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Heavy Metal Concentrations of Groundwater in the East of Ergene Basin, Turkey

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Abstract The aim of this research was to investigate the concentrations of the heavy metals (copper, iron, zinc, chromium, cadmium and lead) and determine their relationship between pH and EC in the east of Ergene Basin, Turkey. For this purpose 18 groundwater samples were collected in May 2013. Results show that mean concentrations of Cu, Fe, Zn, Cr, Cd and Pb were, 0.005, 0.012, 0.083, 0.016, 0.000 and 0.0006 mg L^{-1} respectively, with the decreasing sequence of Zn > Cr > Fe > Cu > Pb > Cd. No significant correlations were found among metals. Only moderate positive correlation was determined between Pb and pH ($r = 0.451$; $p < 0.05$). All metal pollutants studied in the groundwater were below international and national guidelines except Cr.

Keywords Heavy metal · Contamination · Water quality · Ergene Basin

Industrialization is an unavoidable stage in the improvement of a society. Nonetheless, it brings many problems with it and one of the most severe problems is groundwater pollution due to the improper disposal of industrial waste. Water is a vital resource for all human beings, plants, and animals. Hence, the quality of water affects human welfare and is of the utmost importance (Patil and Patil 2010). The main sources for fresh water are aquatic systems such as rivers, lakes, or groundwater obtained from wells. However, one of the purest forms of water available in nature is groundwater and it still meets the overall demand of rural and semi-urban people (Mansouri et al. 2012).

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As water has unique chemical properties due to its polarity and hydrogen bonds, it is able to dissolve, absorb, adsorb or suspend many different compounds. Thus, water can be easily contaminated as a result of surrounding activities such as agriculture or industry (Mendie 2005). The term “heavy metal” is often used as a group name for metals and semimetals (metalloids) that are associated with contamination and potential toxicity or ecotoxicity (Duffus 2002). Heavy metals exist in water in colloidal, particulate, and dissolved phases (Adepoju-Bello et al. 2009), and these occurrences depend on either geogenic origins such as eroded sediments, leaching of ore deposits etc., or anthropogenic origins such as solid waste disposal sites or sewage effluents (Wang et al. 2011). Agriculture has also been identified as a source of heavy metals due to its use of fertilizers (Kidd et al. 2007; Mico et al. 2006).

The human intake of heavy metals through water has been widely reported (Muchuweti et al. 2006). If the occurrence of heavy metals is beyond tolerance limits of the standards, there are negative consequences that damage the environment, reduce the quality of human life, and may even be fatal (Nagajyoti et al. 2010). As heavy metals are non-biodegradable and have a persistent nature, they easily accumulate in the vital organs such as kidneys, bones, and liver and they can cause many serious health disorders (Duruibe et al. 2007). Because of the importance of uncontaminated water, the aim of this study is to test groundwater quality in in the eastern part of the Ergene Basin in northwest Turkey.

The study area is located in the northwest of Turkey, between the coordinates 41°05′47″–41°22′8″ North and 27°04′15″–25°28′39″ East (see Fig. 1). This area is about 100 m above sea level. The area experiences a terrestrial climate, with cold and rainy winters and hot and arid summers. Long-term annual average precipitation is

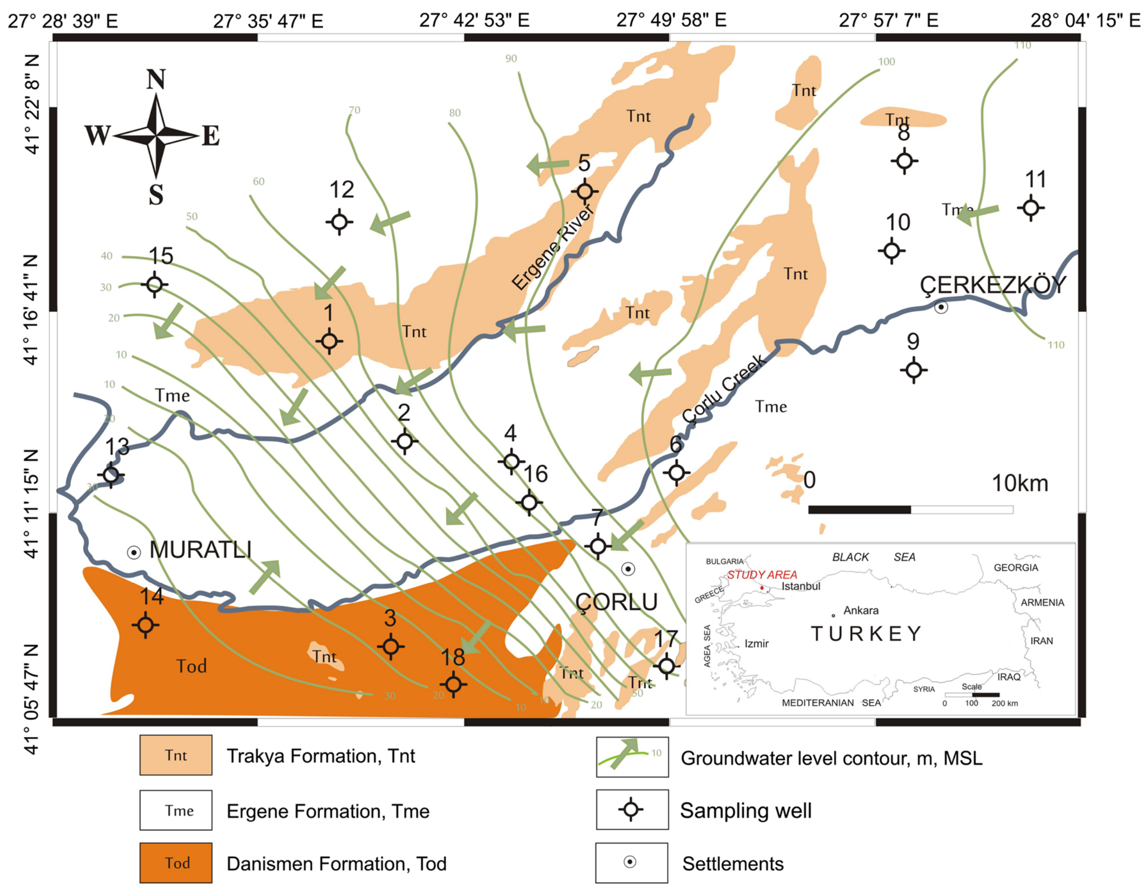

Fig. 1 Location, geological and groundwater level map of the study area

509.6 mm, the average temperature is 12.1°C, and long-term annual evaporation is 791.3 mm. The coldest months are January and February with an average temperature of 4°C while the hottest months are June and July with an average temperature of 30°C (Arkoc and Erdogan 2006). The northern part of the study area is mountainous and the rest is covered with low sloping hills. The well dendritic type of drainage system indicates the occurrence of rocks of uniform resistance (Thornbury 1969).

The upper middle Oligocene aged Danişmen Formation (Tod) consists of clays and siltstones and forms the basement rocks of the study area. The upper Miocene and Pliocene aged Ergene Formation (Tme) consists of gravestone and sandstone intercalations, and the Trakya Formation (Tnt) consists of gravel and sandstones, come over Danişmen Formation conformably (see Fig. 1). Ergene and Trakya Formations constitute the main deep unconfined aquifer in the region. The permeability (K) of this aquifer varies from 10 to 15 m/day. There are hundreds of deep wells with depths of 250–350 m drilled into these formations. The depths of the wells from which the samples were collected are provided in Table 1. The most important fresh water resources in the area are the Ergene River and the Çorlu Creek. The catchment area of these is about 812 km^2. There are no lakes or other natural water resources. Fifteen percent of the study area is flat and 75 % has an undulated topography. The groundwater flow direction is Northeast to Southwest. The groundwater level contours from the mean sea level (MSL) are outlined in Fig. 1.

Agriculture and industry are the main sources of livelihood in the study area. The area constitutes 7 % of the arable fields of wheat and 13 % of overall national production in Turkey (TTAE 2014). The sunflower is another important agricultural product grown in the study area with 75 % of national sunflower production coming from the region (GTB 2013). Therefore, the quality of water is very important. Besides this agricultural production, there are two industrial zones (IZ), namely Çerkezköy and Çorlu. While the one situated in the north east of the study area (Çerkezköy IZ) hosts textile, chemistry, and electronics industries, Çorlu IZ largely hosts the leather industry. Besides these major zones, there are many small or medium sized textile production factories throughout the study area.

The textile industry discharges yarn-dyeing waters into the rivers. As there are no restriction parameters for color pollution in the water pollution regulations of Turkish law (SKKY 2004), all the yarn-dyeing waters are discharged without any treatment. Until recently, chromium salts have been

Table 1 Concentrations of heavy metals (mg L^{-1}), pH and EC (μS/cm) in the study area

Well No.	Coordinates		Well depth	Metals						pH	EC
	Easting	Northing	(m)	Cu	Fe	Zn	Cr	Cd	Pb		
1	27° 38′ 9″	41° 16′ 14″	315	0.0021	0.009	0.03	BDL	BDL	BDL	8.2	1,550
2	27° 39′ 44″	41° 13′ 55″	270	0.0028	0.009	0.05	BDL	BDL	BDL	7	481
3	27° 39′ 29″	41° 08′ 46″	208	0.008	0.063	0.03	0.027	BDL	0.0002	8	570
4	27° 44′ 24″	41° 12′ 25″	294	0.004	0.009	0.02	BDL	BDL	BDL	7.1	835
5	27° 47′ 13″	41° 18′ 31″	281	0.01	0.009	0.04	0.002	BDL	0.0007	7.41	1,468
6	27° 50′ 6″	41° 12′ 1″	285	0.004	0.009	0.04	0.006	BDL	BDL	7.32	487
7	27° 46′ 50″	41° 10′ 13″	293	0.005	0.009	0.96	BDL	BDL	BDL	7	1,280
8	27° 59′ 8″	41° 18′ 54″	300	0.007	0.009	0.04	0.002	BDL	BDL	6.56	470
9	27° 58′ 21″	41° 16′ 18″	300	0.004	0.009	0.05	0.1	BDL	BDL	6.1	683
10	27° 57′ 25″	41° 17′ 53″	308	0.004	0.009	0.033	0.006	BDL	BDL	7.2	723
11	28° 02′ 21″	41° 20′ 30″	251	BDL	BDL	0.026	0.04	BDL	0.0009	7.8	987
12	27° 36′ 32″	41° 20′ 41″	306	0.008	0.009	0.005	BDL	BDL	0.002	7.9	434
13	27° 28′ 27″	41° 12′ 5″	250	0.0021	0.009	0.02	0.09	BDL	0.002	7.6	523
14	27° 30′ 52″	41° 09′ 21″	297	0.006	0.009	0.014	BDL	BDL	0.0009	8.5	763
15	27° 32′ 43″	41° 17′ 51″	331	0.003	0.009	0.03	BDL	BDL	0.0009	7	343
16	27° 43′ 48″	41° 10′ 34″	321	0.007	0.01	0.007	BDL	BDL	0.0009	7.8	386
17	27° 48′ 25″	41° 08′ 8″	268	0.005	0.009	0.021	BDL	BDL	0.0009	8.2	549
18	27° 41′ 55″	41° 06′ 50″	296	BDL	0.001	0.03	BDL	BDL	BDL	8	565
Overall mean				0.005	0.012	0.083	0.016	BDL	0.0006	7.5	737

BDL below detection limits

extensively used in dying wool with synthetic mordant dyes. Although the use of these mordants is restricted, they are still commonly used (Guzel and Akgerman 2000). Another important source of groundwater pollution is the leather industry. During the processing of crude leather by chemicals, many pieces of leather are split and the process waters become polluted. Chromium (IV) and Sulfur are the most important pollutant parameters in these waters (Özdemir et al. 2004).

Published work on the quality of groundwater in this region reported Chromium, Cadmium, and Lead contamination (Arkoc 2011; TU 2002; DSI 2003; COB 2008). In order to eliminate water pollution, an appropriate quality management plan is crucial and an assessment of water quality could be the first and most important step in applying such a plan (Sanchez et al. 2007). The objectives of this study are to assess the heavy metal (Copper, Iron, Zinc, Chromium, Cadmium, and Lead) concentrations, pH, and electrical conductivity (EC) of groundwater in the eastern part of the Ergene Basin, and to unveil the status of contamination in the region.

Materials and Methods

Standard methodology for the analysis of the analyzed parameters was applied during the collection and handling of the samples. The samples were collected from 17 wells drilled for drinking water and the coordinates of all sample locations were recorded with Garmin Etrex® hand-held GPS. All samples were preserved in polypropylene (PP) plastic bottles that were pre-washed with acid and filtered in situ through Whatman® no: 40 filter prior to analysis. Electrical conductivity, total dissolved solids (TDS), and pH were measured in situ on unfiltered water using a portable Hanna HI 98312 tester and a Toledo Mettler pH meter. The water samples collected from the field were preserved in a cooler during the field study. The samples that could not be analyzed immediately were kept in a refrigerator at 4°C. The water samples for dissolved trace elements were acidified by Nitric acid (HNO_3) to pH < 2 due to the problems of absorption or precipitation. The concentrations of metals were measured by inductively coupled plasma-mass spectrometer (ICP-ES/ICP-MS depending on the adequate detection limits of the instruments) analysis (ACME Labs. Vancouver, Canada). STD TMDA-70 reference material was used as a control material in analytical measurements.

The detection limits (mg L^{-1}) for each metal were as follows: Cu (0.00001), Fe (0.01), Zn (0.0005), Cr (0.00005), Cd (0.000005), and Pb (0.0001). SPSS V.16 was used for statistical calculations and Pearson's correlation was used to test the accuracy of the correlations.

Results and Discussion

The overall and mean concentrations of the metals investigated in the study are given in Table 1. According to Table 1, the concentrations of the metals decreased in the following order: Zn > Cr > Fe > Cu > Pb > Cd. According to the results, the mean concentrations of Cu, Fe, and Zn were 0.005, 0.012, and 0.083 mg L^{-1} respectively. While the mean concentrations of Cr, Cd, and Pb were 0.016, 0.000, and 0.0006 mg L^{-1} respectively.

Cd, Cr, and Pb are the most significant of all the metals as they are toxic and commonly present. Cadmium is used in the steel industry and in plastics and battery production. The contamination of groundwater by cadmium is caused by fertilizers and impurities in the zinc of galvanized pipes of metal fittings. Kidneys are the main target organs for cadmium toxicity. Chromium can exist in valances of either +2 or +6 and it is widely distributed in the earth's crust. The total concentration of chromium in drinking water is usually <0.002 mg L^{-1}, and Chromium (+6) is classified as a human carcinogen (WHO 2006). In this study, Chromium was detected as 0.1 and 0.09 mg L^{-1}, levels that are above both the Turkish Standards (TS) and World Health Organization (WHO) limits.

Lead is rarely present in tap water as it is dissolved from natural sources. Its presence depends primarily on household plumbing systems. Lead is toxic to both the central and peripheral nervous systems. Copper, zinc, and iron are essential elements and they are necessary for human metabolism. However, if they are too concentrated, they may have adverse effects. Copper concentrations in drinking water vary widely as the corrosion of copper plumbing is one of the primary sources of copper in drinking water. Long-term exposure to copper (>3 mg L^{-1}) results in gastrointestinal disturbances. Zinc is an essential trace element found in potable water in the form of salts or organic complexes (WHO 2006). If the zinc concentration in water exceeds 3 mg L^{-1}, it might taste bitter. Iron is one of the most abundant metals in the earth's crust and it is found in natural waters at levels ranging from 0.5 to 50 mg L^{-1}. It is an essential element for human nutrition. There is no noticeable taste of iron concentrations below 0.3 mg L^{-1} and a concentration of up to 1–3 mg L^{-1} is applicable for people (WHO 2006).

In Table 2, the international and national threshold standards for drinking water according to TS (2005), WHO (2006), and Environmental Protection Agency (EPA) (2013) are outlined. The suitability of the drinking water in the study area was determined according to these standards. The results of this study show that concentrations of the metals (Cu, Fe, Zn, Cr, Cd and Pb) in the water in the study area were below the admissible limits of all these standards. However, chromium at wells 9 and 13 exceeded the threshold of the TS and WHO standards by 0.1 and 0.09 mg L^{-1} respectively, and cadmium was not detected.

Table 2 Comparison of average heavy metal (mg/L) concentrations with international and national standards

Metals	TS (2005)	WHO (2006)	EPA (2013)	Present study
Cu	2	2	1.3	0.005
Fe	0.2	0.3	0.3	0.012
Zn	–	3	5	0.083
Cr	0.05	0.05	0.1	0.016
Cd	0.005	0.003	0.005	BDL
Pb	0.01	0.01	0.015	0.0006

BDL below detection limits

pH and EC are two of the most important and frequent tests used in water chemistry to identify the chemical and biological properties of water. pH condition may influence the nutrient availability, solubility of metals, and buffering capacity of water. EC is a measure of water's ability to transmit an electric current and it is affected by the presence of inorganic dissolved solids. Groundwater EC is directly affected by the properties of formations through which the water flows. According to TS and EPA, the pH of drinking water should be in the range of 6.5–9.5 and 6.5–8.5. The mean of the pH obtained in this study was 7.5, which is within the stipulated range. The overall mean of the EC values in the study area ranged between 676 and 737 µS/cm. These values were all below TS standards (2,500 µS/cm).

In order to establish the relationship between two variables, a correlation coefficient is generally used. This is simply a measure to exhibit how well one variable predicts the other (Kurumbein and Graybill 1965). Pearson's correlation was used to compute the correlation coefficient (r) of the ions in the groundwater in the study area to find the relationships between variables with the data in Table 1. The results are presented in Table 3. Only moderate positive correlations were found between Pb and pH ($r = 0.451$; $p < 0.05$). No significant correlations were found among the other trace elements. This shows that the source of these metals were independent from each other.

The high concentrations of metals reported in the published work were not observed in this study. Only chromium in two wells exceeded the admissible limits. The wastewater treatment plant at Çerkezköy IZ was constructed in 1994 and the second part of the facility became operational in 2008, and the treatment plant at Çorlu IZ became operational in 2007. Moreover, the European Council restricted chromium salts in mordants in 2005 (EC 2005). The results of the study show that the treatment facilities and the European Council restrictions have had a positive impact on metal contamination in the region as

Table 3 Correlation coefficients (r) among parameters

	Cu	Fe	Zn	Cr	Cd	Pb	pH
Cu	1						
Fe	0.393	1					
Zn	0.008	−0.050	1				
Cr	−0.329	0.053	−0.117	1			
Cd	−0.273	−0.052	−0.061	−0.130	1		
Pb	0.084	−0.150	−0.248	0.208	−0.210	1	
pH	0.091	0.197	−0.222	−0.303	0.304	0.451[a]	1

[a] Correlation is significant at the 0.05 level

metal pollutants, except Cr, were all below international and national guidelines (Table 2).

In light of the obtained values of this study, monthly sampling research should be carried out to assess the pollution status of groundwater and determine the specific areas that might have potential pollution risks in the study area.

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