

Water quality and geochemistry evaluation of groundwater upstream and downstream of the Khirbet Al-Samra wastewater treatment plant/Jordan

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Abstract Groundwater in the northeastern Amman-Zarqa basin is an important source of water for irrigation. The quality and quantity of water has deteriorated due to mismanagement and misunderstanding of the hydrogeological system. Overexploitation of groundwater resources upstream of the Khirbet Al-Samra wastewater treatment plant (KSWTP) has lowered the water table 43 m since the beginning of groundwater development in 1968. Heavy pumping of groundwater downstream of KSWTP has not dropped the water level due to constant recharge from the Zarqa river bed. The water level of groundwater is rising continuously at a rate of 20 cm per year since building the KSWTP in 1985. Groundwater salinity has also shifted the quality of the aquifer from fresh to brackish. Continual irrigation from the groundwater upstream of KSWTP dissolves accumulated salt from the soil formed by evaporation, and the contaminated water infiltrates back to the aquifer, thereby increasing both salt and nitrate concentrations. The intense irrigation from the reclaimed water downstream of KSWTP and leakage of treated wastewater from the Zarqa River to the shallow groundwater is a secondary source of salt and nitrates. The isotopic composition of groundwater varies over a wide range and is associated with the meteoric water line affected by

Mediterranean Sea air moisture. The isotopic composition of groundwater is represented by evaporation line (EL) with a low slope of 3.6. The enrichment of groundwater in $\delta^{18}\text{O}$ and δD is attributed mainly to the two processes of evaporation before infiltration of return flow and mixing of different types of water in KSWTP originating from different aquifers. The EL starts from a location more depleted than the weighted mean value of the Amman rainfall station on the Eastern Meteoric Water Line indicating that the recharge took place under the climate regime prevailing today in Jordan and the recharge of the groundwater originates from a greater elevation than that of the Amman station. Elevated high tritium levels observed in wells in close proximity to a regional fault system signify local recharge and short residence time. The Khaldyia dam is a local source for groundwater recharge.

Keywords Salinity · Over-exploitation · Return flow · Recharge · Environmental isotope · Fault

Introduction

Jordan is categorized as the fourth water poorest country in the world, the allocation per capita reaches less than 150 l/capita/day (Alkhaddar et al. 2005). This water scarcity restricts economic growth (Al-Hadidi 2011), and decision makers are challenged to secure additional potable water for an increasing population, agricultural activities, and growing industry. Very soon, more water will be required for cooling a proposed nuclear power plant in the study area. The climate of the region is considered arid, and water resources in the study region depend on precipitation. Average precipitation and evaporation is 150 and 1,500 mm/year respectively in the study area (WAJ 2003).

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The intensive use of groundwater for agricultural activities disturbed the aquifer balance, and a major decline in water level accompanied by deterioration in groundwater quality has taken place. The decline of groundwater levels due to over-pumping exceeds the recognized safe yield. The salinity increased from 265 part per millions (ppm) to more than 4,000 ppm at present and nitrate concentration in some wells has reached more than 300 ppm.

To reduce the amount of groundwater use for agriculture and prevent further decline in the water table of the aquifer, the water authority built in 1985 the Khirbet Al-Samra wastewater treatment plant (KSWTP) in the region with an intent to make the plant a reliable and sustainable water resource for irrigation purposes.

Wastewater use in irrigation is a widespread practice worldwide. For centuries, farmers in China, northern Europe, and Mediterranean countries used human and animal manure as fertilizers. In the Middle East, countries such as Egypt, Lebanon, and Morocco have used wastewater a source of crop nutrients over many decades (Jiménez and Asano 2008). Worldwide, the land irrigated with wastewater or polluted water is estimated to be 40–60 thousand square kilometers (Keraita et al. 2008). A study by the World Health Organization estimated that the land irrigated by wastewater is nearly equivalent to 7 % of the total irrigated land in the world (WHO 2006).

The biggest user of wastewater in undeveloped countries is the agriculture sector, which makes wastewater a valuable and reliable source of water. It is available all year round, unlike precipitation or perennial streams especially in arid areas (Jiménez and Asano 2008; Raschid-Sally et al. 2005). This allows farmers to produce year-round production with multiple cultivation cycles (Keraita et al. 2008).

Despite the great benefit of using the treated wastewater in agriculture, it becomes apparent that this application comes with a negative impact on the environment and health risks to human from microbiological pathogens. Risks of infection with the bacteria “*Giardia*” in developing countries have been associated with wastewater reuse, and have been reported in Mexico (Cifuentes et al. 2000) and in the Jordan Valley, Jordan (Mutaz 2007). Heavy metals in plants grown in wastewater-irrigated soil were also observed in high concentration in China (Khan et al. 2008). It generates high rates of solute infiltrate into the underlying aquifers, and has had an effect on the rates and compositions of groundwater recharge and aquifer geochemistry. It dissolves and transports excess quantities of fertilizers to the subsurface, enhancing the water–rock interactions in soils and aquifers caused by increased concentrations (Böhlke 2002).

Numerous studies at various locations worldwide showed that the chemical makeup of shallow aquifers have been altered from agricultural practices and fertilizers.

Agricultural contaminant loads in recharging groundwater have resulted in problems related to water quality and its suitability for different uses (Fan and Steinberg 1996; Bajjali 2006).

Agricultural activities usually lead to higher salinity and affected the concentrations of a large number of inorganic chemicals in groundwater, for example: NO_3^- , Cl^- , SO_4^{2-} , H^+ , PO_4^{3-} , HCO_3^- , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} (Ma et al. 2005; Böhlke 2002). The long-term irrigation, irrigation-return-flow, application of unlimited agricultural fertilizers, and recycling of saline groundwater act to further increase the salinity in the groundwater. This changes the chemical makeup of the recharging water, thus resulting in the change of the molal ratios of Na/Cl and Ca/Cl (Subba Rao 2008; Kass et al. 2005; Bajjali and Al-Hadidi 2006).

Other studies also indicate that agricultural practices with treated wastewater have resulted in nitrate contamination of groundwater, with concentrations commonly exceeding the drinking-water maximum contaminant level of 45 ppm. In the state of California, 10 % of public water-supply wells exceed the maximum contamination level of nitrate due to agricultural activities (Ekdahl et al. 2009). Irrigation resulted in groundwater becoming contaminated by nitrate to great depth (Chena et al. 2006; Seiler 2005; Moore et al. 2004). High NO_3^- concentration (>100 ppm) in the region’s water table was derived from nitrification of the NH_4 in the wastewater used for irrigation (Kass et al. 2005).

Contamination of groundwater adjacent to wastewater facilities discharging into surface water has been observed. The hydrological conditions created by treated wastewater discharge into streams raises the potential for contamination of shallow groundwater aquifers, especially in arid areas (Foster and Chilton 2004). In such settings, wastewater facilities act as a significant groundwater recharge zone, with high hydraulic gradients that enhance the transport of water solute transport to the nearby aquifer (Lapworth et al. 2012).

Study area

The study area is in the northeastern part of the Amman-Zarqa basin in Jordan with a total area of about 1,847 km² and consists of two main governorates: Mafraq and Zarqa (Fig. 1a).

Expansion of agricultural development in the study area began in the middle 1960s and 1970s and many wells were drilled by the private sector for irrigation. Increased pumping rates throughout the whole area, especially in Dhuleil, Halabat, and Khaldyia, caused a severe decline in the water levels in the wells in this area (Bajjali 1997).

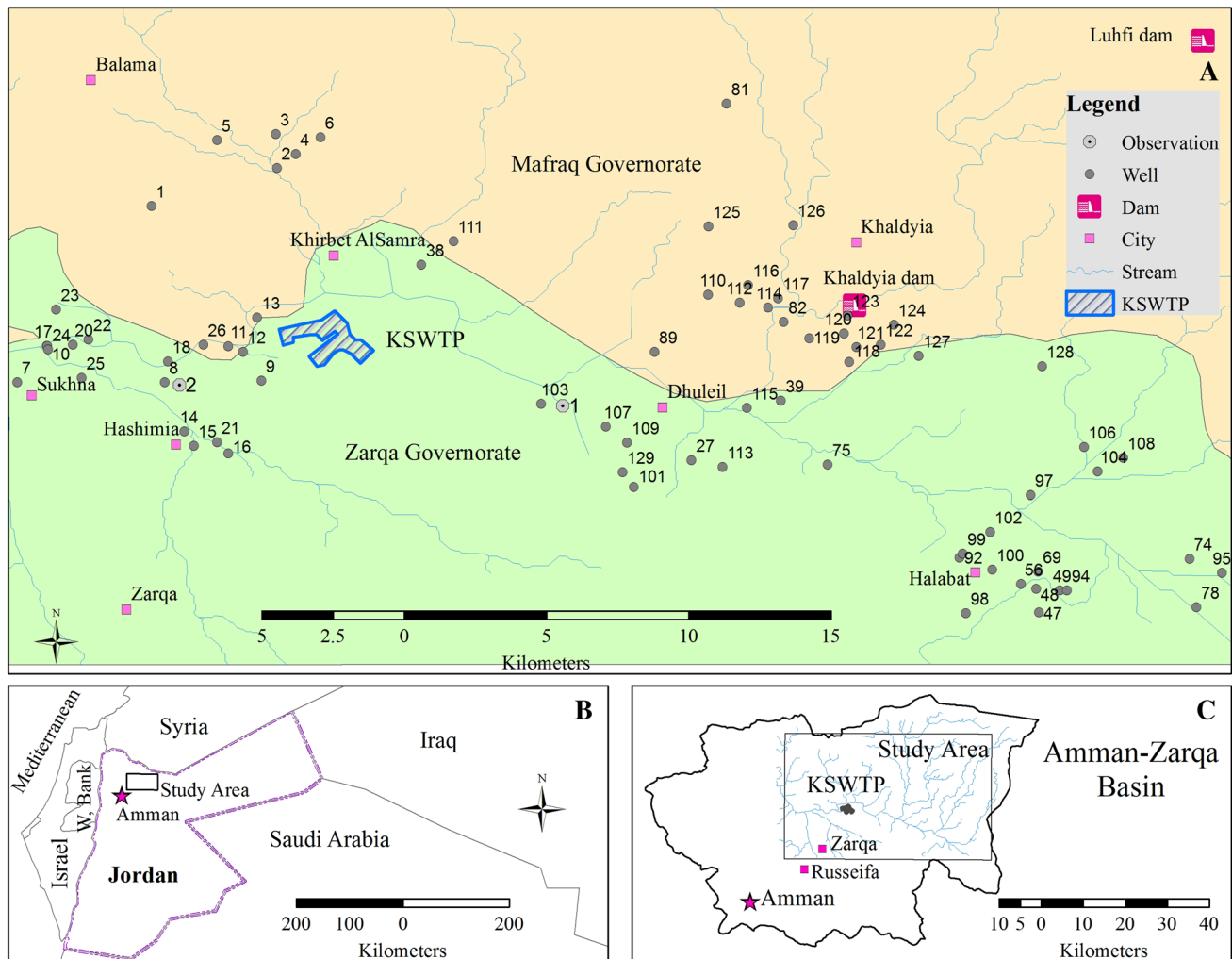


Fig. 1 Site location

The KSWTP was constructed along the Zarqa River in 1985 for treating domestic wastewater from the cities of Amman, Zarqa, and Russeifa (Fig. 1c). From 1985 to 2008 the capacity of the plant increased from 68,000 to 267,000 m³/day (RSS 2012). The plant treats around 72 % of all the wastewater in the country and currently the treated wastewater is used for agriculture. On its course to the Jordan Rift Valley (JRV), the reclaimed water is mixed with surface runoff from wadis (dry valleys) before it is stored in King Talal Dam (KTD), and spills out downstream until it reaches the JRV, where it is mainly used for irrigation (WAJ 2004).

Wastewater use for agricultural irrigation in the country is cost effective since the study area has limited water resources. It provides low cost water resources, increases crop production, reduces the dependence upon groundwater, saves the use of synthetic fertilizers (treated wastewater is rich in plant nutrients), and increases employment opportunities in the rural population.

Two small dams, Khaldyia and Al Luhfi, were constructed in 1985 to store the water from rainy seasons and are used locally for agricultural purposes and for watering livestock (Fig. 1a).

The study area is highly faulted and these fault systems can facilitate rapid infiltration of the return flow by acting as channels from the surface causing groundwater contamination (Benson 1995). Wells that were drilled along a fault system to tap the highest permeable area of the aquifer, are very likely to be affected by agricultural activities.

This study focuses on the conditions that brought the groundwater system to its current state, causing both the quality and the quantity of water to be affected. Three issues related to the groundwater upstream and downstream of KSWTP have been examined in this study: (1) fluctuation of the groundwater levels (2) salinity distribution in groundwater and its source (3) and the mechanism of recharge using the environmental isotopes.

Geology and hydrogeology of the study area

The study area is part of the Amman-Zarqa basin in northern Jordan. The geological formations in the area are mainly Cretaceous carbonate rocks with thick flows of Cenozoic basalt and Holocene alluvial deposits along the flow of the Zarqa River (Fig. 2).

The limestone and the overlying basalt are hydraulically connected and form one aquifer unit. The direction of the regional flow over the whole basin is from the northeast highlands of the Al Druz Mountains in Syria, southwest towards the area downstream of the KSWTP. There is a major NW–SE trending fault system in the area, and the basalt filled a major synclinal structure having a pitch to ESE. Both the fault system and the syncline in the area influence the permeability and groundwater recharge of the aquifer system.

Fluctuations in ground-water levels

Water levels in aquifers are a dynamic balance between recharge, storage, and discharge. If recharge exceeds

discharge, the volume of water in storage will increase and water levels will rise; if discharge exceeds recharge, the volume of water in storage will decrease and water levels will fall. Therefore, water-level measurements provide understanding into the physical properties that control aquifer recharge, storage, and discharge. These properties affect the timing and intensity of responses to hydrologic stresses such as precipitation, infiltration or pumping. Long term fluctuations of water levels, over periods of decades, can provide insight into the effects of climate and man-made activities such as pumping, irrigation, and changes in land use. Short term fluctuations can also occur in response to rainfall, pumping, barometric-pressure variations, or other phenomena (Healy and Cook 2002). The water levels in the observation wells in the study area show a completely different pattern upstream versus downstream of the KSWTP. Over the last 40 years the wells upstream of the plant, especially in Dhuleil-Halabat-Khaldyia area, show steady long-term declines with or without seasonal variations. The greatest declines in the aquifers were in the south of the study area and upstream of the KSWTP where groundwater level in observation well 1 dropped as much as 43.17 m in 44 years (Fig. 3). The decline was almost 1 m per year between 1968 and 2012.

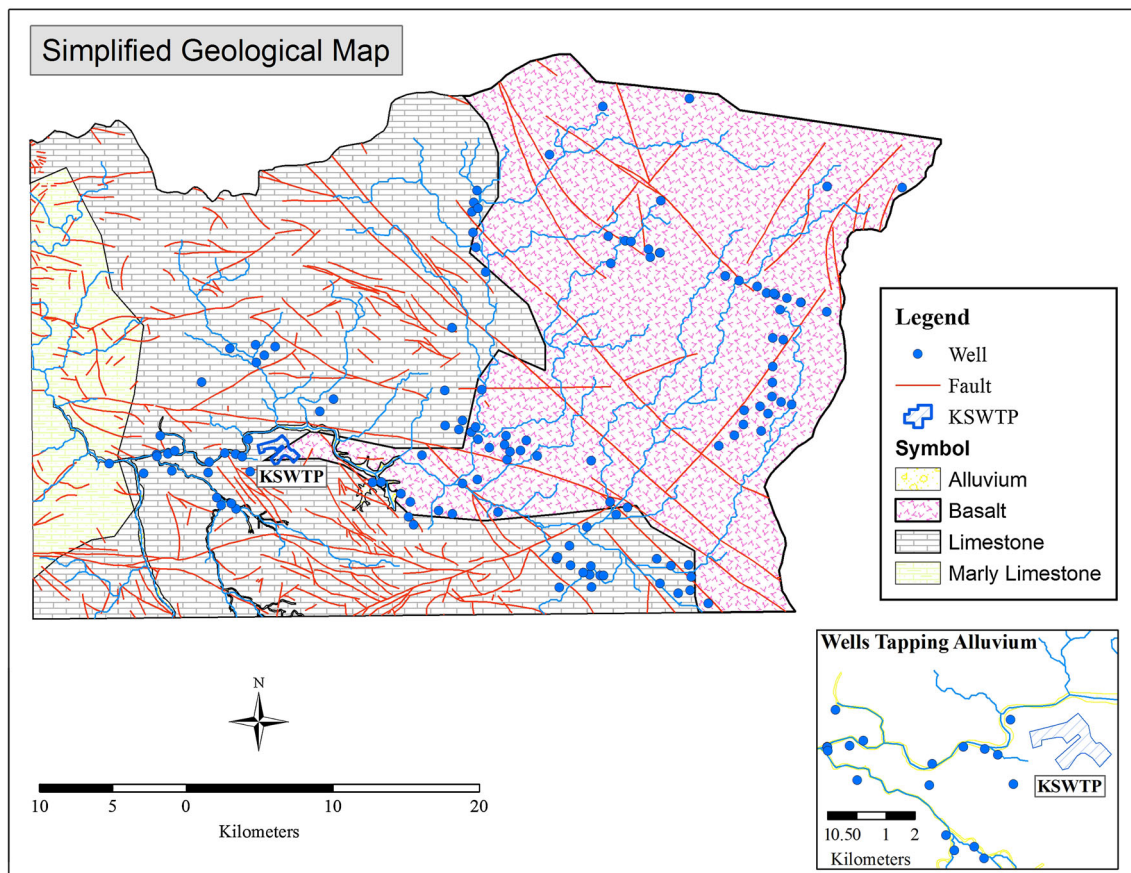


Fig. 2 Simplified geological map

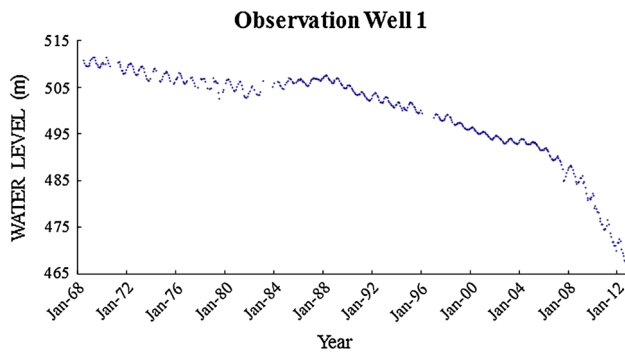


Fig. 3 Groundwater level fluctuation in observation well 1

The sharp decline in the water level can be attributed mainly to anthropogenic activities and slight changes in climate (Bajjali 1997). Groundwater upstream of KSWTP was subject to high extraction for irrigation purposes, and greatly exceeds the recharge rate from precipitation, which caused the groundwater level to decline sharply without replenishment. The amount of rain in the country has decreased for several decades and the general trend of the data in Mafraq station in the study area indicates that the amount of rain has been decreasing there since 1988 (Bajjali 2012).

The area downstream of KSWTP is also an agricultural area, and groundwater withdrawal for irrigation is significant. Nevertheless, groundwater levels in the wells are showing a remarkably constant rise in the water levels. The rise in the water levels in the wells downstream are related to the hydraulic connection between the base flow of the Zarqa River and the groundwater (Bajjali 1997). The groundwater receives direct recharge through the riverbed and return flow from irrigation. The majority of the shallow wells tapping the alluvium deposits of the flood plain are located along the Zarqa River, which receives treated wastewater from KSWTP. Some of the wells have a direct and rapid response to the base flow of the river that consists of treated wastewater. Furthermore, the majority of the groundwater wells are used for intensive irrigation, and the return irrigated water infiltrates back to the aquifer and acts as artificial recharge. Observation well 2 is located close to the KSWTP along one of the tributaries of the Zarqa River. The rise in water level during 1968–2012 was almost 9.16 m, almost 0.2 m per year (Fig. 4).

Methodology

The geology of the study area was digitized using ArcGIS from 1:50,000 geological maps (NRA 1993). Groundwater database information about the water chemistry and environmental isotopes (Appendix 1) was also integrated into a GIS. Weighted mean value (WMV) precipitation at

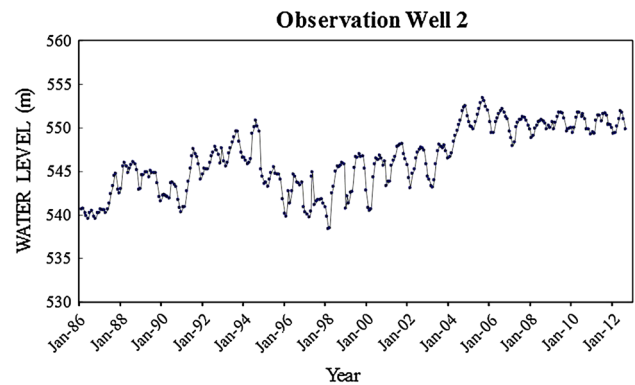


Fig. 4 Groundwater level fluctuation in observation well 2

Amman rainfall stations was used from published precipitation data (Bajjali 2012). Groundwater was sampled from 120 wells and analyzed for major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , HCO_3^- , SO_4^{2-} and NO_3^-).

The samples were collected from each well and generally, at least two casing volumes of water were extracted to ensure that the sample was from groundwater in the aquifer and not from water stored in the well. Sample were collected in cleaned polythene bottles (1,000 ml). Two samples were collected from each well for cation and anion analysis, in which samples for cations were acidified with HNO_3 acid. All the sample were analyzed using standard procedure (APHA 1995). Electrical Conductivity (EC) and pH were analyzed using portable field kit. Major ions (Ca^{2+} , Mg^{2+} , Cl^- , and HCO_3^-) were analyzed using titration, Na^+ and K^+ were measured by flame photometer, and SO_4^{2-} by UV–visible spectrophotometer. Ion balance error of the samples was observed below 5 %. At some wells water was also analyzed for oxygen-18, deuterium, and tritium (Appendix 1). The environmental isotope and chemical analyses were carried out in the Water Authority of Jordan (WAJ) laboratories. Oxygen-18 and deuterium contents were determined by mass spectrometry with an overall precision of 0.15 and 1 ‰, respectively. Tritium was measured by β -counting on electrolytically enriched samples, with 1 tritium unit (TU) analytical precision. The geochemical program AquaChem was used to identify mineralization trends, mineral saturation indices, and interpret and plot water quality data.

Result and discussions

Salinity of groundwater

The majority of the wells upstream of KSWTP penetrate only the upper part of the aquifer which consists of basalt. These wells yielded good quality water with large flows in the 1960s. The range of groundwater salinity at the initial

Table 1 Salinity Increase in groundwater from 1965 to 1989

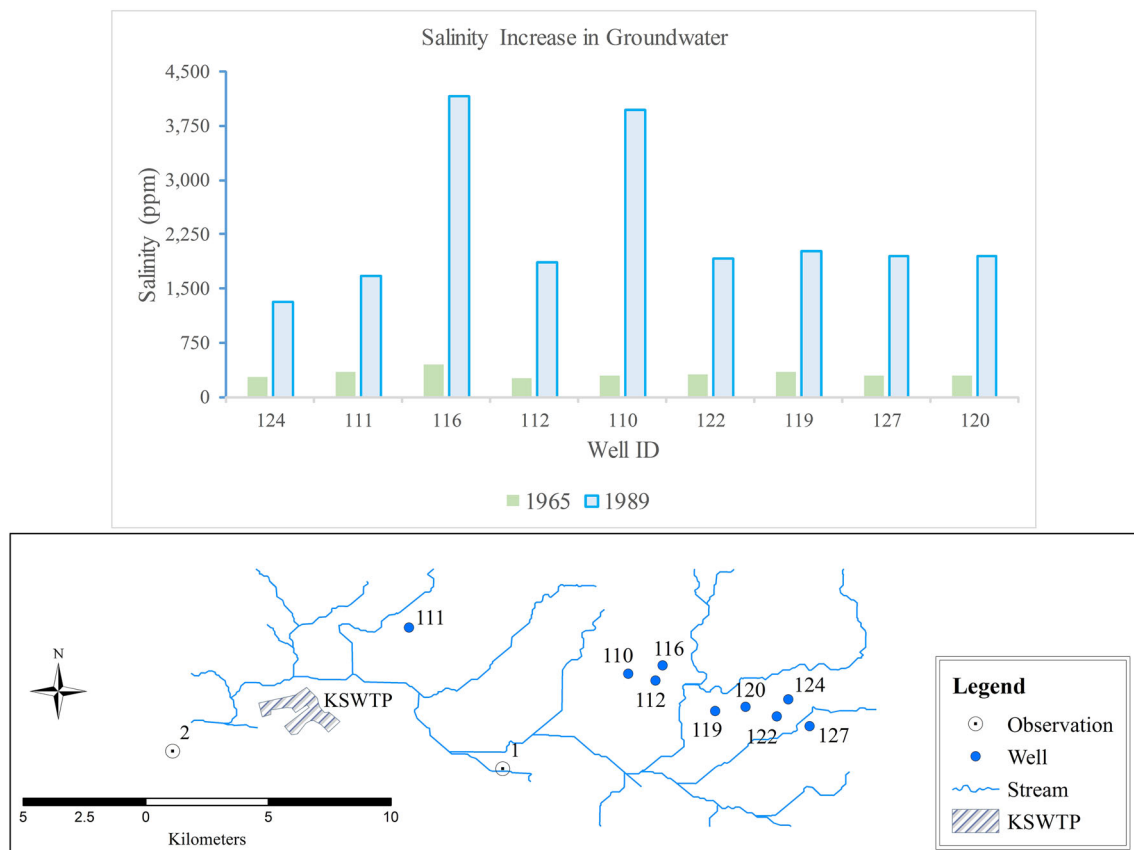
Well ID	1965 TDS (mg/l)	1989 TDS (mg/l)	Rate of increase (%)
101	275	1,307	475
103	314	1,911	609
104	288	1,931	670
108	346	1,950	564
121	291	3,965	1,363
122	346	1,670	483
125	265	1,862	703
128	448	4,160	929

stages was good as it was between 265 and 448 ppm. Therefore, groundwater was at that time suitable for different uses: drinking, agriculture, and industry. However, continuous pumping of groundwater for irrigation over a period of 25 years has resulted in very poor water quality. The salinity of some wells in the Dhuleil-Halabat-Khaldyia area have increased 4.7–13.6 times above the initial level for the period from 1965 to 1989 (Table 1; Fig. 5).

Effectively, the groundwater within the agricultural lands changed from fresh to saline. Over-pumping deteriorated the groundwater in three ways. First, the withdrawal rate was much higher than the actual recharge rate, which

caused the groundwater levels to decline steadily since 1968 (Fig. 3). The water level dropped around 43 m in 44 years and there was no sign that the water level is able to recover during subsequent periods of recharge, which is limited in this area due to low rainfall. Second, the quality of groundwater deteriorated considerably and shifted from good to saline water that has restricted use, and some of the wells were closed due to high salinity. Third, the drop in water level caused an increase in the cost of pumping.

Salinity was also significantly increased downstream of KSWTP areas. The wells there mainly penetrate the carbonate aquifer which consists of limestone and alluvium along the Zarqa River. The salinity there, as in the upstream area, also increased dramatically due to two major factors. All the wells in this area are extensively used for irrigation. Despite huge extraction rates for irrigation, the groundwater levels in the downstream wells have increased (Fig. 4). The rise in water level was almost 20 cm per year after the KSWTP was built in 1985. The rise in the water levels in the wells is attributed to irrigated wastewater infiltration to groundwater, and the infiltration commonly occurs unplanned and uncontrolled. The infiltration could occur directly from the streambed that receives discharge from treatment facilities (Diaz-Cruz and Barcelo 2008; Eckert and Irmscher 2006), or indirectly

**Fig. 5** Salinity increase in groundwater

from excess agricultural irrigation in downstream riparian areas (BGS et al. 1998). A wide range of salinity between 186 and 9,000 ppm was recorded in the downstream groundwater wells. The low salinity value represents a shallow hand dug pit made of bricks and coated with cement to collect the rainwater and surface runoff during rainy season and is used for livestock and crop growing. The hand dug pit is located in close proximity to KSWTP, but not hydraulically connected with the water table of the shallow aquifer. Shallow well No. 12 penetrates the alluvium formation of the floodplain of the Zarqa River 1.5 km downstream of KSWTP, and recorded a high salinity of 9,067 ppm. This well is located only 25 m from the channel of the river. Since all wells are used for intensive irrigation, the return irrigated water infiltrated back to the aquifer and acted as an artificial recharge, as in the area upstream of KSWTP.

Groundwater salinity and faulting

The study area is highly fractured (Fig. 2), and the structure has been tested to see if it has an influence on the quality of the groundwater. This phenomenon has been tested at two locations. The first location is along a main fault running in close proximity to the Zarqa River between Dhuleil, Khaldyia, and KSWTP (Fig. 6a). 22 wells are located within a 2 km buffer zone, where the wells inside the buffer are classified into two groups: group 1 are the wells located within 1 km from the fault (blue), while group 2 are the wells located between 1 and 2 km from the fault (green).

The average total dissolved solids (TDS) and NO_3^- concentrations in group 1 are higher than in group 2. The TDS and NO_3^- in group 1 are 6.19 and 34.4 % higher respectively than the concentrations in group 2 (Table 2). This may indicate that the farther the wells are from the fault, the less effect there is on return flow. At the second location, a group of wells in a faulty area within 3 km from KSWTP (downstream) were compared with a group of wells located in an area with no faults within 3 km of the agricultural centers of Dhuleil and Khaldyia (upstream) (Fig. 6b). The TDS and NO_3^- of the wells in the second location demonstrated higher concentration downstream of KSWTP than the upstream area (Table 2).

A statistical “*t* test” is used to test for a significant difference between TDS and NO_3^- in location 1 and location 2. The *t* test analysis assumes that the variances of both TDS and NO_3^- are unequal and a 95 % significant level ($\alpha = 0.05$) is adopted to run the test. The *t* test was performed using a data analysis package in Microsoft Excel. The result of the analysis shows that the two-tailed *p* value in both locations is more than 0.05, yielding no significant difference at the 5 % level (Table 2).

The entire region, both up- and down-stream of KSWTP, is an active agricultural area. The upstream region, however, relies on groundwater for irrigation, while the downstream region relies on reclaimed water from KSWTP. The irrigation mechanism in both regions allows for return flow to the aquifer; deteriorating its quality. The influence on the quality of the groundwater of using reclaimed water for irrigation far exceeds the influence of irrigation from groundwater. This is clear when we compare the chemical makeup of the groundwater wells located in close proximity to KSWTP. The water chemistry of Well No. 108 upstream of the plant is different than Well No. 13 that is located 767 m downstream of it. Well No. 108 recorded a TDS of 499 ppm and NO_3^- concentration of 26.6 ppm, while Well No. 13 recorded a TDS of 3,510 ppm and NO_3^- concentration of 119 ppm.

It is obvious that we are dealing with a complex hydrological scenario since the local fault system, as well as the irrigation practices of the region, allow irrigation water to infiltrate through the unsaturated zone at different rate.

Source of salinity in groundwater

There are several ways in which the salinity of groundwater can be increased. One possibility is cyclic salting. This is a term applied to salt input to the groundwater from precipitation. However the range of TDS in precipitation in 10 rainfall stations throughout the country ranged between 38 and 210 ppm (Bajjali 2012). For this reason, precipitation in the region could not be the source of the high salt levels in the local groundwater. A second possibility for the source of salts could be rock weathering; however the bedrock is basalt and limestone, neither of which could contribute significantly to salt accumulation in the top soil. The third possibility to rising salt levels is invasion of saline water from the deeper aquifer. A previous study was conducted to evaluate the salinity build up upstream of KSWTP in specific wells in the Dhuleil-Halabat-Khaldyia area, and concluded that an invasion of saline water from the deep layer to the upper aquifer was caused by over-pumping (Nitsch 1990). The over-pumping from the upper aquifer lowered the water table below the piezometric head of the lower aquifer, which caused the deeper saline water aquifer to invade the upper aquifer and raise salinity. Invasion from the deeper aquifer in this particular case is unlikely for the following reason: if saline water moves from the lower saline aquifer to the upper fresh aquifer due to the difference in hydraulic head caused by heavy pumping, the salinity concentration and chemical composition of the water in the productive wells should be more or less homogeneous. However, this is not observed in the chemical makeup of the area’s groundwater, as seen in the hydrochemical facies. The piper diagram (Fig. 7) shows

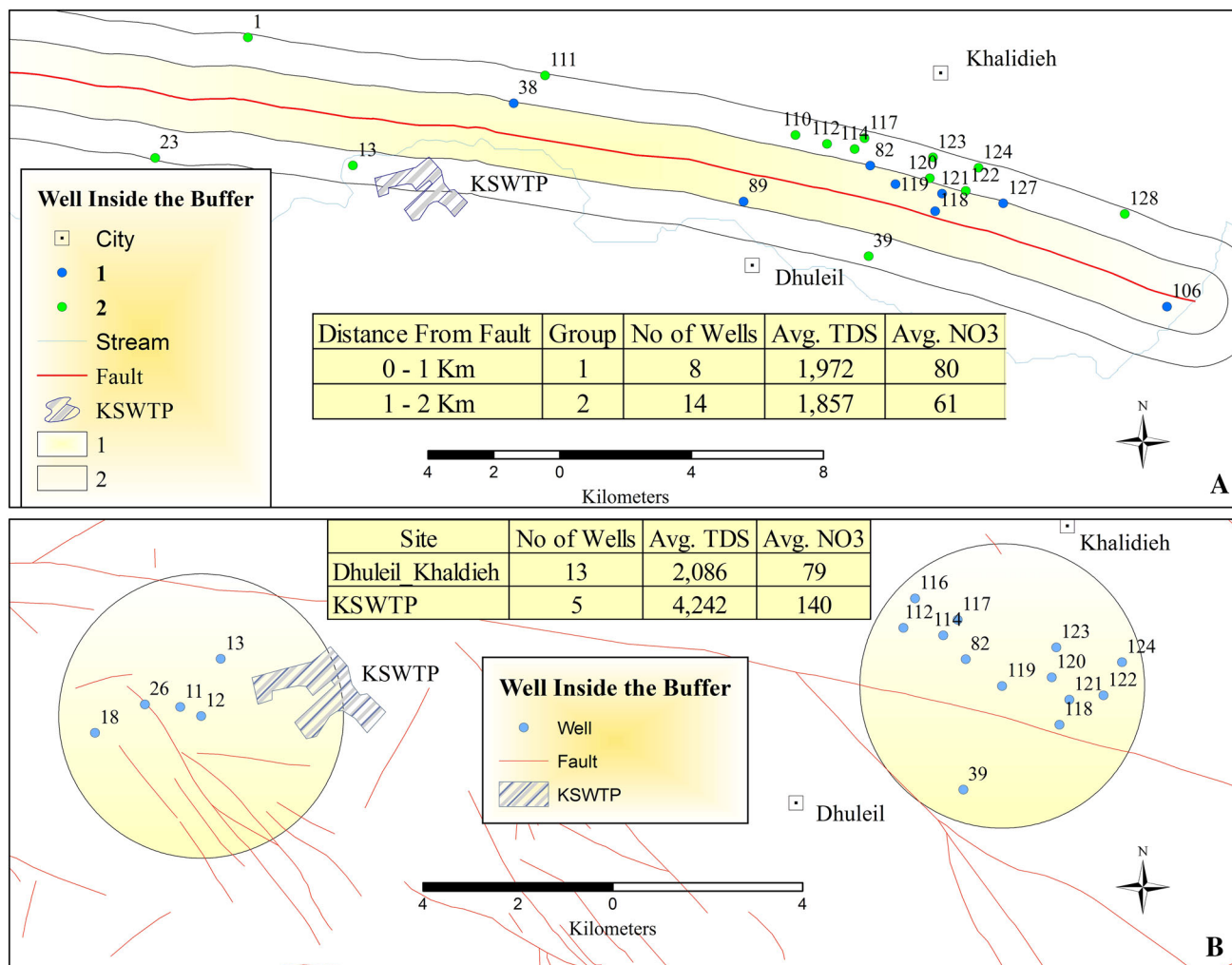


Fig. 6 TDS and NO_3^- concentration of groundwater along major fault

differences in major ion chemistry in groundwater in both areas upstream and downstream of KSWTP. Furthermore, the water in the study wells have differing water types and molal ratios of Ca/Mg, Cl/Ca, and Cl/Na (Table 3). The heterogeneity of the chemical facies and the diverse calculated ionic ratios identified in groundwater indicate that both anthropogenic sources from organic and inorganic pollution, and the water–rock interaction formed the chemical composition of groundwater. The Cl/Na and Cl/Ca ratios show that the concentrations of Na^+ and Ca^{2+} are much less than that of Cl^- , which indicate that the evaporation process is not the main mechanism that lead to the lower concentrations of Na^+ and Ca^{2+} in this aquifer. If the evaporation process is dominant, assuming that no mineral species are precipitated, the Cl/Na ratio would be unchanged (Jankowski and Acworth 1997). However, the majority of the samples have Cl/Na and Cl/Ca ratios much higher than would indicate the possibility of some other chemical processes, such as ion exchange influence the

chemical makeup of groundwater. The Ca/Mg ratio is less than 1, possibly due to domestic sewage and animal waste affecting the groundwater.

Therefore, the most likely source of potential salinity throughout the study area is local irrigation and leakage from treated wastewater along the river bed downstream of the KSWTP. It is believed that continued irrigation from the groundwater aquifer is causing a buildup of salinity in the soil and the aquifer. Various techniques have been used for irrigation, including open channel at the beginning of this are of agricultural development, and sprinkler and drip irrigation at the later stages. The open channel approach made the irrigation water subject to intensive evaporation. Irrigation water evaporates from the soil and the roots of plants, and precipitates salts above and below the soil surface. Incessant irrigation from the groundwater wells in the same agricultural area would continually precipitate and simultaneously dissolve the accumulated salts from the soil surface and the unsaturated zone.

Table 2 TDS and NO₃⁻ comparison at two locations and *t* test results

Group	TDS-mean	TDS-variance	NO ₃ -mean	NO ₃ -variance
Location 1				
Group 1	1,972.00	10,36,972.50	80.1	2,138.40
Group 2	1,856.60	8,38,287.10	61.4	1,860.50
<i>t</i> Stat (TDS)	<i>P</i> (<i>T</i> ≤ <i>t</i>) two-tail (TDS)		<i>t</i> Stat (NO ₃)	<i>P</i> (<i>T</i> ≤ <i>t</i>) two-tail (NO ₃)
Statistics of location 1	0.27	0.8	0.93	0.37
Site	TDS-mean	TDS-variance	NO ₃ -mean	NO ₃ -variance
Location 2				
Downstream of KSWTP	4,242.20	76,67,733.70	140.4	14,545.30
Upstream of KSWTP	2,085.90	9,65,513.10	78.9	1,354.00
<i>t</i> Stat (TDS)	<i>P</i> (<i>T</i> ≤ <i>t</i>) two-tail (TDS)		<i>t</i> Stat (NO ₃)	<i>P</i> (<i>T</i> ≤ <i>t</i>) two-tail (NO ₃)
Statistics of location 2	1.7	0.16	1.12	0.33

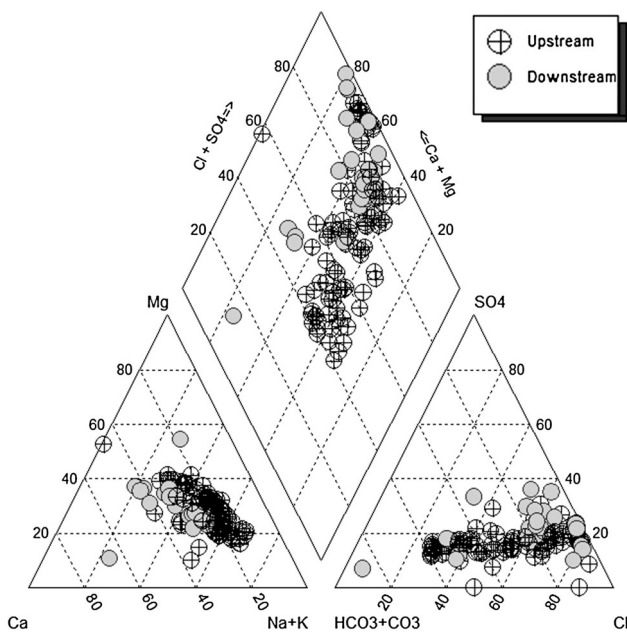


Fig. 7 Piper diagram showing type of groundwater facies

The salt is flushed from the soil repeatedly by the irrigation water, causing the solute to infiltrate down-gradient into the subsurface thereby increasing the salinity of groundwater. This practice has continued for more than four decades near the productive wells. The white color of the soil surface throughout the study area in dry seasons is evidence of salt accumulation. Soil analyses in the mid-sixties (the beginning of the current era of agricultural development), indicates that NaCl and Na₂CO₃ are the major salts in the soil (Nitsch 1990). The dissolution of

Table 3 Molal ratio of some wells upstream of KSWTP

ID	TDS	Ca/Mg	Cl/Ca	Cl/Na
100	2,340	0.72	2.65	2.51
106	2,210	0.84	2.50	3.10
107	2,080	0.77	3.78	1.07
110	3,965	0.64	3.02	1.87
112	2,145	0.64	3.09	2.12
116	4,160	0.63	3.01	2.00
118	3,835	0.74	2.79	1.88
119	2,015	0.70	2.75	2.50
121	2,535	0.70	2.63	2.73

these mineral salts is achieved by chemical attack by carbonic acid. A hydrochemical model in AquaChem was used to calculate the log PCO₂ value of the groundwater wells in the Dhuleil-Halabat-Khaldyia area. Values range from 0.0018 to 0.0078, which exceed the partial pressure of the carbon dioxide of the air which is only 10^{-3.5} (Freeze and Cherry 1979). This allows the irrigation water to dissolve the highly soluble minerals in the soil. Moreover, the excess use of fertilizers had resulted in groundwater pollution and an increase in the concentration of the major cations and anions of concern. The salinity of groundwater in some wells upstream of KSWTP (110, 116, and 118) was above 3,800 ppm (Appendix 1). Such elevated salinity levels is undesirable not only for drinking purposes but also for irrigation use.

In the case of wells downstream of KSWTP, three sources could simultaneously be responsible for increasing the salinity. The first source could come from direct river

loss by leakage through the riverbed. This leakage is dependent on stream flow and properties of the riverbed sediment. The stream flow is estimated to be 267,000 m³/day and the leakage was recorded through the rise in the water table in observation well 2, which is located within 1 km downstream from KSWTP. The water level rose 7.72 m between 2000 and 2005, averaging 1.5 m per year (Fig. 4). The hydrogeological setting of the aquifer system downstream of the KSWTP allows this infiltration to occur. The upper part of the shallow aquifer consists of alluvium which is highly permeable material. The second possible source of salinity is the dissolution of the accumulated salts in the soil by the irrigation water (similar to the situation upstream of KSWTP). The third source is due to direct evaporation from the water table for the wells tapping the relatively shallow alluvium, its average depth around 10 m.

Concentrations of Cl⁻, SO₄²⁻, and Ca²⁺ were highest downstream of KSWTP compared with the concentrations upstream in groundwater, the ratio is almost 3–4 times higher. Various factors contribute to high sulfate, calcium, and chloride levels downstream and upstream, including mineral constituents of aquifers and irrigation return flow. The difference in both regions is that the return flow upstream consists of groundwater, while the downstream return flow is from reclaimed water (Table 4). This high variation in these ions indicates that the reclaimed water used for irrigation downstream has higher concentrations than the groundwater upstream. The variation in Cl⁻, SO₄²⁻, and Ca²⁺ upstream and downstream of KSWTP indicates an irrigation return flow contribution. This is seen from the high concentration of NO₃⁻ (Appendix 1).

Groundwater contamination

Nitrate is another chemical parameter in addition to salinity that was found in high concentrations in some wells throughout the study area. Nitrate is the most available indicator of organic (sewage and manure) and inorganic (artificial fertilizer) sources of contamination. Nitrate is easily dissolved in groundwater, very mobile in subsurface flows and spreads very quickly through the fractured subsurface water-bearing formation.

The nitrate concentration in groundwater in the entire study area had increased beyond the level of natural abundance of nitrate in groundwater, less than 5 ppm as adopted for this study. Nitrate levels in groundwater wells

upstream and downstream of KSWTP have increased by 17.3 and 32 % respectively above the World Health Organization's (WHO) standard of 45 ppm for drinking purposes (WHO 2011).

Chemical fertilizers, particularly urea (46 % nitrogen content), are used extensively and without control in the agricultural area to increase soil fertility and crop yields. However, the most noticeable increase in nitrate is observed in wells downstream of KSWTP. Well No. 12 recorded a nitrate concentration of 324 ppm. This high concentration is due to the sewage effluent of KSWTP, which is high in ammonium (NH₄) concentration (Saqqar et al. 1989). Through the process of nitrification the NH₄ is converted to NO₃⁻ by oxidation. This process normally occurs above the water table, generally in the soil zone where organic matter and oxygen are abundant (Freeze and Cherry 1979). Figure 8 shows that NO₃⁻ concentration is highly correlated with the TDS of the groundwater ($R^2 = 0.89$).

The high association between TDS and NO₃⁻ is strong evidence that the source of high salinity originates from the surface rather than from the subsurface due to the absence of nitrate in non-developed groundwater resources.

Environmental stable and radioactive isotopes

Environmental isotopes techniques using the ¹⁸O, ²H, and ³H have become an integral part of geochemical studies in groundwater projects. Isotopes provide information that complements chemical data, giving insights into geochemical pathways, and processes in groundwater resource and groundwater quality studies. It was used extensively to study the mechanism of infiltration of water into the subsurface, recharge origin, evaporation, mixing, and residence time of recharge (Mathieu and Bariac 1996; Kass et al. 2005; Darling and Bath 1988; Böhlke 2002; Bajjali 2008).

The stable isotope data for all groundwater in conjunction with weighted mean value (WMV) of the rain in the Amman station for the period of 1987–2005 (Bajjali 2012) are plotted on a δ¹⁸O–²H diagram (Fig. 9). The Amman rainfall station is located at 900 m above sea level east of the Mediterranean Sea. Due to the world-wide variation in isotopic composition of precipitation (Dansgaard 1964; Yurtsever and Gat 1981), the long-term WMV was chosen to monitor the isotopic signature of the rain, so it could be used as a guideline to evaluate groundwater recharge processes and the origin of groundwater in the study area.

Figure 9, shows that the groundwater samples reveal a wide variation in stable isotope content, and a close look at the isotopic composition of all the data indicates that there is at least a 3.5 and 15.8 % range in δ¹⁸O and δD respectively.

Table 4 Ratio of some parameters up-downstream of KSWTP

Location	Ca	SO ₄	Cl
Upstream	62.60	107.20	294.09
Downstream	265.34	465.13	951.31
Ratio	4.24	4.34	3.23

Fig. 8 TDS versus nitrate in groundwater

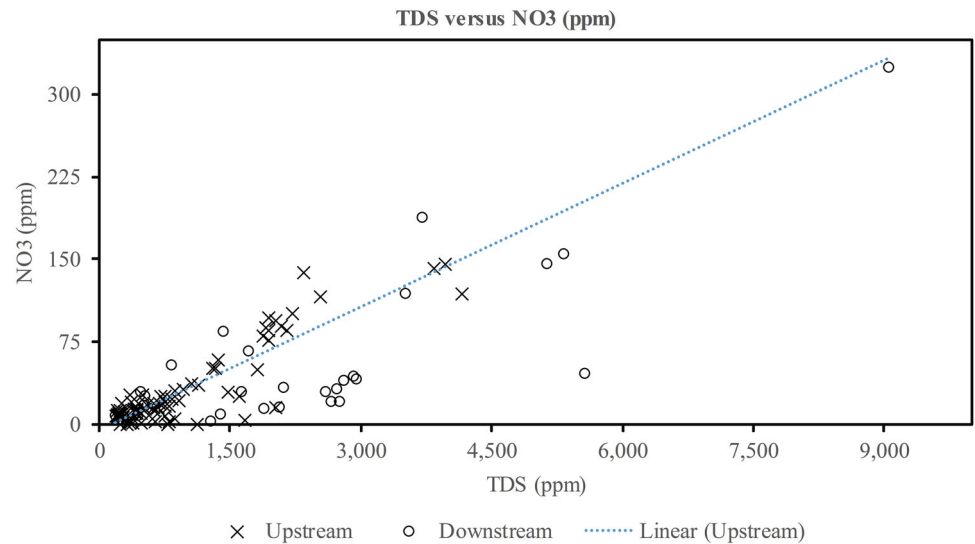
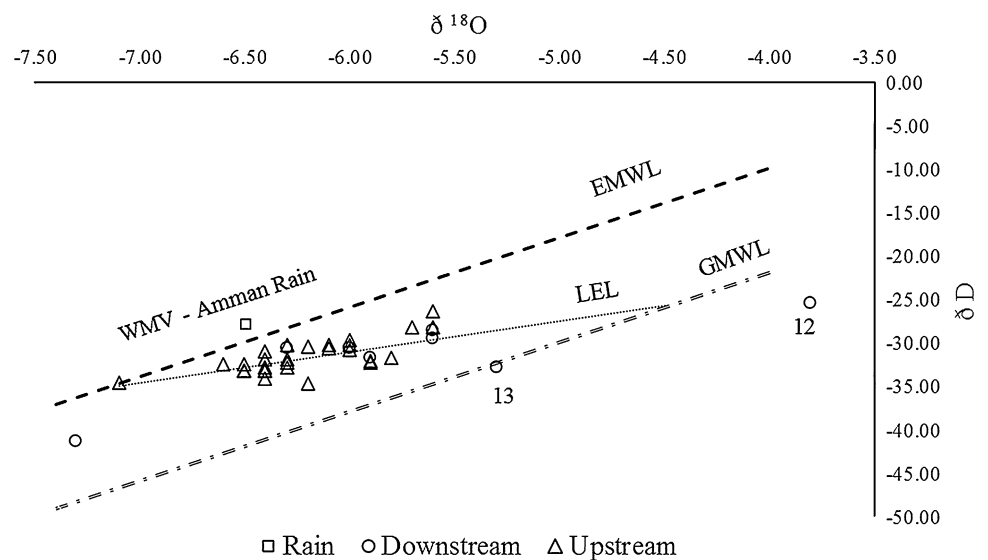


Fig. 9 $\delta^{18}\text{O}$ – δD diagram of the groundwater and WMV of Amman Rain



The samples originated from the Eastern Meteoric Water Line (EMWL), defined by (Gat and Carmi 1970) and clustered widely between the EMWL and the Global Meteoric Water Line (GMWL) defined by Craig (1961) with the exception of two samples (12 and 13) from groundwater downstream of KSWTP. This indicates that the water was subject to evaporation before infiltration down-gradient into the aquifer. This is clearly shown from their plot along an evaporation line represented by the Local Evaporation Line (LEL). The LEL was calculated to be:

$$\delta\text{D} = 3.6\delta^{18}\text{O} - 9.53 (n = 36 \text{ and } R^2 = 0.57)$$

The LEL representing the isotopic composition of groundwater starting at the EMWL. The point of

intersection of the LEL with EMWL on the $\delta^{18}\text{O}$ – δD diagram is a location where we assume that the recharge of the groundwater took place. If we compare this location with the location of the WMV of Amman rain at the EMWL, we observe that the location of the intersection is more depleted in environmental isotopes than the WMV of the isotopic composition of the Amman rain. The altitude at the Amman rainfall station is 900 m. Therefore, we can suggest that the recharge took place under the climate regime which predominates today in Jordan and the recharge altitude of the groundwater originates from a greater elevation than that of the Amman station. It is well known that the heavy isotope contents (^{18}O and ^2H) of rain decrease with increasing altitude. This is attributed to the

progressive condensation of atmospheric vapor and rainout of the condensed phase, which take place when air masses climb up along the slopes of high mountains and cool off as a consequence of adiabatic expansion (Gonfiantini et al. 2001).

The groundwater samples falling along the LEL, are the most divergent values relative to EMWL and usually enriched in both $\delta^{18}\text{O}$ and δD . This is clear evidence that the effect of evaporation is the driving force for the enrichments and variations. The variation in isotopic composition of groundwater wells in the entire study area is attributed to three mechanisms:

First, the groundwater wells upstream of KSWTP in the Dhuleil, Halabat, and Khaldyia areas are tapping the basalt aquifer. It is possible that the isotopic variation is due to stratification of the groundwater. The basalt aquifer is divided by six clay layers, so every layer represents a separate path for the groundwater from the recharge area to the point where the water is captured by a drilling well (Bajjali 1994). Heavy pumping in the summer time can also create a mixing condition of different groundwater circulating through these layers.

Second, the groundwater wells downstream of KSWTP especially in the Samra area are tapping the shallow alluvium aquifer (well No 11, 12, 13, 18, and 26). A portion of the water source in the alluvium aquifer is leakage from the Zarqa River that its base flow that consists of the effluent of treated wastewater from KSWTP. The treated water originates from different sources and when entering the treatment plant becomes subject to mixing and evaporation.

Third, the return flow from irrigation water in both locations upstream and downstream of KSWTP were subject to evaporation before infiltration back to the aquifer. This practice enriches the groundwater that has been used for agriculture with $\delta^{18}\text{O}$ and δD due to direct evaporation. The excess water eventually returns to the aquifer with the signature of the evaporation effects. The isotopic composition of the wells downstream of the Samra area are distinct and more enriched in heavy isotopes than the upstream groundwater. Broad variation in isotopic composition was found for wells 12 and 13 located within 2 km downstream of the KSWTP, indicating that the water infiltrating into the aquifer was subject to extensive evaporation before infiltration.

The tritium concentration in the groundwater enables us to determine when this groundwater was recharged; i.e. pre- or post-bomb testing in 1952. A tritium concentration in excess of 2 ± 1 Tritium Unit (TU) indicates that the well was recharged after 1952. Some of the wells show relatively high concentrations of tritium. The tritium level in the wells downstream of the KSWTP range from 2.5 to 6.7 TU. This could be due to the contribution of wastewater

leakage from the treatment plant into the aquifer through the base flow of the Zarqa River. The treated wastewater in KSWTP originates from some part of the tritiated shallow carbonate aquifer in the Amman Zarqa basin (Bajjali 1997). Therefore, the leakage of the treated wastewater from the river bed into the shallow alluvium aquifer raised the tritium level in the wells. This is clearly observed in some of the wells (No. 7, 11, and 13) that are tapping the alluvium aquifer and located in close proximity downstream of the KSWTP. Their tritium levels range from 3.6 to 6.7 TU, while the tritium levels decrease in the wells that are located far away from the KSWTP.

Some of the wells upstream of the KSWTP also revealed a wide range of tritium levels, from 2 to 15.3 TU. The highest tritium level (15.3 and 6.8 TU) was observed in the wells (No. 125 and 108) that are located in close proximity to the fault systems. A relatively high tritium concentration (5.3 TU) and enrichment in isotopic composition of $\delta^{18}\text{O}$ and δD was measured in the well No. 123 that is located 545 m downstream from the Khaldyia dam. This dam receives its water from precipitation and surface runoff during the wet season. Both rain and surface runoff are tritiated, and a surface runoff sample from the vicinity was found to have a 10 TU value (Bajjali 1990). This indicates that wells located downstream and in close proximity to the dam may receive direct recharge from the stored water in the dam.

Conclusions

The groundwater deterioration upstream and downstream of KSWTP was mainly due to mismanagement by irrigation practices and over-exploitation of the aquifer beyond its sustainable yield. This practice reflects the misunderstanding of the water budget for this aquifer. Over-pumping upstream of the KSWTP lowered the water table around 44 m since 1968, without any sign of replenishment. The heavy pumping did not affect the wells downstream of KSWTP, but water has been rising around 20 cm per year since 1985 due the direct recharge from the Zarqa River.

Despite the high rate of groundwater pumping for irrigation, a slight recharge returned to the aquifer from excess irrigation water and leakage from treated wastewater through the river bed of the Zarqa River. It has been apparent that using wastewater for irrigation resulted in high rates of infiltration to the subsurface water-bearing formation. The infiltration process replenished the groundwater, but also deteriorated the quality of groundwater. The regional fault systems enhance the infiltration by permitting the return flow from irrigation and surface runoff to recharge the aquifer.

The high salinity in the groundwater is associated with return flow of the irrigation water and leakage from the

treated wastewater of KSWTP along the Zarqa river bed. The high nitrate concentration in groundwater was attributed to organic and inorganic origin. Organic and inorganic fertilizers are heavily used in agricultural areas to improve fertility and crop yield, but easily leech into the subsurface via run off and infiltration. The chemical fertilizers dissolved in the irrigation water usually ended up in the aquifer and this resulted in a major increase in cations and anions in the water chemistry. For the majority of groundwater wells, the quality shifted from fresh water (salinity less than 500 ppm) to brackish water (salinity higher than 1,000 ppm). There is evidence that Khaldyia dam serves as an artificial recharge during the winter season and replenishes downstream wells.

The stable isotopes (^{18}O and ^2H) show that the water is of meteoric origin affected by the Mediterranean Sea air moisture. The recharge area of the study area originates at

altitudes greater than 900 m. The wide scatter of the isotope composition is due to an evaporation effect. The radioactive tritium found in some wells is a sign of local recharge. Since farmers applied both inorganic and organic fertilizers for agricultural purposes, it would be helpful for future study to apply the nitrogen isotope techniques to trace the source of nitrate contamination.

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Appendix

See Table 5.

Table 5 Chemical and isotope data

ID	Tritium (TU)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	Depth (m)	pH	TDS (ppm)	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	Cl (ppm)	HCO_3 (ppm)	SO_4 (ppm)	NO_3 (ppm)
1	–	–	–	426	7.5	1,280	40.1	24.3	46.0	78.2	71.0	122.0	96.0	2.0
2	–	–	–	292	7.64	1,427	138.3	78.2	180.8	9.0	424.2	177.5	199.7	83.5
3	–	–	–	300	7.58	524	52.3	32.4	54.0	3.1	100.5	222.0	41.8	24.9
4	–	–	–	300	7.89	488	48.5	34.2	55.7	3.1	99.4	227.5	36.5	28.6
5	–	–	–	340	8.15	451	25.6	46.8	41.9	4.3	78.1	218.4	61.0	7.4
6	–	–	–	300	7.45	840	85.0	53.4	104.9	4.7	293.9	184.8	121.4	53.8
7	3.6	–5.6	–29.5	103	7	1,716	160.0	70.0	290.0	8.0	532.0	299.0	269.0	66.0
8	1.1	–5.9	–31.6	90	7.1	5,330	543.0	366.0	748.0	8.0	2,297.0	116.0	965.0	154.0
9	0.0	0.0	0.0	5	7.7	186	40.0	4.0	12.0	8.0	7.0	159.0	10.0	7.4
10	2.5	–6.0	–30.5	–	7.3	5,135	509.0	347.0	702.0	20.0	2,244.0	122.0	854.0	145.0
11	6.7	–5.6	–28.5	120	7.1	3,705	475.0	260.0	315.0	4.0	1,578.0	128.0	403.0	187.0
12	3.5	–3.8	–25.4	76	6.9	9,067	1,371.0	716.0	706.0	27.0	4,098.0	159.0	1,738.0	324.0
13	5.2	–5.3	–32.8	85	7.2	3,510	455.0	233.0	274.0	12.0	1,521.0	128.0	350.0	119.0
14	–	–	0.0	175	7.16	2,761	230.0	146.0	485.0	11.2	1,060.0	268.0	560.0	20.7
15	0.0	0.0	0.0	289	7.23	1,392	125.0	70.0	259.0	6.4	505.0	299.0	187.0	8.3
16	0.0	0.0	0.0	128	7.28	1,888	165.0	90.0	356.0	7.2	697.0	330.0	290.0	14.0
17	2.5	–6.0	–30.5	–	7.48	2,950	249.0	159.0	494.0	13.0	902.0	370.0	601.0	40.5
18	1.1	–6.3	–30.5	250	7.11	2,816	219.0	142.0	509.0	10.2	815.0	422.0	606.0	39.4
19	–	–	–	30	7.55	2,604	237.0	141.0	441.0	12.4	892.0	276.0	556.0	28.6
20	–	–	–	298	7.2	2,736	294.0	182.0	345.0	11.4	1,011.0	214.0	532.0	31.6
21	–	–	–	102	7.25	2,069	166.0	95.0	408.0	7.7	755.0	290.0	369.0	15.8
22	–	–	–	12	7.31	2,929	251.0	159.0	502.0	11.8	833.0	366.0	452.0	43.4
23	–	–	–	100	7.74	1,636	134.0	85.0	282.0	7.8	515.0	240.0	259.0	28.8
24	–	–	–	–	8.12	2,658	213.0	128.0	475.0	11.5	785.0	295.0	728.0	20.5
25	–	–	–	35	7.09	5,566	471.0	297.0	931.0	26.0	1,906.0	256.0	1,503.0	45.6
26	–	–	–	79	7.38	2,113	202.0	111.0	354.0	10.3	714.0	277.0	305.0	32.5
27	–	–	–	130	7.97	476	33.9	22.6	89.9	4.7	114.0	182.4	56.6	10.2
28	–	–	–	371	7.79	918	58.9	53.3	133.4	12.5	312.8	78.1	125.3	20.9
29	–	–	–	373	8.37	310	16.0	17.8	52.4	5.5	69.2	98.2	26.9	9.9
30	–	–	–	400	8.1	319	23.6	14.6	65.8	4.3	66.0	145.8	43.7	5.1

Table 5 continued

ID	Tritium (TU)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	Depth (m)	pH	TDS (ppm)	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	Cl (ppm)	HCO_3 (ppm)	SO_4 (ppm)	NO_3 (ppm)
31	–	–	–	339	8.19	629	37.9	38.5	100.5	9.4	225.1	87.2	73.0	15.2
32	–	–	–	400	8.21	626	36.9	39.4	94.5	10.2	219.4	92.1	62.9	12.7
33	–	–	–	386	8.33	428	23.3	25.9	69.9	7.4	117.9	105.5	40.8	10.3
34	–	–	–	407	8.28	387	20.0	21.3	61.6	4.3	109.7	98.2	37.9	12.6
35	–	–	–	305	8.13	471	25.4	21.4	92.7	3.9	137.0	121.4	55.2	11.7
36	–	–	–	320	8.14	294	14.4	10.1	69.9	2.4	55.7	125.1	33.1	9.1
37	–	–	–	351	8.32	417	23.6	27.0	65.5	7.0	103.0	106.8	57.1	10.3
38	–	–	–	103	5.74	1,363	156.3	71.4	117.3	11.3	537.8	108.0	90.2	58.5
39	–	–	–	210	0	511	33.5	19.0	102.6	2.7	149.5	117.7	66.7	12.3
40	–	–	–	395	7.81	436	24.1	24.8	64.4	5.5	129.6	86.0	43.2	14.2
41	–	–	–	400	8.4	541	52.3	35.3	71.5	2.7	135.3	186.7	52.3	17.9
42	–	–	–	375	8.09	873	49.3	41.6	165.4	1.6	269.4	167.8	97.9	30.5
43	–	–	–	386	8.16	540	51.9	35.5	0.0	1.6	124.6	206.2	49.0	17.1
44	–	–	–	450	8.15	692	38.1	36.5	109.9	9.8	233.9	78.7	84.0	18.6
45	–	–	–	346	8.43	464	17.6	16.7	98.9	5.1	133.5	108.0	55.7	11.1
46	–	–	–	445	8.22	427	16.0	16.8	94.1	5.9	106.9	129.9	39.8	14.1
47	–	–	–	169	8.12	870	62.1	34.7	166.1	6.3	332.3	151.9	102.2	4.9
48	–	–	–	135	8.23	365	27.9	14.5	82.3	4.3	99.8	144.6	36.0	6.8
49	–	–	–	136	8.06	753	55.9	29.3	170.2	7.0	272.3	126.3	92.6	7.4
50	–	–	–	367	8.12	751	48.9	43.9	120.3	10.6	267.0	78.7	107.0	20.1
51	–	–	–	382	8.14	628	49.5	36.4	94.8	1.2	154.8	197.0	68.6	18.4
52	–	–	–	342	7.57	484	41.7	28.9	65.5	2.0	102.6	211.1	59.0	1.2
53	–	–	–	400	7.99	804	54.7	39.4	162.4	3.5	254.2	166.5	107.5	2.1
54	–	–	–	380	6.94	410	22.0	22.6	66.5	7.0	108.6	114.1	35.5	9.7
55	–	–	–	359	8.16	749	42.3	40.9	128.1	10.6	255.3	77.5	94.1	16.6
56	–	–	–	137	8.27	401	26.1	15.9	81.0	4.3	122.1	104.3	42.7	13.6
57	–	–	–	267	8.32	204	8.8	11.8	35.0	3.9	30.2	93.3	21.6	7.5
58	–	–	–	321	8.17	205	11.0	9.2	34.7	3.9	29.5	105.5	23.0	8.1
59	–	–	–	350	8.3	204	9.6	11.6	32.7	3.9	29.5	97.0	22.1	8.5
60	–	–	–	303	7.98	806	42.3	44.8	152.3	9.0	295.0	90.9	86.9	16.7
61	–	–	–	358	7.87	600	34.5	27.2	113.4	1.2	171.5	158.0	60.5	15.9
62	–	–	–	395	8.18	327	17.0	20.9	43.0	5.5	85.9	108.0	32.2	0.0
63	–	–	–	350	8.05	210	12.4	13.5	39.1	5.1	33.4	115.9	22.6	13.0
64	–	–	–	350	8.4	240	12.6	13.7	35.9	4.3	46.5	95.8	24.5	0.0
65	–	–	–	350	8.09	262	22.4	13.5	42.3	5.5	53.3	99.4	31.7	18.8
66	–	–	–	350	8.31	200	12.2	8.3	34.3	3.9	32.7	95.8	20.2	8.0
67	–	–	–	351	8.29	230	12.4	10.2	43.0	4.7	36.2	89.7	25.0	8.2
68	–	–	–	350	8.24	236	13.0	13.0	34.0	4.3	39.4	115.3	27.4	7.7
69	–	–	–	142	8.39	486	32.3	21.0	84.4	5.1	177.5	76.3	39.4	9.7
70	–	–	–	330	8.2	625	36.3	35.1	102.1	9.4	214.1	90.9	70.1	15.1
71	–	–	–	423	8.23	424	26.3	25.7	62.3	7.0	117.5	106.1	39.4	12.6
72	–	–	–	415	8.37	282	14.8	15.8	53.8	5.5	58.6	117.7	26.4	8.9
73	–	–	–	445	7.62	1,811	95.8	59.2	282.9	15.6	809.4	193.4	0.0	50.1
74	–	–	–	170	8.33	208	9.8	9.5	43.9	3.9	39.8	109.8	20.6	8.2
75	–	–	–	–	8.01	1,472	94.0	67.1	325.9	8.2	576.5	101.9	266.4	28.6
76	–	–	–	350	6.91	196	14.2	7.7	38.2	4.7	30.9	110.4	16.8	7.6
77	–	–	–	351	8.2	197	10.4	10.9	39.1	4.3	29.1	104.3	18.2	7.5

Table 5 continued

ID	Tritium (TU)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	Depth (m)	pH	TDS (ppm)	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	Cl (ppm)	HCO_3 (ppm)	SO_4 (ppm)	NO_3 (ppm)
78	–	–	–	219	8.14	243	12.4	8.2	45.5	3.9	70.3	120.8	0.0	9.9
79	–	–	–	324	7.92	205	22.6	3.8	36.1	3.9	29.1	99.4	20.2	8.3
80	–	–	–	170	8.39	215	9.6	5.8	45.1	2.7	31.9	98.2	17.8	6.8
81	–	–	–	400	7.79	789	66.7	29.3	93.4	5.5	161.9	205.6	99.4	0.0
82	–	–	–	250	7.22	1,600	161.9	46.2	315.6	6.7	591.4	376.4	242.9	25.3
83	–	–	–	245	7.79	218	12.2	7.4	45.3	4.3	30.5	104.3	21.1	9.4
84	–	–	–	124	8.16	235	10.8	10.7	45.3	4.3	46.1	102.5	25.0	12.2
85	–	–	–	386	8.32	216	15.0	10.3	39.3	4.7	31.2	100.7	18.2	7.1
86	–	–	–	596	8.21	454	16.4	16.8	103.0	7.8	102.6	120.2	95.5	18.5
87	–	–	–	404	8.06	280	20.4	12.7	46.5	5.1	52.2	114.1	29.8	8.5
88	–	–	–	350	8.44	284	15.8	16.4	57.7	5.5	63.2	105.5	32.6	11.2
89	–	–	–	267	8.18	268	21.4	11.7	60.0	4.3	69.6	127.5	36.5	6.3
90	–	–	–	615	8.23	367	17.4	18.0	72.5	7.0	76.0	129.3	46.1	20.7
91	–	–	–	570	7.76	642	50.3	29.4	111.1	7.0	182.8	175.1	71.5	2.7
92	–	–	–	160	8.33	669	59.9	39.8	126.0	5.9	301.4	104.3	104.2	15.6
93	–	–	–	200	8.53	204	11.4	7.1	54.5	3.5	39.4	94.5	24.5	8.2
94	–	–	–	283	7.94	607	46.3	30.5	100.5	9.4	185.7	155.6	61.9	5.5
95	–	–	–	257	8.6	191	8.2	7.3	47.6	3.1	35.1	90.9	17.8	7.0
96	–	–	–	165	8.38	246	13.2	8.6	52.0	3.5	47.2	98.8	27.4	8.4
97	–	–	–	350	8.06	390	39.1	17.5	55.9	5.1	83.4	137.9	61.4	1.2
98	–	–	–	–	7.35	1,124	123.3	51.7	176.9	10.9	432.0	240.3	129.6	0.3
99	–	–	–	132	7.92	536	35.5	28.1	77.5	5.5	180.3	107.4	40.8	13.8
100	0.6	–6.5	–33.2	140	7.2	2,340	198.0	164.0	239.0	16.0	929.0	73.0	230.0	138.0
101	0.0	–6.3	–31.9	130	7.7	1,133	78.0	46.0	200.0	8.0	422.0	98.0	130.0	35.8
102	0.0	–6.5	–33.1	121	7.3	218	12.0	7.0	46.0	4.0	43.0	92.0	14.0	10.1
103	0.2	–6.4	–34.0	161	8	710	44.0	29.0	129.0	8.0	223.0	104.0	86.0	25.0
104	0.1	–6.4	–33.1	106	7.8	960	64.0	64.0	136.0	12.0	287.0	92.0	202.0	32.0
105	0.0	–7.1	–34.6	234	8	333	20.0	16.0	67.0	4.0	64.0	153.0	43.0	1.9
106	0.6	–6.2	–34.6	90	7.8	2,210	210.0	150.0	193.0	16.0	929.0	79.0	125.0	101.0
107	0.0	–6.4	–31.0	85	7.7	2,080	108.0	84.0	437.0	8.0	723.0	98.0	389.0	89.4
108	6.8	–5.8	–31.6	105	8.2	499	40.0	32.0	64.0	8.0	145.0	110.0	62.0	26.6
109	0.0	–6.5	–32.4	–	7.8	755	42.0	31.0	150.0	8.0	227.0	104.0	130.0	25.4
110	0.6	–5.9	–32.2	100	7.6	3,965	309.0	287.0	570.0	23.0	1,652.0	79.0	701.0	145.0
111	0.0	–7.3	–41.2	200	7.3	1,670	124.0	82.0	294.0	16.0	560.0	183.0	346.0	3.4
112	0.1	–6.0	–30.1	100	7.5	2,145	152.0	142.0	253.0	16.0	833.0	73.0	230.0	85.2
113	1.8	–6.4	–31.9	210	7.8	826	42.0	30.0	159.0	8.0	241.0	104.0	134.0	22.9
114	0.1	–6.3	–32.7	100	7.8	1,872	150.0	136.0	223.0	16.0	759.0	67.0	230.0	80.6
115	0.0	–6.6	–32.4	155	8.2	352	12.0	13.0	76.0	8.0	99.0	128.0	19.0	1.0
116	2.2	–6.1	–30.1	101	7.2	4,160	337.0	318.0	577.0	20.0	1,794.0	73.0	710.0	119.0
117	1.2	–6.3	–30.1	100	7.7	1,950	148.0	140.0	244.0	16.0	773.0	67.0	288.0	76.4
118	0.0	–6.0	–30.7	98	7.7	3,835	339.0	275.0	573.0	23.0	1,673.0	55.0	720.0	142.0
119	0.0	–6.1	–30.5	100	7.5	2,015	176.0	151.0	221.0	20.0	858.0	61.0	240.0	94.3
120	0.0	–5.9	–32.1	100	7.6	1,950	240.0	97.0	205.0	16.0	783.0	67.0	250.0	85.0
121	0.0	–6.2	–30.4	100	7.5	2,535	230.0	196.0	253.0	20.0	1,071.0	61.0	312.0	116.0
122	0.0	–6.4	–32.8	101	7.7	1,911	176.0	140.0	193.0	16.0	787.0	67.0	216.0	88.0
123	5.3	–5.6	–26.3	95	7.7	1,326	96.0	88.0	161.0	8.0	486.0	98.0	178.0	51.3
124	2.0	–5.6	–28.1	192	7.8	1,307	92.0	89.0	161.0	12.0	471.0	98.0	163.0	50.5

Table 5 continued

ID	Tritium (TU)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	Depth (m)	pH	TDS (ppm)	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	Cl (ppm)	HCO_3 (ppm)	SO_4 (ppm)	NO_3 (ppm)
125	15.3	-5.7	-28.1	165	8	352	26.0	20.0	55.0	4.0	50.0	183.0	43.0	26.0
126	0.8	-6.3	-32.2	125	7.5	1,056	64.0	77.0	131.0	4.0	358.0	171.0	96.0	36.7
127	0.0	-6.4	-33.2	94	7.7	1,950	176.0	144.0	205.0	16.0	808.0	67.0	221.0	97.2
128	2.7	-6.0	-29.6	97	7.8	960	64.0	64.0	136.0	12.0	287.0	92.0	202.0	32.0
129	-	-	-	99	7.61	2,020	162.0	101.0	365.0	10.2	857.0	111.0	276.0	15.1

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