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Spatial and Seasonal Characteristics of Inorganic Chemicals in Armağanköy Dam Water, Thrace Region

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Abstract: The study provides a baseline for the assessment of the inorganic pollution specially, metal contamination in the water Armağanköy dam, Ergene River basin. A survey of inorganic chemicals was performed in water samples collected in Armağanköy dam reservoirs during 2015. Water samples from six sampling sites were collected and analyzed for 10 different water quality parameters. Using these data, a regional irrigation water quality was assessed using one technique: United States Department of Agriculture Method (USDA). This method revealed that the dam water salinity, as represented by electrical conductivity, EC_w, ranges from low salinity (C1: EC_w < 250 micromhos cm^{-1}) to medium salinity (C2: EC_w < 750 micromhos cm^{-1}). The sodium adsorption ratio (SAR) is low (S1) sodicity. Therefore, the water of the dam is dominantly of the C2–S1 class and C1–S1 classes at the sampling site of 1, 2, 3, 4, 6 and 5, respectively. Inorganic analyses were performed according to USEPA method. The cation concentrations are gradually decreases from the February towards the April. Cu^{2+} and Mo^{2+} displayed higher values in the dry season, while higher values for Fe^{2+} and Mn^{2+} in the wet season. The concentrations of Fe^{2+}, Mn^{2+} and Mo^{2+} are generally higher than the other sampling sites at the sampling sites 1 and 6. Correlation analyses showed that metal content of Armağanköy dam water was affected by pH, EC_W and TSS. The heavy metal concentrations in the water samples from the dam reservoirs followed the order: $Mn^{2+} > Fe^{2+} > Mo^{2+} > Cu^{2+}$.

Key words: Hydrochemistry, dam waters quality, irrigation, inorganic chemicals, heavy metals.

1. Introduction

Water pollution and scarcity are the most important anthropogenic causes of global change in aquatic ecosystems. Escalating human populations and economic development have significantly contributed to the current worldwide deterioration in water quality (Varol, M., 2013). Aquatic ecosystems act directly or indirectly as sinks for metals. Increasing industrialization leads to ever increasing pollution of surface waters.

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The loading of surface waters with metals is of increasing importance because these are sources of drinking and irrigation water.

Surface water, which is more susceptible to contamination, is often used for irrigation. Moreover, in the face of a shortage of fresh water in some regions, reclaimed wastewater is used for agricultural purposes in an effort to conserve hydrological resources (Mara et al., 2007).

Lakes, rivers and groundwater are the important potential sources of irrigation water. Chemical analysis of water indicates its suitability for irrigation purposes. Irrigation agriculture depends on adequate water supplies of usable quality. Chemical impurities can be harmful when present above certain fairly well defined limit. The main soluble constituents in water are Ca^{2+}, Mg^{2+}, Na^{+} as cation are of prime importance in determining the quality of irrigation water and its suitability for irrigation purpose. The intensive use of nearly all good quality water supplies means that new irrigation projects and those seeking new additional supplies must rely on lower quality and less desirable sources which will require proper design for environmental management (Akinyemi and Souley, 2014).

Sodium content is the ratio of sodium concentration to the concentrations of calcium and magnesium (beneficial elements) which is also known as sodium adsorption ratio (SAR). High values of soil salinity and SAR cause soil structure deteriorations, decrease of soil permeability and reduction of crop yields due to toxic and osmotic effects (Al-Hamaiedeh and Bino, 2010).

Among the numerous contaminants, pollution by heavy metals in aquatic environment has become a global phenomenon because of its toxicity, persistence for several decades, bioaccumulation and biomagnifications in the food chain. Heavy metals are usually present at low concentration in aquatic ecosystem, but deposits of anthropogenic origin have raised the heavy metal concentration, creating environmental problems in coastal zones, lakes and rivers (Kamala-Kannan et al., 2008; Kabir et al., 2011). They are affect environmental quality by accumulating in reservoirs and resulting in serious human health hazards (Wang et al., 2012).

Many research projects on the irrigation water and assessment of inorganic chemicals in surface waters have been conducted, such as studies of south China (Gu et al., 2016), Lahore in Pakistan (Mahmood and Malik, 2014) in Spain (Garcia-Garizabal and Causape, 2010; Isıdoro et al., 2010) in Benin (Koumolou et al., 2013) the Jilh aquifer in Saudi Arabia (Al-Bassam and Al-Rumikhani, 2003).

Very few studies have been conducted on the Ergene River basin where located the Armağanköy dam, especially on the subject of inorganic pollution (Öngen et al., 2008; Ekmekyapar et al., 2011; Ekmekyapar et al., 2015). Surface and ground waters in the basin are constantly subject to pollution caused by the rapid increase in population and the intensity of agricultural and industrial activities. Consequently, it is necessary to observe the physico-chemical properties in the aquatic ecosystem and explicate the results.

The aim of this study was to determine the physical properties and the concentration /distribution of some metals and in the Armağanköy dam waters and to assess the degree of contamination. A suite of 7 metals (Ca, Mg, Na, Fe, Mn, Cu, and Mo) and pH, EC_w , TSS and SAR were investigated for waters from the reservoir of Armağanköy dam to examine their spatial distribution, seasonal characteristics, possible sources, and potential impacts to the local environment. This study documents the inorganic contamination of environmental concern in the water from the reservoir dam and is intended to provide guidance for managerial decisions in this important irrigation and drinking water. The study places the reported contaminant concentrations in context through extensive comparisons with previous research both for Armağanköy dam and other Turkish locations. The comparison of our results with comparative international studies also provides basic knowledge for Turkish Environment Ministry in the development of their own water quality criteria.

2. Methodology

Study Area

Armağanköy dam is located on the north of the Ergene River basin at the northwest part of Turkey. The dam is one of the most important reservoirs in the Ergene River basin. It supplies the drinking water to province and it is also used as irrigation water. Major land use in the common watershed of lake is agriculture and settling area. It was chosen in this study as it is a major recreation area serving Kırklareli city. Being the largest city in the north section of the Ergene River basin, Kırklareli is plays a key role not only in storing water, agricultural irrigation, water supply and climatic regulation, but also in producing a good deal of marketable grain, freshwater fish. One of the main activities in the city is agriculture. Agricultural products such as cereals, sunflower, sugar beet, pulse, corn and forage crops are the most frequently cultivated (URL 1).

As the fast industrial development in the Ergene River basin the inorganic pollution is common. There are mainly textile factories, white goods, glass, oil, food, and chemical factories in Kırklareli Organized Industrial Zone. These factories in the basin discharge their waste into the Ergene River and its branches (Kırklareli Environmental Information Report, 2014). Therefore, the environmental quality in aquatic system of the Armağanköy dam has direct and significant effects on drinking water safety of the city, stability and biodiversity of the aquatic ecosystem and so on.

The dam has been operating since 1998 and was built across the stream Kocadere. The body volume of dam is 1.553.000 m^3 and the area of lake is 3 km^2. The average height from the stream Kocadere is 61m. It covers a maximum of 5623 ha.

Sampling and Sample Preparation

Seasonal water samples (February, March, April) were taken in 2015 at six sampling sites (stations 1, 2, 3, 4, 5, and 6; Fig. 1) from surface layer and at the banks of dam. Samples which were put in the acid-rinsed polyethylene containers were immediately taken to the laboratory. Field water sampling and measurements followed standard methods (APHA 1998). All chemicals used were of the highest purity available (Merck) and all glassware and the laboratory equipment used was carefully cleaned with HCl to minimize potential contamination. The samples were collected in plastic bottles and brought to the laboratory where filtered. Electrical conductivity (EC_w) and pH were measured directly after collection. They were also monitored in the samples using a multi-parameter measurement instrument (Thermo Orion 3 star) after appropriate calibrations with standard buffer solutions. Concentration of TSS was measured using drying method at 103–105 ^{0}C described by standard methods (APHA 1998).

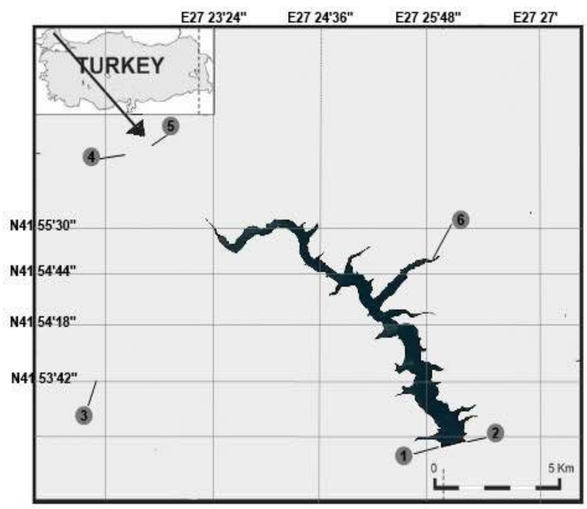

Fig. 1. Map of Armağanköy dam and selected sites (1-6).

The USEPA Method, 3005A (USEPA, 1992), and USEPA Method 200.2 inductively coupled plasma-optical emission spectrometry ICP-OES (USEPA, 1996) were used, respectively, to digest and analyze Ca^{2+}, Mg^{2+}, Na^{+}, Fe^{2+}, Mn^{2+}, Cu^{2+} , and Mo^{2+}. A 100 ml representative aliquot of the well-mixed sample was placed into an acid washed glass beaker to which 3 ml of concentrated nitric acid (HNO_3, Merck) were added, and the beaker covered with a watch glass. The sample was heated on a hotplate and evaporated to approximately 5 ml at 95 ^{0}C without boiling. The beaker was then allowed to cool, after which, 3 ml of concentrated nitric acid (HNO_3) were added and the beaker covered with a watch glass. The solution was again heated at 95 ^{0}C and refluxed. Additional acid was added and the reflux repeated until the appearance of the digestate was unchanged. The digestate was evaporated to 3ml at 95 ^{0}C, without boiling. After cooling, a small quantity of 1:1 hydrochloric acid, HCl (10 ml/100 ml of final solution) were added to the sample digest and covered with a watch glass to reflux for an additional 15min to dissolve any precipitate or residue resulting from evaporation. After cooling, the digestate was transferred to a 100 ml volumetric flask, diluted to 100 ml with milli-q deionised water (analytical grade), and the flask transferred to a 125 ml high density polyethylene (HDPE) sample bottle for storage (USEPA, 1996). Sample solutions were analyzed for trace metals following the ICP-OES (Spectro Blue model). Reagent and procedural blanks were determined in parallel to the sample treatment using identical procedures. Each calibration curve was evaluated by analyses of these quality control standards before, during and after the analyses of a set of samples. The analytical precision was within the range of ±10%.

The United States Department of Agriculture method (USDA) was used for water quality assessment. The USDA method is mainly based on water electric conductivity (EC_w), representing the total concentration of soluble salts in irrigation waters, usually expressed in micromhos cm^{-1} at 25 ^{0}C and its sodium adsorption ratio (SAR). Sodium hazard (alkali hazard) is due to excessive SAR values. The sodium adsorption ratio is expressed as:

$$\boldsymbol{SAR} = \frac{Na}{\dfrac{\sqrt{Ca + Mg}}{2}}$$

Where Na is the concentration of sodium ions (meq L^{-1}), Ca the concentration of calcium ions (meq L^{-1}), and Mg is the concentration of magnesium ions (meq L^{-1}).

Statistical Analyses

Statistical analyses of data were performed using SPSS statistical software package (Version 10).

3. Conclusions

Physico-chemical Parameters

Physico-chemical parameters show that the sampling sites is from the study area (Fig.2). The pH values are ranges between 7 and 7.8. The pH values are generally lower than other months in February. The TSS values are ranges between 0.006 and 0.1540 mg/L. The TSS values are generally higher than other months in March and at the sampling sites 1, 6. In this study, the values of pH and TSS are within an acceptable range for irrigation and drinking water.

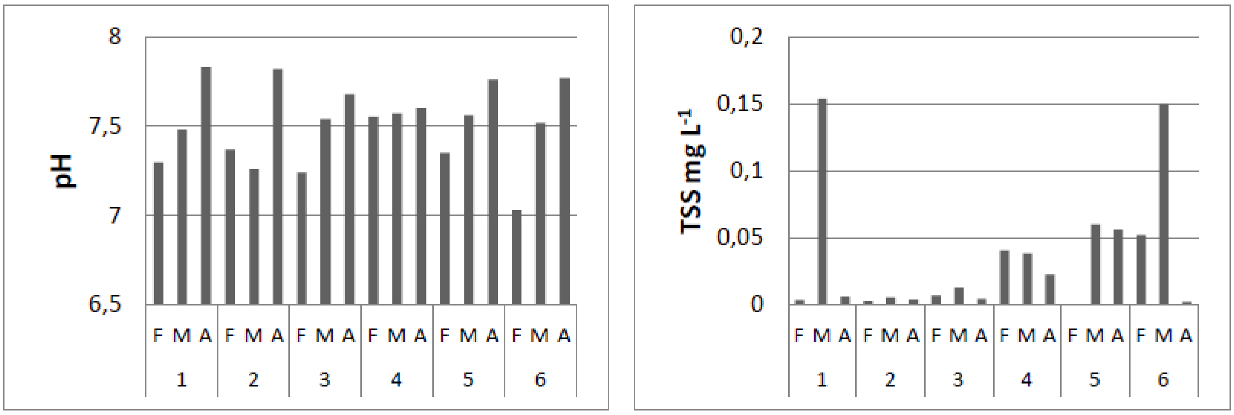

Fig. 2. Physico-chemical parameters, at the sampling sites from the study area, during 2015. Sampling sites: 1, 2, 3, 4, 5, 6.

Distribution of Ca^{2+}, Mg^{2+}, Na^{+}, SAR and EC

The distribution of the Ca^{2+}, Mg^{2+} and Na^{+} cations indicates in Fig.3. The cation concentrations are gradually decreases from the February towards the April. The Mg^{2+} concentration (51.38 - 133 meq L^{-1}) is higher than the other cations at the sampling sites 3 and 4. The Ca^{2+} concentrations range from 36.21 to 79.27 meq L^{-1} and the Na concentrations range from 30.35 to 75.71 meq L^{-1}. In this study, sodium, magnesium and calcium contents are within an acceptable range for irrigation water.

The SAR contours are ranging from 3.2 to 10.8 (Fig 4a). Hazardous SAR tends to develop leading to the breakdown of the soil structure and dispersion with decreased water permeability. The dam waters demonstrate suitability for all kinds of the cultivation of sensitive plants to sodium. These results obtained were similar to the work done by Xiao et al., (2014); Shaki and Adeloye, (2006) and Palma et al., (2014).

The areal distribution of ECw at 25 ^{0}C for dissolved salts in the dam water ranges from 107 to 533 micromhos cm^{-1}(Fig. 4b). According to regulation of Turkish irrigation water quality, dam water is a very good (I. class) at the 5 sampling site and it is good (II. class) at the sampling sites of 1, 2, 3, 4 and 6.

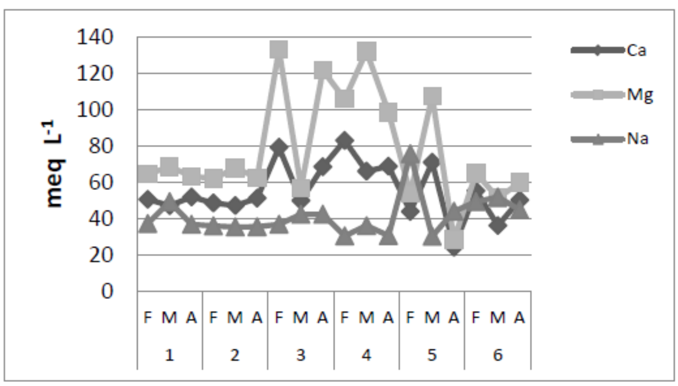

Fig. 3. Cross section of sodium, calcium, magnesium of the sampling sites: 1, 2, 3, 4, 5, 6.

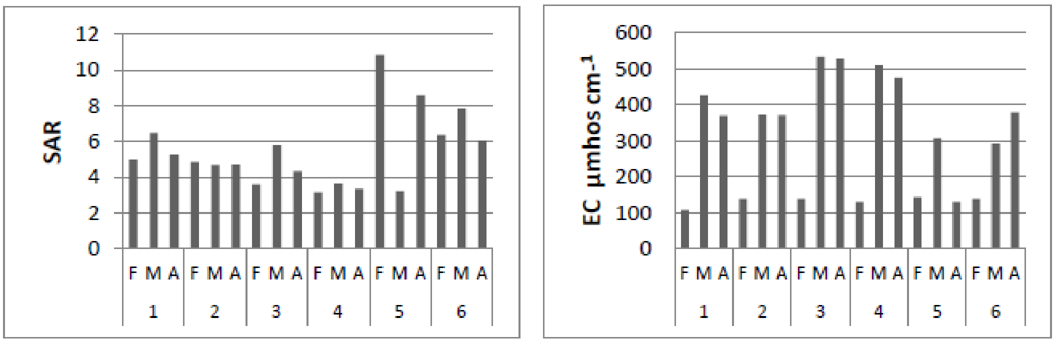

Fig. 4. Cross section of (a) SAR of the sampling sites; (b) ECw of the sampling sites: 1, 2, 3, 4, 5, 6.

Classifications of the Armağanköy Dam Water for Irrigation

The areal distribution of cations and other irrigation water quality assessment components have been discussed previously. In order to derive a simple technique appropriate to describe the suitability of dam waters for irrigation, the distribution of the major cations in the aquifer were subjected to the USDA classification techniques.

Classification According to USDA Method

The USDA classification for salinity (C) and sodicity hazards (S) in the Armağanköy dam are shown in Fig. 5. Most of the sampling sites within the low salinity hazard zone are in the S1 class. Following the USDA classification system, the water from the dam in the salinity class is in the C2 class, which is of a medium quality for irrigation waters. It is only low at the number of 5 sampling site and it is in the C1 class. On the other hand, the combined ECw/SAR classification the Armağanköy dam water in the C2–S1 and C1–S1 classes in the sampling sites of 1, 2, 3, 4, 6 and 5, respectively.

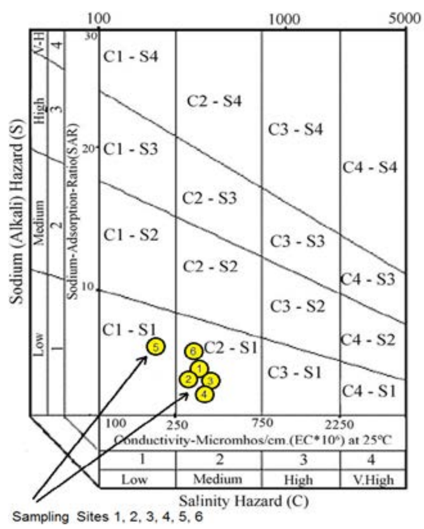

Fig. 5. Classification of water in the Armağanköy dam based on the USDA method

Distribution of Fe, Mn, Cu, Mo

The distribution of the iron, manganese, copper and molybdenum metals indicates in Fig.6. The concentrations of Fe^{2+}, Mn^{2+} and Mo^{2+} are generally higher than the other sampling sites at the sampling sites 1 and 6. The Fe^{2+} concentrations are range from 1093 to 7341 µg L^{-1} and the Mn^{2+} concentrations are range from 1120 to 43630 µg L^{-1}. The Mo^{2+} concentrations are range from 1084 to 8590 µg L^{-1}. The Cu^{2+} concentrations (0-3090 µg L^{-1}) is very high according to the limits values of Turkish regulation of surface water quality classes. The Fe^{2+} and Mn^{2+} concentrations are very high according to the Water Intended for Human Consumption Standard (Council Directive 98/83/EC). The abundance of heavy metals analyzed in decreasing order were: Mn^{2+} >Fe^{2+}>Mo^{2+}>Cu^{2+}.

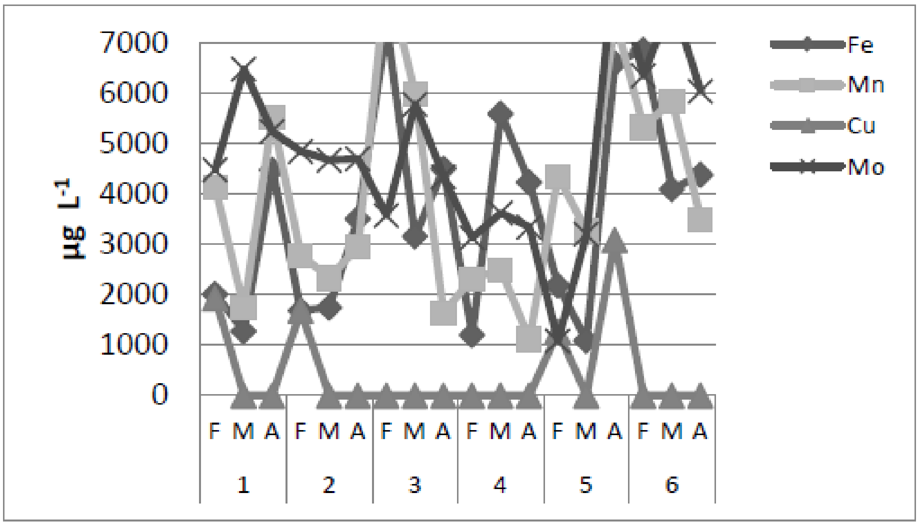

Fig. 6. Cross section of iron, manganese, copper and molybdenum of the sampling sites: 1, 2, 3, 4, 5, 6.

The comparison between the present concentrations and those in the literature concluded that the concentrations observed in the Armağanköy dam were lower or higher than those recorded (Table 1).

Table 1 Maximum concentrations of heavy metals in the Armağanköy dam reservoirs, and comparison with other studies and guidelines (MCL).

	Heavy Metals		
	Fe	Mn	Cu
This study (μg L^{-1})	7341	43630	3090
Hough Park Lake (mg L^{-1})[a]	0.298	0.093	0.001
Burullus Lake (μg L^{-1})[b]	3000	nd	50
Dicle Dam (μg L^{-1})[c]	189.24	nd	9.63
Atatürk Dam (ppm)[d]	19.265	514.07	22.70
Water quality criteria for drinking water			
EC (1998), (mg L^{-1})	0.2	0.05	2
WHO (2004), (mg L^{-1})	0.3	0.1	2
USEPA (2009), (mg L^{-1})	0.3	0.05	1.3

[a]Ikem and Adisa (2011), [b]Ebrahem et al. (2012),

[c]Varol (2013), [d]Karadede and Ünlü (2000)

The results of correlation analysis were shown in Table 2. The significant positive correlations are between pH and EC, TSS and EC, SAR and EC-TSS, Ca and pH-SAR, Mg and TSS-SAR, Na and SAR-Ca, Mn and Ca-Na, Cu and SAR-Na-Fe, Mo and Fe, respectively. The significant negative correlations are between, Ca and TSS, Mg and Ca, Na and EC-TSS-Mg, Fe and pH-EC, Mn and TSS-Mg, Cu and pH-EC, Mo and pH-Ca-Mn, respectively. That was maybe due to the differences of local heavy metal sources.

Table 2 Correlations matrix for heavy metal concentrations and the physicochemical parameters in dam waters.

	pH	EC	TSS	SAR	Ca	Mg	Na	Fe	Mn	Cu	Mo
pH	1										
EC	**0.41***	1									
TSS	-0.03	**0.42***	1								
SAR	0.01	**0.58***	**0.97****	1							
Ca	**0.91****	-0.17	**-0.92****	**0.97***	1						
Mg	-0.15	0.21	**0.95****	**0.95***	**-0.99****	1					
Na	-0.03	**-0.74****	**-0.90****	**0.99****	**0.67***	**-0.73***	1				
Fe	**-0.98****	**-0.56***	0.01	0.03	-0.09	0.10	0.10	1			
Mn	0.28	-0.10	**-0.86****	0.03	**0.99****	**-0.97****	**0.57***	-0.16	1		
Cu	**-0.58***	**-0.97****	-0.26	**0.42***	0.06	-0.10	**0.58***	**0.72***	0.02	1	
Mo	**-0.94****	-0.20	0.16	0.03	**-0.41***	0.35	-0.01	**0.89****	**-0.51***	0.34	1

Bold values are significant.

* Correlation is significant at the 0.05 level

** Correlation is significant at the 0.01 level

Fe, Mn, and Cu were the most abundant elements in the reservoirs, whereas Mo was the less abundant. During the study period, heavy metals studied did not show significant spatial variations. The highest the metal concentrations in the dam reservoirs were observed at sites, which are located at the entrance of the streams to the reservoirs (sites 1,6). pH, TSS, EC, SAR and cation contents are within an acceptable range for irrigation water. When compared to drinking water quality guidelines established by WHO, EC and USEPA, Fe, Mn and Cu were determined as potential pollutant in the dam reservoirs and it may pose health risk for the residents in the region. All heavy metals showed significant temporal variations. Cu and Mo displayed higher values in the dry season, while higher values for Fe and Mn in the wet season. The anthropogenic activities contributed more to the main sources of heavy metals, and contamination factors indicated that Fe, Mn and Cu pollution was serious in study area.

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