

Interpretation of Water Chemistry and Stable Isotope Data from a Karst Aquifer According to Flow Regimes Identified through Hydrograph Recession Analysis

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Abstract

In this study the relation between flow regime and chemistry of a major karst groundwater resurgence zone in southwestern Slovenia was examined using spring hydrograph recession analysis. Long-term (>2 weeks) recession periods were isolated from 6 years of flow data. Breaks in slope on a plot of the natural log of the discharge versus time allowed for the identification of four separate flow regimes of the aquifer outflow. Major ion chemistry and stable isotopic composition ($\delta^{18}\text{O}$ of water and $\delta^{13}\text{C}$ of DIC) of samples collected twice monthly for two years were then grouped according to where they had been collected within each identified flow regime. Patterns in the chemical and isotopic data emerged which indicated shifting sources of water contributing to the outflow of the spring under different hydrologic conditions. This type of analysis may be a valuable water resource management tool in other karst regions.

INTRODUCTION

A primary challenge for the management of karst water resources is to characterize water quality changes with discharge variability. In order to accomplish this goal, managers must be able to efficiently assess two aspects of the karst aquifer system that interact and determine overall water quality: the hydrologic and the hydrochemical variability. Often, however, resources for characterizing water quality across the full range of hydrologic variability are limited, resulting in a frequency of water sampling that is far lower than the actual time scale of chemical changes taking place at the point of measurement. Therefore, a need exists for a method through which relatively infrequent water quality data can be used to accurately understand and possibly predict major changes in water quality as the hydrologic conditions change.

In this paper, we describe a technique in which long-term records of discharge and relatively infrequent water quality sampling can be combined for the purpose of studying water quality changes with flow. The steps are not mathematically complex, allowing for

straightforward and rapid culling of information from data which already exists for many springs. The analysis begins with examination of the recession limbs of a long-term (several years) record of discharge. First suggested by Maillet (1905), several authors have since proposed that the recession limb of a karst spring hydrograph can be approximated by a function that is the sum of several exponential segments of the total recession (Forkasiewicz and Paloc, 1967; Hall, 1968; Milanović, 1981; Bonacci, 1993; Tallaksen, 1995). Thus, the entire discharge-time relationship of the recession is expressed as:

$$Q(t) = \sum_{i=1}^N q_o^i e^{-(\alpha_i)t} \quad (\text{eq. 1})$$

Where Q is the discharge at time t , N is the number of exponential segments of the recession, q_o^i is the discharge at the beginning of each recession segment, and α_i is the recession coefficient for each segment. In this model, each exponential segment is interpreted to represent the depletion of an aquifer reservoir, with the rate of depletion of that reservoir being

represented by the recession coefficient (α_i). Accordingly, the segment with the greatest recession coefficient would represent the most rapid drainage of the karst network (presumably surface runoff or displacement of water into the largest conduits) and the recession segment with the smallest coefficient would represent the baseflow (i.e., the slow drainage of that portion of the aquifer with the lowest transmissivity). The latter is often termed the *diffuse flow* portion of the aquifer, while the most transmissive conduits are referred to as the *quickflow* portion of the aquifer. Intermediate segments of the total hydrograph recession are thought to represent the emptying of aquifer volumes having intermediate values of hydraulic conductivity.

In reality, it is not clear whether the above conceptual interpretation has any definitive physical validity. It is extremely difficult to quantify the proportions of various transmissive elements of a karst aquifer given the high degree of heterogeneity in karst. Moreover, the conceptual model of a karst aquifer having separate “diffuse flow” and “quickflow” components may be misleading, as the physical connectivity between fractures and solutionally enlarged conduits exists more as a continuum of transmissivities within the aquifer. Nonetheless, the full recession of the hydrograph contains much useful information, particularly concerning (1) the volume of water drained from the system over time after peak flows, regardless of where the flow originates in the body of the aquifer, and (2) changes in the rate of discharge that occur at discrete values of discharge, thus placing quantifiable limits on aquifer flow regimes.

Constructing a Master Recession Curve

Assuming individual recession segments can be identified, the mean values of q_o and α for each segment can be used to construct a Master Recession Curve (MRC) of the spring or well (in the absence of identifiable linear segments on a semi-log plot of discharge vs. time, other models may be applied to estimate the segments of the MRC; see Sujono and others, 2004 for examples). Each segment of the MRC is only a portion of an individual exponential recession

curve, the constants of which are defined by the values of the recession constant (α) and the initial discharge defining the upper limit of the recession segment (q_o). Taken individually, each of these curves represents aquifer drainage under a particular flow regime, defined by the discharge measured over a specified time interval after the onset of the recession. Except for the tail end of the baseflow recession curve, the time intervals of all of the recession segments overlap. Thus, the volumes of water contributed by the underlying curves must be accounted for as part of the volume of water drained solely by an individual segment.

For example, let us assume an arbitrary master recession curve of a karst spring, represented in semi-log space in **Figure 1**. Three exponential recession curves ($Q_f(t)$ =fast flow, $Q_i(t)$ =intermediate flow and $Q_b(t)$ =baseflow) combine to give the overall recession, which is represented by the uppermost surface of the intersecting lines shown in Figure 1. The total volume of water drained across the fast flow portion of the recession is equivalent to the integration of recession curve $Q_f(t)$ on the interval t_o to t_i . In this way, the calculation sums together the volumes V_f^f , V_i^f and V_b^f . Lacking any *a priori* knowledge of the physical significance of these volumes for the functioning of the aquifer, their estimation may not seem consequential. However, for the purposes of water quality interpretation it may be desirable to separate the fastest flow portion from the other volumes drained across the MRC. Thus, we may calculate the fast flow volume (V_F) determined solely by the largest recession constant (α_f) and separated from the baseflow and intermediate flow volumes as:

$$V_F = V_f^f = \int_{t_o}^{t_i} Q_o \exp(-\alpha_f t) dt - \int_{t_o}^{t_i} q_o^i \exp(-\alpha_i t) dt \quad (eq. 2)$$

By integrating the MRC only on the interval from the time of peak flow until the break in slope and intersection with the next recession curve, the expression in eq. 2 quantifies the volume drained solely under the fastest draining

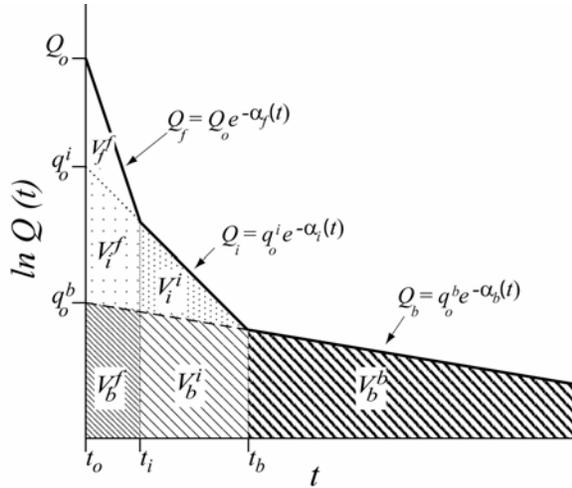


Figure 1: Schematic representation of a Master Recession Curve (MRC) and the theoretical drainage volumes obtained by integration beneath individual linear segments (see text for details).

portion of the MRC; it is only the volume of the fast flow regime that we seek to define. The “fast flow” volume is not equivalent to the total theoretical volume drained by the uppermost recession curve—rather, it is a flow regime we are defining independent of (but dominated by) that recession curve. The fast flow regime thus includes theoretical contributions from all 3 recession segments.

Similarly, the intermediate flow (V_I) and baseflow (V_B) volumes (represented in Figure 1 by the stippled region and cross-hatched region, respectively) can be calculated by the following equations:

$$V_I = \int_{t_0}^{t_b} q_o^i \exp(-\alpha_i t) dt - \int_{t_0}^{t_b} q_o^b \exp(-\alpha_b t) dt \quad (\text{eq. 4})$$

$$V_B = \int_{t_0}^{\infty} q_o^b \exp(-\alpha_b t) dt \quad (\text{eq. 5})$$

Thus, the total volume of water, V_T drained across the entire recession, from $t=0$ to $t=\infty$ is:

$$V_T = V_F + V_I + V_B. \quad (\text{eq. 6})$$

Using these expressions to quantify theoretical volumes of outflow for a particular spring, one may now look to characterize the quality of water drained from those volumes based upon chemical and/or isotopic data. This was the approach taken for the case study described herein.

STUDY SITE AND BACKGROUND

This study was conducted within the Classical Karst, located along the border between southwestern Slovenia and northeastern Italy. The Slovene name for this region is *Kras*, and this term will be used hereafter in order to signify the geographic location. The Kras region is an uplifted, overturned anticlinal block of Cretaceous limestone forming a plateau at approximately 400 m above sea level. The Kras region is 40 km long, up to 13 km wide, and covers approximately 440 km², with mean annual precipitation between 1400 and 1600 mm (Kranjc, 1997). Rainfall easily infiltrates into the limestone bedrock, due to thin soil thickness (0 to 0.5 m) and the abundance of bare karst bedrock surfaces. No surface streams exist on the Kras plateau. Given the abundant annual precipitation, highly permeable land surface, and lack of surface water runoff, autogenic recharge on the Kras surface is a major component of recharge to the underlying aquifer.

In the past, hydrogeological research on the Kras focused mainly on the source of water of the Timavo springs. The Timavo springs are the largest natural source of groundwater in the region, and have been an object of curiosity for centuries (Galli, 1999). The largest of these springs has been dived to a depth greater than 80 m below sea level, where phreatic conduits of diameters in the tens of meters have been mapped (Guglia, 1994). Collectively, the long-term average discharge of the springs is approximately 30.2 m³/sec (variable within the years studied between 18 m³/sec and 39.4 m³/sec), with low flows averaging around 9 m³/sec, and maximum flows over 130 m³/sec (Gemiti, 1984).

The Timavo springs represent the major component of outflow (85%) of the regional

karst groundwater system (Civita and others, 1995). Several other springs in proximity to the Timavo springs form the remainder of the groundwater resurgence zone. Of these, Sardos spring and Moschenizze North spring are also reclaimed for water supply. These springs, as well the water from a supply well (B-4) and a monitoring well (B-3) were sampled in this study (**Figure 2**). The water supply well B-4 provides the sole water source for the inhabitants of the Kras region in Slovenia, serving a population of approximately 25,000 people. The monitoring well B-3 is completed within a zone of fluctuating water level, and was observed to be dry after a drought period. Samples collected from the well before and after the drought exhibited nearly identical water chemistry; thus, this well contains water that is displaced from storage within the local vadose zone. A large river, the Soča River, drains the high Julian Alps along the western border between Italy and Slovenia. This river loses a large amount of flow into the karst aquifer ($20 \text{ m}^3/\text{sec}$), and is believed to account

for much of the flow from the springs in the summer (Mosetti & D'Ambrosi, 1963; Urbanc & Kristan, 1998). The primary goal of this study was to determine how the contribution from the Soča River affects the outflow of the springs with changing flow conditions.

Daily discharge measurements exist at the Timavo springs as a consequence of their reclamation for water use. In order to quantitatively define the flow regimes considered here, a hydrograph analysis of the Timavo springs discharge was performed. Six years of discharge records were available, from 1995-2000. Out of the six-year record, six of the longest recession periods were chosen for detailed analysis. The recession flows at the Timavo springs were fit by a series of linear segments of the hydrograph recession in semi-log space. The simple exponential decay relation (*eq. 1*) appears to provide an adequate model for the analysis of all discharge regimes at the springs.

METHODS

From our hydrograph recession analysis, a Master Recession Curve (MRC) (**Figure 3**) was constructed. Individual storm event recessions from the long-term discharge records of the Timavo springs were compiled to form the MRC. Four distinct segments to the Timavo MRC were identified, each corresponding to a characteristic flow regime. The breaks in slope define the approximate discharge limits of each flow regime.

The MRC construction was performed manually by visual inspection of the individual event hydrographs. Individual event recession periods were isolated from the entire discharge record and were plotted as the natural log of the flow ($\ln Q$) vs. time (t). **Figure 4** shows one of these recession hydrographs of the Timavo springs. Linear ordinary least-squares regression lines were then fit to each segment of each event hydrograph in semi-log space. The slopes of the regression lines are equal to the values of the recession coefficient (α) for each flow regime of the MRC in units of day^{-1} , and the y-intercept of the regression lines are the value of discharge at

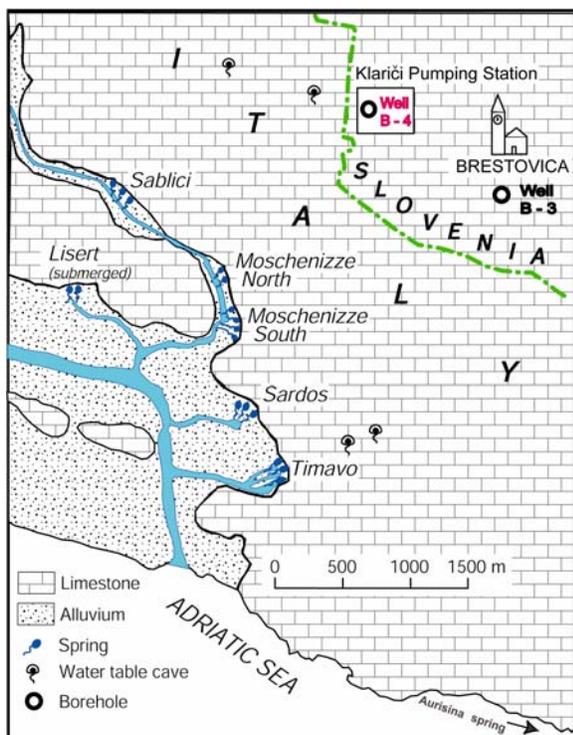


Figure 2: The groundwater resurgence zone of the Kras region (after Krivic, 1981).

the start of the recession (q_0 at $t=0$). The values of α and q_0 that were obtained from the linear regressions of the six event hydrographs were tabulated for each segment of each event, and averaged. These results are presented in **Table 1**.

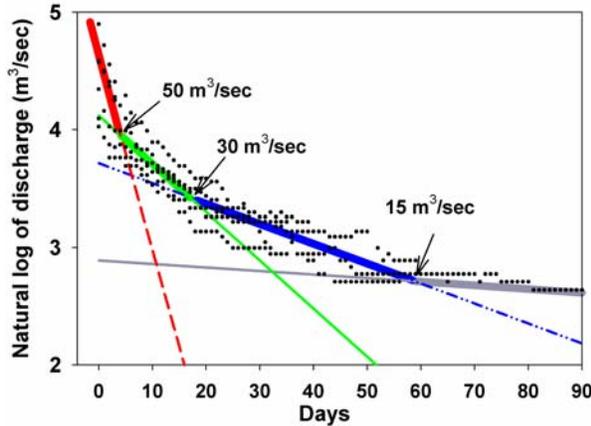


Figure 3: Master Recession Curve for the Timavo springs. Lines indicate ordinary least-squares regression through recession segments. Average daily discharge data are shown as dots.

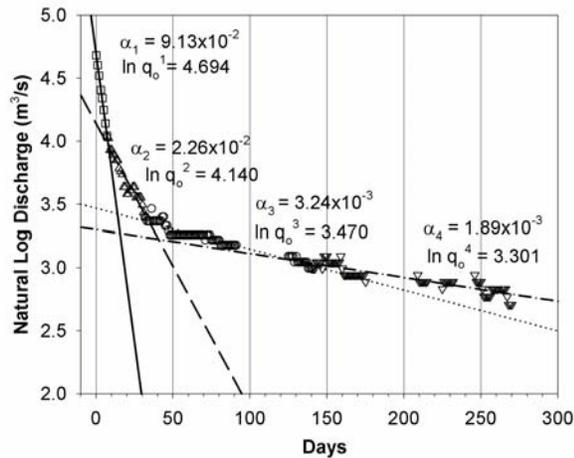


Figure 4: Representative recession hydrograph of the Timavo springs.

Since it was a common occurrence that recession segments would be cut off by increases in discharge resulting from new recharge events, the values of α and q_0 were weighted according to the time duration of each segment prior to an increase in discharge. Thus, values of α and q_0 obtained from individual recessions that persisted for longer time periods were more heavily weighted in the calculation of the mean values for that portion of the MRC. This practice lends a deliberate bias towards the

larger events; the largest events recharge a greater portion of the vadose zone as the water table of the aquifer rises, thus they produce longer, more informative, recessions.

A limitation to the analysis in this case is that the Timavo springs, having been engineered for water reclamation, are fitted with a sluice gate that controls the discharge at low flow. The consequence of the control structures is that the baseflow never drops below 9 m³/sec. Thus, the true baseflow recession slope may be absent. Nonetheless, significantly long periods of recession that were not influenced by the control structures were observed such that reproducible recession segments could be fit to the discharge record.

RESULTS AND DISCUSSION

Four flow regimes of the Kras aquifer were defined through the hydrograph analysis: (1) flood flow, (2) high flow (3) moderate flow, and (4) baseflow. The flood flow regime is for flows of the Timavo springs above approximately 50 m³/sec, high flow is between 30 and 50 m³/sec, moderate flow is between 15 and 30 m³/sec, and baseflow discharge is below 15 m³/sec.

The individual segments of the MRC were integrated to provide an area below the curve that represents the total theoretical storage volume of the aquifer that supplies the discharge of the Timavo springs. These results are shown in **Table 1**.

Comparison between flow regimes, isotopes, and chemistry

The isotopic and chemical data collected in this study were grouped into the four flow regimes according to the discharge measured at the Timavo springs on the date the water sample was collected. Oxygen ($\delta^{18}\text{O}$ of water) and carbon ($\delta^{13}\text{C}$ of dissolved inorganic carbon, or $\delta^{13}\text{C}_{\text{DIC}}$) stable isotope data of the Timavo springs collected between November 1998 and November 2000 were grouped together by flow regime, and box plots were constructed.

TABLE 1: Results of Timavo springs hydrograph recession analysis

Recession segment	Flow regime	Discharge range (m ³ /sec)	α (day ⁻¹)	q_0 (m ³ /s)	Recession Period (days)	Storage volume (m ³)	% of total storage
1	Flood flow	> 50	1.64×10^{-1}	101.49	0 (peak Q) – 4	0.06×10^8	1.0%
2	High flow	30 to 50	4.10×10^{-2}	61.56	4 – 17	0.13×10^8	2.2%
3	Moderate flow	15 to 30	1.70×10^{-2}	40.98	17 – 58	0.48×10^8	8.2%
4	Baseflow	<15	3.00×10^{-3}	18.00	58 or more	5.18×10^8	88.5%
Total:						5.85×10^8	100%

The relation between $\delta^{18}\text{O}$ and flow regime is opposite to the relation between $\delta^{13}\text{C}_{\text{DIC}}$ and flow regime (**Figure 5a & 5b**). The $\delta^{18}\text{O}$ values become more negative with higher flow while $\delta^{13}\text{C}_{\text{DIC}}$ values become more positive. The increase in $\delta^{18}\text{O}$ and corresponding decrease in $\delta^{13}\text{C}_{\text{DIC}}$ with increasing flow is consistent throughout the sampling period. In addition, similar seasonal trends are apparent among the isotopic variation of all of the groundwaters (**Figure 6**). Note that all the groundwaters can be approximated as a mixture between the water of well B-3 (autogenic recharge) and the Soča River.

The high-altitude (>2000 m) alpine source of the Soča River lends it $\delta^{18}\text{O}$ values that are more negative than the water derived from local rainfall on the Kras. The $\delta^{18}\text{O}$ of weighted mean annual precipitation is -6.5‰, essentially equal to the composition of well B-3. Thus, the difference in $\delta^{18}\text{O}$ between these sources of water allows for discrimination between them in the mixtures of the groundwaters.

Similarly, the difference in $\delta^{13}\text{C}_{\text{DIC}}$ values between the Soca River and autogenic recharge (represented by the composition of well B-3) adds a second parameter by which to discriminate between these sources in the outflow. Lower $\delta^{13}\text{C}_{\text{DIC}}$ values in the autogenic recharge water reflect a greater proportion of DIC derived from soil CO_2 , which tends to be low in $\delta^{13}\text{C}_{\text{DIC}}$ as a result of the oxidation of organic matter (Deines, 1980; Deines and others, 1974). The partial pressure of CO_2 in the unsaturated zone is 10-100 times that of the

atmosphere with $\delta^{13}\text{C}$ values between -20 and -25‰ (Doctor, 2002), thus lower $\delta^{13}\text{C}_{\text{DIC}}$ values indicate water that has been stored within the vadose zone of the karst.

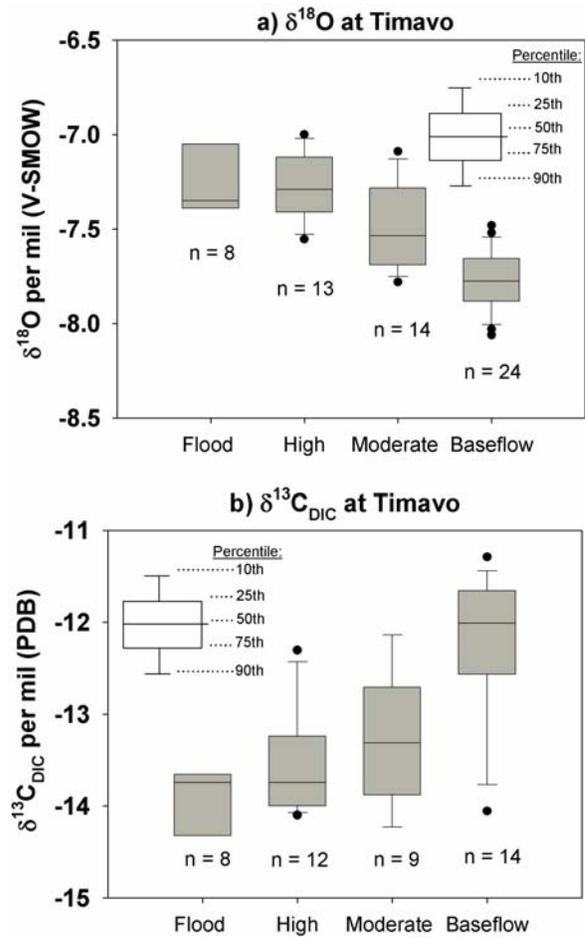


Figure 5: Changes in stable isotopic composition with flow regimes at the Timavo springs. Outlier values correspond to samples collected immediately after or during storm events.

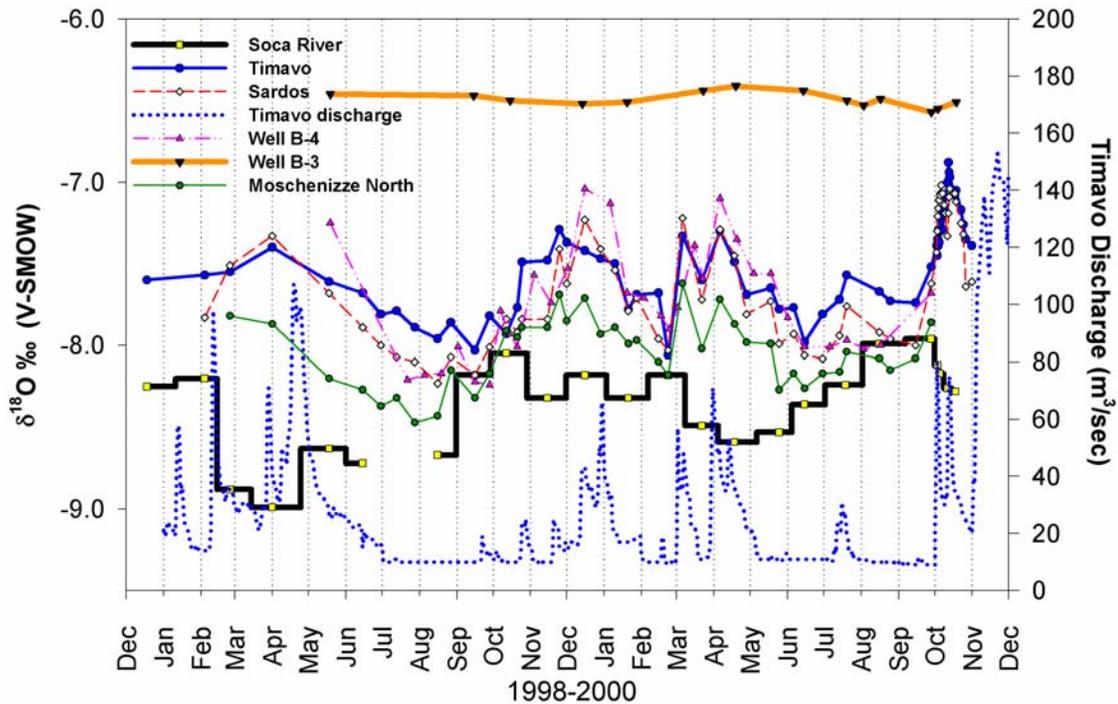


Figure 6: Time series of oxygen isotope values of the Kras groundwaters, with the average daily discharge of the Timavo springs shown for reference. Note that all the groundwaters are a mixture between the water of well B-3 (autogenic recharge) and the Soča River.

Together, these isotopic data present a conceptual model of two component mixing between allogenic Soča River water and autogenic recharge from local precipitation to account for the observed isotopic compositions of the Kras groundwaters. The proportion of Soča River water issuing from the springs is apparently greatest under lower flow conditions, while increasing amounts of autogenic recharge water are released from storage in the vadose zone during higher flows.

The chemistry data from the present study was combined with the chemistry data of Gemiti & Licciardello (1977) and of Cancian (1987), assuming similarity between the flow regimes determined by those authors and the flow regimes determined by the recession analysis of the present study. For the combined chemistry data it was possible to characterize only three flow regimes, since Cancian (1987) reports only three in his data summary. Therefore, the mean values of the flood flow and high flow regime from the recession analysis were combined into “high flow”, and the baseflow values are defined as “low flow”.

The results of the water chemistries grouped according to flow regime are shown in **Figures 7 to 9**. **Figure 7** shows the Ca/Mg ratios of all the groundwaters tend to approach that of the Soča River as the flow decreases with the exception of well B-4, which shows a relatively constant Ca/Mg ratio regardless of flow regime. Of the other springs, Timavo has the highest Ca/Mg values, followed by Sardos and then by Moschenizze North. Well B-3 has a much higher and constant Ca/Mg than the other waters, thus the progressive shift toward higher Ca/Mg values with increasing flow regime implies a shift toward a greater proportion of autogenic recharge water supplying the springs.

For Cl⁻, all of the groundwaters show similar concentrations except for well B-4, which has the highest Cl⁻ concentrations of all of the groundwaters (**Figure 8**). Cl⁻ levels in the other groundwaters are relatively constant at 5-10 ppm across the flow regimes, while for well B-4 the Cl⁻ is highest at high flow (>50 ppm on average) and decreases to approximately 20 ppm on average at low flow. Well B-3 has a low and constant Cl⁻ concentration of 3.0 ppm.

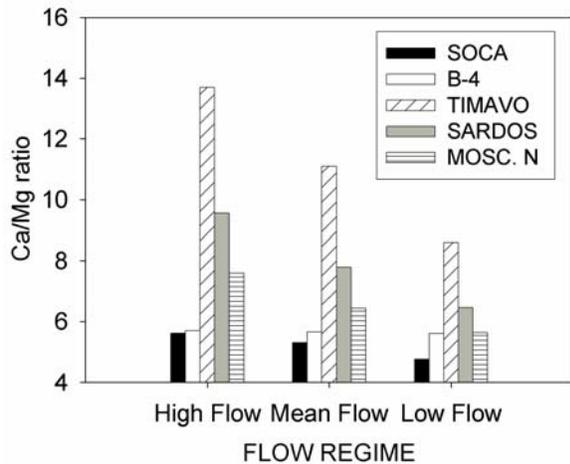


Figure 7: Ca/Mg ratio of Kras groundwaters with flow regime.

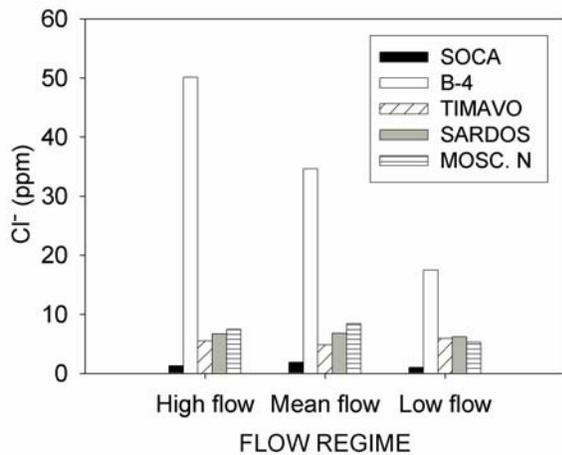


Figure 8: Cl⁻ of Kras groundwaters with flow regime.

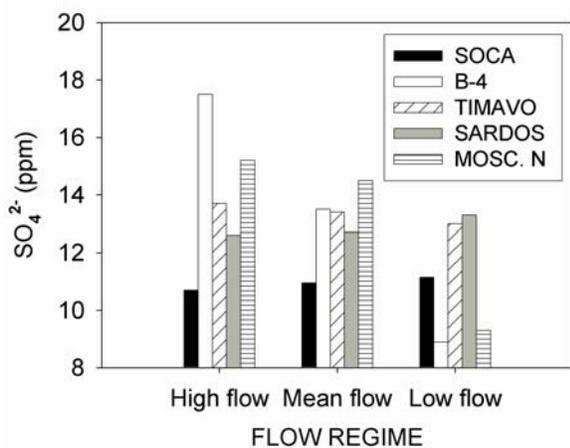


Figure 9: SO₄²⁻ of Kras groundwaters with flow regime.

Well B-4 also shows anomalous chemistry with respect to SO₄²⁻; it has the highest SO₄²⁻ concentrations of all the groundwaters at high flow and the lowest SO₄²⁻ at low flow (Figure 9). SO₄²⁻ concentrations at Timavo and Sardos stay relatively constant regardless of flow regime, at between 12-14 ppm on average. SO₄²⁻ at well B-4 and Moschenizze North decreases with decreasing flow regime, and at low flow they exhibit the lowest SO₄²⁻ concentrations of all the groundwaters.

High chloride (>100 ppm) and sulfate (>30 ppm) concentrations have been observed from two shafts intersecting the water table nearby the Timavo springs (Gemiti, 1994). The water in these shafts is derived from local storage of autogenic recharge within the epikarst, and may be influenced by anthropogenic activities. This water stored within the unsaturated zone impacts well B-4 and Moschenizze North spring under elevated hydraulic head conditions, and to a lesser extent at low flow. Because these two sites exhibit higher Cl⁻ and SO₄²⁻ when the water table rises, it is likely that an overflow connection permits the higher salinity water to affect both well B-4 and, to a lesser degree, Moschenizze North spring under high flow conditions.

CONCLUSIONS

Hydrochemical and isotopic data collected at a frequency of approximately twice monthly over a two-year period was interpreted through identification of discrete flow regimes of the karst aquifer by means of hydrograph recession analysis. Grouping the chemistry data together within the defined flow regimes illuminated broad patterns of water quality variability according to changing discharge conditions.

The simple exponential decay model used for fitting multiple linear recession segments to the outflow of the Timavo springs was adequate for determining the flow regimes of the groundwater resurgence of the Slovene Kras region. As a result of the recession analysis, four distinct flow regimes of the Timavo springs have been defined: flood flow (>50 m³/s), high flow (30–50 m³/s), moderate flow (15–30 m³/s), and

baseflow (<15 m³/s). The estimated storage volume of the baseflow regime represents the greatest proportion (88.5%) of the total theoretical storage volume, with the flood and high flow regimes together representing 3.2%. These percentages highlight the importance of the baseflow regime for providing the majority of flow at the Timavo springs. Although high flows do not drain those portions of the aquifer with a large capacity for water storage, floods are responsible for recharging other parts of the aquifer system, thus flood waters may remain in storage for longer periods of time than otherwise may be indicated by the rapid drainage under higher flow regimes.

The flow at the Timavo springs serves as an adequate proxy for the flow of the other local springs that drain the aquifer. Similar trends in the stable isotopic composition ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}_{\text{DIC}}$) of the water exist among the Timavo springs, Sardos spring, and well B-4 when compared to the discharge of the Timavo springs. For each of these groundwaters, the $\delta^{18}\text{O}$ values are lowest during lowest flow periods and highest during the highest flow periods, while the $\delta^{13}\text{C}_{\text{DIC}}$ values are lowest during high flow and highest during low flow. These results indicate mixing between similar sources at each of these outflow points, as well as a change in the proportions of each source under changing hydrologic conditions. The more negative $\delta^{18}\text{O}$ and more positive $\delta^{13}\text{C}_{\text{DIC}}$ values of the waters are consistent with a predominant Soča River source during low flow periods, while the more positive $\delta^{18}\text{O}$ and more negative $\delta^{13}\text{C}_{\text{DIC}}$ values are consistent with a predominant source of storage within the vadose zone.

The relations among the flow regimes and water chemistry are similar to the results previously reported by Gemiti and Licciardello (1977) and Cancian (1987). There is a general trend of decreasing Ca/Mg ratio with decreasing flow regime in all of the groundwaters sampled, except for well B-4. Since the Soča River shows the lowest Ca/Mg ratio of all the waters, and autogenic recharge water (well B-3) shows the highest Ca/Mg ratio, the decreasing trend supports the conclusion of variable mixing

between the Soča River and autogenic recharge such that under lower flow conditions Soča River water has a greater influence on the groundwater of the aquifer.

The anomalous Cl^- and SO_4^{2-} chemistry observed at the Klariči supply well (well B-4) indicates a high salinity component that affects this well when phreatic head levels are elevated during high flows. Water chemistries of local vadose shafts indicate that the source of this high salinity water is likely a shallow perched zone of water in storage within the epikarst. This water may be anthropogenically impacted.

The trends observed in both isotopic and chemical composition of the groundwaters as flow regimes change indicate that pronounced shifts in the water sources feeding the groundwaters of the Kras aquifer resurgence zone occur as hydrologic conditions vary. These data show that under low flow conditions the outflow contains a greater proportion of Soča River water, while under high flow conditions more water discharged from the springs is derived from the vadose zone. In addition, a third source of water with high levels of Cl^- and SO_4^{2-} exists in vadose storage and influences some of the groundwaters under elevated flow conditions. The techniques developed in this study may be applied to other karst aquifers where water quality and flow monitoring is taking place.

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REFERENCES

- Bonacci, O. (1993) Karst springs hydrographs as indicators of karst aquifers. *Hydrological Sciences- Journal des Sciences Hydrologiques*, 38 (1,2), 51-62.
- Cancian, G. (1987) L'idrologia del Carso goriziano-triestino tra l'Isonzo e le risorgive del Timavo. *Studi Trentini di Scienze Naturali*, vol. 64, p. 77-98.
- Civita, M., Cucchi, F., Eusebio, A., Garavoglia, S., Maranzana, F. & Vigna, B. (1995) The Timavo hydrogeologic system: an important reservoir of supplementary water resources to be reclaimed and protected. Proc. Int. Symp. "Man on Karst", Postojna 1993, *Acta Carsologica*, 24: 169-186.
- Deines, P. (1980) The isotopic composition of reduced organic carbon. In: Handbook of Environmental Isotope Geochemistry, Vol. 1 (P. Fritz and J.Ch. Fontes, eds.). Amsterdam: Elsevier, pp. 329-406.
- Deines, P., Langmuir, D., and Harmon, R. (1974) Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters. *Geochimica et Cosmochimica Acta*, vol. 38, p.1147-1164.
- Doctor, D.H. (2002) The Hydrogeology of the Classical Karst (Kras) Aquifer of Southwestern Slovenia. Ph.D. dissertation, University of Minnesota, 252 pp.
- Forkasiewicz, J. and Paloc, H., (1967) Le régime de tarissement de la Foux de la Vis. Etude préliminaire. *AIHS Coll. Hydrol. des roches fissurées, Dubrovnik (Yugoslavia)*, vol. 1, pp. 213-228.
- Galli, Mario (1999) Timavo: Esplorazione e studi. Supplemento no. 23 di *Atti e Memorie della Commissione Grotte "Eugenio Boegan"*, Trieste, 195 pp.
- Gemiti, F. (1984) La portata del Timavo alle risorgive di S. Giovanni di Duino. *Annali Gruppo Grotte Ass. 30°Ott., Trieste*, 7:23-41.
- Gemiti, F. (1994) Indagini idrochimiche alle risorgive del Timavo. *Atti e Memorie della Commissione Grotte "E. Boegan"*, vol. 30, pp 73-83.
- Gemiti, F., and Licciardello, M. (1977) Indagini sui rapporti di alimentazione delle acque del Carso triestino e goriziano mediante l'utilizzo di alcuni traccianti naturali. *Annali Gruppo Grotte Ass. XXX Ott.*, sez. C.A.I. Trieste, 6, 43-61.
- Guglia, P. (1994) Risultati esplorativi del Progetto Timavo (1990-1993). *Atti e Memorie della Commissione Grotta "E. Boegan"*, 31/1992-93: 25-48.
- Hall, F.R. (1968) Base-flow recessions—a review. *Water Resources Research*, vol. 4 (5): 973-983.
- Kranjc, A.,ed., (1997) Slovene Classical Karst- "Kras". Postojna: Institut za raziskovanja krasa ZRC SAZU, 254 pp.
- Krivic, P. (1981) Etude hydrodynamique d'un aquifère karstique côtier: le Kras de Slovenie, Yougoslavie. *Accadémie Montpellier, Univ. Sc. Techn. Languedoc, Thèse de Docteur-Ingénieur Université Montpellier II*: 108 pp.
- Maillet, E. (1905) *Essai d'Hydraulique Souterraine et Fluviale*. Librairie Scientifique A. Hermann: Paris.
- Milanović, P. T. (1981) Karst Hydrogeology. Littleton, Colorado: Water Resources Publications, 434 pp.
- Mosetti, F. & D'Ambrosi, C. (1963) Alcune ricerche preliminari in merito a supposti legami di alimentazione fra il Timavo e l'Isonzo. *Boll. Geograf. Teor. ed Appl.*, n. 17.
- Sujono, J., Shikasho, S., Hiramatsu, K. (2004) A comparison of techniques for hydrograph recession analysis. *Hydrological Processes*, 18, 403-413.
- Tallaksen, L.M. (1995) A review of baseflow recession analysis. *Journal of Hydrology*, **165**: 349-370.
- Urbanc, J., and Kristan, S. (1998) Isotope investigation of the Brestovica water source during an intensive pumping test. *RMZ - Materials and Geoenvironment*, vol. 45, no. 1-2, p. 187-191.