Published in Applied Geochemistry, 5, issues 5-6, 563-569, 1990
which should be used for any reference to this work

Hydrology of a spring complex, studied by geochemical time-series data, Acquarossa, Switzerland

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Abstract—A case study of three springs in Switzerland is used to demonstrate the value of geochemical time-series data as a powerful tool to study the dynamics of groundwater systems. Values of repeatedly measured parameters revealed intermixings of two water types: (a) a 29°C water, circulating to a depth of ~1100 m and containing approximately 700 mg/l Ca, 2000 mg/l SO_4, 700 mg/l HCO_3, 20 mg/l of Na and Cl, 6 mg/l Fe, at least 47 mg/l SiO_2, and with an isotopic composition of $\delta D = -73.0‰$ and $\delta^{18}O = -10.9‰$, and (b) a 12°C or colder water, shallow, and of a post-1953 age, containing 420 mg/l TDI or less, very low in Na and Cl (4 mg/l or less), isotopic values of $\delta D = -71.0‰$ and $\delta^{18}O = -10.5‰$ and tritium as in recent (post-bomb) precipitation.

SCOPE OF THE PROBLEM

GROUNDWATER systems are dynamic and this is reflected in the behaviour of individual springs and wells, which are often variable in their characteristic parameters e.g. discharge, level of water table, temperature, concentrations of dissolved ions and isotopic composition. Single measurements do not adequately describe the dynamic picture and provide sporadic and limited insight into groundwater systems.

Most hydrological and hydrochemical properties have a meaningful definition only for single groundwater components e.g. flow direction, modes of flow (porous versus conduit-dominated media), depth of circulation, chemical equilibrium with associated rocks, ionic geotemperature, recharge altitude (calculable from isotopic data), and water age. However, mixing of different water types is common in nature (MAZOR, 1985), and a crucial stage in the study of a groundwater system is to establish whether one deals with one type of water or with a mixture of waters from different reservoirs. In the first case the properties of the system may be deduced straight from the measured parameters, but in the second case meaningful age, depth of circulation, recharge altitude or chemical equilibria may not be deduced, except for the intermixing water types, or end members, provided their parameteric values have been derived. Periodically repeated measurements, or time-series data, are in many cases the sole approach to establish whether one deals with a simple uniform water system or with a mixed one (MAZOR *et al.*, 1985).

Ideally, data are collected at the same source (spring or well) over long periods at regular time intervals. In such cases the results are best presented in a graphic mode as a function of time, the best known example being the hydrograph. If however, the repeated measurements are taken irregularly, leaving long time gaps, or the number of repeated measurements is small, a plot as a function of time is of limited value. In such cases other approaches are needed.

The present communication addresses the methodology of processing sporadically collected hydrochemical time-series data, demonstrated on the Acquarossa spring complex, southeast Switzerland (Fig. 1).

THE ACQUAROSSA SPRING COMPLEX

The thermal area of Acquarossa is located in the Blenio Valley (Tessin). Its name originated from the red oxidised iron deposits precipitated at the point of emergence. The springs issue from the Penninic overthrust of Simano. Cadisch (in HÖGEL, 1980) suggested that Triassic dolomite, sandstone and gypsum act as the aquifer rocks, and that the thermal water ascends through faults and fractures in overlying gneiss and micaschist and flows out in a talus fan.

One spring, Albergo, emerges at an altitude of 550 m. About 450 m south of it, at an altitude of

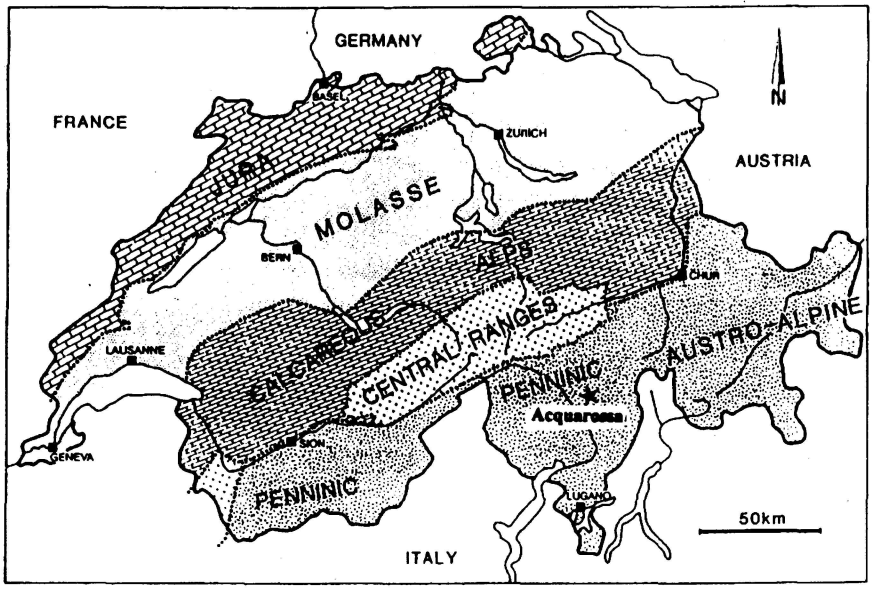

FIG. 1. Location map of the studied springs.

450 m, issue three springs, of which two have been included in the present study: Satro Left and Satro Central.

RESULTS

The results of repeated measurements are given in Tables 1 and 2. The analytical procedures were described by VUATAZ (1982). The observed patterns are described below.

Variability with time

Figure 2 reveals an overall picture of the nature of temporal variations. Albergo was remarkably steady over 14 months—the maximum/minimum discharge ratio was ~2, the concentration of the total dissolved ions (TDI) remained at 2600 mg/l with fluctuations of <10%, and the temperature remained constant at 25 ± 0.5°C. The Albergo spring has shown such steady behaviour since 1882 (VUATAZ, 1982). The Satro Central spring, observed over a period of 4 months, revealed a similar behaviour: the discharge de-

Table 1. Results of the Albergo spring

Date	14-05-1977	21-06-1977	08-08-1977	06-10-1977	03-03-1978	30-04-1978	08-06-1978	16-07-1978
Discharge (l/min)	72	120	72	120	90	75	75	72
Temperature (°C)	24.6	24.9	25.1	25.2	25	24.8	24.8	25.1
pH	6.3	6.7	6.8	6.45	6.8	6.8	6.55	6.5
TDS (mg/l)	2674	2663	2451	2633	2565	2650	2570	2578
Sum of cations (meq/l)	37.65	36.08	36.4	37.47	36.98	36.87	36.65	36.78
Sum of anions (meq/l)	37.1	37.54	33.16	36.42	35.23	36.99	35.42	35.55
Ca^{2+} (mg/l)	581	549	555	574	571	565	562	566
Mg^{2+} (mg/l)	86.7	85.5	85.8	87.8	84.5	85.3	83.6	84.1
Na^+ (mg/l)	17	18.4	18.2	17.8	17	19.9	18.6	18.3
K^+ (mg/l)	16.7	18.3	17.1	16.4	16.4	16.6	17.2	17.2
Sr^{2+} (mg/l)	11.4	11.3	11.2	11.2	11.7	11.5	11.6	11.1
Fe^{2+} (mg/l)	2.36	2.86	3.9	3.89	2.64	2.56	5.59	3.13
Mn^{2+} (mg/l)	0.15	0.17	0.16	0.18	0.15	0.17	0.17	0.17
Li^+ (mg/l)	0.09	0.11	0.11	0.1	0.1	0.1	0.1	0.1
SO_4^{2-} (mg'l)	1250	1300	1100	1250	1200	1275	1200	1200
HCO_3^- (mg/l)	659	621	615	622	615	626	622	628
Cl^- (mg/l)	6.5	7	6.5	7	6	6.5	5	6.5
F^- (mg/l)	1.73	1.84					1.87	1.75
SiO_2 (mg/l)	41.5	47.1	38.1	42.5	40.5	41.8	42.3	41.8
Tritium (TU)		38			26			
Deuterium (‰)		−73.4			−72.6			
Oxygen-18 (‰)		−10.88			−10.83			

Table 2. Results of the Satro springs

	Left spring				Central spring			
Date	03-03-1978	30-04-1978	08-06-1978	16-07-1978	03-03-1978	30-04-1978	08-06-1978	16-07-1978
Discharge (l/min)	120	30	25	10	70	60	36	30
Temperature (°C)	13.9	14.8	16.1	18.1	23.8	23.8	24.4	24.5
pH	7.3	6.95	6.75	6.65	6.5	6.45	6.25	6.3
TDS (mg/l)	420	596	776	1397	2643	2787	2753	2879
Sum of cations (meq/l)	5.57	8.3	11.02	19.03	36.98	39.43	38.97	30.19
Sum of anions (meq/l)	5.68	8.03	10.53	19.47	36.7	38.68	38.07	40.25
Ca^{2+} (mg/l)	82.5	127	171	299	564	615	610	626
Mg^{2+} (mg/l)	13.5	18.8	23.9	43	87.7	86.6	83.6	87.6
Na^{+} (mg/l)	4.18	5.15	6.39	10.5	18.2	18.5	19	19.5
K^{+} (mg/l)	4.18	5.01	5.92	9.46	17.1	16.9	17.7	19.1
Sr^{2+} (mg'l)	1.65	2.31	3.24	6.02	12.5	12	12.4	12.2
Fc^{2+} (mg/l)	0.31	0.19	0.22	0.68	2.37	2.33	2.01	2.95
Mn^{2+} (mg/l)	0.02	0.02	0.04	0.04	0.2	0.18	0.18	0.19
Li^{+} (mg/l)	0.02	0.02	0.03	0.05	0.11	0.1	0.1	0.11
SO_4^{2-} (mg'l)	160	245	340	650	1250	1350	1300	1400
HCO_3^- (mg/l)	137	171	200	342	641	639	655	659
Cl^- (mg/l)	3.5	4.5	5	10	8	3.5	5.5	7
F^- (mg/l)			0.6	0.87			2.1	1.96
SiO_2 (mg/l)	13	16.5	19.2	25.3	44.3	42.4	45.5	43.5
Tritium (TU)	64				35			
Deuterium (‰)	−71				−73.9			
Oxygen-18 (‰)	−10.45				−10.85			

creased only by a factor of ~2, and the TDI and temperature remained steady. These two springs, 450 m apart, have the same TDI concentrations and the same temperature. The Satro Left spring differs significantly: during a 5 month period the discharge decreased by a factor of 12, the TDI concentrations increased by a factor of 3, and the temperature increased by 4°C. A water cannot have different TDI concentrations, e.g. in the Satro Left case from 420 to 1400 mg/l (Table 2). Hence, at least two different

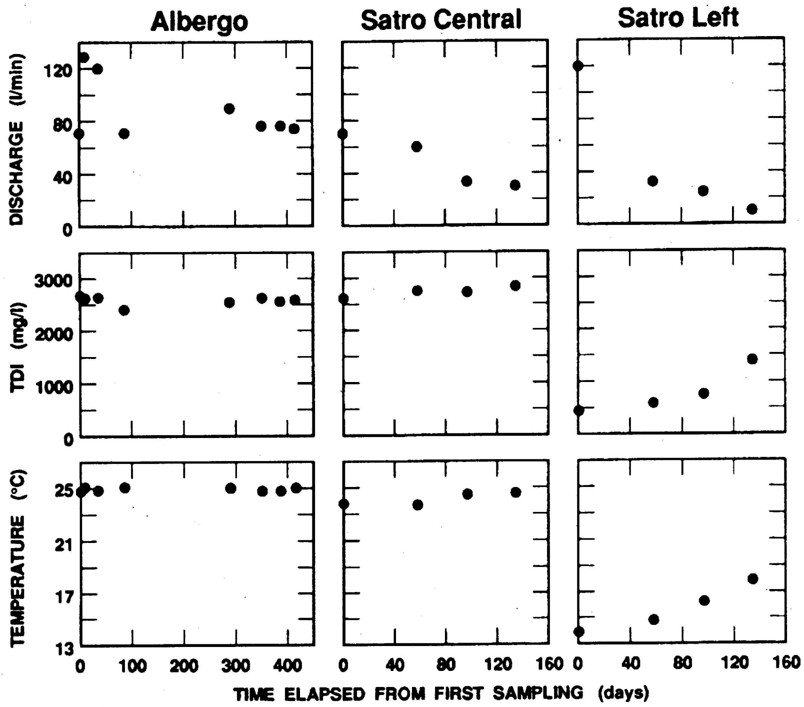

Fig. 2. Discharge, total dissolved ions and temperature as functions of measurement and sample collection date. Sampling began on 14-05-1977 at Albergo and on 03-03-1978 at the Satro Central and Satro Left springs and it was terminated on 16-07-1978.

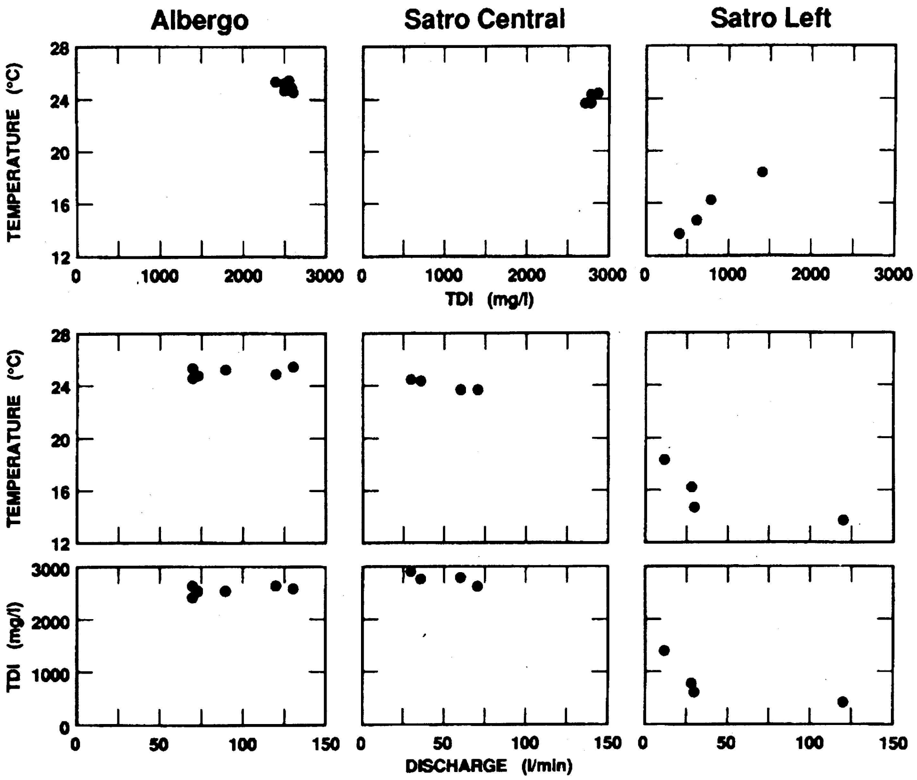

FIG. 3. Temperature and total dissolved ions (TDI) as functions of discharge, and temperature–TDI plots.

water types intermix at this spring: a relatively fresh cold water and a more saline warm water, their ratios being correlated to the discharge (Fig. 2).

Variability as a function of discharge

Temperature and TDI remained practically stable at the Albergo and Central Satro springs, although the discharge varied by a factor of ~2, as seen in Fig. 3. In contrast, in the Satro Left spring the temperature and TDI revealed a marked negative correlation with discharge (Fig. 3), suggesting flow of warm saline water and seasonal additions of cold fresh water.

Temperature variations as a function of salinity

As seen in Fig. 3, the Satro Left spring revealed a positive correlation between temperature and TDI, extrapolating to 12°C at 0 mg/l TDI. This temperature is the lowest possible temperature of the intermixing cold water end member, the real value lying between this extrapolated value and the lowest measured value of 13.9°C. The high temperature–TDI correlation suggests that mixing of a warm saline water with a cold fresh water occurs in the Satro Left spring immediately prior to emergence at the surface. Cooling after mixing would disturb the temperature–TDI correlation. The Satro Central spring had little variation in its salinity and temperature, yet a positive TDI–temperature correlation can be seen in this case as well (Fig. 3).

Dissolved major ions variability and water composition

The relative ion abundances are the same in the three springs, namely:

$$\mathrm{Ca} > \mathrm{Mg} > \mathrm{Na} = \mathrm{K} \quad \text{and} \quad \mathrm{SO_4} > \mathrm{HCO_3} \gg \mathrm{Cl}.$$

These ions and SiO_2 in the Satro Left spring show linear positive correlations with TDI (Fig. 4) and with each other. The high variability of the ion concentrations in the Satro Left spring may indicate intermixing of several water types. The high correlations, reflected in straight lines in Fig. 4, suggest that only two water types intermix: a relatively saline water, diluted by a very fresh water. The latter is, most probably, local recharged water that underwent minimum interaction with rocks. The Albergo and Satro Central data show positive linear correlations for SO_4 and possibly Ca (Fig. 5). The range of concentration variations are in the latter cases smaller than in the Satro Left case, but they suggest that mixing, or dilution, also occurs in the Albergo and Satro Central springs.

The SO_4 concentration is high in the springs, up to

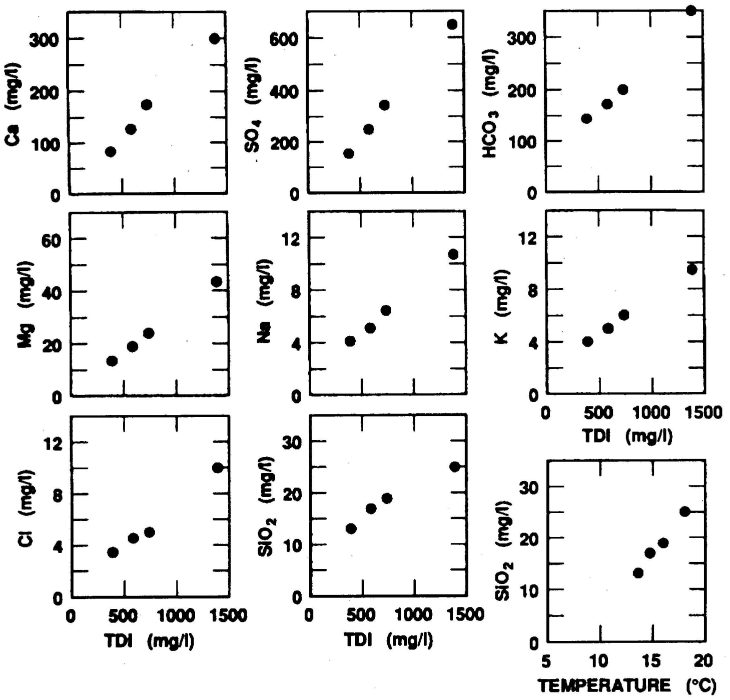

FIG. 4. Ionic concentrations in samples of the Satro Left spring as a function of total dissolved ions.

1400 mg/l, paralleled by the presence of Ca as the dominant cation, suggesting interaction with gypsum or anhydrite. Even the highest observed SO_4 concentrations are below saturation concentration with respect to gypsum or anhydrite under the prevailing conditions, indicating that one observes water not in direct contact with gypsum, but a diluted version. The TDI–SO_4 line of Satro Left extrapolates to the origin of the axes, suggesting that no secondary interactions changed the SO_4 concentration after the mixing event. This suggestion is in agreement with the conclusion that dilution occurs immediately prior to emergence at the surface, based on the TDI–temperature correlation. In contrast, the TDI–SO_4 lines of the Albergo and Satro Central springs extrapolate toward the TDI axes (Fig. 5), suggesting SO_4 is involved in a secondary process that consumes part of it.

The HCO_3 concentration is high in the most saline samples, up to 660 mg/l, in contrast to the samples with more fresh water of Satro Left, that contains as little as 140 mg/l HCO_3 (Table 2). Thus, CO_2 has been added to the mineral water at intake, or along its underground path, followed by interaction with carbonate rocks, e.g. limestone and/or dolomite. Magnesium might originate from the latter interaction as well as from evaporites associated with the gypsum or anhydrite.

Chloride and Na occur in the three springs in exceptionally low concentrations: 3–10 mg/l Cl and 4–20 mg/l Na. These low concentrations imply that practically no NaCl has been added to the water underground, not even to the mineralised water end-member. Thus, no halite is present in the rocks associated with either the fresh or mineralised waters. The Na:K ratio is ~1, an exceptionally low value in groundwater. In the present case this is probably another reflection of the very low Na concentration.

Silica is present in concentrations of 38–47 mg/l in the Albergo and Satro Central springs, and 13–25 mg/l in the Satro Left spring. The SiO_2 concentration is positively correlated to TDI in the Satro Left and Albergo springs, suggesting it is relatively high in the saline water end member, in agreement with the higher temperature deduced for the latter.

Iron concentrations were 2–5 mg/l at the Albergo and Satro Central springs, as compared to 0.3–0.7 mg/l in the Satro Left spring. Thus, an enrichment in dissolved Fe characterises the warm saline water end member.

Tritium data

The four tritium values assign 26–38 TU for the Albergo and Satro Central springs, and 64 TU for the sample of highest discharge of the Satro Left spring (Tables 1 and 2). This indicates that the fresh cold-water end member, most abundant in the Satro Left spring, has a post-bomb, i.e. post-1953 age. In contrast, the saline warm water end member, most represented in the Albergo and Satro Central springs, is low in tritium and most probably devoid of it (warm waters generally predate the bomb tritium contamination).

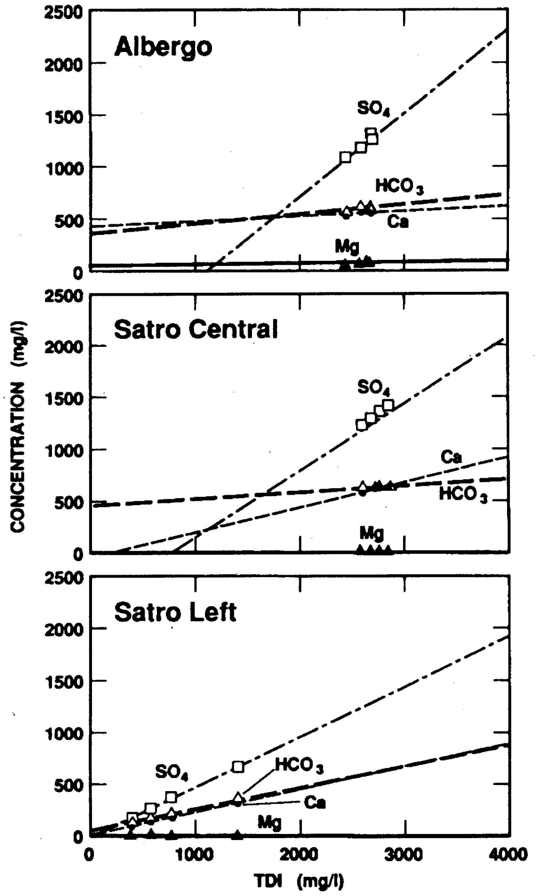

FIG. 5. Composition scatter diagrams revealing ionic linear correlations with total dissolved ions in the studied Acquarossa springs. Extrapolation of the Satro Left spring data to 3900 mg/l TDI, the highest value reconstructed via tritium data for the Satro Central spring, provides the extrapolated ionic concentrations in the undiluted saline water end member.

The presence of some tritium in the most saline samples of the Albergo and Satro Central springs suggests that these waters contain some amount of the recent water end member. Taking the value of 64 TU, observed in the freshest sample of the Satro Left spring, as representing the local fresh groundwater at the time of the study, the percentage of recent water may be estimated in the saline samples. The sample collected at the Albergo spring on 03-03-1978 (same date at which the Satro Left sample was collected) contained 26 TU, suggesting that this spring water contained about 26 × 100/64 = 40% post-bomb water.

Ion concentrations and temperature of the saline water end member

The tritium concentration, observed in the most saline water sample, suggests that the dissolved ion concentrations in the undiluted mineralised water end member could be higher by about 40% than observed in the most concentrated sample. Thus, the TDI concentration of the undiluted saline end member is 2800 × 1.4 = 3900 mg/l. A temperature of 29°C, representing the undiluted warm end member, is obtained by extrapolation in Fig. 3 of the best fit TDI–temperature line to 3900 mg TDI/l (not marked on Fig. 3). Similarly extrapolated values of about 2000 mg SO_4/l, 700 mg HCO_3/l and 700 mg Ca/l are obtained in Fig. 5 for the saline end member by extrapolation to a TDI concentration of 3900 mg/l.

Deuterium and oxygen-18

The isotopic values available for δD yield an average value of $-73.0‰$ for the Albergo and Satro Central springs, and $-71.0‰$ for the sample of the highest discharge of the Satro Left spring (Table 1). The $\delta^{18}O$ values were -10.83 to $-10.88‰$ in the Albergo and Satro Central springs, and $-10.45‰$ in the sample of highest discharge in the Satro Left spring. Thus, the fresh, cold and young end member has an isotopic composition that is slightly, but analytically significant, heavier as compared to the saline, warm and old water end member. This observation suggests that the old water end member was recharged at an altitude that was slightly higher than that of the recent end member, or that the old end member was recharged during a paleoclimatic regime that differed from the present one. An accurate calculation of the recharge altitude of the recent water end member has to be postponed until local isotopic recharge–altitude relations are available.

A CONCEPTUAL HYDROLOGICAL AND HYDROCHEMICAL MODEL

The repeated measurements conducted in the three Acquarossa springs provided a long list of boundary conditions that may be put together into a conceptual model of the studied water system. Two water types have been identified in the Acquarossa system.

A warm (~29°C) end member, that is relatively old (pre-1953), saline (~3900 mg/l TDI), containing Ca (~700 mg/l), SO_4 (~2000 mg/l), HCO_3 (~700 mg/l), and poor in Na and Cl (20 mg/l each or slightly more), Fe (~6 mg/l), SiO_2 (at least 47 mg/l), and isotopic values of $\delta D = -73.0‰$ and $\delta^{18}O = -10.9‰$. A cold (12°C or less) end member, that is recent (post-1953), fresh (420 mg/l or less), very low in Na and Cl (4 mg/l or less), isotopic values of $\delta D = -71.0‰$ and $\delta^{18}O = -10.5‰$ and tritium as in recent (post-bomb) precipitation.

A crucial question pertains to whether the warm mineral water component in the relatively salt poor Satro Left spring is the same as in the more concentrated water of the Albergo and Satro Central springs. This question can be answered using the Satro Left spring plots of the various ions as functions of TDI (Fig. 4). Selecting the representative TDI value (2800 mg/l) of the Satro Central spring, the following extrapolated values are obtained: SO_4 = 1350 mg/l, HCO_3 = 640 mg/l, Ca = 600 mg/l, and SiO_2 = 40 mg/l (not marked on Fig. 4). These extrapolated values agree very well with the corresponding values of the Satro Central spring (Table 1) and the same holds true for the comparison with the Albergo spring. Hence there is a common mineral-water end member that occurs in the three springs.

A similar extrapolation can be made on the temperature–TDI plot of Satro Left (Fig. 3): a TDI value of 2800 mg/l reveals a corresponding value of 24°C (not marked on Fig. 3). This value is the same as the average temperature observed in the Satro Central spring (Table 1), indicating that no conductive cooling of the ascending warm water takes place in the springs. The combination of Figs 3–5 provides the full picture of the Satro Left spring as a mixed system of saline warm water that is diluted by fresh cold water.

The data indicate that the saline water type has a relatively deep circulation, because it is warm. Taking the extrapolated value of 29°C for the undiluted end member, and 7°C for the shallow and fresh recharge water, the warm water was heated by ~22°C due to its deep circulation. Taking a regional geothermal gradient of 2°C/100 m (Rybach, 1982), a circulation depth of 1100 m is obtained.

CONCLUSIONS

The present study demonstrates that single measurements, conducted on springs or wells, have little meaning in terms of the understanding of the dynamics of a water system. A single point out of the Satro Left points on the plots of Fig. 4 could not tell that one deals with a mixed system. However, even a limited set of 4–7 repeated measurements reflected the time dependent dynamics, including types of aquifer rocks, depth of circulation and age of the components of the system. Because mixing of waters is common in nature, time-series data are essential to the understanding of water systems.

Editorial handling: H. L. Barnes.

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