The investigation of mass transfer in the Karasu karstic aquifer, Konya, Turkey

Adnan Ozdemir · M. Tahir Nalbantcilar

Abstract In this study, the changes in the chemical composition of the groundwater along a flow path were examined by using the water samples collected from unconfined, semi-confined and confined parts of the Karasu karstic aquifer. It was determined that transport of bicarbonate, calcium, and magnesium was dominant in unconfined and semi-confined parts of the aquifer, whereas calcite and dolomite precipitate in the confined parts. On the other hand, gypsum dissolution is present in all parts of the aquifer. In addition, the computed saturation indices explain the occurrences and precipitation of travertines in the Goksu Valley, which is the discharge area for the aquifer.

Résumé Les modifications de la composition chimique de l'eau souterraine le long d'un axe d'écoulement ont été étudiées à partir d'échantillons prélevés dans les parties libres, semi-captives et captives de l'aquifère karstique de Karasu. On a mis en évidence que le transport de carbonate, de calcium et de magnésium est prépondérant dans les parties libres et semi-captives de l'aquifère, alors que la calcite et la dolomite précipitent dans les parties captives. En outre, la dissolution du gypse se produit dans toutes les parties de l'aquifère. Par ailleurs, les indices de saturation calculés rendent compte de l'existence et de la précipitation des travertins dans la vallée du Göksu, qui est la zone de décharge de cet aquifère.

Resumen En este estudio, se han examinado los cambios de composición química en las aguas subterráneas a lo largo de una línea de corriente mediante el análisis de muestras recogidas en partes libres, semiconfinadas y cautivas del acuífero cárstico de Karasu. Se ha determinado que el transporte de bicarbonato, calcio y magnesio es dominante en las zonas libres y semiconfinadas, mientras que la calcita y la dolomita precipitan en las zonas confinadas. Por otro lado, la disolución de yesos ocurre en todo el ámbito del acuífero. Además, los índices de saturación calculados explican la existencia y precipitación de travertinos en el Valle de Goksu, situado en el área de descarga del acuífero.

Keywords Mass transfer · Hydrogeology · Karstic aquifer · Konya · Turkey

Introduction

As a result of chemical reactions between groundwater and carbonate minerals, either new carbonate minerals precipitate or carbonate minerals of the aquifer dissolve, causing karstic structures to form. Theoretical and experimental studies on carbonate equilibria (Freeze and Cherry 1979; Back and Lesser 1981; Back et al. 1982; Domenico and Schwartz 1990) provide a detailed description of this phenomenon. Carbonate reaction environments have been generally classified as open and closed systems. "These systems are defined by whether or not the amount of CO_2 is constant. An aqueous system in which the dissolved CO_2 is constant because of relatively unobstructed interaction with an abundant gaseous environment of constant pressure of CO_2 such as the earth's atmosphere is commonly referred to as an open system. If the H_2CO_3 consumed by mineral-water reactions is not replenished from a gaseous reservoir, the system is denoted as a closed system" (Freeze and Cherry 1979).

This study was carried out in an area of 115 km^2 located between Kartal Mountain (Hadim-Konya, south Turkey) and Goksu Valley (Fig. 1). The central and northern parts of the investigated area are forestland whereas the southern part is covered by maquis.

Changes in chemical composition of rain and/or snow water in the Kartal Mountain area, moving along a flow path to the point where these emerge at the surface in the Goksu Valley, were investigated. Groundwater in the study area first passes through an unconfined part of the aquifer, interpreted as open system conditions where the reactions given in Moran et al. (1978) occur. It then flows through a semi-confined part and a confined part, interpreted as closed systems of the aquifer, to emerge at the surface in the Goksu Valley.

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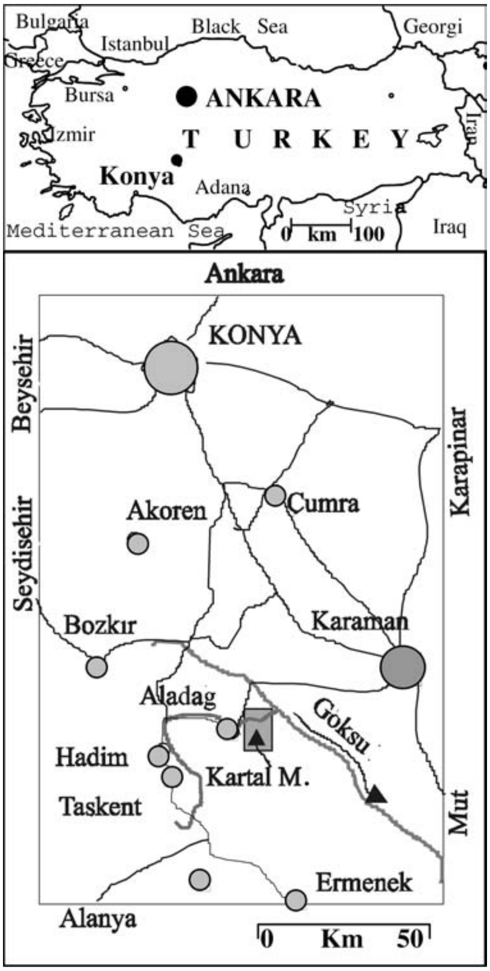

Fig. 1 Location map of the study area

Geology and Hydrogeology

The detailed geology of the area and its vicinity is given in Turan (1990, 1995) and Uguz et al. (1994), and a hydrogeologic description is given in a study by Baskan (1988). The Taskent complex (limestone, radiolarite, tuffite, diabase, and serpentinite – Upper Cretaceous) in the region is overlain by the Zindancik complex (metasandstone, quartzite, mudstone, fillite, and marble – Triassic) and both are overlain by the Kahtepe formation (limestone, and sandstone – Upper Permian – Middle Triassic) with a tectonic contact. All these units are uncomformably overlain by the Sinatdagi formation (conglomerate, dolomitic limestone, and limestone – Jurassic – Lower Cretaceous). Travertine (Quaternary – Recent) is the youngest unit in the study area (Fig. 2).

The Kahtepe formation, Sinatdagi formation, and the limestone blocks in the Zindancik complex (Fig. 2) comprise the Karasu aquifer which has a high permeability associated with karstification and secondary fracture porosity. The Taskent complex is weakly permeable whereas the remainder of the Zindancik complex is impermeable. Since karstification is well developed in the Kahtepe and Sinatdagi formations, dissolution voids, dolines, carens, and caves are often present. Karasu Spring is the only spring associated with this aquifer. Limestone strata of the Taskent complex and marble blocks of the Zindancik complex are moderately permeable and comprise the reservoir of numerous springs with low discharge.

Investigation Method and Sampling Techniques

The changes in chemical composition of groundwater from recharge to discharge areas were studied using the analysis of spring waters in the unconfined, semi-confined, and confined sections of the Karasu aquifer. The water infiltrating to the aquifer from snow in the Kartal Mountain was sampled (S1). The water discharging from the aquifer was collected from the Karasu Spring (S7), and other waters were sampled (from S2 to S6) from the springs between these two points (Fig. 2).

Temperature (T, °C), electrical conductivity (EC, μS/cm), and pH were measured at each sampling site. Ion concentrations of principal constituents (in mmol/l) and the saturation indices of calcite (Sicc), dolomite (Sidol), and gypsum (Sigyp), which were determined by using the PHREEQE computer program (Parkhurst et al. 1990), are given in Table 1.

Results and Discussion

The Variation of Parameters Along the Flow Path

The temperature of the waters at the sample sites ranges from 1 to 19.1 °C and increases along the flow path (except for S5; Table 1). The pH of the water recharging the Karasu aquifer is 6.72 whereas the pH of discharging water is as much as 8.1 for sample S6 at the discharge of the aquifer (Fig. 3). Three areas can be distinguished for EC changes along the flow path. These are strongly increasing values in the unconfined part of the aquifer (between S1 and S3), slightly increasing values in the semiconfined part of the aquifer (between S3 and S5), and very strongly increasing values in the confined part of the aquifer (between S5, S6 and S7). In addition, the concentration changes of Ca, Mg, Na and K along the flow path are similar (Fig. 4). On the other hand, Cl generally has an increasing trend, except for the intermediate samples S2 to S5 (Fig. 5). Ca, Cl and HCO_3 in the S7 sample have excess concentrations. Variations of Ca, HCO_3 and Cl concentrations along the flow path are very similar (Figs. 4, 5).

Mass Transfer and Reactions Along the Flow Path

The reservoir rock of the Karasu aquifer is generally composed of calcite, rarely dolomite and, in smaller amounts, clastic rock alternations. Similar concentrations of Na+K and Cl along the flow path indicate that minerals such as halite and sylvite in shallow marine sedi-

Fig. 2 **a** Simplified hydrogeologic map of the study area. **b** Cross section along *I*, *II* and *III*

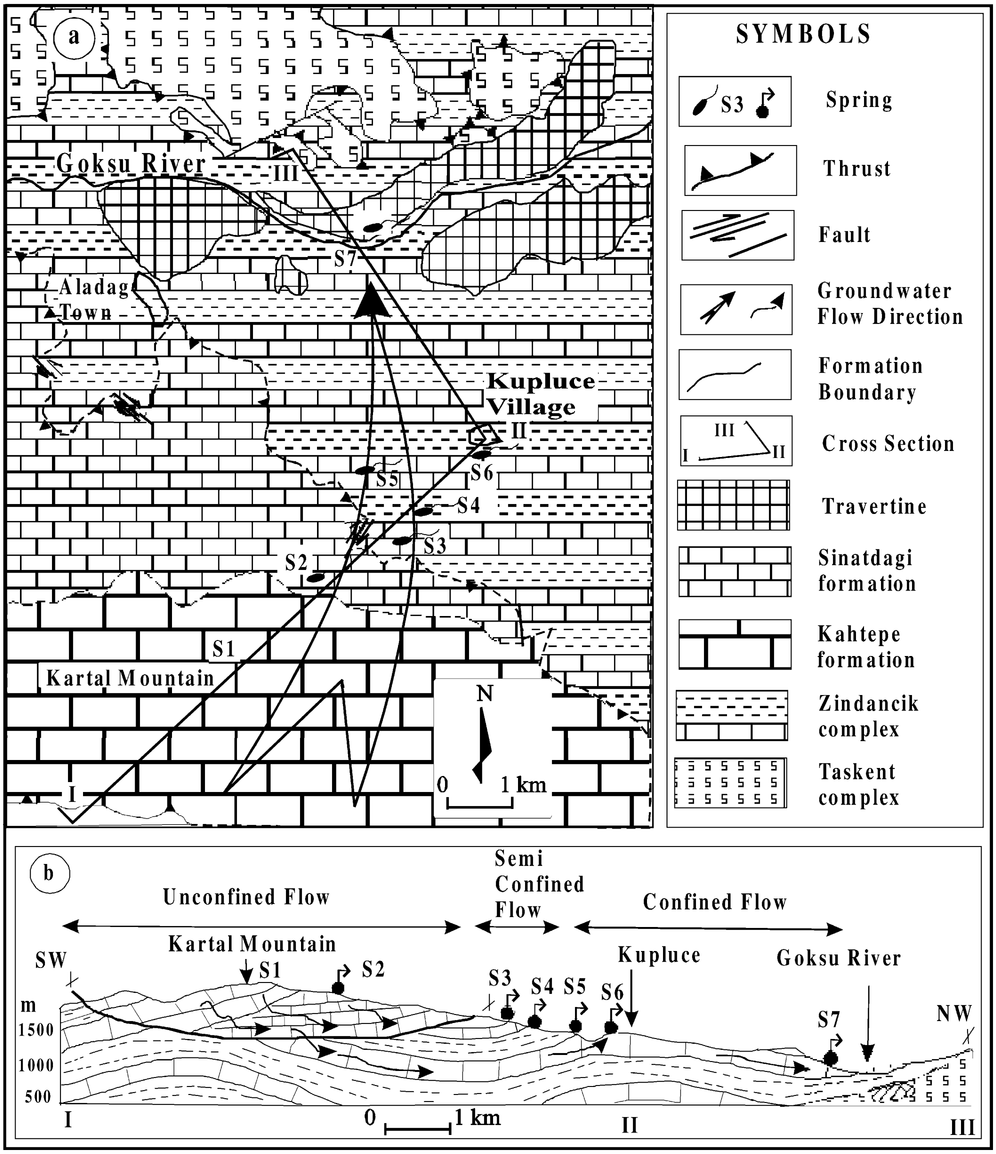

Table 1 Physical and chemical data used in the study

	S1	S2	S3	S4	S5	S6	S7
pH	6.72	6.74	6.80	7.14	7.90	8.10	8.06
T (°C)	1.4	6.9	10.5	13.6	12.2	19.0	19.1
EC (μS/cm)	16	285	300	327	350	460	987
Ca	0.060	1.160	1.480	1.550	1.610	1.640	3.980
Mg	0.040	0.125	0.308	0.308	0.316	0.466	1.337
Na	0.120	0.370	0.020	0.020	0.029	0.333	0.079
K	0.200	0.156	0.010	1.000	0.012	0.145	0.034
Cl	0.100	0.141	0.140	0.169	0.169	0.281	0.620
SO_4	0.008	0.037	0.040	0.052	0.059	0.060	0.229
HCO_3	0.443	2.967	3.295	3.295	3.524	4.290	9.672
Saturation index of calcite (Sicc)	−3.360	−1.210	−0.900	−0.420	0.410	0.780	1.380
Saturation index of dolomite(Sidol)	−7.170	−2.600	−2.570	−1.570	0.050	1.080	2.340
Saturation index of gypsum (Sigyp)	−4.810	−3.120	−2.960	−2.850	−2.790	−2.750	−2.050

ments are dissolved whereas calcite and dolomite are deposited. It is believed that mixing dissolved calcite and dolomite crystals, which have fossil seawater inclusions, increases Na, K, and Cl concentrations in the groundwater. Cation exchange plays an important role in ion concentration increases. However, it is not the purpose of this study to determine the effect of these factors.

CO_2, which originates from the oxidation of organic material and the respiration of plant roots and microorganisms, has been dissolved by recharge of acidic rain

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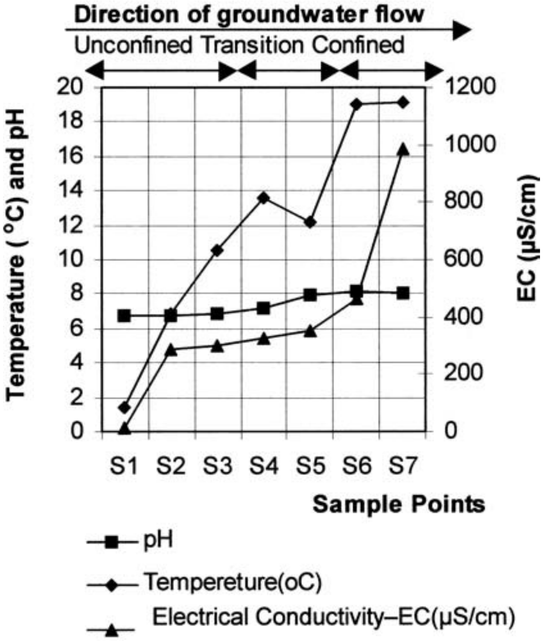

Fig. 3 Variation of pH, temperature and electrical conductivity along the regional flow path

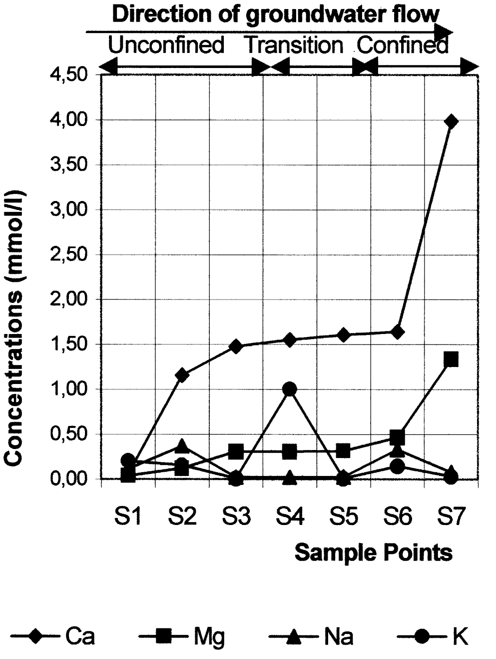

Fig. 4 Variation of cationic composition along the regional groundwater flow path

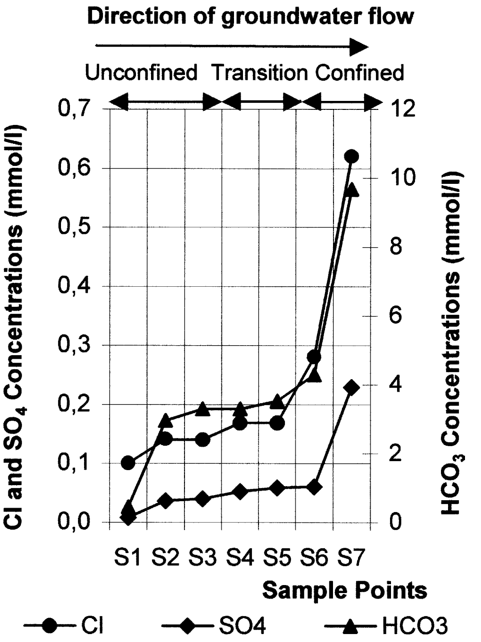

Fig. 5 Variation of anionic composition along the regional groundwater flow path

Table 2 Results of mass transfer calculations between S1 and S5

Species	Mass gained from the aquifer (mmol/l)			
	S2–S1	S3–S2	S4–S3	S5–S4
Ca	1.100	0.320	0.07	0.06
Mg	0.085	0.183	0	0.008
SO_4	0.029	0.003	0.012	0.007
HCO_3	2.524	0.328	0	0.229
Gypsum dissolution	0.029	0.003	0.012	0.007
Dolomite dissolution	0.085	0.183	0	0.008
Calcite dissolution	0.986	0.134	0.058	0.045
H_2CO_3 dissociation	1.156	0.500	0.058	0.061
Calculated HCO_3	2.312	1.000	0.116	0.122
Observed HCO_3	2.524	0.328	0	0.229
Difference	0.212	–0.672	–0.116	0.107

and/or snow water (S1) as it moves downwards into the aquifer (Palmer and Cherry 1984). In the open system condition of both the recharge and discharge areas, water enriched in CO_2 dissolves the carbonate minerals and increases the concentrations of HCO_3, Ca, and Mg in the groundwater. At the weak acid/strong base reaction stage (Moran et al. 1978) and with a constant (CO_2) gas pressure, HCO_3 ion concentration and pH increase linearly to the saturation point (Langmuir 1971). This has occurred between samples S1 and S2 in the area (Table 2). It is also shown that the saturation index values of dolomite, calcite, and gypsum decrease from S1 to S2.

Groundwater, containing CO_2 left over from carbonate dissolution in the confined part of the aquifer, can dissolve calcite, dolomite, and gypsum in the semi-confined area between S1 and S4. Down-gradient from the S4 spring, groundwater becomes saturated with respect to calcite and dolomite. A saturation index of –2.790 (Fig. 6; cf. Figs. 7, 8) for gypsum indicates that groundwater can still dissolve this mineral. Figures 2 and 3 show that groundwater further north (down-gradient) is confined, and closed system conditions prevail. In this area (S5, S6, and S7), saturation indices higher than +0.1 show that groundwater will precipitate both calcite and dolomite (Fig. 6; Table 1).

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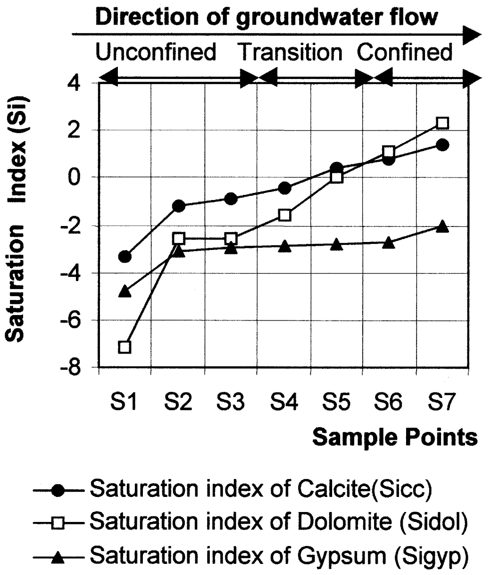

Fig. 6 Variation of calcite, dolomite and gypsum saturation index values

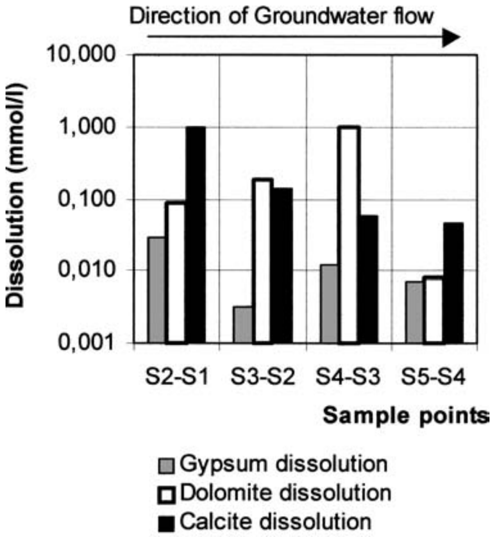

Fig. 7 Variation of calcite, dolomite and gypsum dissolution along the regional flow path

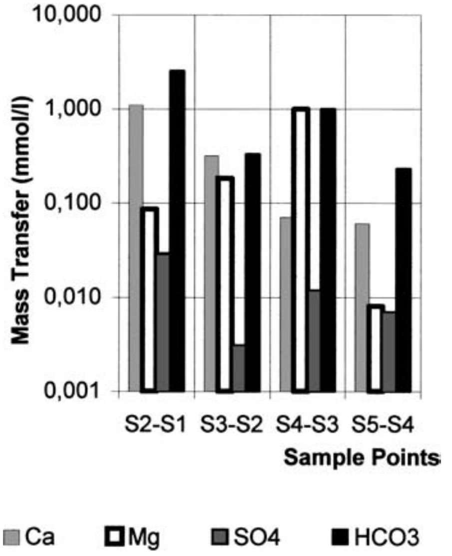

Fig. 8 Mass transfer between S1 and S5

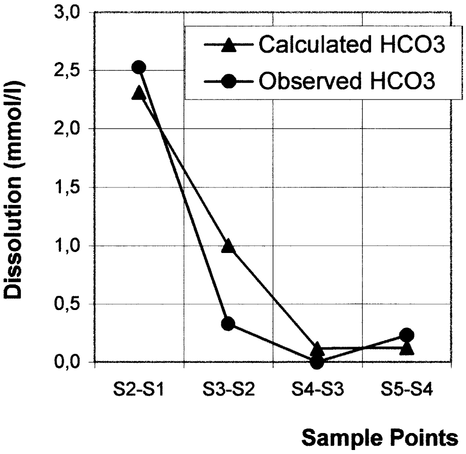

Fig. 9 Observed and calculated HCO_3 dissolution

The aquifer is mainly composed of limestone, dolomite, and gypsum. Ca, Mg, HCO_3, and SO_4 ions comprise 89–98% of total ions in the spring waters. In the mass transfer calculations, the principles given by Plummer and Back (1980) and Appelo and Postma (1992) were used. Calculation of the Ca/Mg ratio (in mmol/l) of dolomite was taken as 1, and it was assumed that all SO_4 in the system comes from the dissolution of gypsum. Based on these assumptions, it is shown that the differences in observed and computed mass transfer values (Fig. 9; Table 2) between S1–S2, S2–S3, S3–S4 and S5–S4 springs are quite low. Higher differences between S2 and S3 may indicate that hydrodynamic conditions in the transition part of the aquifer are more complex in comparison to the recharge and discharge areas of the aquifer. The dissolution rate histogram (Fig. 7) shows that dissolution of calcite in the flow direction continuously decreases. However, dissolution of dolomite increases in S2–S1, S3–S2, and S4–S3. Dissolution of gypsum decreases in all pairs of sample points. It also seems that the present dissolution potential of the system is between S2 and S3 waters, and is mainly used for obtaining HCO_3 and Ca and the remaining for Mg and SO_4 (Fig. 8). Also, solubility of gypsum is higher compared with calcite and dolomite (Bogli 1980; Fig. 6).

Groundwater becomes supersaturated with respect to calcite and dolomite between samples S4 and S5. This

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explains why travertines are precipitating on both sides of the Goksu River.

Conclusions

The conclusions of this study are as follows. The Karasu karstic aquifer is composed of three parts, namely, unconfined, semi-confined, and confined parts. Changes in HCO_3–Ca and Na+K–Cl concentrations show similarities along the flow path in the aquifer. Dissolution of calcite, dolomite, and gypsum is observed in the part between the recharge area and S4–S5. Gypsum dissolution and dolomite and calcite precipitation are found in the S4–S5 springs in the Goksu Valley, which is in the discharge area for the aquifer. Solubility of gypsum is not much affected by the hydrodynamic conditions of the aquifer. Mass transfer of HCO_3 and Ca along the flow path to the S5 spring continuously decreases whereas mass transfer of SO_4 and Mg first decreases and then increases. Saturation indices exceeding +0.1 for calcite and dolomite, calculated from the water chemistry of spring S5, explain the presence of precipitated travertines in the Goksu Valley.

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