	45.9 ± 1.8	46.4 ± 2.1
Cu	63.9 ± 1.9	38.9 ± 1.5	40.9 ± 1.5	73.9 ± 2.1	33.0 ± 1.4	44.2 ± 1.5	38.0 ± 1.5	28.5 ± 1.3	208.3 ± 3.4
Zn	141.0 ± 2.3	116.0 ± 2.1	62.2 ± 1.5	96.7 ± 1.9	84.2 ± 1.7	93.5 ± 1.7	107.0 ± 1.9	77.1 ± 1.6	349.3 ± 3.7
Ga	9.4 ± 0.8	4.8 ± 0.6	10.3 ± 0.8	8.5 ± 0.8	9.9 ± 0.8	7.4 ± 0.6	7.6 ± 0.7	9.7 ± 0.8	5.0 ± 0.7
Ge	ND	ND	1.0 ± 0.4	1.1 ± 0.4	0.8 ± 0.4	0.9 ± 0.4	ND	ND	0.9 ± 0.4
As	21.7 ± 1.2	9.0 ± 0.7	15.4 ± 0.9	13.6 ± 1.1	8.0 ± 0.8	8.8 ± 0.8	5.4 ± 0.7	14.2 ± 1.0	8.5 ± 1.4
Br	3.7 ± 0.3	1.4 ± 0.3	1.1 ± 0.3	1.9 ± 0.3	2.0 ± 0.3	1.4 ± 0.2	1.5 ± 0.3	2.6 ± 0.3	3.5 ± 0.3
Rb	35.8 ± 0.5	18.2 ± 0.4	35.5 ± 0.5	40.1 ± 0.6	37.3 ± 0.5	35.5 ± 0.5	29.4 ± 0.5	40.6 ± 0.5	29.4 ± 0.5
Sr	369.5 ± 1.4	293.4 ± 1.3	311.4 ± 1.3	305.3 ± 1.3	308.7 ± 1.3	314.7 ± 1.2	295.0 ± 1.2	329.0 ± 1.3	314.4 ± 1.3
Y	9.1 ± 0.5	3.6 ± 0.5	8.5 ± 0.5	9.7 ± 0.5	8.0 ± 0.5	7.3 ± 0.4	5.7 ± 0.5	8.4 ± 0.5	6.5 ± 0.5
Zr	128.2 ± 5.9	45.2 ± 4.2	109.4 ± 5.6	98.4 ± 5.0	92.3 ± 5.1	133.6 ± 5.6	96.6 ± 5.3	93.8 ± 5.1	92.6 ± 5.4
Nb	11.6 ± 2.2	3.2 ± 1.7	10.2 ± 2.1	6.9 ± 2.0	11.4 ± 2.1	10.9 ± 1.8	7.1 ± 1.9	10.7 ± 1.9	ND
Mo	ND	ND	ND	ND	ND	3.9 ± 1.4	ND	3.2 ± 1.3	8.2 ± 1.9
Ag	0.7 ± 0.6	ND	ND	ND	ND	ND	ND	ND	ND
Cd	ND	ND	0.4 ± 0.4	ND	ND	ND	ND	ND	ND
Sn	5.3 ± 0.6	1.1 ± 0.3	4.2 ± 0.5	4.7 ± 0.5	3.1 ± 0.5	4.0 ± 0.5	2.3 ± 0.5	1.6 ± 0.4	5.7 ± 0.6
Sb	6.0 ± 0.5	3.2 ± 0.5	2.2 ± 0.5	3.9 ± 0.5	1.9 ± 0.5	2.9 ± 0.5	3.2 ± 0.5	3.6 ± 0.5	6.0 ± 0.6
I	3.3 ± 1.4	2.0 ± 1.2	ND	3.5 ± 1.3	ND	ND	2.2 ± 1.3	ND	ND
Cs	ND	ND	ND	ND	ND	ND	ND	5.2 ± 1.8	4.1 ± 1.7
Ba	449.1 ± 4.7	153.8 ± 3.7	323.9 ± 4.4	403.9 ± 4.4	328.0 ± 4.3	356.4 ± 4.4	275.1 ± 4.0	358.5 ± 4.4	299.5 ± 4.2
La	20.0 ± 4.7	ND	17.8 ± 4.7	12.8 ± 4.5	16.6 ± 4.7	19.1 ± 4.6	18.0 ± 4.4	17.6 ± 4.6	13.2 ± 4.5
Ce	32.9 ± 6.2	14.4 ± 5.8	31.0 ± 6.2	40.0 ± 6.0	35.4 ± 6.2	37.2 ± 6.2	16.9 ± 5.8	30.7 ± 6.2	25.7 ± 6.0
Hg	1.0 ± 0.7	ND	ND	ND	ND	ND	ND	ND	ND
Tl	ND	ND	ND	ND	1.0 ± 0.7	1.0 ± 0.6	0.7 ± 0.7	ND	ND
Pb	65.8 ± 1.5	18.4 ± 0.9	25.1 ± 1.0	60.4 ± 1.4	30.1 ± 1.1	35.5 ± 1.0	25.9 ± 1.0	42.6 ± 1.2	107.4 ± 1.9
Bi	ND	ND	ND	ND	ND	0.8 ± 0.4	ND	1.2 ± 0.5	ND
Th	3.9 ± 0.4	1.8 ± 0.3	3.6 ± 0.4	5.5 ± 0.5	4.9 ± 0.5	4.4 ± 0.4	2.5 ± 0.4	5.4 ± 0.5	2.6 ± 0.3
U	12.1 ± 4.1	ND	ND	ND	6.3 ± 3.3	ND	ND	ND	ND

[a]Concentrations of elements are given in μg/g except for those of major elements, which are in percentages. Precision is given as standard deviation in each case for five different measurements.
[b]ND: not detected.

mélange at the far south and north of the city. Eocene and Miocene volcanic rocks crop out at the central part and to the north–northeast of the city center.[26,27] Clay-rich sedimentary deposits are the main lithology of Ankara City and mostly represent the central and western parts of the area (Fig. 1). Clay-rich sedimentary deposits mostly form the decompositions of the volcanic rocks of Ankara. The volcanic rocks of Ankara are mainly composed of andesite with rare amounts of dasite and basalt. Most of the andesite lithology altered to clay and clay-rich deposits. Clay and calcite feldspar with minor amounts of gypsum, pyroxene, amphibole, hematite, and other iron hydroxide minerals form the main mineralogical compositions of the lithology. The lithology of the studied area are enriched with Si, Al, and Ca with less amount of Na, K, Mg, Fe, and other light elements.

MATERIALS AND METHODS

Dust particulate samples were gathered by street sweeper vehicles directly from various roads of Ankara in September. A total of nine samples were collected from nine main locations and kept in plastic bags until analysis. In order to determine the sources of heavy metal contents, samples of exhaust ashes of gasoline, LPG, and diesel fuel and from brake pads of the vehicles were also collected and analyzed for comparison purposes. Because the sweeper vehicle collects the dust directly from the road by wetting, the dust samples were dried at room temperature. Samples containing large objects were screened to remove the course fraction. The dust samples were sieved into particle size range of less than 250 μm and then pressed into thick pellets of 32 mm diameter using wax as a binder. The sources of heavy metal contents of road dust samples are assumed to originate from lithology, exhaust gases, and the abrasion of brake pads of motorized vehicles. Therefore, accumulated dust at the inner part of the exhaust was also stripped and analyzed for different types of fuels such as gasoline, diesel, and LPG to compare its composition with the road dust samples. The composition of the brake pads was analyzed to compare with the composition of the dust collected directly from the road.

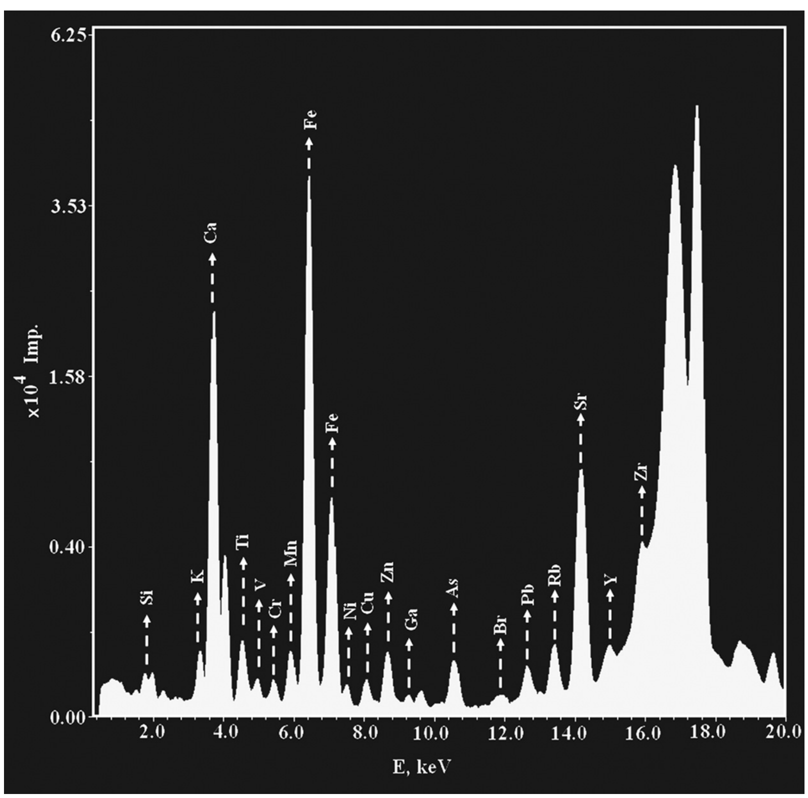


FIGURE 2 Part of the XRF spectrum of CC-U road dust sample in Ankara.

Elemental concentration of dust, exhausts, and brake pad samples was determined by using PEDXRF. The instrument used was a Spectro XLAB 2000 PEDXRF spectrometer (Germany) equipped with an Rh anode X-ray tube. The detector of the spectrometer was a Grefham Sirius 50/BE/XRF (Germany). The detector of the spectrometer is liquid nitrogen cooled Si(Li) with a resolution of less than 150 eV at Mn Kα, 1000 cps. The sample to be analyzed was excited with linear polarized X-ray radiation.[28]

The results of the measurements of the Spectro XLAB 2000 PEDXRF spectrometer controlled by determining the elemental concentration in a standard sample[29,30] which is prepared by CRM 2126–81, a certified material from ASSO and shown in Table 1.

RESULTS

All the collected samples were coded and are shown in Table 2.

All data are the results of an average of three measurements for each sample. The concentration values of road dust samples were searched for 42 elements as given in Table 3. A representative spectrum for a road dust sample taken from the city center Ulus is given in Fig. 2.

TABLE 4 PEDXRF Result for the Exhaust Dusts and Brake Pad Samples in Ankara[a]

Element	EG	ELPG	ED	BP
Al	ND[b]	ND	ND	1.311 ± 0.089%
Si	ND	4930 ± 110	ND	5040 ± 160
P	ND	1029 ± 67	621 ± 34	ND
S	2705 ± 45	9578 ± 72	1.349 ± 0.006%	2.763 ± 0.013%
Cl	171 ± 11	106.2 ± 8.6	95.7 ± 5.0	431 ± 15
Ca	545 ± 27	1.866 ± 0.012%	2500 ± 28	2470 ± 110
Ti	ND	420 ± 16	61.5 ± 6.0	491 ± 16
V	ND	ND	ND	97.3 ± 7.0
Cr	165.3 ± 5.8	ND	70.1 ± 2.9	1.450 ± 0.008%
Mn	1692 ± 29	525 ± 20	326.4 ± 8.7	951 ± 36
Fe	43.99 ± 0.06%	39.18 ± 0.05%	13.63 ± 0.02%	10.39 ± 0.02%
Co	93.6 ± 5.7	80.2 ± 4.8	36.6 ± 2.9	45.1 ± 3.7
Ni	18.4 ± 1.8	11.7 ± 1.9	5.4 ± 0.4	11.3 ± 1.9
Cu	211.7 ± 8.7	36.6 ± 3.8	46.9 ± 2.3	6.608 ± 0.013%
Zn	3225 ± 29	1074 ± 15	465.9 ± 5.6	7.879 ± 0.013%
As	25.7 ± 2.1	48 ± 15	9.7 ± 0.8	ND
Se	ND	ND	1.7 ± 0.3	ND
Br	17.7 ± 1.3	109.7 ± 2.7	ND	ND
Rb	ND	5.2 ± 1.5	ND	6.1 ± 0.9
Sr	1.5 ± 0.9	150.6 ± 2.2	5.7 ± 0.4	18.2 ± 0.9
Zr	ND	17.0 ± 4.5	ND	21.7 ± 6.7
Mo	38.2 ± 4.0	29.6 ± 3.8	12.5 ± 1.6	9627 ± 41
Ag	ND	6.2 ± 1.1	ND	ND
Cd	2.1 ± 0.8	4.2 ± 1.0	1.0 ± 0.4	ND
Sn	14.7 ± 0.8	ND	4.3 ± 0.4	3.625 ± 0.005%
Sb	3.4 ± 0.7	ND	ND	ND
I	ND	ND	ND	950 ± 24
Cs	ND	ND	1.7 ± 1.3	ND
Ba	10.7 ± 2.7	357.5 ± 4.3	3.9 ± 1.8	306.1 ± 6.6
La	ND	7.5 ± 3.7	ND	ND
Ce	ND	ND	ND	13.8 ± 5.9
Pb	ND	3096 ± 22	5.0 ± 1.9	16.2 ± 2.9
Th	ND	36.7 ± 4.0	ND	ND

[a]Concentrations of elements are given in μg/g except for those of major elements, which are in percentages. Precision is given as standard deviation in each case for five different measurements.

[b]ND: not detected.

TABLE 5 **PEDXRF Result for the Volcanic (V) and Clay-Rich Soil Samples (CS) of Ankara Region[a]**

Element	CS-1	CS-2	CS-3	V-1	V-2	V-3	V-4	V-5
Na	3.37 ± 0.14%	1200 ± 100	1.58 ± 0.12%	3.41 ± 0.13%	3.39 ± 0.13%	3.74 ± 0.14%	3.22 ± 0.13%	3.58 ± 0.13%
Mg	3390 ± 220	1.089 ± 0.030%	2.126 ± 0.035%	2540 ± 200	5550 ± 230	2590 ± 210	2540 ± 210	1740 ± 190
Al	8.196 ± 0.031%	7.395 ± 0.030%	9.645 ± 0.034%	7.805 ± 0.028%	7.957 ± 0.029%	7.891 ± 0.029%	8.027 ± 0.029%	7.549 ± 0.028%
Si	30.76 ± 0.05%	22.80 ± 0.04%	29.20 ± 0.05%	30.67 ± 0.05%	31.41 ± 0.05%	32.30 ± 0.05%	32.13 ± 0.05%	32.99 ± 0.05%
P	2001 ± 24	246 ± 10	486 ± 13	ND[b]	1580 ± 20	1346 ± 19	1380 ± 20	1060 ± 17
K	2.109 ± 0.013%	3993 ± 57	2.188 ± 0.013%	2.200 ± 0.012%	1.996 ± 0.012%	2.363 ± 0.013%	2.312 ± 0.013%	2.384 ± 0.013%
Ca	2.785 ± 0.012%	1.285 ± 0.008%	2774 ± 48	2.062 ± 0.010%	2.108 ± 0.010%	2.022 ± 0.010%	2.062 ± 0.010%	1.669 ± 0.009%
Ti	4185 ± 35	2617 ± 26	4270 ± 32	2715 ± 27	2736 ± 27	2765 ± 28	2751 ± 28	2063 ± 25
V	47 ± 11	135 ± 10	118 ± 32	47.8 ± 9.6	36.5 ± 9.1	37.8 ± 9.5	38.8 ± 9.8	30.9 ± 8.7
Cr	44.4 ± 4.7	ND	33.1 ± 6.8	32.1 ± 4.3	32.4 ± 4.2	28.2 ± 3.9	25.4 ± 3.6	ND
Mn	370 ± 10	322 ± 16	315 ± 13	236.5 ± 8.1	306 ± 13	280.1 ± 8.8	269.2 ± 8.7	388.9 ± 9.6
Fe	3.313 ± 0.008%	7.249 ± 0.012%	5.193 ± 0.010%	2.310 ± 0.006%	2.423 ± 0.006%	2.457 ± 0.006%	2.562 ± 0.006%	1.93 ± 0.005%
Co	41.5 ± 7.3	75.7 ± 9.1	51.9 ± 8.1	33.0 ± 6.3	35.5 ± 6.7	19.4 ± 4.8	33.5 ± 6.4	26.7 ± 5.7
Ni	26.0 ± 1.6	34.6 ± 3.7	28.4 ± 2.6	18.7 ± 1.3	10.9 ± 1.0	20.2 ± 1.4	21.6 ± 1.4	13.2 ± 1.1
Cu	29.9 ± 1.6	28.2 ± 2.1	18.8 ± 1.2	2.4 ± 0.4	3.3 ± 0.5	ND	6.4 ± 0.7	3.8 ± 0.5
Zn	55.4 ± 1.5	209.9 ± 2.9	101.7 ± 2.1	67.4 ± 1.6	69.8 ± 1.6	62.5 ± 1.6	60.3 ± 1.5	33.9 ± 1.2
Ga	19.0 ± 0.9	26.4 ± 1.0	20.0 ± 0.9	19.6 ± 0.9	18.1 ± 0.9	17.7 ± 0.9	19.2 ± 0.9	17.7 ± 0.8
Ge	ND	3.3 ± 0.5	ND	1.0 ± 0.4	0.6 ± 0.3	1.3 ± 0.5	0.8 ± 0.4	1.8 ± 0.5
As	9.0 ± 0.8	9.4 ± 0.9	8.2 ± 0.6	8.7 ± 0.8	3.4 ± 0.7	6.7 ± 0.9	7.8 ± 0.8	4.8 ± 0.8
Br	ND	1.0 ± 0.2	ND	0.7 ± 0.2	ND	0.5 ± 0.2	ND	1.2 ± 0.2
Rb	57.7 ± 0.6	41.7 ± 0.6	91.0 ± 0.8	69.2 ± 0.7	75.2 ± 0.7	67.2 ± 0.7	69.1 ± 0.7	69.1 ± 0.6
Sr	683.0 ± 1.9	200.4 ± 1.1	38.8 ± 0.5	599.7 ± 1.7	596.4 ± 1.7	598.3 ± 1.7	594.0 ± 1.7	548.5 ± 1.6
Y	20.6 ± 0.6	22.5 ± 0.6	19.2 ± 0.6	20.4 ± 0.6	18.3 ± 0.6	18.9 ± 0.6	19.4 ± 0.6	19.9 ± 0.6
Zr	231.6 ± 7.2	183.1 ± 5.4	188.5 ± 5.2	260.8 ± 7.1	263.4 ± 6.9	240.0 ± 6.5	245.8 ± 6.6	261.7 ± 6.4
Nb	21.1 ± 2.2	27.1 ± 2.2	18.4 ± 2.3	25.0 ± 2.2	24.3 ± 2.2	22.6 ± 2.1	24.5 ± 2.2	22.4 ± 2.0
Mo	5.2 ± 1.6	2.6 ± 1.1	5.0 ± 1.6	ND	4.5 ± 1.4	5.8 ± 1.5	4.2 ± 1.4	6.0 ± 1.5
Ag	ND	15.9 ± 0.7	ND	ND	ND	ND	ND	ND
Cd	0.6 ± 0.1	ND	1.9 ± 0.5	ND	ND	0.4 ± 0.1	ND	0.6 ± 0.4
Sn	4.8 ± 0.6	2.6 ± 0.5	3.7 ± 0.5	1.4 ± 0.4	ND	ND	2.2 ± 0.5	2.5 ± 0.4
Cs	5.2 ± 1.2	5.1 ± 1.5		6.6 ± 1.2	4.5 ± 1.1	ND	4.7 ± 1.0	14.1 ± 1.6
Ba	1119 ± 6	650.5 ± 4.9	339.1 ± 4.0	1584 ± 7	1280 ± 6	1273 ± 6	1627 ± 7	1311 ± 6
La	52.9 ± 4.5	33.9 ± 4.5	23.0 ± 4.4	54.6 ± 4.6	62.8 ± 4.6	50.1 ± 4.5	47.2 ± 4.6	78.9 ± 4.4
Ce	84.8 ± 6.0	90.4 ± 6.0	36.0 ± 5.8	73.8 ± 6.0	79.0 ± 6.0	77.1 ± 5.8	67.6 ± 5.8	101.8 ± 5.8
Tl	0.8 ± 0.1	ND	ND	0.8 ± 0.6	ND	ND	ND	1.0 ± 0.6
Pb	22.7 ± 1.0	16.2 ± 1.1	4.6 ± 0.8	26.1 ± 1.0	28.1 ± 1.1	25.6 ± 1.0	26.0 ± 1.0	28.3 ± 1.0
Bi	1.1 ± 0.5	ND	ND	ND	0.9 ± 0.5	ND	ND	0.4 ± 0.3
Th	9.1 ± 0.7	7.0 ± 0.8	8.5 ± 0.7	8.8 ± 0.7	8.6 ± 0.7	9.8 ± 0.7	16.9 ± 0.7	14.7 ± 0.7
U	ND	ND	12.8 ± 4.0	10.1 ± 3.5	ND	8.9 ± 3.1	15.5 ± 3.8	14.5 ± 3.4

[a]Concentrations of elements are given in μg/g except for those of major elements, which are in percentages. Precision is given as standard deviation in each case for five different measurements.
[b]ND: not detected.

The heavy metal contents of the road dust samples were assumed to be the sum of the various sources such as lithology, motor fuels, and brake pads.[31] The results of the exhaust and brake pad samples are given in Table 4. Concentrations of elements are given in μg/g units except for those of major elements, which are given as percentages. The standard deviations in Tables 3 and 4 were calculated for five replicate measurements. The results of the chemical analyses reveal that there are no geological effects in the environmental pollution of the city.

DISCUSSION

The results of the collected samples from the different lithology of Ankara region is given in Table 5.

The distribution of some selected elements, which are mostly toxic, present in the road dust samples and their correlation with the exhaust and brake pad samples are shown in Table 6 and in histograms in Fig. 3. Most of the selected elements given in Table 6 are the most hazardous and toxic for human health. For example, lead may cause intelligence and behavioral disorders. In addition, it may cause hypotension, bradicardia, nausea and vomiting, anemia, and kidney function abnormalities.[32,33] Arsenic in the human body can cause polyneuritis, liver and kidney function abnormalities, and cancer. Chromium can cause respiratory tract irritation, pneumoconiosis, lung cancer, gastrointestinal disorders, and dermatitis. Manganese can cause airway irritation, peripheral muscle tonus disorder, and liver function abnormalities. Nickel may cause skin eruptions and gastrointestinal adverse signs. Considering data in Tables 3–5, the elements of Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sn, Pb, and Th should not derive from the lithology of Ankara but from the motor fuel and brake pad samples. The concentrations of Cr, Mn, Fe, Ni, Cu, Zn, As, Sn, Pb, and Th toxic elements are lower in volcanic and clay samples than in polluted road dust, exhaust dust, and brake pad samples (Tables 4 and 5). Although the concentration of Co seems to be higher in clay samples than that of road dust samples, the compatible and immobile nature of this element[34,35] fixes it in its source material, preventing contamination of the environment. It is interesting to note that the source of some elements is mainly due to the exhaust dust and/or brake pads. For example, high contents of Cr, Mn, Cu, Zn, and Sn (Table 6) show that these elements mainly come from brake pad samples. On the other hand, As and Pb come mostly from exhaust dust rising from the fuel. Although the main source of Zn seems to be the brake pad, gasoline, LPG, and diesel fuels also contribute to the amount of this element in the road dust. The presence of Th and Ba in road dust samples in considerable amounts can be explained with the high concentration of

TABLE 6 **Results of the Selected Elements within Nine Different Localities of Ankara and Their Correlations with the Exhaust and Brake Pad Samples of the Vehicles**[a]

Element	Sample code												
	CC-U	YM	AD	CK	MM	KO	SC	EM	CC-K	EG	ELPG	ED	BP
Cr	246.4	97	433	257	129.5	114.2	120.1	97.5	992	165.3	ND	70.1	14,500
Mn	720	296.2	606	549	591	379.6	417	400.9	411	1692	525	326.4	951
Fe	35,520	17,180	30,500	27,990	26,010	21,420	19,590	21,290	29,200	439,900	391,800	136,300	103,900
Co	27.4	27.7	27.5	ND[b]	ND	29.2	24.2	19.5	ND	15.7	10.2	3.6	45.1
Ni	51.1	37.9	92	63.6	45.5	28.7	42	45.9	46.4	8.4	7.7	5.4	11.3
Cu	63.9	38.9	40.9	73.9	33	44.2	38	28.5	208.3	211.7	36.6	46.9	66,080
Zn	141	116	62.2	96.7	84.2	93.5	107	77.1	349.3	3225	1074	465.9	78,790
As	21.7	9	15.4	13.6	8	8.8	5.4	14.2	8.5	25.7	48	9.7	ND
Sn	5.3	1.1	4.2	4.7	3.1	4	2.3	1.6	5.7	14.7	ND	4.3	36,250
Ba	449.1	153.8	323.9	403.9	328	356.4	275.1	358.5	299.5	10.7	357.5	3.9	306.1
Pb	65.8	18.4	25.1	60.4	30.1	35.5	25.9	42.6	107.4	ND	3096	5	16.2
Th	3.9	1.8	3.6	5.5	4.9	4.4	2.5	5.4	2.6	ND	36.7	ND	ND

[a]Concentrations of elements are given in μg/g.
[b]ND: not detected.

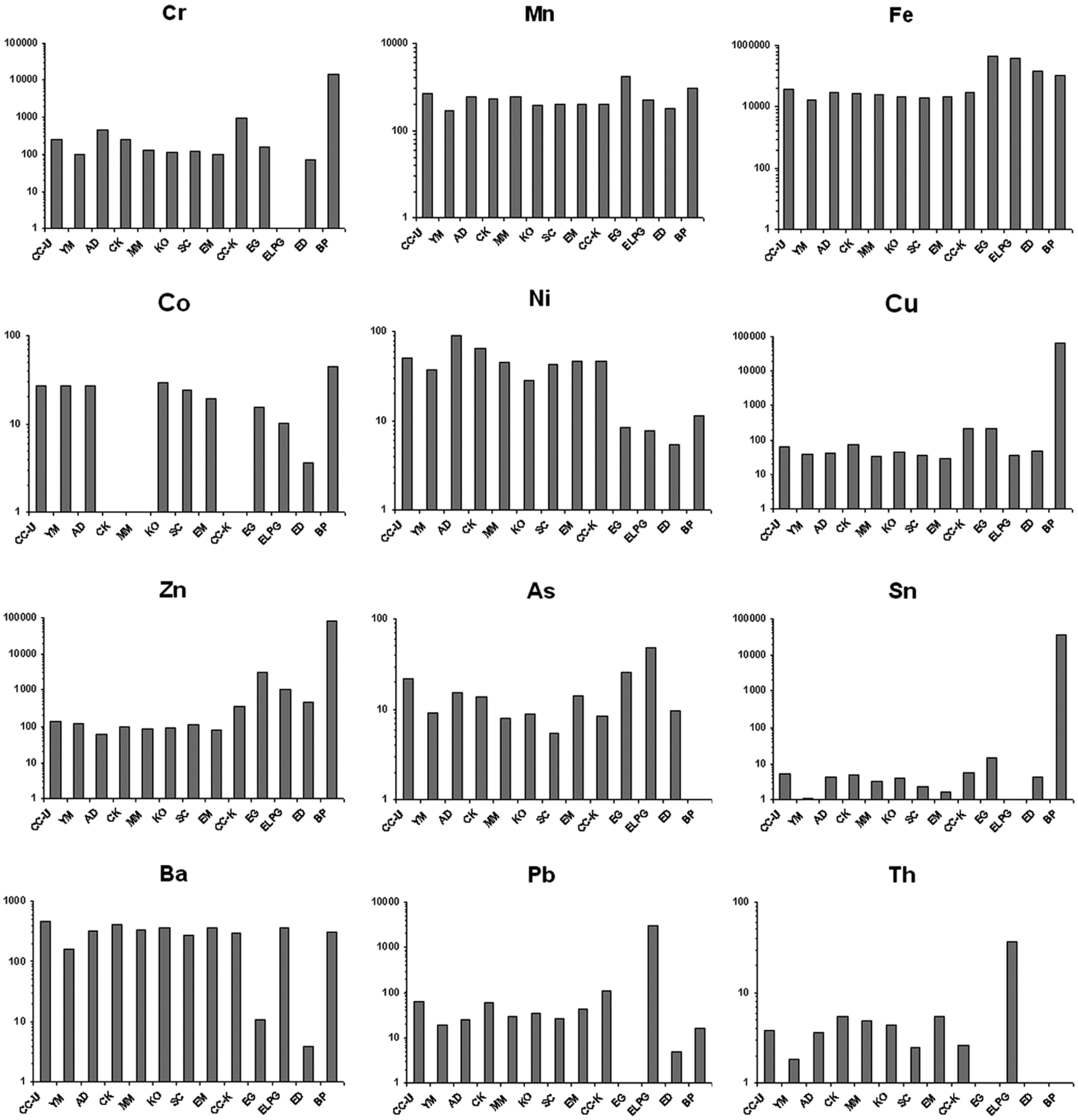


FIGURE 3 **The histogram of the elements within nine different localities of Ankara and their correlations with the exhaust and brake pad samples of the vehicles.**

these elements in volcanic and clay samples and their mobile nature. Fe is found in significant amounts in road dust samples in Ankara as can be seen from Table 6. Because Fe has diverse sources, it cannot be used as a criterion in the interpretation of the nature of the polluted city road dust samples.

To differentiate the heating and traffic sources of heavy metals pollution in the Ankara road dusts, the samples were collected in summer. In this season, heating fuel should not have any effect on pollution within the collected road dust samples. Therefore, the heavy metals found in the road dust samples seem to be from the fuel consumption of the vehicles in Ankara on the main roads. Regarding these events, the chemical compositions of the exhaust and brake pad samples of the vehicles are analyzed and compared with chemical compositions of the road dust.

CONCLUSIONS

The PEDXRF analysis of main road dust samples collected from the nine different densely populated residential settlement regions of Ankara showed that the heavy metal pollution was mainly due to the motor vehicle exhausts and abrasion of brake pads rather than the lithology of the region. The contribution of lithology and industrial plants to the concentration of elements of Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sn, Pb, and Th in road dust samples is negligible. Because the analyses were performed during the summer, the contribution to the heavy metal pollution from heating sources was also ignored. Another project is underway to determine the effects of chimney gases from domestic heating to the heavy metal pollution of road dust in Ankara. It is interesting to note that Pb is found in exhaust dust samples in considerable amounts. Because most motor vehicles in Ankara use LPG and diesel fuels, Pb pollution will be a real health problem in Ankara in the near feature. Generally, urban environmental pollution due to toxic trace metals from traffic is harmful for the human health as well as the ecosystems near Ankara.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Ankara University Scientific Research Fund under Grant No. 2003-07-45-015 and State Planning Organization (DPT) Project Grant numbers of 2003-K120190-4-6 and 2003-K12019011-5-6.

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