JOURNAL OF ENVIRONMENTAL HYDROLOGY

The Electronic Journal of the International Association for Environmental Hydrology On the World Wide Web at http://www.hydroweb.com

VOLUME 16

2008

TRACING SOURCES OF POLLUTION IN GROUNDWATER **USING HYDROCHEMICAL AND ISOTOPIC METHODS: BEIRUT AND ITS SUBURBS**

Véronique Kazpard^{1,2} Zeinab Saad^{1,2}

¹Lebanese University, Faculty of Sciences, Hadath, Lebanon ²Lebanese Atomic Energy Commission, Beirut, Lebanon Antoine El Samrani^{2,3} ³Holy Spirit University of Kaslik, Jounieh, Lebanon

Analyses of hydrochemical and stable isotopes of deuterium and oxygen-18 were conducted on groundwater samples that tap into a limestone aquifer in Beirut city and its suburbs. The analyses document the chemical and isotopic characteristics of the natural groundwater and establish its origin. Hydrochemical data are classified on the basis of dominant anions. Mineral groundwater quality was found to be affected by different pollution sources in the southern suburb of Beirut. Isotopic analyses delineate two major groundwater groupings. The first is influenced by direct recharge into the aquifer from precipitation. The second, showing elevated mineral characteristics, is influenced by a secondary evaporation process that results in isotopic enrichment of groundwater. Investigation of the isotopically enriched d15N samples shows the origin of nitrate pollution to be from infiltration of either animal waste or septic systems to groundwater.

INTRODUCTION

In Lebanon, groundwater is an important source of water supply. It is mainly developed for domestic and industrial uses because of the poor management of surface water. The population and industrial development of Beirut city are increasing. In urban areas, a 205 l/day/capita consumption is considered the norm for Lebanon. Large-scale groundwater abstraction in the Beirut area has resulted in adverse economic and environmental problems, such as declining groundwater levels and deterioration in groundwater quality. These problems will become more serious in the future. Management of groundwater resources requires an understanding of the main processes controlling its geochemical evolution and origin. Interpretation of the environmental isotope record of both precipitation and groundwater, coupled with hydrochemical characteristics, provide a good comprehension of the groundwater system in a basin (Shama and Hughes, 1985; Wood and Sandford, 1995; Kendal and McDonell, 1998). In fact, the chemical characteristics of groundwater provide information on its geological history and its mode of origin within the hydrogeologic cycle (Ward, 1975; Freeze and Cherry 1979; Fetter, 1988). Isotopic characteristics as evaluated from stable isotopic abundance of deuterium and oxygen-18 give clues to the origin and recharge of the groundwater (Matthew and William, 2002; Dindane et al., 2003). The application of the environmental isotope method to recharge problems is based on the spatial and temporal variability of the isotopic content of water.

In this study the combined chemical and isotopic characteristics of water are used to determine the origin of groundwater and the hydrologic relations between precipitation and groundwater in the Beirut region and its suburbs. The study was designed to develop a database of the hydrochemical and the isotopic composition (²H and ¹⁸O) of groundwater in Beirut; it will also assess the groundwater quality and the causes of its deterioration.

MATERIALS AND METHODS

To study the groundwater quality in the Beirut region, 13 samples were taken within the aquifer and analyzed for their chemical and isotopic constituents. The location of these samples is given in Figure 1. The depth of the wells varies from 50 to 300 m with an average of about 150 m. The discharge averages 35 l/sec/well with a range of 20 to 80 l/sec. The aquifer is located in Cretaceous and mid-late Miocene strata. The lithology consists of thin-bedded limestone and conglomerates. The lithology has a strong influence on the chemistry of groundwater.

Water samples were collected in polyethylene containers. Each sample was divided into three aliquots. The first was filtered through 0.45 mm Millipore filter for elemental analysis using ion chromatography. The second was pre-concentrated and acidified with concentrated HCl prior to δ^{15} N isotopic analysis for nitrate. The third was acidified with HCl for deuterium and oxygen-18 analysis in water.

RESULTS AND DISCUSSION

Hydrochemical characteristics of groundwater

Figure 2 shows the total dissolved solids (TDS) variation in Beirut groundwater. Typical TDS concentrations in the Beirut aquifer are below the recommended level of 500 mg/L. Only concentrations in samples 6, 7, 8 (in Beirut's southern suburb) and 11 are higher, with values ranging up to 7000 mg/L, and exceeding the drinking water standard.



Figure 1. Location of sampling sites in Beirut basin.

High TDS concentrations may indicate that the concentration of one or more dissolved constituents is high and that more detailed water quality analysis is warranted.

The mineral quality of water can be classified based on the predominant cations and anions. Figure 3 shows additional analysis for chloride and sulfate variation in groundwater. The drinking water standard for chloride is 600 mg/L. Chloride concentrations above 600 mg/L were detected in the area of wells 6, 7, 8 and 11. One of these wells (number 11) is an upper zone well in the Beirut area of known seawater intrusion (Saad et al., 2004). The other wells are in the principal aquifer zone in the Beirut area. Elevation of sulfate is observed in the same contaminated wells.

To determine the sources of high-chloride water to wells, the molar ratio of chloride and sulfate was calculated and compared to the value in seawater (Figure 4). Most of the groundwater is situated below the seawater molar ratio (dashed line). Only values for sites 6, 7, 8 and 11 are found higher than seawater. The high-chloride water may originate from soluble salts trapped in the aquifer sediments from repetitive seawater intrusion. The constituents dissolved within the groundwater may retain a chemical composition consistent with a seawater origin.

Since Beirut suburbs and some principal areas still have septic systems in use, monitoring for nitrate contamination is an essential groundwater management function. Figure 5 shows that in the principle aquifer zone, wells 6, 7, 8 and 11 contained nitrate concentrations above the drinking water standard (50 mg/L). Nitrate in water comes from both natural and anthropogenic sources such as fertilizers, septic systems, and animal waste.

In order to delineate the sources of pollution in groundwater, additional isotopic analysis is performed for deuterium, oxygen-18 and $\delta^{15}N$ of nitrate ions in water.

Isotopic Characteristics of Groundwater

Isotopic compositions of groundwater in the Beirut basin are plotted separately in a spatial δ^{18} O and δ D diagrams (Figure 6). Oxygen-18 and deuterium are naturally occurring stable isotopes of







Figure 3. Chloride and sulfate distribution in the Beirut groundwater basin.



Figure 4. Molar ratio of chloride and sulfate in groundwater (circles) and seawater (square).

oxygen and hydrogen, respectively. Oxygen-18 and deuterium abundances are expressed as ratios, in delta notation as per mil (parts per thousand) differences, relative to the standard known as Vienna Standard Mean Ocean Water (VSMOW). The δ^{18} O and δ D composition of a water sample, relative to the global meteoric water line and relative to the local meteoric water line, provide a record of the source and evaporative history of the water, and can be used as a tracer of the movement of the water. Differences in the δ^{18} O and δ D composition of water from the global

Journal of Environmental Hydrology



Figure 5. Nitrate variation in the Beirut groundwater basin.

meteoric water line may result from differences in the temperature of condensation of precipitation that recharged the ground water. Partial evaporation of a water sample shifts the δ^{18} O and δ D composition to the right of the local meteoric water line (Craig, 1961).

Figure 6 shows that samples having high chloride, nitrate and sulfate (sites 6, 7 and 8) content are enriched in δ^{18} O and δ D. Maximum enrichment reaches -2‰ for δ^{18} O and -10‰ for δ D relative to the mean groundwater composition. To understand this feature, isotopic data were plotted against the Lebanon and Mediterranean meteoric water baselines (Saad et al., 2005).

In the δD - $\delta^{18}O$ diagram (figure 7), the isotopic composition of groundwater is close to that of the Lebanese Meteoric Water Line (LMWL). The more negative values indicate that groundwater recharge arises from local precipitation and infiltration. The karstic feature of the aquifer promotes the direct and fast infiltration of precipitation into groundwater. The less negative samples plot to the right of the local meteoric water line along an evaporative trend line. All high-chloride water plots to the right of the meteoric water line and chloride concentrations consistently increase with the evaporative shift in $\delta^{18}O$ and δD isotopic composition. These data suggest that the high-chloride concentrations are the result of evaporative process concentration of groundwater influenced by seawater intrusion.

In order to establish the origin of nitrate pollution in samples 6,7,8 and 11, isotopes for $\delta^{15}N$ were determined by Geokarst Engineering in Trieste, Italy. Values of $\delta^{15}N$ in wells 6 and 7 are respectively 16.15‰ and 15.5‰; whereas values for wells 8 and 11 are 12.6 and 13.32‰. These results showed that the origin of nitrate in wells 6 and 7 is the infiltration of animal waste used as



Figure 6. Spatial variation of isotopic parameters in the Beirut groundwater basin.

Journal of Environmental Hydrology



Figure 7. Oxygen-18 and delta deuterium composition of water from selected wells in the Beirut groundwater basin.

fertilizers in landscaping (Wassenaar, 1995; Komor and Anderson, 1993). The source of nitrate in wells 8 and 11 is the infiltration of septic systems to groundwater (Heaton, 1986; Böhlke and Denver, 1995).

CONCLUSIONS

In this study we have reported the hydrochemistry and the stable isotopic content of groundwater in the Beirut region and its suburbs. The mineral quality of water was found to be different in the southern suburb of Beirut where groundwater is characterized by elevated amounts of anions. Additional sources to the natural recharge of groundwater are thus suggested in the highly polluted samples. In the upper coastal area of Beirut, seawater intrusion affects groundwater quality.

The stable isotope composition of groundwater was found to be close to the Lebanese Meteoric Water Line (LMWL). Samples that fall between the Mediterranean Meteoric Water Line (MMWL) and LMWL indicate that groundwater recharge arises from local precipitation and infiltration. Samples showing high chemical parameters deviated from the LMWL. This may reflect the evaporation of recharge water as it moves through the unsaturated zone. $\delta^{15}N$ values of these samples confirm that the high nitrate content originated from either infiltration of animal waste or septic systems to groundwater.

REFERENCES

- Böhlke, J.K., and J.M. Denver. 1995. Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic Coastal Plain, Maryland. Water Resour. Res., Vol. 31, pp. 2319-2339.
- Craig, H. 1961. Isotopic variations in meteoric waters. Science, Vol. 133, pp. 1702-1703.
- Dindane, K., L. Bouchaou, Y. Hsissou, and M. Krimissa. 2003. Hydrochemical and isotopic characteristics of groundwater in the Souss Upstream Basin, Southwestern Morocco. Journal of African Earth Science, Vol. 36, pp. 315-27.
- Freeze, W.H., and J.A. Cherry. 1979. Groundwater. America; Prentice-Hall.
- Fetter, C.W. 1988. Applied Hydrogeology. America; Mirrill.
- Heaton, T.H.E. 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: A review. Chem. Geol., Vol. 59, pp. 87-102.

Kendal, C., and J.J. McDonell. 1998. Isotope Tracers in Cathment Hydrology. Amsterdam; Elsevier.

- Komor, S.C., and H.W. Anderson. 1993. Nitrogen isotopes as indicators of nitrate sources in Minnesota sand plain aquifers. Ground Water, Vol. 31, pp. 260-270.
- Matthew, S.L., and P.P. William. 2002. Stable isotope value of Costarican surface water. Journal of Hydrology, Vol. 260, pp. 135-150.
- Shama, M.L., and M.W. Hughes. 1985. Groundwater recharge estimation using chloride, deuterium and oxygen-18 profiles in the deep coastal sands of Western Australia. Journal of Hydrology, Vol. 81, pp. 93-109.
- Saad, Z., V.A. Kazpard, M.A. Geyh, and K. Slim. 2004. Chemical and Isotopic Composition of Springs and wells in the Damour River Basin. Journal of Environmental Hydrology, Vol. 12, Paper 18.
- Saad, Z., V. Kazpard, A.G. El Samrani, and K. Slim. 2005. Chemical and isotopic composition of rainwater in coastal and highland regions in Lebanon. Journal of Environmental Hydrology, Vol. 13, Paper 29.
- Wassenaar, L.I. 1995. Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes of N-15 and O-18 in nitrate. Appl. Geochem., Vol. 10, pp. 391-405.
- Weiskel, P.K., and B.L. Howes. 1992. Differential Transport of Sewage-Derived Nitrogen and Phosphorus through a Coastal Watershed. Environmental Science and Technology, Vol. 26(2), pp. 352-360.

Ward, R.C. 1975. Principles of Hydrology. London; McGraw-Hill.

Wood, W.W., and W.E. Sandford. 1995. Chemical and isotopic methods for quantifying groundwater recharge in a regional, semiarid environment. Journal of Groundwater, Vol. 33, pp. 458-468.

ADDRESS FOR CORRESPONDENCE Zeinab Saad Lebanese Atomic Energy Commission CNRSL PO Box 11-8281 Beirut, Lebanon

Email: zsaad@cnrs.edu.lb