ORIGINAL ARTICLE

Deciphering factors controlling trace element distribution in the soils of Karaduvar industrial-agricultural area (Mersin, SE Turkey)

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Abstract In this study, 30 topsoil samples were collected from Karaduvar area (Mersin, SE Turkey) where at present various industrial and agricultural activities are occurring. Using a Þve-step ultrasound-assisted sequential extraction (UASE) procedure, trace elements in soil samples were partitioned into the following: (1) soluble-exchangeable; (2) bound to carbonates; (3) bound to Fe- and Mn-oxides; (4) bound to organic matter and sulÞde compounds, and (5) residual fraction. Concentrations of 11 trace elements in the extracts were determined using ICP-MS. Total concentrations ranged between (in mg Kg^{-1}) 3.35 and 7.26 for As; 1.18 and 3.96 for Cd; 10.76 and 20.26 for Co; 37.99 and 63.48 for Cr; 18.55 and 243.1 for Cu; 338.7 and 565.6 for Mn; 4.42 and 6.44 for Mo; 148 and 279.3 for Ni; 10.12 and 73.71 for Pb; 17.93 and 36.55 for V, and 25.46 and 331.7 for Zn. Factor analysis was applied to dataset in order to discriminate between natural and anthropogenic pollution sources and factors controlling the spatial distribution of trace elements in the area. Results suggest that distributions of Co, Cr, Mn, and Ni are mainly controlled by lithological factors, whereas, distributions of Cu, Pb, and Zn can be attributed to agricultural activities such as pesticide/herbicide use and fertilizer application, as well as irrigation with petroleum hydrocarbon-contaminated groundwater. Highest concentrations of Cd and Mo are generally observed around the diesel-Þred thermal power plant and ATAÞ reÞnery. Highest concentrations of As and V are generally observed at the NW sector of the area; however, no deÞnitive source can be designated for both of these elements.

Keywords Soil pollution Trace elements Sequential extraction Anthropogenic factors Factor analysis Turkey

Introduction

Increasing concerns regarding the possible environmental risks associated with the heavy metal pollution of soils has led to growing number of studies in the recent literature (e.g. Lu et al. 2003; Falk et al. 2006; Li and Huang 2007). Heavy metals are the most important source of trace element toxicity in the environment given that most organisms and plants are not adapted to tolerate high concentrations of them (Abimbola et al. 2007). Studies have shown that heavy metals can be taken up and accumulated in roots, leaves, and edible parts of the plants (Chopin et al. 2008) with a resulting risk to human and animal health (Gupta and Gupta 1998). Soil pollution is commonly caused by various point and non-point sources including natural parent material weathering, mining activities, urban and industrial discharges/spills/wastes/emissions in the form of liquid, solid or gas, and agricultural activities such as pesticide/herbicide use, fertilizer application and irrigation. Pollution of soils by trace elements is critical because they can be persistent in the environment and have a tendency to accumulate in soils (Kabata-Pendias 2001) by preferential adsorption onto silt- and clay-size fractions and adsorption by Fe- or Mn-oxides and organic matter (Abderahman and Abu-Rukah 2006). In soils, the forms of trace elements strongly depend on their nature and origin (Ma and Uren

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1998). Trace elements naturally exist as impurities on the crystal structure of mineral phases and more importantly as exploitable minerals. On the other hand, the anthropogenic trace elements may exist on the surfaces of soils as reactive forms (Levy et al. 1992; Ramos et al. 1994). Although the total concentrations of trace elements in soil give some indication of the level of contamination, it provides no insight into element fractionation, mobility, bioavailability, or toxicity (Ahnstrom and Parker 1999; Romaguera et al. 2008).

Trace elements in soils are associated with a number of physicochemical forms (Shuman 1985) which in turn critically affect leaching behavior of trace elements. Fractionation studies of trace elements in soils using a sequential extraction procedure can provide an understanding of their chemical forms and occurrences of elements (Tessier et al. 1979). Many single and sequential extraction schemes (ranging from 3 to 7 steps) have been proposed for determination of specific chemical forms of trace elements and studying the mobility/availability of them in soil samples (e.g. Tessier et al. 1979; McGrath and Cegarra 1992; Gimeno-Garcóa et al. 1995; Ho and Evans 1997; Ahnstrom and Parker 1999; Polyák and Hlavay 2001; Väisänen and Kiljunen 2005). A comprehensive review on the subject, including remarks on the reagents used and their selectivity as well as their extraction capability, can be found in Filgueiras et al. 2002. Principle of sequential extraction procedure is based on the selective extraction of trace elements bound by specific soil fractions. Most of the sequential extraction procedures are based on Tessier's scheme, which has been modified by several researchers (Campanella et al. 1995; Borovec 1996; Gómez Ariza et al. 2000; Väisänen and Kiljunen 2005) in order to optimize sequential extraction of trace elements in different geo-environmental media. In this study, ultra-sound-assisted sequential extraction (UASE) method proposed by Väisänen and Kiljunen (2005) was used to perform a five-step sequential extraction on the soil samples.

Karaduvar site is one of the most interesting and dramatic examples of an area experiencing various environmental problems. Pollution from past petroleum refining and thermal power generation activities, petrochemical accidents (explosive burning of storage tanks and spills), untreated industrial discharges, agricultural activities and disordered urbanization are believed to be the main environmental problems in the study area. These activities have co-existed nearly half a century at the site and have all had profound effects on the environment. Nevertheless, at the site no serious pollution characterization or remediation studies have been taken so far. The aims of this study were to (1) report on the mineralogical and geochemical composition of the soil samples; (2) assess the mobility and fractionation of the 11 trace elements (As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V and Zn) using UASE procedure, and (3) make an inventory of the spatial extent of the pollution and define the pollution sources (natural vs. anthropogenic) using univariate and multivariate statistical techniques.

Materials and methods

### Site history and description of the study area

The study area (Karaduvar site) is located at the eastern side of the city of Mersin (in SE Turkey) along the coast of the Mediterranean Sea, and it is bounded by latitudes $36^0 48' 12''$–$36^0 50' 09''$N and the longitudes $34^0 23' 03''$–$34^0 43' 40''$E (Fig. 1). The history of Karaduvar (ancient name Anchiale) dates back to Neolithic period (ca. 3600 BC) and continues unbroken through Chalcolithic and Early Bronze ages. The area has been traditionally associated with agricultural activities although the agricultural areas have been markedly decreasing since the past three decades due to industrial and urban expansions. Crops grown in the area include pepper, green bean, tomato, radish, leek, cauliflower, savoy cabbage, leaves and salad herbs, and citrus fruits, most of which are native to Mediterranean region. Given that the region has fertile alluvial soils and mild climate, agricultural activities continue all year long.

At the Karaduvar site, industrial areas are found side by side with areas of intensive agriculture. After the establishment of ATAŞ petroleum refinery in Karaduvar in 1962, the area has become the center of attraction for a wide variety of industrial activities ranging from petrochemical to energy and chemical to fertilizer production. In 1970, a diesel-fired thermal power plant was established in the area with a capacity of 4 $\times$ 25 MW and closed down in 1994. In 1972, a nitrogen fertilizer factory was also established in the area, which currently produces CAN and DAP fertilizers (total production is 740 $\times$ 10^3 t year^{-1}). In 2005, ATAŞ refinery phased out its crude oil-refining operations; however, its petroleum hydrocarbon storage and transport activities are still operative. Additionally, there are 11 actively operating storage facilities in the area, which are dealing with storage and marketing of refined petroleum products (e.g. gasoline, diesel fuel, fuel oil, etc.) and/or liquefied petroleum gas (LPG). According to year 2000 census, there were 1,154 active enterprises and 2,137 residential houses in the area.

Rocks and unconsolidated deposits found in the area and surrounding region can be divided into three major geologic units (Şenol et al. 1998): (1) Permo-Carboniferous Karahamzauşağı formation and upper Cretaceous Mersin ophiolitic mélange; (2) tertiary sedimentary rocks, and

Fig. 1 Locations of soil sampling sites and land use/land cover map of the study area
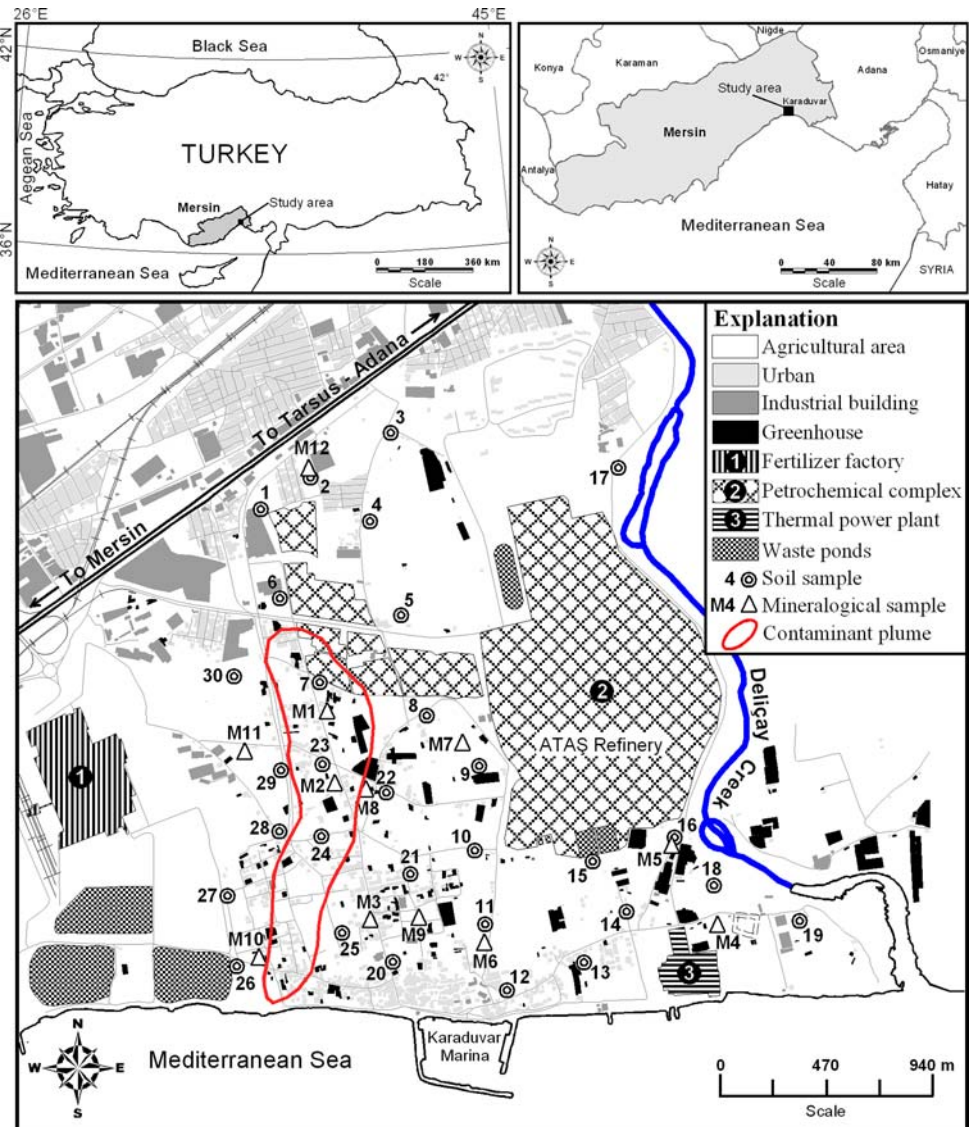
(3) quaternary unconsolidated deposits (Fig. 2). Karahamzauşağı formation is the oldest rock unit of the area and it consists of marble, schist, and quartzite. Mersin ophiolitic melange contains various rocks with differing compositions including gabbro, harzburgite, verlite, dunite, clinopyroxenite, diabase, and radiolarite. Ophiolitic melange also contains substantial amounts of chromite (Cr_2O_3) mineralizations with chromite contents between 52 and 60% (Yaman 1991). Ophiolitic melange is generally found in the northern part of the study area within deep canyons and shows serpentinization. Tertiary sedimentary rocks are composed of lower-middle Miocene Karaisalı and Güvenç formations (limestone and clayey limestone, respectively), middle–upper Miocene Kuzgun formation (sandstone, conglomerate and limestone), and upper Miocene–Pliocene Handere formation (clay–siltstone, marl, limestone, sandstone, gypsum) (Fig. 2). Tertiary sedimentary rocks consist of a succession of marine, lacustrine, and fluvial deposits which display transitional characteristics both vertically and areally (Şenol et al. 1998). Quaternary unconsolidated deposits are described by Şenol et al. (1998) as heterogeneous mixture of rock detritus ranging from clay to boulder size. The mixture includes shore and sand dune deposits, deltaic sediments, stream alluvium, talus deposits, caliche, and Terra Rosa deposits (Mediterranean red soil) (Şenol et al. 1998).

The study area is a low-lying deltaic plain with slopes ranging from 0.57 to 0.96% and the elevations between 0 and 30 m above mean sea level. The study area has a typical Mediterranean climate that is characterized by hot and dry summers, mild winters and low precipitation. According to 72-year-long records (1930–2002), mean annual temperature in the area is 18.8°C with a mean temperature above 20°C from May through October. The
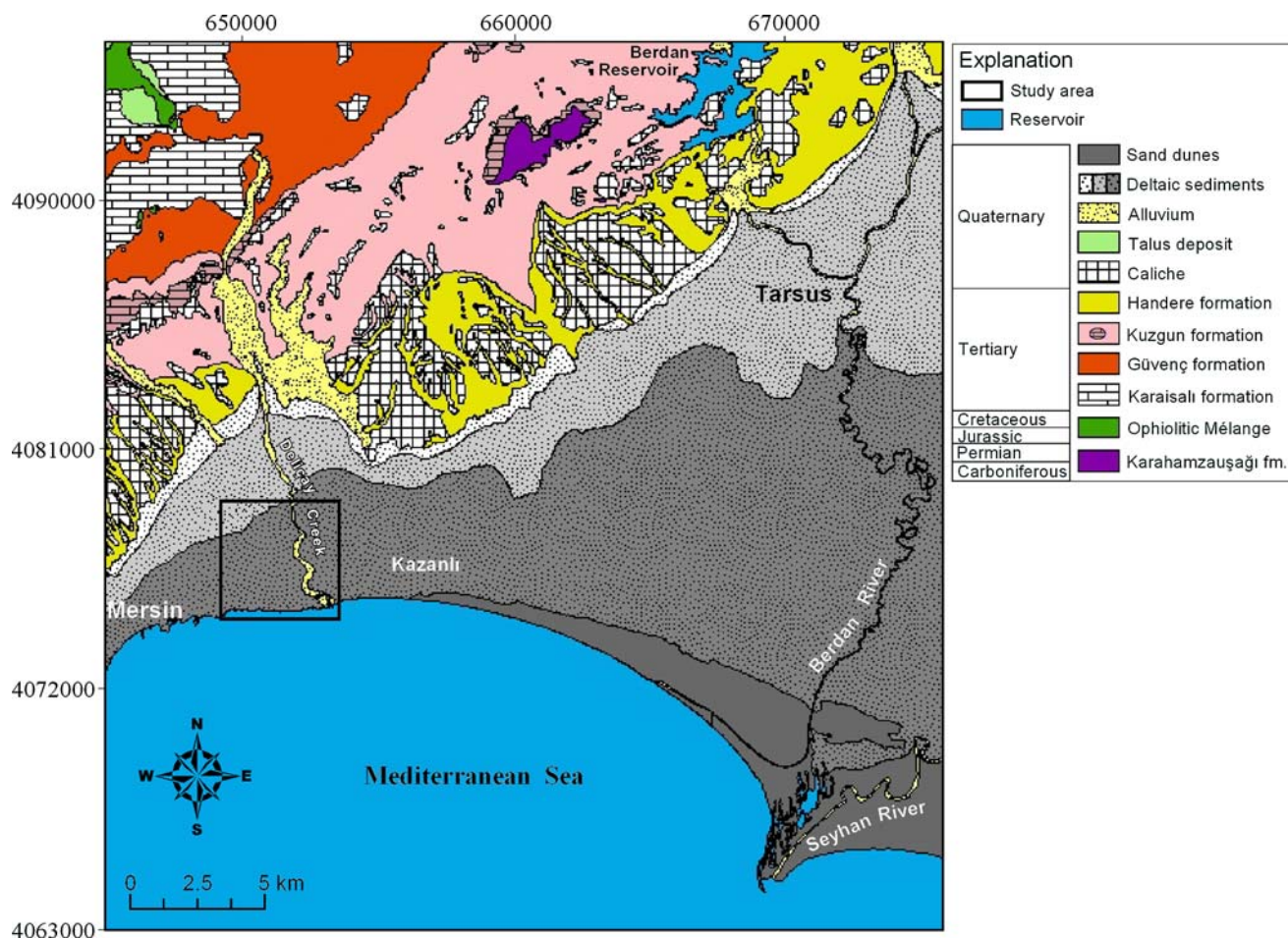
Fig. 2 Geology map of the study area and surrounding region (coordinates are in UTM meters and datum is WGS84)

area receives mean annual precipitation of ~500 mm, and extended periods (i.e., 4–5 months) without precipitation are common (Demirel and Güler 2006). Alpine climate conditions prevail in the northern part of the study area (at the Taurus Mountains).

Soil sampling and sample preparation

For geochemical studies, 30 cultivated topsoil samples from a depth interval of 0–20 cm were collected from the agricultural plots located around various industrial facilities. For mineralogical studies, additional soil samples were taken from 12 different locations and from three different depth intervals (0–30, 50–80 and 90–120 cm) in each location. Field work was completed in 1 day (2 February 2007) to rule out any seasonal effects. Sampling locations are depicted in Fig. 1. All soil samples were taken by so-called Edelman hand auger (Eijkelkamp Agrisearch Equipment, The Netherlands) and transported to the laboratory in tightly sealed 1-kg polyethylene bags to exclude loss or addition of moisture or pollutant. All soil

samples were subsequently air-dried at room temperature and carefully disaggregated in a ceramic mortar before sieving through a 2-mm nylon sieve to remove large particles and other debris. Finally, the fraction <2 mm was powdered in an agate mortar and was used for further mineralogical (XRD) analyses.

Analytical procedures

Reagents

All the chemicals used were of the analytical grade unless otherwise stated. Deionized water (ELGA Purelab Prima, UK) was used as feed water to produce ultra pure water from the ELGA Purelab UHQ (UK). The water used throughout the period of experimentation had a resistivity of 18 MΩ cm at room temperature. All extractant, standard and rinse solutions were made from this water. The acids used were nitric acid (65%), hydrochloric acid (37%), and acetic acid (≥99.5%). The reagents used in the production of the extracting solutions were sodium acetate anhydrous

(C99%), hydroxylamine hydrochloride (C99%), hydrogen peroxide (35%), magnesium chloride hexahydrate (C99%), sodium hydroxide pellets (98%) and ammonium acetate (C98%). All glassware and plastic vessels used for the experiments was previously soaked in 10% HNO_3 for 48 h and rinsed with ultra pure water. All extracts were kept in thoroughly cleaned plastic bottles.

XRD measurements and soil pH

X-ray diffraction (XRD) analyses of soil samples were carried out at the Hacettepe University Geological Engineering Department in Ankara, Turkey. The mineralogical composition of the powdered samples and clay fraction (<2 μm) was determined on random and oriented samples using a Rigaku D/Max-2200/PC X-ray diffractometer (Japan) with Cu-$k\alpha$ radiations generated at 40 kV, 30 mA. The scanning rate was 2θ min^{-1}. To prepare oriented mounts, selected Þve subsamples of clay fraction were treated with hydrogen peroxide overnight to oxidize organic matter. Then, each sample was divided into three parts. The Þrst part was saturated with ethylene glycol, the second was heated up to 550 and the third part was left without treatment. XRD data for all samples were collected for values of 2θ between 2 and 50.

Soil pH (pH-H_2O) was determined by saturating soil sample (<2 mm fraction) with deionized water (1:5 solid to solution ratio) and shaking it mechanically at 15 rpm for 1 h (Rayment and Higginson 1992). The pH-H_2O of the supernatant was measured by means of a digital WTW Multi 340i/SET (Wissenschaftlich-Technische Werksta ten, Germany) multi-parameter instrument attached to a glass pH electrode, which was calibrated at pH 4.01 and 7.00 using standard buffer solutions.

Sequential extraction procedure

In this study, UASE procedure proposed by Väisänen and Kiljunen (2005) was employed to perform a Þve-step sequential extraction procedure (Table 1) on the soil samples and to characterize the occurrences or phases of As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V, and Zn in the studied soil samples. The UASE procedure is advantageous in terms of simplicity, operation time and consumption of sample and reagents. The UASE procedure fractionates soil elements into: (F1) soluble-exchangeable; (F2) bound to carbonates; (F3) bound to Fe- and Mn-oxides; (F4) bound to organic matter and sulÞdes; and (F5) residual (crystalline-bound) fractions using a series of progressively harsher reagents to dissolve increasingly refractory forms (Väisänen and Kiljunen 2005).

Using a precision balance with readability of 0.0001 g (Mettler Toledo AL204, USA), untreated 0.5 g subsample

Table 1 Five-step ultrasound-assisted sequential extraction (UASE) procedure (Väisänen and Kiljunen 2005) used in this study for analyzing chemical forms of trace elements

Step	Dissolved fraction	Material	Extraction procedure	Sonication time (min)	Temperature (°C)
F1	Soluble-exchangeable	Soil sample	8 mL of 0.5 mol L^{-1} $MgCl_2$ at pH 7 (pH adjusted with diluted NaOH or HCl)	3 (19 3 min)	20
F2	Bound to carbonates	Residue from F1	10 mL of 1.0 mol L^{-1} CH_3COONa at pH 5 (pH adjusted with CH_3COOH)	15 (59 3 min)	20
F3	Bound to Fe- and Mn-oxides	Residue from F2	10 mL of 0.1 mol L^{-1} $NH_2OH·HCl$ at pH 2 (pH adjusted with CH_3COOH)	18 (69 3 min)	85
F4	Bound to organic matter and sulÞde compounds	Residue from F3	3 mL of 0.02 mol L^{-1} HNO_3 and 10 mL of 15% H_2O_2 (pH adjusted to 2 with HNO_3)	9 (39 3 min)	85
F5	Residual phase (silicate-bound)	Residue from F4	10 mL of 1:1 (v/v) diluted Aqua Regia	93 (6 min)	60

of soil sample accurately weighed into a 50-mL polypropylene centrifuge tube into which an appropriate amount of extracting solution is added (Table 1). The residues from each step were sequentially treated to obtain the operationally defined fractions shown in Table 1. In this study, UASE procedure was performed with Bandelin Sonorex brand ultrasonic water bath with 880 W power and 35 kHz frequency (Progen Scientific Ltd., UK). Sonication times were divided into equal 3-min steps so that after each 3-min step, the centrifuge tube is shaken by hand to prevent sedimentation (Väisanen and Kiljunen 2005). Then, the sample is placed into the ultrasonic water bath for the next sonication step. After each extraction procedure, the supernatant was collected by centrifugation at 3,000 rpm for 10 min using a Sigma 2-16 centrifuge (SIGMA Laborzentrifugen GmbH, Germany). Then, the solution is pipetted into a 50-mL volumetric flask. After centrifugation, the residues from steps F1, F2, F3, and F5 were washed once with 5 mL of ultra pure water. Whereas, residue from F4 was washed with a solution of 5 mL of 3.2 mol L^{-1} CH$_3$COONH$_4$ (CH$_3$COONH$_4$ in 20% v/v HNO$_3$). These rinse solutions were centrifuged and pipetted into same volumetric flasks with the preceding extracts. Later, pooled extracts diluted to volume with ultra pure water (Väisanen and Kiljunen 2005).

Soil standard reference material, SRM 2710 (Montana Soil), was also subjected to UASE procedure and analyzed to check the accuracy of the results and elemental recoveries. The SRM 2710 contains moderately elevated level of trace metals, certified by the National Institute of Standards and Technology (NIST 2003) and was received air-dried, pulverized, and homogenized. Certified reference materials play a vital role in the analytical quality assurance (NIST 2003) and they also allow the comparability of results produced by different laboratories (Polya and Hlavay 2001).

ICP-MS measurements

ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) analyses were performed in the Environmental Geochemistry laboratory at the Mersin University Geological Engineering Department, Mersin, Turkey. Concentrations of 11 elements (As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V and Zn) in the solution extracts were determined in triplicate by Agilent 7500ce ICP-MS (Tokyo, Japan) equipped with a collusion/reaction cell in the form of octopole reaction system (ORS). The argon gas utilized was of spectral purity (>99.998%). The external standard calibration method was applied to all determinations, using ^{6}Li, Sc, Ge, Y, In, Tb and Bi internal standard mix (in 2% HNO$_3$ matrix). NIST single-element reference standards are used to construct five-point calibration curves. At regular intervals during analysis, calibration standards were analyzed as samples to monitor instrument drift. Furthermore, extractant and ultra pure water blanks were frequently analyzed alongside samples to check for contamination. Blanks were prepared by completion of the full analytical procedure without samples. The analytical accuracy was checked from replicate measurement of several samples and by measuring certified reference materials. The relative error is less than 5% for all analyzed elements.

Statistical analyses and data treatment

Statistical associations do not necessarily establish cause-and-effect relationships, but do present the information in a compact format as the first step in the complete analysis of the data and can assist in generating hypothesis for the interpretation of occurring processes (Guet al. 2002). First, descriptive univariate statistics were examined to study the distributions of the variables. Then, Kolmogorov–Smirnov (K–S) statistic test was used for the confirmation of normal distribution of the variables. R-mode factor analysis (FA) was used for the multivariate statistical analysis of the soil geochemical data. Detailed technical descriptions of FA technique is provided in detail in Harman (1967) and Rummel (1970), hence, only brief mention of this technique is made here. As a pattern recognition method, FA can provide a powerful tool for analyzing soil geochemical data. This approach has been applied successfully to extract related variables and infer the processes that control soil chemistry (Tao 1998; Al-Khashman and Shawabkeh 2006). The assumptions of FA include homoscedasticity (equal variance) and normal distribution of the variables (Bretzel and Calderisi 2006). Therefore, equal weighing of all variables requires the normalization and subsequent standardization of the relevant variables. FA technique reduces a large number of variables to a minimum number of ''new'' variables called ''factors'' by linearly combining measurements made on a number of variables (Davis 1986). Kaiser's Varimax rotation is generally applied to the ''new'' variables in order to find factors that can be more easily explained in terms of natural or anthropogenic processes (Closs and Nichol 1975). This rotation is called varimax because the goal is to maximize the variance of the ''new'' variable, while minimizing the variance around the ''new'' variable (StatSoft, Inc. 1997). The number of factors extracted is defined by using the ''Kaiser criterion'' (Kaiser 1960) where only the factors with eigenvalues greater than unity are retained. Statistical software R version 2.5.1 (R Development Core Team 2007) was used to perform the data analysis.

Results and discussion

Soil mineralogy and pH

Mineralogical composition of the soil samples was determined by XRD analysis. The results presented here are semi-quantitative values that were obtained after the evaluation of a total of 36 individual XRD diffractograms. The analysis results show that clay minerals are the dominant phase in the soil samples with no discernible differences in clay mineral content of the soil profile. XRD analysis of the <2-μm clay fraction separated from the five mineralogical soil samples (M1, M3, M5, M7, M12; see Fig. 1) revealed the presence of illite with lesser amounts of vermiculite, kaolinite, and serpentine. XRD data also indicate that the soils contain quartz > feldspar > calcite ? dolomite ? mica ? serpentine ± hornblende minerals. This composition greatly reflects the mineralogy of the geologic units found in the drainage area (e.g. ophiolitic melange, sandstone, marl, limestone and dolomite etc.) (Fig. 2).

The soil pH-H_2O values indicate a neutral to slightly alkaline character (7.50–8.15) with a mean value of 7.89 (n = 30). High pH values are possibly due to presence of carbonates (calcite and dolomite) in soils. It is also known that after the application of nitrate fertilizers such as calcium nitrate and potassium nitrate the soil pH values can increase remarkably. These types of fertilizers are liberally applied throughout the area. Soil pH is one of the main factors controlling the solubility of trace elements in soils (Ross 1994). Previous studies have shown that each unit of increase in pH results in approximately a twofold decrease of the concentration of trace elements (e.g. Cd, Ni, and Zn) in the soil solution (Christensen 1984; Sanders et al. 1986), hence limiting the mobility of trace elements.

Evaluation of the analytical performance

In this study, accuracy of the analytical performance was evaluated by means of the NIST certified standard reference material SRM 2710 (Montana Soil) (NIST 2003). Standard soil reference material was analyzed by ICP-MS using seven replicates and each measurement was repeated three times. The total extractable trace element contents and the mean recoveries of the standard reference material used are presented in Table 2. It should be noted that the final step of UASE procedure (Fraction 5) uses 1:1 diluted aqua regia (HCl:HNO_3 3:1 solution), which extracts most of the potentially mobile element fractions, however, leaves the more resistant silicate minerals undissolved (Peltola and Åström 2003). Therefore, total concentrations obtained by this study should be treated as ''pseudototal''.

Table 2 Analytical results of NIST SRM 2710 (Montana Soil) obtained by UASE procedure (in mg/kg)

Element	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Total	NIST certified value	Recovery (%)	NIST recovery (%)
As	1.17 ± 0.18	26.75 ± 1	389 ± 2	64 ± 1	128 ± 3	609 ± 4	626 ± 38	97.3	94
Cd	7.9 ± 1.0	4.4 ± 1.0	4.1 ± 0.9	1.4 ± 0.3	3.1 ± 0.4	20.9 ± 2.2	21.8 ± 0.2	96.2	92
Co	0.39 ± 0.13	0.42 ± 0.05	3.14 ± 0.13	0.12 ± 0.01	2.56 ± 0.10	6.64 ± 0.31	10[a]	66.4	82
Cr	0.82 ± 0.02	1.05 ± 0.08	2.89 ± 0.44	8.27 ± 0.77	10.26 ± 1.28	23.28 ± 1.74	39[a]	59.7	49
Cu	181 ± 47	656 ± 9	1,024 ± 43	361 ± 36	348 ± 41	2,570 ± 66	2,950 ± 130	87.1	92
Mn	736 ± 92	298 ± 18	2845 ± 45	585 ± 60	2,484 ± 226	6,947 ± 176	10,100 ± 400	68.8	76
Mo	0.24 ± 0.04	0.57 ± 0.03	3.79 ± 0.02	11.38 ± 0.27	3.93 ± 0.00	19.91 ± 0.17	19[a]	104.8	100
Ni	3.04 ± 1.16	0.43 ± 0.13	1.79 ± 0.61	3.23 ± 0.66	1.05 ± 3.84	12.32 ± 0.54	14.3 ± 1	86.2	71
Pb	608 ± 181	1565 ± 45	2,222 ± 90	359 ± 27	522 ± 3	5,275 ± 79	5,532 ± 80	95.4	92
V	0.20 ± 0.04	0.48 ± 0.05	14.58 ± 0.29	12.82 ± 0.04	22.37 ± 0.82	50.45 ± 1.11	76.6 ± 2.3	65.9	56
Zn	682 ± 27	275 ± 7	1426 ± 19	787 ± 69	2,344 ± 239	5,514 ± 332	6,952 ± 91	79.3	85

The concentrations of the elements are given as mean of seven replicate samples ± standard deviation

Total = fraction 1 + fraction 2 + fraction 3 + fraction 4 + fraction 5

[a] Non-certified values

soil elements. Analysis of the SRM 2710 showed satisfactory accuracy, with the recoveries for As 97.3%; Cd 96.2%; Cu 87.1%; Mn 68.8%; Ni 86.2%; Pb 95.4%; Zn 79.3%, and V 65.9%. Recoveries for Cu, Mn, and Zn were slightly lower than the NIST recoveries given in Table 2.

Trace element fractionation and mobility

Table 3 summarizes the results from trace element sequential extraction in soils at Karaduvar. In this study, mobility of trace elements is deÞned as the sum of the Þrst four sequential extraction steps (F1, F2, F3, and F4). The relative amounts of each metal in each fraction, expressed as a percentage of the cumulative total extracted from soil samples, are presented in Fig. 3. In all the analyzed soil samples As, Cr, Cu, and Ni were prevalently held in residual fraction (F5) of soils, with other forms making up for much less than 30%. Therefore, these elements must be mostly present either in silicate minerals of which they are constituent parts, or as impurities in the crystal structure of other silicate minerals. Other important fractions for As, Cr, Cu, and Ni are the F4 (8.8Ð13.9%) and F3 (2.1Ð10.2%) fractions, and to a lesser extent F2 (1.3Ð 4.5%) fractions. Co was concentrated in the F5 (46.2%) and F3 (43.8%) fractions and the surplus distributed in F4 (5.4%) and F2 (4.6%) fractions. Compared to other elements (except for Mn), signiÞcantly larger amounts of Co are found in the reducible fraction (F3). The excessive Cr, Co, and Ni contents in some of the samples may come from chromite deposits within the ultramaÞc rocks located in the catchment area (Fig. 2). Weathering of ophiolitic rocks can also be responsible for elevated concentrations of these potentially toxic elements. Ophiolitic "range contains metallurgical-grade chromite mineralizations with Cr₂O₃ contents between 52 and 60% (YamÞ 1991). Cd was found mostly in the F5 (30.8%) fraction, while approximately 64% was distributed almost evenly between F2 (18.9%), F3 (22.5%), and F4 (22.2%) fractions (Fig. 3). Mo shows a similar pattern to Cd. Up to 39% of total soil fractionated Mo was bound to F5 fraction. The remaining 61% is distributed between F4 (28.5%), F3 (17.9%), F2 (9.1%), and F1 (5.2%) fractions. This fact shows that the Cd and Mo compounds can be easily mobilized when in contact with natural waters. In general, it can be said that Cd is more mobile than the other elements, which has often been reported in literature (Mench et al. 1994). In all analyzed samples, the proportion of total Mn found in the reducible fraction (F3) was rather high (62%), which is not surprising because NH₂OH HCl is a reducing agent speciÞcally used to dissolve Mn-oxides in soils (Chao 1972). As Mn-oxides are highly susceptible to reduction due to a high groundwater level, this pool may easily be released into the groundwater (Bundt et al.

1997). The remaining 38% of Mn is distributed between F2 (22.6%), F5 (13.7%), F4 (1.2%), and F1 (0.6%) fractions. For Pb, V and Zn F3 (32.7, 22.1 and 16.5%, respectively), and F4 (14.3, 22.1, and 12.1%, respectively) fractions are signiÞcant. Zn seems, however, to be less mobile, since the residual fraction (64.3%) is relatively larger than for Pb (44.4%) and V (52.5%). In general, mobility of trace elements in soil samples in decreasing order can be given as: Mn > Cd > Mo > Pb > Co > V > Zn > Ni > Cu > As > Cr. Overall, the results show that signiÞcant portions of these trace elements can be mobilized under changing pH or redox conditions.

Elemental concentrations and distributions

The concentrations of trace elements in the studied soils are extremely variable (Table 3). The range of values for average total extractable concentration is (in mg kg⁻¹) 3.35Ð7.26 for As; 1.18Ð3.96 for Cd; 10.76Ð20.26 for Co; 37.99Ð63.48 for Cr; 18.55Ð243.1 for Cu; 338.7Ð565.6 for Mn; 4.42Ð6.44 for Mo; 148Ð279.3 for Ni; 10.12Ð73.71 for Pb; 17.93Ð36.55 for V and 25.46Ð331.7 for Zn. Clearly, large variations in trace element contents are found, with locally elevated concentrations for Cd, Co, Cu, Ni, Pb, and Zn. The results suggest that these trace elements have different distribution patterns, which can be related to different sources and dissimilar leachability of the elements. The comparison of trace element concentrations in soils of Karaduvar area to Turkish soil quality control regulation (SQCR), the world median values and the levels given in the literature (Table 4) reveals high concentrations of Cd and Ni in the studied soil samples. Median concentrations of these elements far exceeded the values given in Turkish soil quality standard (OfÞcial Gazete 2005) and levels given in the literature for different sites (Wilcke et al. 1998; Loska et al. 2004; Wang and Qin 2007). Locally high concentrations of Co, Cu, Pb, and Zn also occurs in the area; however, their median concentrations are lower than the values given in Turkish soil quality standards (Table 4). Occurrences of high percentages of some of these trace elements (especially Cd, Co, Pb and Zn) in the mobile fractions (see Fig. 3) indicate an environmental concern for these elements. Among these metals, Cd, Zn and to a lesser extent Pb, can be potentially mobilized in consistent amounts as a consequence of pH and redox changes. In general, despite high total concentrations, most of the trace elements appear to be speciated for the most part as rather insoluble geochemical forms (silicate-bound) (Fig. 3).

The spatial distributions of the trace element concentrations of the soils in the Karaduvar site are presented by contour maps in Figs. 4 and 5. The contours allow identiÞcation of possible problem areas and their related sources. A close examination of the trace element contour maps in

Table 3 Statistical summary of concentration of elements in different fractions of Karaduvar soil samples (depth 0–20 cm) (concentrations in mg kg^{-1})

Fraction	Statistics (n = 30)	As	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	V	Zn
F1	Range	0.004–0.117	0.060–0.186	0.00–0.00	0.00–0.263	0.042–0.661	0.0–10.140	0.194–0.345	1.182–2.24	0.00–0.284	0.103–0.716	0.012–8.656
	Median	0.028	0.077	0.00	0.000	0.152	2.390	0.265	1.644	0.000	0.265	0.503
	AM ± ASD	0.033± 0.022	0.085± 0.025	0.00± 0.00	0.041± 0.074	0.219± 0.154	3.178± 2.864	0.263± 0.037	1.66± 0.30	0.029± 0.066	0.299± 0.149	1.113± 1.988
	GM ± GSD	0.028± 1.810	0.083± 1.270	0.00± 0.00	0.074± 1.681	0.178± 1.900	3.053± 2.040	0.261± 1.150	1.643± 1.19	0.040± 1.936	0.264± 1.630	0.420± 4.180
F2	Range	0.118–0.396	0.206–1.001	0.00–1.624	0.250–1.893	0.329–3.477	37.4–168.4		2.838–9.15	0.744–5.352	0.268–1.021	0.757–20.14
	Median	0.202	0.261	0.765	0.627	0.675	116.2	0.426	5.954	1.364	0.586	3.084
	AM ± ASD	0.215± 0.062	0.294± 0.140	0.770± 0.460	0.650± 0.331	0.843± 0.646	109.9± 33.1	0.456± 0.079	6.203± 1.68	1.926± 1.227	0.60± 0.207	3.777± 3.422
	GM ± GSD	0.207± 1.315	0.278± 1.321	0.652± 1.996	0.584± 1.582	0.710± 1.697	104.1± 1.417	0.451± 1.157	5.974± 1.32	1.630± 1.747	0.564± 1.432	3.068± 1.821
F3	Range	0.174–0.794	0.243–0.823	3.324–9.717	0.410–3.406	0.00–26.550	230.7–366.8		8.70–40.06	2.727–22.17	2.635–12.29	1.979–40.49
	Median	0.304	0.304	7.277	0.976	2.495	293.8	0.799	21.14	6.024	5.542	9.806
	AM ± ASD	0.342± 0.134	0.349± 0.126	7.153± 1.735	1.098± 0.598	3.111± 4.629	297.6± 33.3	0.911± 0.336	21.47± 7.24	7.255± 4.289	6.057± 2.241	10.965± 7.26
	GM ± GSD	0.321± 1.407	0.333± 1.323	6.926± 1.301	0.979± 1.597	2.180± 2.161	295.8± 1.12	0.878± 1.270	20.24± 1.42	6.334± 1.655	5.689± 1.422	9.315± 1.774
F4	Range	0.233–0.832	0.251–1.099	0.00–1.563	2.026–10.83	0.234–216.0	0.00–216.0		9.72–36.62	0.328–17.07	3.688–9.972	0.026–136.9
	Median	0.405	0.284	0.959	7.420	2.643	4.678	1.352	28.925	2.606	5.670	6.087
	AM ± ASD	0.423± 0.134	0.356± 0.184	0.870± 0.397	7.138± 2.334	10.28± 38.93	5.633± 5.017	1.418± 0.136	27.18± 5.96	3.516± 3.51	6.046± 1.813	10.91± 24.09
	GM ± GSD	0.404± 1.352	0.329± 1.422	0.813± 1.614	6.680± 1.481	2.816± 3.054	4.527± 3.212	1.412± 1.095	26.39± 1.30	2.409± 2.393	5.79± 1.335	5.419± 3.585
F5	Range	2.528–5.119	0.358–0.917	4.230–8.721	31.77–50.49	15.58–41.93	26.61–85.79		95.0–205.8	4.462–41.93	9.261–17.93	19.15–303.7
	Median	3.573	0.400	7.413	42.06	26.66	67.065	1.929	150.2	8.027	14.395	36.815
	AM ± ASD	3.808± 0.765	0.476± 0.161	7.389± 1.011	42.26± 4.904	27.72± 5.612	66.21± 12.73	1.952± 0.200	152.1± 27.0	9.657± 6.715	14.023± 1.99	45.74± 49.59
	GM ± GSD	3.734± 1.221	0.456± 1.310	7.310± 1.164	41.98± 1.123	27.19± 1.218	64.68± 1.263	1.943± 1.100	149.7± 1.20	8.547± 1.552	13.878± 1.16	38.41± 1.571
Total	Range	3.352–7.258	1.182–3.957	10.76–20.26	37.99–63.48	18.55–243.1	338.7–565.6		148–279.3	10.12–73.71	17.93–36.75	25.46–331
	Median	4.663	1.335	16.616	51.210	31.834	487.206	4.776	209.224	17.682	27.033	56.620
	AM ± ASD	4.821± 0.881	1.560± 0.594	16.18± 2.425	51.18± 5.59	42.17± 39.13	482.5± 43.64	5.00± 0.543	208.6± 33.9	22.36± 13.07	27.02± 4.425	72.50± 59.57
	GM ± GSD	4.746± 1.192	1.489± 1.319	15.99± 1.171	50.89± 1.115	36.38± 1.542	480.4± 1.10	4.973± 1.107	206.0± 1.17	19.81± 1.598	26.67± 1.179	61.22± 1.664

Total = fraction 1 + fraction 2 + fraction 3 + fraction 4 + fraction 5

AM ± ASD Arithmetic mean ± arithmetic standard deviation

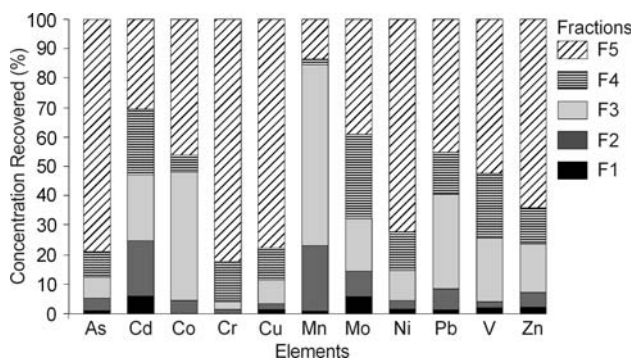*GM ± GSD* Geometric mean ± geometric standard deviation

Fig. 3 The extent of release of elements in soluble-exchangeable (*F1*); bound to carbonates (*F2*); bound to Fe- and Mn-oxides (*F3*); bound to organic matter and sulþde compounds (*F4*), and residual (*F5*) fractions for the ultrasound-assisted sequential extraction (UASE) of the Karaduvar soil samples. For each element total recovered amounts (in mg kg⁻¹) across þve fractions is given in Table 3

Fig. 4 reveals that the highest Co, Cr, Mn, and Ni concentrations were observed in the NE sector of the area close to Deliþay Creek suggesting a natural and common source for these elements. Sampling points 16, 17, and 18 showed the highest or among the highest concentrations for Co, Cr, Mn, and Ni. The excessive Cr contents in some samples may come from chromite (CrO_3) deposits within the ultramaþc rocks located in the drainage area (Fig. 2) where these rocks also contain substantial amounts of Co and Ni (Yaman 1991). Weathering of ophiolitic parent material possibly has a major control on the distribution of

these trace elements. The decline in metal content with distance along the course of Deliþay Creek also supports this contention (Fig. 4).

A similar elemental association is also observed for Cu, Pb, and Zn. Highest concentrations of these trace elements is observed in the SW sector of the area where agricultural activities are very intense (Fig. 5). This part of the study area also overlies the petroleum contaminated part of the aquifer (red line in Fig. 1), which is the only source of water for irrigation. Analysis of ground water samples taken from wells located within the contaminant plume (Fig. 1) contains Pb concentrations up to 43.5 µg L⁻¹ (Kurt et al. 2008). Therefore, high concentrations of some trace elements, especially Pb, can be attributed to this source. The additional sources for Cu, Pb, and Zn can be attributed application of pesticides/herbicides containing Cu and Pb and fertilizers containing Zn. The fertilizers used in this area are composite fertilizers containing up to 1% Zn as micronutrient. Both pesticides/herbicides and fertilizers are liberally applied to agricultural soils of the area. Gradually decreasing concentrations of Cu, Pb, and Zn away from cultivated areas also conþrms an agricultural source for these elements.

Elevated values of both Cd and Mo (samples 12, 13, 14, 15 and 16) correspond to the sites situated near diesel-þred thermal power plant and ATAÞ reþnery, both of which can be considered as point sources of anthropogenic contamination for these elements (Fig. 6). Both of these establishments ceased their operations fairly recently (in 1994

Table 4 Comparison of Turkish soil-quality standard with range/median values of studied trace elements in polluted soils around the world and this study (values in mg kg⁻¹)

Elements	SQCR[a]	World median[b]	This study[c]	Poland[d]	China[e]	Thailand[f]
As	20	6	3.35–7.26 [4.66]	4.98–17.4 [8.64]	8.7–577 [13]	–
Cd	1	0.35	1.18–3.96 [1.34]	0.2–2.07 [0.77]	0.11–2.9 [0.42]	0.05–2.53 [0.15]
Co	20	8	10.76–20.26 [16.62]	–	8.9–19 [11]	–
Cr	100	70	37.99–63.48 [51.21]	13.63–81.84 [31.47]	63–162 [72]	4.3–57.4 [25.4]
Cu	50	30	18.55–243.1 [31.83]	4.15–45.36 [8.08]	17–80 [32]	5.1–283 [26.6]
Mn	–	1,000	338.7–565.6 [487.21]	–	430–902 [508]	50–810 [290]
Mo	10	1.2	4.42–6.44 [4.78]	–	0.71–4.9 [1.2]	–
Ni	30	50	148–279.3 [209.22]	2.33–15.91 [5.56]	23–104 [30]	4.1–52.1 [23]
Pb	50	35	10.12–73.71 [17.68]	17.83–212.85 [38.56]	16–120 [36]	12.1–269.3 [28.9]
V	–	90	17.93–36.55 [27.03]	–	62–101 [74]	–
Zn	150	90	25.46–331.7 [56.62]	22.8–177.1 [61.4]	53–380 [102]	3–814 [38]

Median values are given in square brackets

[a] Soil quality control regulation of Turkey (Ofþcial Gazette 2005)

[b] Bowen (1979)

[c] Industry affected agricultural soils of Karaduvar site (0–20 cm, n = 30)

[d] Loska et al. (2004): industry affected farming soils of Suszec commune (0–20 cm, n = 1,228)

[e] Wang and Qin (2007): urban topsoil from the city of Xuzhou (0–10 cm, n = 21)

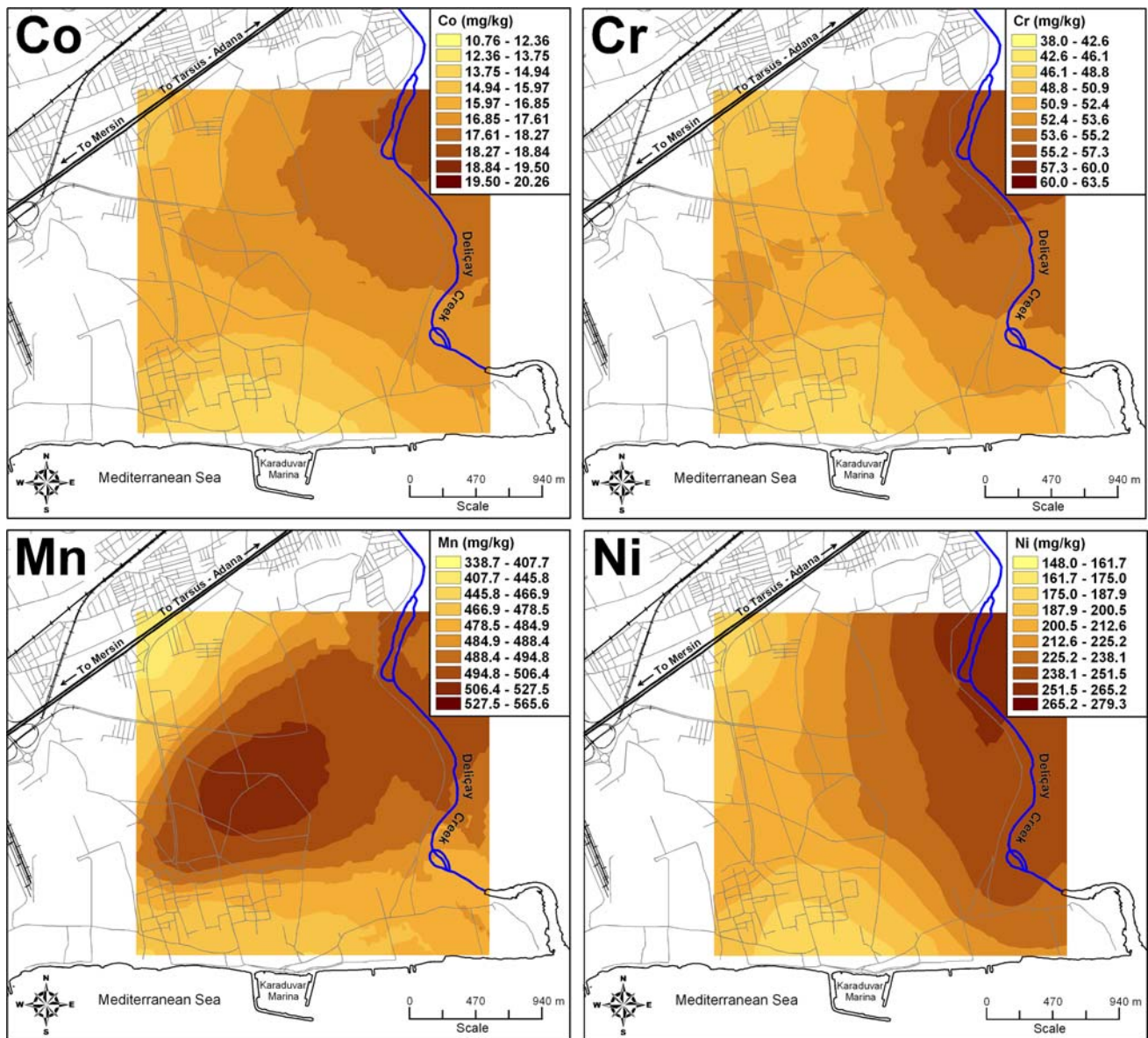[f] Wilcke et al. (1998): urban topsoil from the city of Bangkok (0–5 cm, n = 30)

Fig. 4 Spatial distribution of concentrations of Co, Cr, Mn, and Ni

and 2006, respectively). Dry and wet deposition around these facilities has been possibly contributed to the input of anthropogenic Cd, Mo and possibly other trace elements into agricultural soils.

As and V distribution patterns throughout the study area are different compared to the other elements studied, suggesting that the introduction of these elements to the system occurs through a different mechanism. Highest concentrations of both of these trace elements are found NW sector of the study area, where they show an almost identical distribution pattern (Fig. 6). Although this suggest a common contaminant source for these elements, no definitive source can be designated for As and V. However, it is worth noting that, this part of the study area is very close to nitrogen fertilizer factory and these elements might come from this source and occurred as a result of atmospheric deposition. Burning of fossil fuels also increases the amount of V in the air (Merian 1991). Vanadium is a major trace element in petroleum products, especially in the heavier fractions with concentration ranging from 0.6 to 1,400 mg kg^{-1} (Alloway 1995).

Statistical data analysis

Kolmogorov–Smirnov (K–S) normality test results showed that the variables Cd, Cu, Mo, Pb, and Zn are lognormally distributed (P values < 0.05), while the variables As, Co, Cr, Mn, Ni, and V are normally distributed (P values > 0.2).
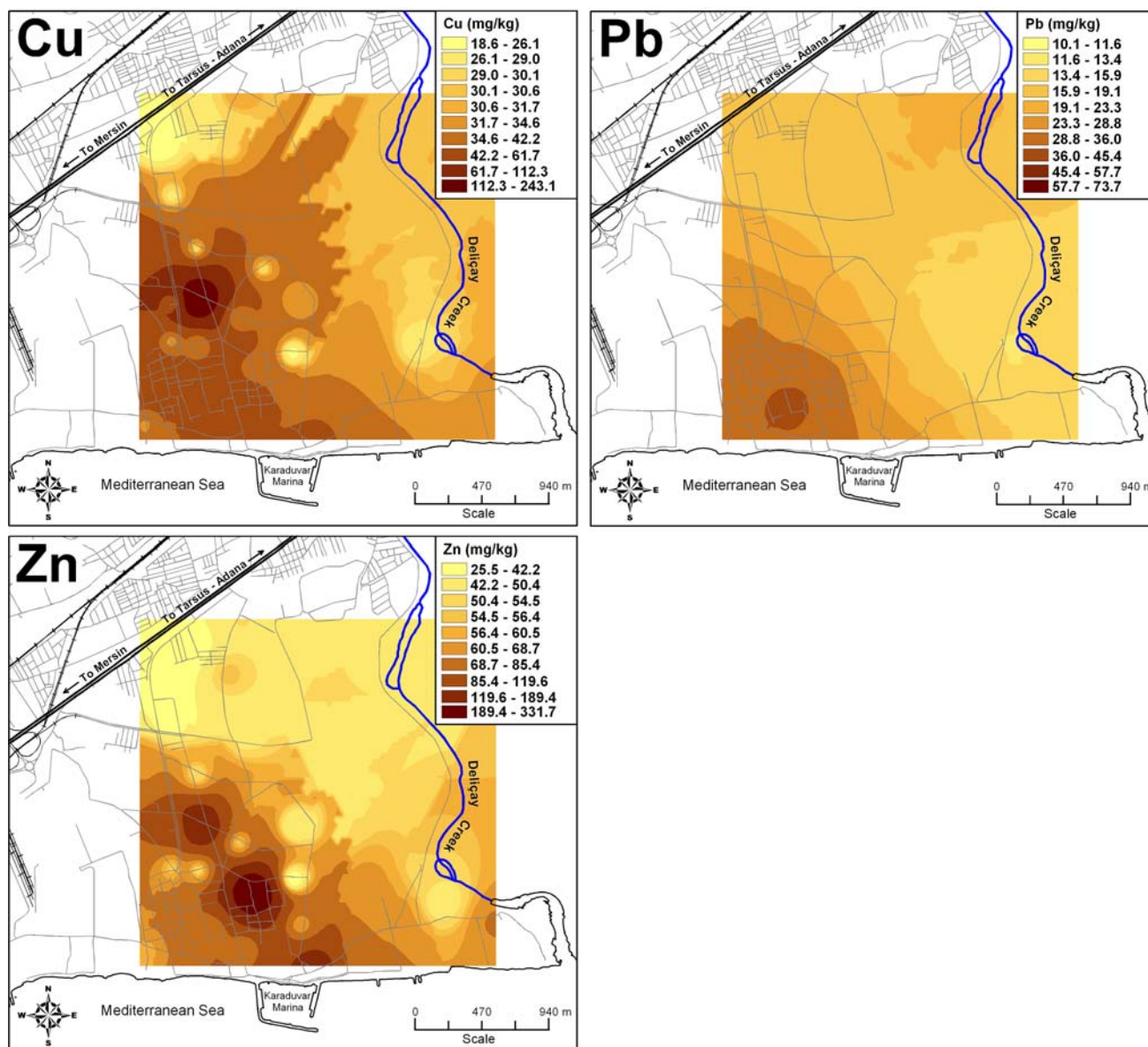
Fig. 5 Spatial distribution of concentrations of Cu, Pb, and Zn

If the KolmogorovÐSmirnov D statistic is signiÞcant (i.e., $P < 0.05$), then the hypothesis that the respective distribution is normal, is rejected (Swan and Sandilands 1995). Therefore, a logarithmic transformation (log) was performed for the variables Cd, Cu, Mo, Pb, and Zn before applying multivariate statistical methods. Subsequently, all variables are standardized to their standard scores (z-scores).

R-mode factor analysis was used to reduce the number of variables and identify the variables most important to separating the groups, in effect extracting the factors that control the geochemical variability in soil samples. In this situation, we anticipate that the geochemistry of soil samples is mainly controlled by parent rock composition

(lithology) of the drainage area. In addition, there may be contributions from anthropogenic sources (i.e., agricultural and industrial) that can produce distinct geochemical differences compared to natural background. The factor solutions provide information on the following: (1) loadingÑthe strength of a particular variable in a factor and takes values between 1 and - 1; (2) communalityÑthe amount of the total variability of each variable explained in given factor model, which is a value close to unity, and (3) eigenvalueÑthe amount of the total data variability explained by each model (Closs and Nichol 1975). If a FA is successful, the number of factors extracted from the dataset will be smaller than number of variables used, communalities will be close to unity, and the factors will be
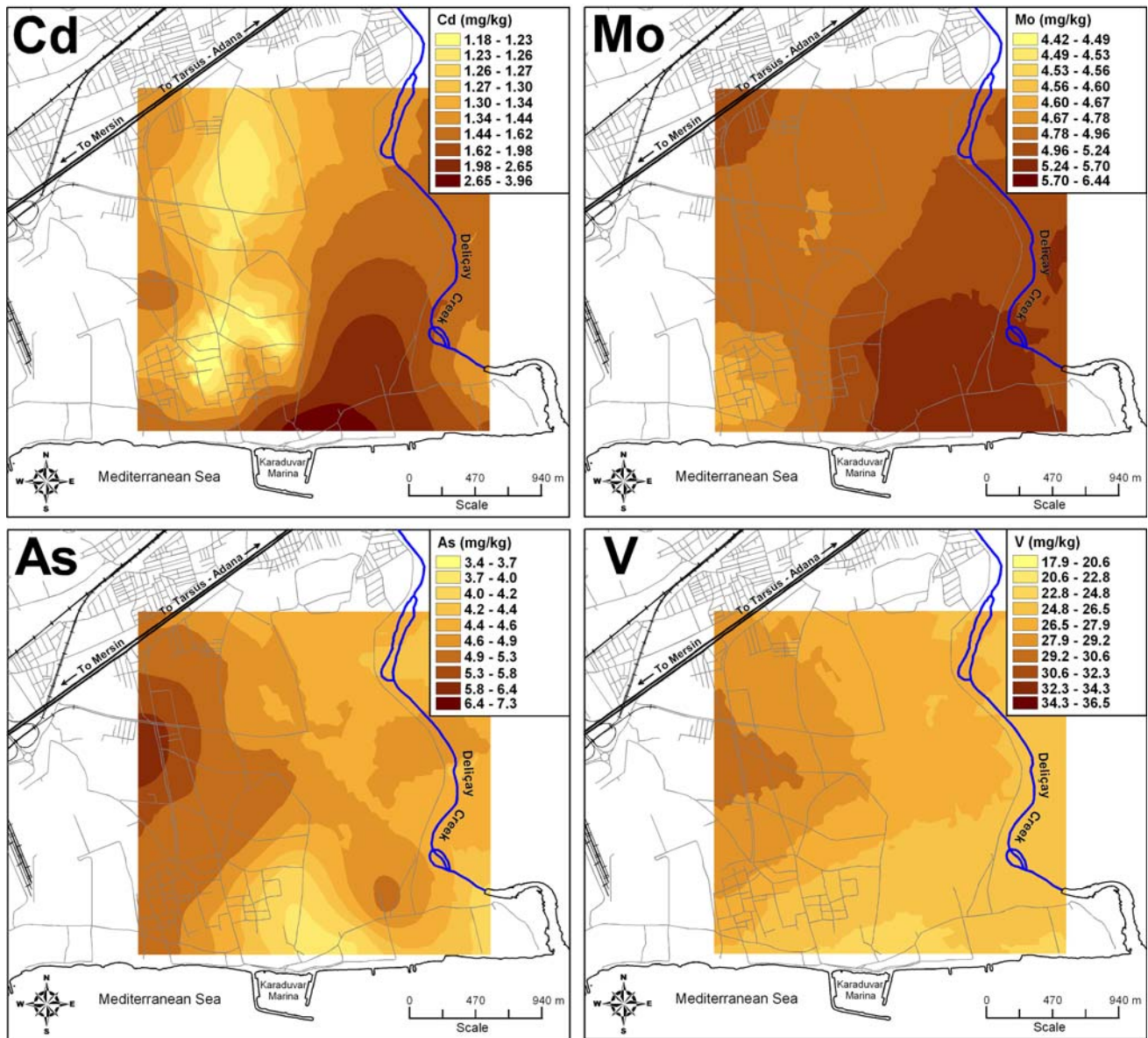
Fig. 6 Spatial distribution of concentrations of Cd, Mo, As, and V

readily associated with particular sources or processes (Davis 1986).

In this study, by applying FA technique, 11 variables (As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V and Zn) combined to produce four new variables or factors explaining 83.2% of the variance of the original dataset (Table 5). The remaining variance (16.8%) can be ignored as ''noise''. Both Kaiser's criterion and scree plot were used to choose the number of factors. Most of the variance (37%) is contained in the Factor 1, which is associated with the variables Co, Cr, Mn, and Ni (with loadings 0.860, 0.844, 0.754 and 0.898, respectively) (Table 5). Highest concentrations of these variables are generally observed at the NE sector of the study area close Deliçay Creek, draining the

area (Fig. 4). Co shows strong correlations with Cr, Mn and Ni, supporting the association of these trace elements to ultramaþc rocks. This suggests that the distribution of Co, Cr, Mn, and Ni are mainly controlled by lithological (natural) factors. Factor 2 explains 20.65% of the variance and is mainly related to Cu, Pb, and Zn (with loadings 0.873, 0.769 and 0.894, respectively) (Table 5). Highest concentrations of these variables are generally observed at the SW sector of the study area (Fig. 6), which is intensely cultivated. Therefore, sources of Cu, Pb, and Zn can be attributed to agricultural (anthropogenic) activities such as pesticide/herbicide use and fertilizer application, as well as irrigation with petroleum hydrocarbon-contaminated ground water. The variables Cd and Mo (with loadings

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Table 5 Factor loadings for soil samples of the Karaduvar area (depth 0Ð20 cm)[a]

Element	Communality[a]	Factor 1	Factor 2	Factor 3	Factor 4
As	0.881	0.134	- 0.021	- 0.075	**0.926**
Cd	0.847	- 0.006	0.198	**0.892**	- 0.111
Co	0.962	**0.860**	- 0.278	- 0.183	0.335
Cr	0.839	**0.844**	- 0.037	0.232	0.268
Cu	0.775	- 0.068	**0.873**	- 0.069	0.059
Mn	0.742	**0.754**	0.121	- 0.397	0.039
Mo	0.801	- 0.066	- 0.254	**0.832**	- 0.203
Ni	0.882	**0.898**	- 0.270	0.049	0.024
Pb	0.742	- 0.335	**0.769**	- 0.165	- 0.106
V	0.836	0.242	- 0.112	- 0.256	**0.837**
Zn	0.846	- 0.004	**0.894**	0.172	- 0.134
Eigenvalue		4.070	2.272	1.705	1.105
Cumulative Eigenvalue		4.070	6.342	8.047	9.152
Explained variance (%)		37.004	20.654	15.497	10.048
Cumulative % of variance		37.004	57.658	73.155	83.203

Statistically signiÞcant loadings (>0.700) are in bold (rotation method: Varimax normalized)

[a] The proportion of a variableÕs variance explained by the factor structure

0.892 and 0.832, respectively) contribute most strongly to the Factor 3 that explains 15.5% of the total variance (Table 5). Highest concentrations of these variables are generally observed at the SE sector of the study area (Fig. 6), around the diesel-Þred thermal power plant and ATAÞ reÞnery. This suggests that soils polluted by atmospheric deposition of Cd and Mo as a result of accidental burning of storage tanks containing petroleum hydrocarbons, historical petroleum reÞning and diesel-Þred thermal power generation activities. Finally, Factor 4 explains 10.05% of the total variance and represents elements As and V (with loadings 0.926 and 0.837, respectively) (Table 5). Highest concentrations of these variables are generally observed at the NW sector of the study area (Fig. 6) but no deÞnitive source can be designated for As and V, as discussed previously.

ophiolitic melange, sandstone, marl, limestone and dolomite etc.).

Results of this study suggest that natural sources (e.g. lithology) and past and present anthropogenic activities (e.g. agricultural and industrial) have caused pollution of soils by several trace elements. High concentrations of Co, Cr, Mn, and Ni in the area can be attributed to a natural source (lithology). Catchment area has important chromite mineralizations related to ophiolitic rocks and possibly weathering of this parent material has a major control on the distribution of these trace elements. On the other hand, close statistical association of Cu, Pb, and Zn and their high concentrations around intensely cultivated agricultural areas also indicate a common anthropogenic source for these trace elements. Sources for Cu, Pb, and Zn can be attributed application of pesticides/herbicides containing Cu and Pb and fertilizers containing Zn as a micronutrient (containing 1% Zn). Both pesticides/herbicides and fertilizers are liberally applied to agricultural soils of the area. Part of the Pb contamination can also be attributed to irrigation with petroleum hydrocarbon contaminated ground water, which is known to contain Pb concentrations up to 43.5 μg L^{-1}. According to results of this study, the most important point sources of trace element (Cd and Mo) pollution in the area found to be related to ATAÞ petroleum reÞnery, diesel-Þred thermal power plant and petrochemical accidents (e.g. burning of storage tanks and leakages). Elevated concentrations of both Cd and Mo correspond to the sites situated near these facilities, where dry and wet deposition has been possibly contributed to the input of anthropogenic Cd and Mo. As and V distribution

Conclusions

In the present study, concentrations of As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V, and Zn in topsoil samples (0Ð20 cm) of the area surrounding Karaduvar district were measured at 30 sampling points in order to decipher their spatial distribution patterns and to evaluate their mobilities and potential sources. In the area, mineralogical composition of soil samples are mainly composed of clay minerals (e.g. illite, vermiculite, kaolinite and serpentine), quartz, feldspar, calcite, dolomite, serpentine, and trace amounts of hornblende. This composition greatly reßects the mineralogy of the geologic units found in the drainage area (e.g.

patterns throughout the study area is different compared to the other elements studied, suggesting that the introduction of these elements to the system occurs through a different mechanism. Although their identical spatial distribution and statistical association suggest a common contaminant source for these elements, no deÞnitive source can be designated for As and V.

Results of this study suggest that despite their locally high total concentrations, most of the studied trace elements appear to be speciated for the most part as rather insoluble geochemical forms and their mobilities in decreasing order can be given as: Mn, Cd > Mo > Pb > Co > V > Zn > Ni > Cu > As > Cr. However, occurrences of high percentages of some of these trace elements (especially Cd, Co, Pb and Zn) in the mobile fractions indicate an environmental concern for these elements, especially under changing pH or redox conditions. In light of the Þndings of the present work, further scientiÞc studies are needed in the Karaduvar site, which evaluate potential toxicity of agricultural products grown in the contaminated soils of the area. This is essential because of the risks caused by these soils for the near populations and the agricultural areas that surround the site.

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