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A comparative view to heavy metal pollution in soil and rainwater in Çanakkale, Turkey

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Abstract: On Earth, atmosphere interact with crust and thus simultaneously monitoring of environmental pollution in both parts of the environment is important. Soil and rainwater samples were taken in different parts of Çanakkale, Turkey, in two seasons. Study sites laid along with the prevailing wind direction (from NE to SW) as wind has the potential to distribute pollutants emitted into the air throughout its path. The concentrations of selected elements were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Also, physical parameters such as pH, temperature, electrical conductivity of the rainwater and temperature and pH value of the soil samples were measured together with the meteorological parameters. Seasonal differences for the selected elements were insignificant in the soil samples ($p>0.05$), while some elements showed seasonal variations in the rainwater samples ($p<0.05$). The highest average heavy metal levels were found for Zn > Pb > Mn> Cu> Cd > Ni> Cr in the rainwater samples and Mn > Zn > Cu > Pb > Cr > Ni > Co in the soil samples, respectively. The highest enrichments were found for Pb in the rainwater and As in the soil samples. Elevated As levels occurred in the samples can pose a great risk for public health and agriculture.

Keywords: Atmospheric pollution; Çanakkale; ICP-MS; meteorological parameters; rainwater; soil pollution.

1. Introduction

On Earth, atmosphere interact with crust and thus monitoring the environmental pollution simultaneously in both parts of the environment is important. Presence of impurities in the atmosphere in quantity and time that harming health, living things, and ecological balance is called air pollution, originated both from natural and human-made sources [1]. Air pollutants can be found in the form of soot,

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smoke, dust, gas, steam, and aerosols in the air which alter the natural composition of the air [1]. Air pollution has reached serious levels in our country and the world mostly due to rapid industrialization and urban sprawl. The increase in the number of vehicles and the need for heating and the failure to take adequate and necessary measures to prevent air pollution from the industrial activities expand the dimensions of air pollution [2]. Heavy metal composition in the air is linked with not only atmospheric pollution, but also soil and water pollution, since molecular weights of typical heavy metals found in the air are heavier than other gaseous pollutants and they adsorb on the particles while settling on any surface due to gravity [3]. Also, meteorological parameters play a role on the distribution of heavy metals in the air.

In general, soil constitutes the largest receiving environment in the ecosystem that exposed to all metal contamination. Also, in aqueous systems such as rivers, lakes, and swamps, heavy metals accumulate in sediments. Therefore, heavy metals found in drinking water and other natural water resources [4]. For this reason, many studies are focused on the analysis of environmental samples such as water, soil, and sediment [5]. Heavy metals are found in the soil discharged from different sources such as traffic, industrial activities, ore-mine processing facilities, excessive fertilizer application, waste water and waste sludge applications [6-8], which pose a risk for arable lands. Also, the total metal concentrations in the soil are directly related to the soil parent material. However, the mobility of metals spread to the environment by human origin is higher than lithospheric sources [9-11].

The aim of this study to determine the heavy metal content in the soil and rainwater samples collected from different parts of Çanakkale city.

2. Experimental

Soil and rainwater samples were taken from 5 different sampling locations in Çanakkale (Turkey) in November 2017 and May 2018. Rainwater samples were collected no later than 6 weeks after the first placement of the samplers at the sampling sites. Time duration of the rainwater sample collection was variable due to local variability in rain events and the amount of rainwater accumulated in the samplers. Duplicate rainwater samplers were placed alongside and triple composite soil samples were taken at the sampling sites. The analyses of the soil and rainwater samples were performed immediately after the collection from the study sites. Meteorological parameters were obtained from Turkish Meteorological Institute throughout the study period. Also, as rain event has an importance on rainwater sample collection, weather forecasts and satellite observations (NOAA) were followed over the sampling periods. Furthermore, atmospheric temperature and relative humidity (RH) values were measured at the time of sampling by a real-time instrument (Testo 435-2).

2.1. Study Sites

The sampling sites were selected through the major wind blowing direction and estimated preliminarily on the city map. Long-term meteorological records indicate that the prevailing wind direction has been from NE to SW and secondarily from opposite direction which was from SW to NE directions [2,12-13]. All sampling sites were chosen at non-residential and rural areas to minimize the contribution of any potential anthropogenic sources such as domestic, traffic, and industrial processes. Final locations of the sampling sites were then determined after the preliminary observations at the field that had the best representation of the study aim. Rainfall forecasts and real-time rain occurrences over the region were followed to determine the sampling period. Çanakkale city is laid on both the European and Asian continents with the transient climatic characteristics of the Mediterranean and Black Sea regions [14]. The sampling points of this study were located at Ayvacik, Bayramic, Çan, Etili, and Karabiga regions of the city (see Figure 1). In terms of distance of the sampling sites from the potential environmental pollution sources, Karabiga and Çan are very close to coal-fired power plants, while Ayvacik and Bayramiç are located in Mount Ida forests. Also, active granite/stone mine quarries are available near Karabiga. Open coal mines and a ceramic factory facilitate in Çan center. Etili is located between Çan and Çanakkale city center. Sampling sites are not close to residential areas nor potential traffic sources.

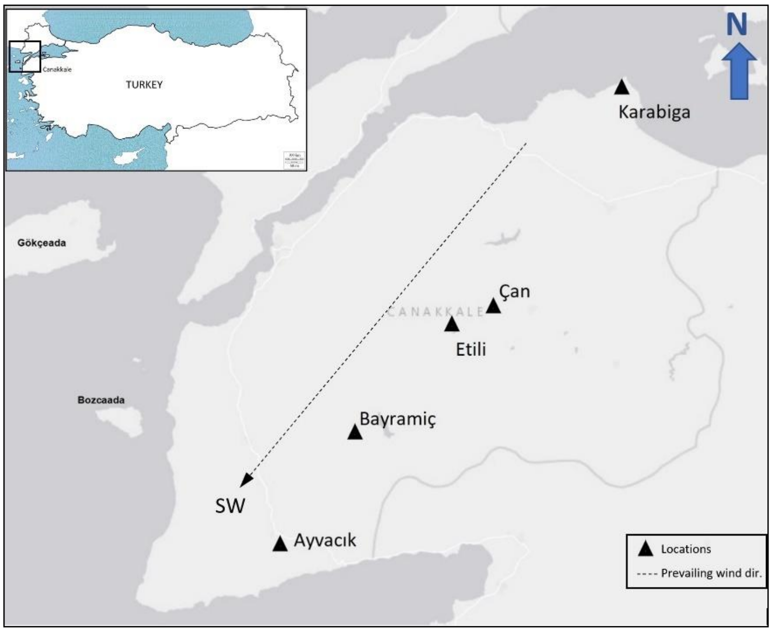

Figure 1. Locations of the study sites (Ayvacik, Bayramic, Çan, Etili, and Karabiga)

2.2. Sampling and Analysis of the Rainwater Samples

Rainwater samplers [15] were placed in the sampling locations in two seasons. As a rainwater collection system, two-step collection vessels made of polyethylene (PE) were placed on top of a rigid wooden stick at 1.50 m above the ground. A glass-fiber filter (2.0 µm pore size and 47 mm diameter: Merck Millipore Inc., Ireland) on a PE filter holder was bonded between two funnel-vessels. Rainfall initially dropped into the first funnel through the holes on the first funnel (at the top). Particles accumulated on the filter and the remaining rain drops were accumulated in the second vessel (*i.e.* collection funnel), which was then analyzed to determine the elemental content. Duplicate rainwater samplers were placed at each sampling point not to lose rainwater sample from the external factors. Containers filled with rainwater (≥ 50 ml) were taken from the sampling points no later than 6 weeks after the placement of the rainwater samplers, depending on the accumulated amount of the rainfall in the meantime. Rainwater samples in the collection vessel were analyzed by ICP-MS. Also, temperature (°C), pH, electrical conductivity (EC; µs/cm), etc. of the rainwater samples were measured by a multi-parameter probe (WTW Multi 3510 IDS multiparameter). The rainwater samples were then sent to an accredited laboratory (ACME Lab, Canada) to be analyzed for the elemental content by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). To determine trace to ultra-trace concentrations of the elements in the rainwater, the samples were analyzed directly by an ICP-MS and higher concentrations were confirmed by Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES).

2.3. Sampling and Analysis of Soil Samples

Soil samples were taken from a 5-15 cm deep hole dug in the form of a "V" at the sampling points in two seasons. A real-time instrument (Floureon, 4 in 1 soil survey instrument) was used to record temperature and pH value of the soil at the time of sampling. The soil samples were taken as a mixture of triple soil samples to represent each sample sites. The soil samples were mixed with approximately 0.5 kg of sample taken from different points of the same sampling sites [16]. Soil samples were stored in a cool and clean environment until the analyses. Coarse matters such as leaves and rocks were taken out from the soil mixture. Humidity content of the soil was determined by the gravitational method [17]. It indicates the mass difference between the soil dried at 105 °C for overnight and wet, raw soil. The size of the soil in the dried soil samples was decreased to several nanometers using the corresponding sieves for further analysis. Afterwards, soil samples were analyzed in an accredited laboratory (ACME Lab, Canada) to determine the composition of the selected elements. Briefly, the soil samples were digested with a modified Aqua Regia solution concentrated with HCl, HNO_3 and deionized (DI) water in a heating block or hot water bath for one hour. The adjusted sample volume diluted with HCl and then analyzed by the ICP-MS.

2.4. Data Evaluation

SPSS 19.0 software was utilized to perform statistical analyses. To find associations between the parameters, simple regression models and Spearman rank correlation tests were used. ANOVA test was applied to the data set to determine the seasonal variation of the measured elemental levels in the soil and rainwater samples. Values with $p<0.05$ were considered statistically significant for all applied tests.

The enrichment factor (EF) of the selected elements in the samples (soil or rainwater) was computed with reference to aluminum, as a conservative crustal element used in soil pollution studies [18-19], according to Equation (1):

$$EF = (C_{element}/C_{ref})_{sample}/(C_{element}/C_{ref})_{earth\ crust} \qquad \text{(Eq. 1)}$$

where $C_{element}$ is the concentration of the metal and C_{ref} is the concentration of the reference element in the sample (soil or rainwater) earth's crust [20].

3. Results and discussion

3.1. Meteorological Parameters and Physical Parameters of the Samples

Atmospheric temperature and RH values at the time of samplings were over 9 °C and 63- 75% in the fall and over 19 °C and 39-56% in the spring, respectively. Strong northern winds and rarely southern winds were the most frequent winds. The minimum and maximum levels of the rain amount occurred in the spring sampling and in the fall, respectively. Soil pH was around 6.5 – 7.0 and the soil temperature was over 6 °C in the fall and over 11 °C in the spring. Humidity content of the soil samples was lower in the spring season than in the fall season due to increased levels of soil temperature and a relatively dry season, observed before the spring sampling campaign.

The lowest pH values (>3.3) in the rainwater samples were measured in the fall season for all sampling sites. Overall, the lowest pH values were recorded in Etili, compared to other locations. Typical rainwater pH is around 5.4 - 5.6 due to the weak acidic effect of CO_2 in the air [1] and thus pH values that lower than 5.4 - 5.6 indicate the acidic rain. Rainwater pH values were lower than 5.6 at all sampling points, except for Karabiga as a result of alkalinity alteration by Ca or Mg ions, as these elements were available there (*e.g.,* active limestone mines). Therefore, the alkalinity level of the rainwater samples might have increased by the aerosols accumulated in the air, which was in accordance with studies conducted in Mugla, Turkey [21] and Iran [22]. Earlier researches carried out in the Aegean or Marmara regions of Turkey also indicated the less acidic rainwater observations with the pH of as high as 7.72 [21,23-30]. Electrical conductivity of the rainwater samples (65 and 436 µS/cm) were in the acceptable range of our national tap water standard, TS 266 [31]. The EC value of the rainwater was likely to increase with cations dissolved in the rainwater. Compared to EC values observed in the rainwater samples in this study, higher EC levels were measured in ground water samples collected in Çanakkale region [32-35].

3.2. Spatial and Seasonal Variations of Minerals and Heavy Metals in the Samples

Minerals and heavy metals in the soil and rainwater samples are presented according to spatial and seasonal variations. Major elements such as Al, Ca, Fe, and Mg are assumed to be vital for the earth's crust [36]. Thus, their levels are mostly not related to pollution, depending on the corresponding enrichment factor (EF) in the soil or air. As general, the anthropogenic heavy metals selected in this study (*e.g.,* As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn, and Hg) were found above the method detection limits

(MDL). Some elements (Ag, Au, and As) were linked with volcanic activity, geo-thermal zones, and/or radioactivity (Th and U). Therefore, those elements are given separately from the indicator elements of the anthropogenic pollution.

3.2.1. Mineral and Heavy Metal Levels in the Soil Samples

The concentrations of the measured elements in the soil samples taken from the sampling points in the fall and spring seasons are given in Table 1. No statistically significant difference was found in terms of seasonality for the selected elemental content of the soil samples taken from each study site (p>0.05).

Table 1. Elemental content of the dry-soil samples taken from the study points.

Element	Unit	MDL	Fall	Spring	Background concentrations
Major elements					
Al	%	0.01	2.1±1.13	1.57±0.48	7.1[a], 7.96[b]
Ca	%	0.01	0.6±0.37	0.65±0.34	3.85[b]
Fe	%	0.01	3.14±1.11	2.81±0.84	4[a], 4.32[b]
Mg	%	0.01	0.35±0.20	0.34±0.11	2.20[b]
K	%	0.01	0.29±0.10	0.17±0.05	2.14[b]
Na	%	0.001	0.02±0.03	0.02±0.01	2.36[b]
P	%	0.001	0.06±0.01	0.05±0.02	0.0757[b]
Anthropogenic pollution indicators					
Cd	mg/kg	0.01	0.5±0.5	0.3±0.3	0.35[a], 0.10[b]
Co	mg/kg	0.1	19.3±6.9	14.8±6.6	8[a], 24[b]
Cr	mg/kg	0.5	39.7±20.2	32.9±31.8	70[a], 126[b]
Cu	mg/kg	0.01	39.7±19.1	43.2±34.0	30[a], 25[b]
Hg	mg/kg	0.005	0.13±0.12	0.07±0.05	0.06[a], 0.04[b]
Mn	mg/kg	1	1222±395	927±255	1000[a], 716[b]
Mo	mg/kg	0.01	1.3±0.7	4.0±7.0	1.2[a], 1.1[b]
Ni	mg/kg	0.1	36.9±21.1	29.3±24.0	50[a]
Pb	mg/kg	0.01	43.7±13.0	30.7±8.4	35[a], 14.8[b]
V	mg/kg	1	66.3±29.7	61.4±22.5	90[a], 98[b]
Zn	mg/kg	0.1	68.6±22.0	61.3±16.3	90[a], 65[b]
Volcanic/Geo-thermal/Radioactive elements					
Ag	µg/kg	2	108.6±85.0	60.4±56.7	50[a], 70[b]
As	mg/kg	0.1	25.5±16.6	18.5±10.2	6[a], 1.7[b]
Au	µg/kg	0.2	4.5±5.4	12.5±26.8	2.5[b]
Th	mg/kg	0.1	7.6±5.1	6.2±3.4	8.5[b]
U	mg/kg	0.1	1.7±1.2	1.6±1.2	2[a], 1.7[b]

[a] [37]; [b] [20]; MDL: method detection limit; fall and spring season concentrations are shown as average ± standard deviation.

Elemental content of the soil is compared with background levels of earth crust given by Bowen [37] and Wedepohl [20]. Major components of the soil had concentration order as follows: Fe > A l > Ca > Mg > K > P > Na, in descending order. Merely proportion of P in the soil was slightly higher than background earth's crust level. Concentration order of the anthropogenic pollution indicators was Mn > Zn > V > Cu > Pb > Cr > Ni > Co, in descending order. Mineral and heavy metal concentrations in the soil samples were compared with Turkish Soil Pollution Control Regulation [38]. With this regard, measured elemental concentrations in the soil samples exceeded merely As limit value (0.4 mg/kg by oral intake or skin contact) at all sampling sites and the Co limit value (23 mg/kg by oral intake or skin contact) at Bayramiç and Etili. The amount of As in the soil samples was quite high compared to the limit values. A study conducted around Ayvacik found very high As levels in the groundwater and they showed that the source of As was linked with alteration zones in the volcanic rocks [33]. Even though relatively low levels of Cu, Pb, and Zn were observed here, Cu-Pb-Zn mines are present particularly around Çan and Etili, while Mn, Au, and Ag are also rarely found close to Etili and between Ayvacik and Bayramiç regions, according to the national mapping study for Çanakkale [39]. Average levels of Ag, As, and Au were markedly higher than the background levels of earth's crust. Specifically, Au availability close to the Mount Ida region (covers Ayvacik, Bayramiç, and Edremit region) is of local concern, since gold has already attracted several international gold exploration companies here. As radioactive elements, average levels of Th and U were slightly higher than the background levels.

Table 2 shows the comparison of average elemental levels of the soil samples collected in the fall and spring seasons at all study sites with the literature: Cd levels were lower than those measured in Pakistan [40], Mexico City [41], and Poland [42]; Cr levels were lower than those measured at India [43]; Cu levels were higher than Mardin [44], Hatay [45], Pakistan [40], Nigeria [46], and Tibet [47]; Ni levels were higher than Hatay [45], Nigeria [46], Pakistan [40], Tibet [47], Germany and Poland [42]; Pb levels were higher than Tibet [47], Pakistan [40], Mardin [44], and Hatay [45]; and Zn levels were higher than Hatay [45], Nigeria [46], and Pakistan [40].

EF values are categorized in five enrichment classes to indicate trace elemental pollution in the soil: *i)* EF < 2: minimal enrichment, *ii)* 2 < EF < 5: moderate enrichment, *iii)* 5 < EF < 20: significant enrichment, *iv)* 20 < EF < 40: very high enrichment, and *v)* EF > 40 shows extremely high enrichment [51-52]. Average EF values of As, Cd, Pb, Hg, Mn, Cu, Ni, and Zn in the soil samples showed variations among the sampling sites in terms of enrichment classes over the study period, as given in Figure 2. The fact that EF values for Ca, Cr, and Mg were in the first enrichment class, no anthropogenic pollution source exists in the study sites in terms of the major components of the soil. Several studies carried out close to Çan and Etili showed the contribution of coal-fired power plants to the As, Cd, Cr, Pb, Zn, and Se contents of water and fly ash samples collected around the region [7,32]. Once the Cd level in Bayramiç in the fourth enrichment class, indicating very high enrichment, was excluded, Cd, Pb, Hg, Mn, and Cu levels were found to be in the second and third enrichment classes, showing moderate to significant enrichment of those heavy metals in the soil samples. The potential sources of those heavy metals were explained as the geomorphological characteristics of the region, presence of coals and other mines, and usage of local coal in the coal-fired power plants located in Karabiga and between Çan and Etili [7,32,33,53,54]. Parallel to that, soil samples collected along the prevailing wind directions to determine the effect of Çayirhan power plant (in Ankara, Turkey) emissions on the region found higher heavy metal levels along the prevailing wind direction, compared to the opposite direction of the prevailing wind [55]. The highest levels of Cr, Cu, Ni, and Pb that given in Table 2 were observed in the soil collected from Kolaghat, India [43], where thermal power plants were shown the main source of heavy metal pollution in the soil. Another study conducted in the industrial region of Samsun-Tekkeköy, Turkey showed that soil samples that were close to the industrial facilities exceeded the critical levels for As, Cr, Cu, Ni, and Zn [56]. The major sources of heavy metal pollution in surface soil around Gebze industrial area, Turkey were shown as hazardous wastes distributed from the industrial plants through rain or wind and traffic [57]. In another study carried out in multiple points of İstanbul, Tukey, proximity to highways showed higher levels of heavy metals than the secondary roads [50]. In an extensive study conducted in multiple cities of different Asian and European countries indicated the remarkable contribution of anthropogenic heavy metals such as Cu, Cd, Zn, and Pb in the roadside soil contents [42]. All sampling locations of our present study were far from the traffic sources. In some studies, traffic appeared to be the major anthropogenic source of the heavy metals (*e.g.,* [3,6,58]). Unlike those studies, traffic was not considered as a major anthropogenic source in this study. Instead, mining activities and coal-fired power plants were the major anthropogenic sources, in addition to the potential contribution of natural rock characteristics of the soil on enrichment of some heavy metals such as As. Relatively high As levels were noted in the previous studies conducted in Çanakkale [7,32,33,53,54].

Table 2. Comparison of levels (mg/kg-dry soil) of the selected anthropogenic heavy metals observed in the soils collected from different countries.

Country (city)	Cd	Cr	Cu	Ni	Pb	Zn
Hong Kong [6]	0.02-5.9	-	5.1-190	-	5.3-404	38.7-435
Tibet [47]	0.05-0.4	35-58	11.3-20.5	10-24.8	16.6-42	28-77.3
Pakistan [40]	0.8	-	13.0	8.8	36.5	56.7
India (Kolaghat) [43]	-	101.4	70.4	52.3	26.6	148.6
Nigeria [46]	0.4-1.1	-	27.7	7-12.3	71-113	44.7-67.9
Mexico (Mexico City) [41]	1.7	-	101.5	-	921	666.5
Dubai [48]	0.17-1.0	-	15.5-65.9	13.3-98	260-278	72.4-170.3
Poland (Zabrze) [42]	5.2	28	70	23	210	870
Germany (Übingen) [42]	0.3	13	80	22	56	200
Italy [49]	-	1.7-73	6.2-286	-	4-3420	30-2550
Turkey (İstanbul) [50]	-	-	68.7[b] 23.4[c]	-	191[b] 29.7[c]	255[b] 96.6[c]
Turkey (Mardin) [44]	0.26-0.4	17-28	9.9-14.2	27-42	0.6-2.2	-
Turkey (Konya) [51]	-	-	144.4	1832	60	225.9
Turkey (Hatay) [45]	0-0.3	0-0.1	0.4-5.4	0.4-4	0.1-0.8	0-4.3
Turkey (Çanakkale)[a]	*0.3 (0.1-1.4)*	*36.3 (6-84)*	*41.5 (14-97)*	*33.1 (7.6-60.2)*	*37.2 (18-57)*	*64.9 (45-103)*

[a] This study; min – max (avg.); [b] surface soil from highway, [c] surface soil from secondary roads.

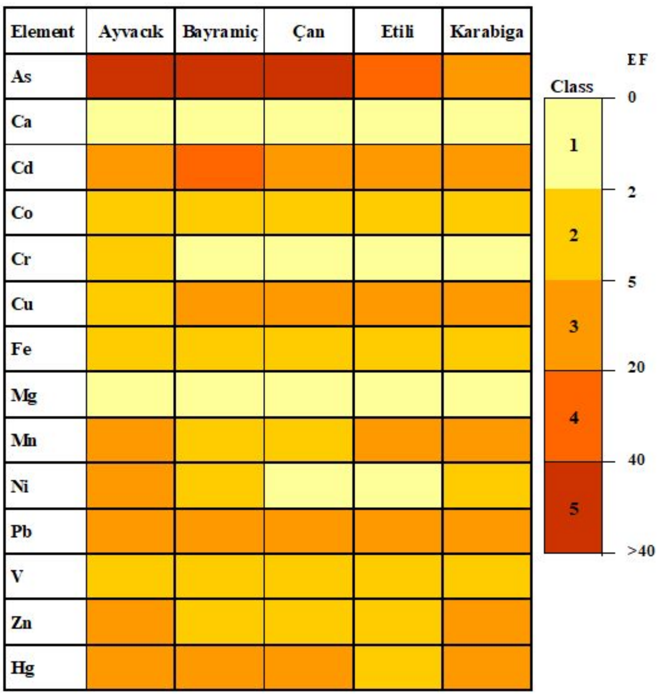

Figure 2. Heat map for enrichment factor (EF_{soil}) of the selected elements in soil over the study period at the study sites

3.2.2. Mineral and Heavy Metal Levels in the Rainwater Samples

The concentrations of the selected elements in the rainwater samples collected at the sampling points in the fall and spring seasons are given in Table 3. Statistically significant differences were found between the rainwater samples taken in the fall and spring ($p<0.05$). Average concentration order in rainwater samples was Zn > Pb > Al > Fe > Mn > Cu > Cd > Ni > Cr, in descending order. Average concentrations of Cd, Cr, Cu, Mn, Ni, Pb, Se, V, and Zn were higher than those in the background freshwater composition [37].

Table 3. Elemental content of the rainwater samples taken from the study points

Element	Unit	MDL	Fall	Spring	Background concentrations [37]
Major elements					
Ca	mg/L	0.05	2.9±1.4	9.6±6.0	-
Mg	mg/L	0.05	0.5±0.3	1.7±1.3	-
Na	mg/L	0.05	3.5±0.9	5.4±2.6	-
K	mg/L	0.05	0.7±0.5	10.2±9.6	-
Anthropogenic pollution indicators					
Al	µg/L	1	30.4±28.4	33.2±36.6	300
Cd	µg/L	0.05	4.6±3.7	6.7±5.5	0.1
Co	µg/L	0.02	0.1±0.04	0.3±0.2	0.2
Cr	µg/L	0.5	0.5±0.3	2.3±1.6	1
Cu	µg/L	0.1	7.1±4.0	9.1±7.6	3
Fe	µg/L	10	35.6±31.8	21.2±16.7	8
Mn	µg/L	0.05	11.0±5.0	39.3±19.3	0.5
Mo	µg/L	0.1	<0.1	0.3±0.3	0.5
Ni	µg/L	0.2	1.3±0.6	5.9±4.0	-
P	µg/L	10	87.6±79.4	3584±7030	3
Pb	µg/L	0.2	124.0±63.5	12.5±14.6	0.2
Se	µg/L	0.5	<0.5	3.0±1.6	-
Si	µg/L	40	225.6±328.5	1147.2±6115.7	0.5
V	µg/L	0.2	0.6±0.2	1.1±0.5	1.5
Zn	µg/L	0.5	153.3±56.4	368.0±382.6	500
Volcanic/Geothermal/Radioactive elements					
Ag	µg/L	0.05	<0.05	0.6±0.6	0.3
Au	µg/L	0.05	<0.05	0.07±0.05	-
As	µg/L	0.5	<0.5	1.0±1.0	0.5
Th	µg/L	0.05	<0.05	0.06±0.04	-
U	µg/L	0.02	<0.02	<0.02	0.4

MDL: method detection limit; fall and spring season concentrations are shown as average ± standard deviation.

Measured levels of the elements in this study are comparable with other studies conducted elsewhere. Except Jordan [59], Cd levels were higher than those measured in the places given in Table 4; Cr levels were lower than Singapore [60] and Russia [61]; Cu levels were lower than Giresun [62], Greece [63], and Jordan [59]; Fe levels were lower than Jordan [59] and Greece [63]; Ni levels were lower than Tibet [64] and France [65]; the highest Pb levels were observed in Çanakkale (this study); and except

Giresun [62], Zn levels were higher than those observed elsewhere given in Table 4. In another study, elevated heavy metal levels were observed in Istanbul [30], probably due to the contribution of dense traffic and industry-related anthropogenic air pollutant emissions. Rainwater samples taken along the Giresun coastal road [62] showed higher concentrations of Fe, Zn, Mn, Cu, Cr, Ni, As, and Co, while lower concentrations occurred for Pb and Cd than those measured in this study. Also, the authors found no statistically significant difference between the stations (p>0.05), whereas the seasonal difference was statistically significant. Major elements that were originated mostly from the earth's crust [30,66] in the rainwater samples were Ca, K, Na, and Mg, in descending order.

Table 4. Comparison of concentrations (µg/L) of the selected anthropogenic heavy metals observed in the rainwater samples taken from different countries

Country (city)	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Mexico [66]	0.04-4.5	-	-	-	0.4-12.9	0.6-9.3	-
USA [70]	1.1[a], 0.27[b]	0.52[a], 0.98[b]	-	-	-	0.33[a], 1.16[b]	-
Brazil [71]	0.17	-	3.6	-	-	1.7	9.8
Tibet [64]	<0.001-0.02	<0.03-3.5	0.05-4.2	<0.6-132	<0.04-4.37	0.011-1.8	0.33-33.4
Singapore [60]	0.05-0.4	0.40-2.8	0.7-34.1	3.2-63.8	0.8-6.5	0.21-12.6	0.93-11.7
China [67]	1	-	5	-	-	-	96
Jordan [59]	42	-	40	21.5	1.75	51	32
Russia [61]	0.08-3.4	0.2-0.5	1.3-31.6	-	-	0.17-0.7	21.6-113
France [72]	0.11	-	1.4	-	-	2.8	21.8
France [65]	<0.01-0.06	-	-	-	0.3-1.15	0.08-0.73	2.4-22.9
Greece [63]	0.06	1.2	2.9	-	-	3.3	39
Greece [73]	0.2	-	15.4	4.4	4.14	0.88	33.5
Turkey (Izmir) [27]	3.1	-	-	-	7.4	7	186
Turkey (Giresun) [62]	4.6	22	50.2	2379	17.7	36.1	713
Turkey (Çanakkale)[c]	*1.6-15.2 (5.6)*	*<0.5-3.9 (1.4)*	*2-21.7 (8.1)*	*<10-87 (28.4)*	*0.5-7.8 (3.6)*	*0.6-201.3 (68.3)*	*92.3-1025 (260.7)*

[a] fall, [b] spring; [c] This study; min – max (avg.)

According to Figure 3, the highest EF values (>200) were observed for As, Zn and Cd in both seasons. Pb, Mg, and Cu had EF values between >10 to >100, depending on the season. The lowest EF values were observed for Ni and Cr, which were slightly higher than 1. A study conducted in İstanbul, measuring fewer elements than this study showed that Pb, V, Cu, Ni, and Co had EF values >100, indicating the major contribution of anthropogenic sources such as industry and traffic [30]. In another study conducted in Singapore, the same elements that we observed in our study were predominant and attributed to the anthropogenic sources [66]. Relatively high contributions of urbanization and industrial activities have been shown the reasons of heavy metal pollution in rainwater of a region, that was close to petrochemical companies in Iran [22]. Even though the lowest heavy metal levels occurred in central Tibetan Plateau, which can be assumed as a remote environment with the least anthropogenic pollution source impact, long-range transport of the pollutants found to have contribution on heavy metal content in the rainwater of Tibet [64]. Like our outcomes, studies conducted in Beijing and İzmir, Turkey found Zn as the predominant heavy metal in the rainwater [27,67]. In another study conducted in Australia, elevated Pb and Zn levels that exceeded the limit values were observed in the rainwater [68]. Zn was shown to be a potential carcinogen and oral reference dose (RfD) was estimated as 0.3 mg/kg-day [69]. On the other hand, no study had As enrichment in the rainwater as high as found in this study.

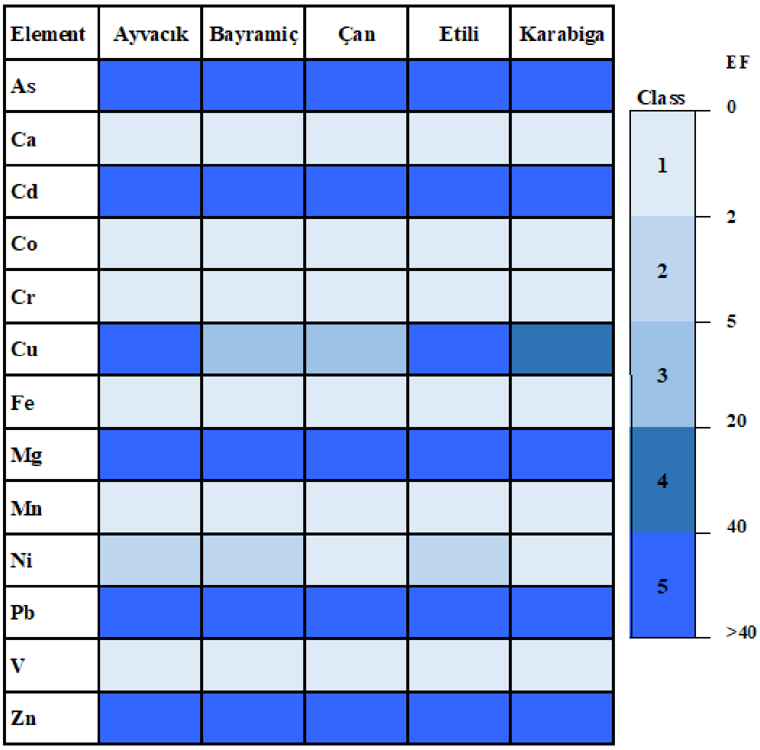

Figure 3. Heat map for enrichment factor ($EF_{rainwater}$) of the selected elements in rainwater over the study period at the study sites.

4. Conclusions

On Earth, atmosphere interact with crust and thus simultaneous monitoring of the environmental pollution in both parts of the environment is important. Soil and rainwater samples were taken in different parts of Çanakkale, Turkey, in two seasons along with the prevailing wind direction (from NE to SW), as wind has the potential to distribute pollutants emitted into the air throughout its path.

Physical parameters of rainwater pH (3.2-8) and EC values (98-486 us/cm) varied in a wide range, depending on the characteristics of the region and the meteorological parameters. Concentrations of the selected elements were measured by ICP-MS. All sampling locations in this study were far from the traffic sources. Unlike some studies conducted in urban sites, traffic was not considered as a major anthropogenic source in this study. Instead, mining activities and coal-fired power plants were major anthropogenic sources, in addition to potential contribution of natural rock characteristics of the soil on some of the heavy metals such as As. In addition to coal-fired power plants and open-pit mines available in the city, agricultural activity is the main socioeconomic activity at all of the sampling sites.

The highest enrichments were found for Pb in rainwater and As in soil samples. Elevated As levels found in the samples can pose a great risk for public health and agriculture. The study result showed that the elemental composition of the samples was influenced by the enhanced air plume dispersion of anthropogenic pollution sources along the prevailing wind directions over the city. The cumulative amount of the pollutants emitted into the air may show increasing trend from Karabiga to Ayvacik by enhanced air plume dispersion due to wind characteristics in the province. Also, As, Zn, and Cd were enriched in the soil and air with high magnitude. Therefore, there is an urgent need to conduct more interdisciplinary studies covering more than one part of the environment.

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