Assessment of Groundwater Pollution Parameters in the Amik Plain

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1. Introduction

Water is one of the most important natural resources to sustain life. Ascertaining its quality is very crucial before it is used for drinking, agricultural and industrial purposes and by aquatic life. However, all available water bodies are not suitable for all different uses (Khan et al. 2003). Freshwater is one of the basic necessities for life sustenance, human consumption, and habitats. But only 2.5% of all waters on Earth are freshwater. Because, nearly 70% of freshwater is frozen in the ice-caps of Antarctica and Greenland, only 1% of world's freshwater is also accessible for direct human uses. This is the water found in lakes, rivers, reservoirs and those underground sources (Ebrahimi et al. 2011). Groundwater is the major source of freshwater for drinking, irrigation, and industrial uses. For its sustainable use, both the quantity and quality issues have to be addressed together (Kumari et al. 2014).

The water quality used for irrigation is very important for agricultural production and to ensure environment protection. Water contains some salts as dissolved ions. Excessive amounts of dissolved ions in irrigation water can affect plant growth, and the physical and chemical properties of the agricultural soil. It also reduces soil fertility and crop yields (Ayers and Westcot 1994).

Groundwater is one of the major sources of exploitation in arid and semi-arid regions (Khasei-Siuki and Sarbazi 2015). Groundwater quality can be affected by numerous types of human activity such as agricultural, residential, industrial and municipal activities (Nas and Berktay 2010). The variety and extent of groundwater chemical composition could also be influenced by natural processes such as evaporation, dissociation of minerals, mixing of water, rock weathering, and human activities. The geochemistry of soil and the geological history of rocks have a significant impact on the chemical contamination of groundwater. Therefore, any groundwater suitability assessment for agriculture should include their chemical composition (Narany et al. 2014). Agricultural, industrial and domestic activities degrade the quality of groundwater supply (Anonymous 1979).

According to the Turkish General Directorate of State Hydraulic Works (DSI), the available surface water potential of Turkey totals 98 billion m^3 while total annual groundwater resource is approximately 14 billion m^3. The total usable annual surface and groundwater potential of Turkey is 112 billion m^3. 37% of the groundwater is used for irrigation, 24% for industrial purposes and 39% domestic purposes. In Turkey, uses of groundwater for irrigation take place to a great extent on lands where irrigation network is inadequate. As of 2012, a total agricultural land area of 667.080 ha is irrigated by groundwater (DSI 2013).

Contamination of groundwater by domestic and industrial effluents and agricultural activities is a serious problem faced by developing countries. The industrial wastewater, sewage sludge and solid waste materials are currently being discharged into the environment indiscriminately. These materials enter subsurface aquifers, resulting in the pollution of irrigation and drinking water (Ebrahimzadeh and Boustani 2011).

All over the world, wherever nitrogenous fertilizers have been used extensively to increase the agricultural productivity, the groundwater shows a high nitrate level. Often, nitrate contamination of groundwater may be also associated with point sources such as domestic sewage, industrial waste, livestock feeding operations and septic tanks, etc. Various physical, chemical, and biological processes in the soil zone and groundwater determine the nitrate level in groundwater (Johnsson et al. 2002). Agricultural systems also contribute to excessive phosphorus (P) additions that are adversely affecting water sources worldwide (Webb et al. 2004).

2. Evaluation of pollution parameters in groundwater in the Amik plain

The Amik plain is situated in the Asi basin and has an area about 75000 ha (Figure 1). It is surrounded by the Amanos Mountain to the west, the Syrian border and the town of Reyhanli on the east, Antakya and Altınözü cities to the south, and the towns of Hassa and Kirikhan to the north. The area has a Mediterranean climate with annual average temperature rainfall and relative humidity 18.8°C 1124 mm and 69% respectively (Gün and Erdem 2003). Parent materials of the Amik Plain consist mostly of alluviums and lacustrine. Lacustrine is relatively flat and often has parent materials with uniform properties. Amik plain is one of the most productive agricultural lands in Turkey. Main crops in the plain are cotton, maize, and wheat (Kilic et al. 2008).

The most important formations bearing groundwater in the Amik plain are quaternary alluvium, Pliocene, Miocene, Sandstone, and conglomerate marl and limestone. Alluvial exist together with hillside rubbles in the eastern parts of Antakya-Kirikhan highway. The groundwater recharge occurs through infiltration from precipitation and from surface runoff and while discharge occurs through evapotranspiration and the flow from springs. Groundwater recharge and discharge capacity is in equilibrium at $57.5x10^6 m^3$/year. The amount of groundwater that can be taken safely from alluvial aquifer in the Amik plain is $9.5x10^6$ m^3/year (DSİ 1975; Karatas and Korkmaz 2012). The depth of the well from the surface range from 35 m to 140 m (mean 92 m).

In the studies conducted by Agca (2014) and Agca et al. (2014), a total of 92 groundwater samples were collected from drilled wells in the Amik plain in June 2012 to evaluate pollution parameters. The groundwater samples were analyzed for electrical conductivity (EC), total dissolved solids (TDS), pH, major cations [sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+})] and major anions [carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), chlorine (Cl^-) and sulfate (SO_4^{2-})], dissolved oxygen, ammonium (DO), (NH_4^+), Nitrate (NO_3), phosphorus (P) and heavy metals (Cd Co, Cr, Cu, Fe, Mn, Pb, Ni, and Zn) contents were determined the groundwater in the Amik plain In addition, sodium adsorption ratio (SAR), residual sodium carbonate (RSC) and total hardness (TH) were calculated from measured data to evaluate groundwater quality and classification.

In order to evaluate the contamination of groundwater regarding physicochemical variables and heavy metal pollution, their concentration were compared with World Health Organization standards (WHO 1997 and 2004), Classification of Turkish Water Pollution Control Regulation (TWPCR 2008) and FAO standards (Ayers and Wescot 1994).

Figure 1 – Asi River basin

https://www.water-security.org/article/the-orontes-a-complex-river

According to results of Agca (2014), among the parameters, the coefficients of variations (CV) were the highest for Ca^{2+} (113.63%) and the lowest for pH (3.59). Usually, CV<10% represents low variability, 10%≤CV≤100% means moderate variability, and CV>100% means high variability (Zhou et al. 2011). According to this classification, all the groundwater parameters except pH, Ca^{2+} and Cl^{-}, have the moderate variability. The pH value has weak variability while Ca^{2+} and Cl^- have the strong variability. Low CV values indicate a homogeneous distribution of soil variables, while high CV values indicate a non-homogenous distribution of variables in the study area. For example, the mean pH values in both seasons were close to that of median values. In other words, the range of pH values were fewer variables than the range of other parameter values.

Na^+ ion (average content of 183.0 mg L^{-1}) dominates while K^+ ion (average content of 3.62 mg L^{-1}) has minimum value among the cations. Mg^{2+} and Ca^{2+} are between Na^+ and K^+. The SO_4^{2-} ion (average content of 303.2 mg L^{-1}) has maximum average value while CO_3^{2-} + HCO_3^- have minimum value among the anions. Cl^- and HCO_3^- are between SO_4^{2-} and CO_3^{2-}. In the bed of the old Amik Lake, EC, Cl^- and SO_4^{2-} concentration in groundwater are very high in comparison with other parts of the region (Agca 2014). This is because of the deposits in this region and the soils that are formed on these deposits. The soils in this region have very high salts and gypsum (DSI 1989; Agca et al. 2000; Kilic et al. 2008. Agca et al. 2006) were found high concentration of EC, Cl^- and SO_4^{2-} in the groundwater in the same area.

According to results of Agca et al. (2014), Fe (Iron) had the highest mean concentration in the groundwater, followed by Mn, Ni, Cr, Cu, Zn, Co, Cd and Pb. The highest Co value was determined as 21.10 µg/L. The 83 of 92 groundwater samples exceeded the permissible limit of Co content (10 µg/L) set by the Turkish Water Pollution Control Regulation (TWPCR) (2008). The highest Cr value was recorded as 353.60 µg/L. 54 of 92 groundwater samples were below the permissible limit of Cr concentration (20 µg/L) set by TWPCR (2008). The highest Cu content was 54.90 µg/L. According to these results, 31 out of 92 groundwater samples exceeded the permissible limit of Cu concentration (20 µg/L) set by TWPCR (2008). The highest Fe value was found as 657.10 µg/L in wells. In this study, 15 of 92 groundwater samples exceeded the permissible limit of Fe concentration (300 µg/L) set by TWPCR. The highest Mn value was recorded as 1026.10 µg/L). A total of 26 groundwater samples exceeded the permissible limit of 100 µg/L set by TWPCR (2008). The highest Ni values in groundwater samples in Amik plain were found to be 161.80 µg/L. Only in 6 out of 92 groundwater samples, Ni contents were below the permissible limit of 20 µg/L set by TWPCR. Pb could not be detected in any of the groundwater samples. Therefore, Pb in all the groundwater samples was below the limit of 10 µg/L set by TWPCR (2008). The highest Zn value in the Amik plain was recorded as 193.90 µg/L. In this study, Zn concentrations of all the groundwater samples were below the permissible limit of concentration (200 µg/L) set by TWPCR (2008).

2.1 Assessment of groundwater quality for drinking purpose

According to results of Agca (2014), in the Amik plain, the pH values varied from 7.10 to 8.37 with an average value 7.79, indicating the slightly alkaline nature of groundwater. All the groundwater pH values in the study area were within the desirable limits (7.0-8.5) prescribed by WHO (1997). Electrical Conductivity (EC) measures the salt concentrations of water and provides indication of ionic concentrations. The EC in 1.1 % of the total samples is lower than the maximum desirable limit of 750 µS/cm and is more than highest permissible limit of 1500 µS/cm in 52.2 % of the total groundwater samples. Higher EC values in the study area indicate the enrichment of salts in the groundwater. Approximately 98.9 % of the samples are above the maximum desirable limit of 500 mg/L of TDS which can be used for drinking without any risk and 29.3% of the total groundwater samples have more than the highest permissible limit of 1500 mg/L of TDS. All the samples are more than the maximum desirable limit of 100 mg/L of TH that can be used for drinking without any risk and TH in 73.9 % of the total groundwater samples are lower than the highest permissible limit of 1500 mg/L. On the other hand, according to the total hardness classification recommended by Sawyer and Mcartly 1967 (Alam et al. 2012), 2.2% of the water samples fall in hard class (150-300 mgL^{-1} total hardness as $CaCO_3$) and 97.8% of the samples also fall in the category of very hard class (<300 mgL^{-1} total hardness as $CaCO_3$).

Na^+ in 12% of total samples are below the most desirable limit of 50 mg/L that can be used for drinking without any risk, while Na^+ content in 66.3% of all the samples are below the maximum allowable limit of 200 mg/L. On the other hand, all the groundwater K^+ values in the study area were below the recommended value of 100 mg/L. Ca^{2+} in 92.4% of the samples were below most desirable limits of 75 mg/L, however only 2.2% of the samples exceed maximum allowable limit of 200 mg/L. All the groundwater Mg^{2+} contents in the study area were between the most desirable limit of 30 mg/L and maximum allowable limit of 150 mg/L. HCO_3^- in 65.2% of total samples were below the desirable limit of 200 mg/L while HCO_3^- in all the groundwater were below the maximum allowable limit of 600 mg/L. In 67.4% of the samples, Cl^- contents are below the most desirable limit of 250 mg/L. However Cl^- in 9.8% of samples exceed maximum allowable limit of 600 mg/L. SO_4^{2-} in 33.7% of total groundwater samples are below the most desirable limit of 200 mg/L while only SO_4^{2-} contents of 9.4% of samples are determined above the maximum allowable limit of 600 mg/L.

According to Agca et al. (2014), in the groundwater of the Amik plain, the temperature values in the groundwater ranged from 18.7 to 33.0 ^0C. In 73.0% of the samples exceeded the permissible limit of 25^0C suggested for very high quality classes by TWPCR (2008). Dissolved oxygen (DO) varied from 08.9 to 13.18 mg/L. The DO concentration in only 5 samples were found to have higher than the permissible limit of 8 mg/L for high quality classes (TWPCR 2008). Nitrates are the end product of aerobic stabilization of organic nitrogen and a product of conversion of nitrogenous material, and as such occur in polluted water. The highest NO_3^- concentration recorded as 300 mg/L and lowest as 0.38 mg/L in this study. The desirable limit of nitrate for drinking water is specified as 50 mg/L recommended by WHO (2004). In this study, only 12 of the 92 groundwater samples from the study area exceeded the desirable limit of 50 mg/L.

P values in groundwater ranged from 0.021 mg/L to 0.250 mg/L. There are no health-based guidelines on P values for water prescribed by the WHO, however, the Food Standards Agency (2003) has determined the guideline value for P in drinking water. According to the Food Standards Agency (2003) PO4-P limits is 2.2 2.0 mg/L.

In this study, all the groundwater samples taken from wells had higher Cd concentration than the guideline value for drinking water of 3 μgL^{-1} recommended by the WHO (2004). In the 7 of 92 samples, Cr concentration exceeded the guideline limit of 50 µg/L while the Cu concentrations of all the groundwater samples were below the guideline limit of 2000 µg/L by WHO. The Fe concentrations of all the groundwater samples were also below the guideline limit of 300 µg/L. In 3 of 92 samples, Mn concentration exceeded the guideline limit of 400 μgL^{-1} while Ni concentrations in a total of 23 samples exceeded the guideline limit of 70 µg/Lby WHO. This situation also results from Ni content of the fertilizers containing P expand, since phosphorus fertilizers a lot of Ni content (Koleli and Kantar 2005). In all the groundwater samples, Zn concentration did not exceed the guideline limit for drinking water of 4000 µg/L suggested by WHO (2004). The cadmium and nickel concentrations exceeded the maximum allowable limit also recommended by WHO in 24% and 70% of sample locations, respectively.

2.2 Assessment of groundwater quality for irrigation purpose

The evaluation of groundwater quality for irrigation is based on pH, EC and TDS values and calculation of chemical index like sodium adsorption ratio (SAR) and residual sodium carbonate (RSC), nitrogen, phosphorus and heavy metals.

Despite the pH values varied from 7.10 to 8.37 with an average value of 7.79 in the two periods, pH values varied between 7.10 and 7.50 in 19.6% of the samples, between 7.5 and 8.0 in 55.4% and between 8.00 and 8.35 in 25%. These results show that approximately 80% of groundwater is suitable for irrigation with respect to pH values. It is doubtful whether the remaining water is suitable for irrigation or not. This is because its pH values are close to 8.5 which is the highest limit for soil alkalinity (Richards 1954). But, research by Keskin et al. (1999), Agca et al. (2000) and Kilic et al. (2008) have not found alkalinity problems in the Amik plain, until now.

Electrical conductivity (EC) is routinely used to measure salinity (Richards 1954). Electrical conductivity (EC) is a good measure of the salinity hazard to crops as it reflects the TDS in groundwater as well as other water resources. The EC values of groundwater in the study area have very large variation from 456.9 to 13112.0 µS/cm. The large variation in EC is mainly attributed to geochemical processes prevailing in this region.

The US salinity laboratory diagram (Richards 1954) was used to evaluate the suitability of groundwater for irrigation purposes by Agca (2014). According to this classification, 3.3% of the groundwater samples in the study area fall in the C4S4 that has very high salinity and very high sodium hazard. These waters have very high salinity and very high sodium hazard. Therefore these waters are not suitable for irrigation under ordinary conditions. Nearly 4.3% of the groundwater samples fall in the C4S3 class. These waters have very high salinity and high sodium hazard. This water is not also suitable for irrigation. Because, these water have very high amount of salt and high amount of Na^{+}. 17.4% of the groundwater samples fall in the category C4S2 that has very high salinity and medium sodium hazard. This water is not suitable for irrigation, since the water has a very high amount of salt and induces a potential hazard dues sodium in fine-textured soils having cation exchange capacity. As much as 3.3% of the groundwater samples in the study area fall in the C4S1 having very high salinity and low sodium hazard. In fact, this water could be suitable for irrigation with respect to sodium adsorption ratio (SAR) values, but because of limiting of very high salt content, is not suitable for irrigation. About 4.3% of the water samples fall in the C3S2. This water has high salinity and medium sodium hazard. This water cannot be used on fine-textured soils with restricted drainage. If drainage is adequate or soils have coarse textured it may be used for irrigation on salt tolerant crops. As much as 66.3% of the water samples fall in the C3S1 having high salinity and low sodium hazard. This water can be used almost all soils with little danger of the development harmful levels of exchangeable sodium with respect to SAR values. However, even then this water cannot be used on soils with restricted drainage. If drainage is adequate or soils have coarse textured it may be used for irrigation on salt tolerant crops.

The residual sodium carbonate (RSC) values of the groundwater samples in the study area were found between -40.6 and 2.39. In all the water samples, the RSC of almost all the water samples have less than 1.25 me/L confirming that the water in the area is suitable for irrigation with respect to RSC. Moreover, RSC values all groundwater samples except 4 samples have negative RSC values. These results indicated that Ca^{2+} + Mg^{2+} did not precipitate completely Ca^{2+} and Mg^{2+} as carbonate. Because the excess of CO_3^{2-} + HCO_3^{-} over Ca^{2+} + Mg^{2+} may cause complete precipitation of Ca^{2+} and Mg^{2+} as carbonate.

The NO3-N values in the groundwater changed between 0.09 mg/L and 67.74 mg/L. In the 12 water samples, The NO3-N values are bigger than the maximum recommended concentration for irrigation water of 10 mg/L NO3-N (44 mg/LNO_3^{-}) proposed by Ayers and Westcot (1994). NH4-N concentrations in groundwater samples were found to vary between 0.11 mg/L and 163.72 mg/L. In 34 of 92 samples, NH4-N contents were higher than maximum permissible limit for irrigation water of 5 mg/LNH4-N (6.1 mg/LNH_4^{+}) recommended by Ayers and Westcot (1994). FAO determined the maximum recommended concentration for P in irrigation water.

According to FAO (Ayers and Westcot 1994), a PO4-P limit is 2.0 mg/L. None of the groundwater samples in this study exceeded P limit.

All the Co, Cu, Fe, Ni and Pb and Zn values in groundwater were below recommended maximum concentration values of 50, 200, 5000, 200 and 5000 µg/L respectively, for irrigation set recommended by FAO (Ayers and Westcot 1994). Cadmium concentration of 76 groundwater samples is higher than recommended maximum concentration of 10 µg/L suggested by FAO. This situation results from phosphorus fertilizers since their Cd contents are very high (Koleli and Kantar 2005). Chromium content of 89 groundwater samples was lower than recommended maximum concentration of 100 µg/L for irrigation water proposed by FAO. Only in 5 groundwater samples, Mn concentrations exceeded the recommended maximum content of 200 µg/L set by FAO. None of the groundwater samples in this study exceeded P limit.

3. Evaluation of pollution parameters in Asi River

The Asi River is one of the most important surface water sources in the Middle East and is the most important surface water for the Amik plain. Asi River is transboundary rivers in the Middle East region. It rises in Lebanon and passes through three countries' territories. These counties are Lebanon (upstream), Syria (midstream) and Turkey (downstream). The Asi discharges into the Mediterranean Sea at the southern edge of Samandag, Hatay in Turkey (Scheumann et al. 2011). The total length of this river is approximately 400 km, the section in Turkey being about 88 km. It is presently used for the irrigation of 12.000 ha land on Amik plain and another 50.000 ha is being planned to be irrigated (Altunlu 2002). The main flow rate of the Asi River ranged annually between 2.39 (in July) and 22.96 $m^3\ s^{-1}$ (in February) according to the data of the period during 1995-2002 (Eie 2003).

In the research by Agca et al. (2009), 12 sampling sites were selected along the Turkish section of the Asi River (Fig. 2). The samplings from these sites were carried out at six different times: starting in October 2004, and continuing in January, May, July, September and November in 2005. Water samples were analyzed for temperature (T), electrical conductivity (EC), pH, Na, K, Ca, Mg, Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, P, CO_3, HCO_3 and Cl were volumetrically determined. In addition, sodium adsorption ratio (SAR) was calculated from Na, Ca and Mg values.

3.1. Evaluation of physicochemical parameters

The electrical conductivity (EC) and sodium adsorption ratio (SAR) values changed between 745.5- 1699.6 S cm^{-1} and 0.75–1.71, respectively, during the study period. According to the classification of USSL (Richards, 1954), irrigation water quality class of the Asi River was C3S1 (with high salinity and low sodium hazard) within all sampling sites and at all times. Similar results were also reported by Agca et al. (2006) and Odemis et al. (2006). The differences in EC values among the sampling times were found to be statistically significant ($p<0.01$). The EC values were the highest in January and the lowest in November. Intensive agricultural activities on the Amik plain elevated the use of fertilizers and other chemicals. The Amik plain has water table (Anonymous 1986) that enables upward transport of salts mainly Na and Mg chlorides in dry summer seasons. These salts are leached away by means of surface run off to the Asi River with winter precipitations. In addition, starter fertilizers applied in wheat sowing can leach, to some extent, with winter rainfall as well. Therefore, leaching of the soil by winter precipitation caused an increase in the values of EC, Na, Mg and Cl at the sampling time of January 2005. The EC values were relatively low from May to September, which is the irrigation season in the study area. This outcome may be considered advantageous for irrigation. But, the EC values of the river were still high for various management. In fact, in a research related to the salinization tendency of the soil, about 28130 ha land was classified as slightly saline and around 2600 ha as saline in the Turkish part of the Asi River basin (DPT 1997). The temperature values of the river water vary significantly within the sampling times. This parameter under the influence of the climate of the region peaked in July and decreased during winter months. The temperature variations within the sampling times, indicated by the standard error values, were the lowest in May and September. Regarding the chemical properties, the highest levels except for K were recorded in January, whereas the lowest pH, Na, and Cl values were measured in November. All of the aforementioned parameters were significantly different within the sampling times (p<0.01). Phosphorus was recorded as a potentially hazardous element to aquatic life and water quality. The P content ranged from 13.64 to 1097.70 µg L-1 during the study period, in general being very low in winter months; but started increasing in May 2005 and attained its maximum in July 2005.

Figure 2 – Sampling sites on the Asi River

The spatial changes in physico-chemical properties of the river water were not statistically significant, except for the pH. The variations of the pH values among sampling sites were significant (p< *0.01*) also. The EC values increased from Demirköprü towards Antakya city center because of discharges from nearby cities and inclusion of drainage water from the drainage channels. The lowest EC values were recorded at sites 1 and 12. Little creeks and streams that flow into the Asi River at sites 10 and 11 decreased salt content of the river water. The highest Cl values were measured at site 12 (Figure 2) along the river. This situation is probably related to the mixing of the river water with the seawater. Measured temperature values of the river water did not differ significantly within sampling sites but it was higher, on average, at site 12 than the other sites (Agca et al. 2009). This situation was probably related to broader river-bed and shallower water depth at this site since the temperature in rivers changes in accordance with the altitude, climate, atmospheric conditions, flow rate, and structure of the river-bed (Cirik and Cirik 1995). The P concentrations of river water were very high at sampling site 8 through 12. For example, in July, the P concentrations at the points 8 and 9 (Antakya city center) were 1061.8 and 1097.7µ g L-1, respectively. The reasons for such an increase in P content of the river may be the addition of drainage waters from agricultural lands, sewage sludge discharges from nearby cities and the inevitable decline in the water content of the river during summer months. In fact, agricultural and urban activities are considered as the major sources of P additions to aquatic ecosystems (Wu 2005; Rogel et al. 2006). Earlier reports showed that detergents are one of the most important factors in the P enrichment of natural surface water resources (lakes and rivers) in Turkey (Sengül 1991).

3.2 Evaluation of heavy metal contents

All metal contents of the Asi River during the study period were found to be considerably lower than the allowed maximum concentration of trace elements in irrigation water recommended by FAO (Pais and Jones 1997). In other words, there was no metal pollution in the river during the period of the investigation. This situation is most likely related to the small number of industrial plants in Turkish part of the Asi River basin. The reports in various basins reveal that the elevated water pollution is related to the regional industrial development and technological levels of the industrial plants. For example, in the Southern Thrace, which is one of the most important industrial centers in Turkey, it was reported that Hg, Cd and Zn contents were low whereas Cr and Pb were high in the surface water owing to automotive, dyeing and textile industry in the region (Aksoy 1993). Until recently, rivers have been utilized as the easiest and cheapest means for the disposal of municipal wastes without proper treatment, especially near highly populated cities. Therefore, organic contaminants and P contents of the rivers have been higher near the cities. Some significant differences were detected between the sampling times for all metal concentration except for Ni (p<0.01). When the mean concentrations of metals were compared, sampling times 3 and 4 (May and July) yielded significantly higher concentration than the other sampling times. The concentrations of Cr, Fe and Mn increased markedly at sampling time 4 and they were the lowest at sampling times 2, 5 and 6. Among the metals, the highest variation in concentration was observed for Al. However, there was no significant seasonal difference in Ni concentration. The remaining metals could be placed in two or three statistically different groups. The spatial differences in metal contents were not statistically significant except for Ba (p>0.05). When the mean values were considered, metal contents except for Cd, Cr, Ni, and Fe were lower at the sites 1, 2 and 3 (on the Syria-Turkey borderline) than those of the other sampling sites. But, the Cd, Cr, Ni, and Fe contents were also found to be relatively high at these sites. In general, it was observed that heavy metal concentrations were high near Antakya city center (sites 8 and 9) because of small industrial estate and leather industry (Agca et al. 2009).

The order of heavy metal was found to be Fe>Mn> Cu > Ni > Cr >Pb> Co > Cd for all water samples. The contents of Cd, Co, Cu, and Pb in all samples and Cr, Fe, Mn and Ni in 90% of all samples were found to be below the limits for class one (high quality) according to Water Pollution Control Regulation (Anonymous 1988). In other words, there was no heavy metal pollution in the water resources investigated. It is most likely that this situation resulted from no intensive industrial and domestic activities in the study area. Because, industrial and domestic activities may degrade the quality of underground water supply (Anonymous 1979).

4. Conclusion

Inadequate rainfall in Amik plain area makes the irrigation requirement peak in the summer. Surface and groundwater are the main sources of the irrigation in the Amik plain. But, drainage water is also used when other sources became inadequate. In addition, local people use well water for drinking purposes. Because of these reasons, groundwater quality is very important in the Amik plain.

The results of Agca et al. (2006) indicated that groundwater in the Amik plain have dominance of physiologically neutral salts such as NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$. Therefore, these salts cannot increase pH of the water environments because such salts do not hydrolyze in water. The pH values of all groundwater sources being below 8.5 (the limit values of alkalinity) supported this situation. The most of the groundwater samples of RSC values were found negative. In addition, the most of the samples of SAR values were lower than 10. Therefore, most of the groundwater can be safely used for irrigation considering alkalinity. Nearly 29% of the total groundwater is not suitable for irrigation because of high and very high EC values (>2250 µS/cm). Other water can be used for irrigation if adequate leaching occurs and plants that can be resistant to salts grow. The results of studies of the groundwater in Amik plain indicated that the number of wells with high NH_4^+content is more than that of with NO_3^-. But there was no NO_3^-, NH_4^+ and PO_4^{3-} pollution in the groundwater of Amik plain. Temperature and salt content seemed to be problems in some of the groundwater, but dissolved oxygen deficiency were the main problem in all the examined groundwater in the Amik plain.

The metal concentrations showed a dominance in the order of Fe >Mn> Ni> Cr> Cu> Zn> Co> Cd>Pb in the groundwater in the Amik plain. They all had much higher Cd concentration than the guideline value for drinking water while the Cu and Fe concentrations of all the groundwater samples were below the guideline limit recommended by the WHO. Physicochemical properties and heavy metal studies of Amik plain indicated that the main sources of nitrogen and some heavy metal pollution in the study area, are because of the agricultural activities. There were no industrial activities or heavy traffic in and around Amik plain.

The Asi River water has a slightly – moderately alkaline reaction ranging from pH 7.47 to 8.57. Therefore, also considering the relatively low SAR values, the river water is not expected to cause sodicity. According to the EPA, optimum pH values of fresh water can be between 6.5 and 9.0. As a concluding remark, it can be stated that content please qualify are soluble salts and P are the most critical parameters, for treating aquatic life and agriculture in the lower Asi River basin. As stated earlier, the quality of the Asi River water is C3S1; thus its use without consideration of soil parameters (i.e. ECe, ESP) and plant requirements (i.e. ECw tolerance) for irrigation and without proper allowances for leaching requirements may cause rapid degradation of the soil. Further, keeping this mind, irrigation methods with minimum water consumption such as drip irrigation should be preferred instead of the conventional methods to minimize the rate of salt accumulation in the soil and save water.

Higher quality surface water resources instead of groundwater resources should be used to prevent increasing soil salinity and protect human health. For this purpose, The Turkish State Hydraulics Work has been constructing dams in the Amik plain. Besides, groundwater and Orontes river quality must be continuously monitored.

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