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Speciation of U, Se, As and Sr in Makook Karstic water system, Kurdistan Region, Iraq

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Abstract

Speciation of trace elements in water system is essential for understanding of the mobility, toxicity, bioavailability and transport characteristics of these elements. This study presents an evaluation of different factors affecting speciation of uranium (U), selenium (Se), arsenic (As) and strontium (Sr) in Makook Karstic water system. Results show a temporal variability of U, Se, As and Sr species within the different karst aquifers. The abundant species are U(VI), U(IV), Se(IV), Se(VI), As(V), As(III), Sr^{2+} and $SrHCO_3^+$. It is observed that these species are significantly controlled by pH, redox (pE), temperature (T), dissolved organic carbon (DOC), dissolution of calcite and dolomite minerals and variation of springs discharge. Mineralogical content of the host rocks controls the speciation of the studied elements as well. Therefore, different aquifers show different speciation responses for the same element. This study illustrates the speciation mechanism in karstic waters.

Introduction

The geochemistry of groundwater is controlled by many factors including pH, temperature, mineralogy, weathering, redox reactions and human impacts. Trace elements have been taking the interest of many researchers because some of it such as selenium (Se) is an essential element for the humans (certain daily intake), but some others are toxic (As). The geochemistry of uranium in groundwater is complex because of many oxidations states, and only two are relevant in natural environments, U(IV) under reducing and U(VI) under oxidizing conditions. The oxidizing U(VI) is more soluble in water, especially at low pH conditions and it can be affected by organic matter, carbonates, phosphates and hydroxides (Erőss et al., 2012; Lauria et al., 2004).

Selenium has recognized to have anti-carcinogenic activity (Ravoori et al., 2010), and can prevents arsenic toxicity effects (Huang et al., 2008). Occurrence of Se in groundwater is due to weathering of rocks, and dissolution of soluble salts in soils. The Se species in groundwater are Se(-II)(in reducing environments), Se(IV) (moderately oxidizing), and Se(VI) in oxidizing environments. (Elrashidi et al., 1987). Selenium speciation in groundwater is controlled by aquifer redox conditions, microbial transformations, dissolved oxygen (DO) and other redox couples (Kumar and Riyazuddin, 2011).

Inorganic As occurs in groundwater predominately. The pH and redox are the main factors that controls the As speciation. Under oxidizing conditions As(V) concentrations in groundwater is predominant and As(III) in reducing environment (Smedley and Kinniburgh, 2002).

Cation exchange capacity of the solid matrix and ionic strength of groundwater are the main factors that control the sorption and speciation of Sr^{2+} (Koss and Kim, 1990).

The Makook karstic water system is composed of Bekhme carbonate karst aquifers and represents one of the largest reserves of groundwater in the Kurdistan region (Stevanović and Iurkiewicz, 2004). Like in many parts of the world, water scarcity is obvious in the study area. Therefore, investigating the available water resources in the Makook karstic aquifers is a valuable endeavor.

The concentrations of trace elements in carbonate karst groundwater are very low because of the short residence time and the low content of trace elements in many calcites. A few accessory minerals and organic matter are the most important sources of trace elements in carbonate karst groundwater (Kilchmann et al., 2004). The geochemistry of trace elements in karstic waters is still not well investigated and in particular not in the region of interest.

The objectives of this study are focused on the factors that control the speciation of U, Se, As and Sr in karst waters of Makook karstic system. The correlation of pH, redox, temperature, DOC, dissolution of calcite and dolomite and springs discharge with the aforementioned trace elements are used for visualization of processes that control the geochemistry of the Makook karstic system.

Materials and Methods

A. *Study Area*

The study area is located in the Kurdistan region in the northeast of Iraq, Sulaimani governorate, Ranya district (*Figure: 1a*). The area is situated within latitudes 36°10'00"– 36°35'00" north and longitudes 44°30'–44°50' east in the elevation range of 500 to >2000 meter (m) above sea level. Makook Anticline Mountain lies in a northwest–southeast direction and is surrounded by Shawre valley in the northeast and Balisan valley in the southwest. The study area is part of the Dokan sub-basin. The climate of the area is of semi-arid type. Rainy season starts from October and mainly ends in May with minor showers in June, July, and September. The mean annual precipitation for the study area is 571 mm and the average annual temperature is 20 °C. The mean annual evaporation (pan) is about 2000 mm and the mean relative humidity is about 47% (Mustafa et al., 2015). The meteorological data are to the sampling period (2011-2012).

Rocks of Mesozoic and Cenozoic age can be found in the study area. Rocks of Jurassic period are cropping out representing Sarki, Sehkaniyan, Sargelu, Naokelekan, Barsarin and Chia Gara Formation (Jassim and Goff, 2006). The Cretaceous unit comprises Balambo, Sarmord, Qamchuqa, Bekhme, Kometan, Shiranish and Tanjero Formation (Bellen et al., 1959). Jurassic and Cretaceous rocks are occasionally overlain by Quaternary fan deposits (boulders, gravel, and fine clastics). Makook Anticline represents a double plunging anticline (NW–SE) within in the parallel trend of Zagros folded structures between Ranya and Palawan anticlines and Shawre and Balisan synclines (in between) in the NE and SW respectively. The area is characterized by tectonic distortion, especially in the northwest part of Makook Anticline (Mustafa and Merkel, 2015a).

The studied springs are within the Makook karst system, which is composed of three karstic aquifers: Bekhme, Kometan and Shiranish (Mustafa et al., 2015).

Bekhme karstic aquifer supplies major springs along Makook anticline including Zewa, Qala Saida and Gullan springs. Bekhme aquifer is a well karstified, thick, semi-confined aquifer underlain by Sarmord Formation (Stevanovic and Markovic, 2004). The Kometan aquifer is represents the source of Sarwchawa, Betwata, Chewa and Bla springs (Mustafa et al., 2015). Kometan Formation is a well karstified, highly fissured aquifer with confined to semi-confined conditions and overlain by Shiranish Formation (Stevanovic and Markovic, 2004). The aquifer is composed of carbonate rocks and contains a large amount of groundwater, varying in space and time. One of the springs (Shkarta) drains poorly developed karst (with small fissures). This spring is located in the Shiranish Formation (marl and marly limestone), which was inconsistently recognized as a fissured aquitard (locally in the marly limestone part) by Al Manmi (2008).The general groundwater flow direction is from the NW to the SE of the studied area (Al Manmi, 2008). Long, medium and short flow paths are recognized (*Figure: 1b*) and both conduit and diffuse flow regime are exists in different aquifers of the study area. Kometan aquifer is characterized by higher degree of karstification, while Bekhme aquifer is of moderate degree and Shiranish aquifer (aquitard) is poorly karstified (Mustafa and Merkel, 2015). Strong karstification cycles took place in the aquifer system during the Paleocene–Miocene period (Stevanovic et al., 2009), and are ongoing process, even recently. Concerning the karst features, depressions and sinkholes are rarely recognized, but remote sensing investigations revealed that cores of some of the major anticlines are pitted due to karstification (Stevanovic and Markovic, 2004). Betka cave near Sarwchawa town was described by Stevanovic et al. (2009). At the entrance of Betka cave a hall with 20 m length, 7 m width and 10 m height was found.

B. Sampling

Three karstic springs (Sarwchawa, Shkarta and Zewa) were sampled six times during September 2011, December 2011, April 2012, June2012, September 2012 and November 2012. The temporal sampling from each spring was planned to be representative for the dry and wet periods during hydrologic year of 2011-2012. Sampling and measurements of field parameters were conducted at the spring's outlet. The water samples were collected in 30, 50 and 100 ml polyethylene bottles. Aliquots for ICP-MS analysis were filtrated with 0.2 µm cellulose acetate filters and then acidified with an ultra-pure nitric acid (30% HNO_3). All samples were stored in a cool box at 4 °C until analysis in the laboratory.

C. Field and Analytical Methods

Redox potential (Eh) was measured via a WinLab redox meter and WTW SenTix-ORP electrode and checked by standard redox buffer (pH=7 and 220 millivolts at 25 °C). The parameters pH and water temperature (T) were measured on-site using a multi-parameter WTW model 3430, WTW pH electrode SenTix-940. A three-point calibration was carried out for the pH electrode via technical WTW buffers (pH=4.01, pH=7 and pH=10). Alkalinity was determined immediately after sampling by means titration and converted to hydrogen-carbonate (HCO_3^-) according to APHA (1998). Because no continuous discharge measurements of the springs were available, different methods current meter (OTT C31)and volumetric readings) were employed to record the discharge of the springs during the monitoring period from September 2011 to November 2012.

The measurement of major cations, anions and trace elements was conducted in the laboratories of the Hydrogeology Department, Technische Universität Bergakademie Freiberg, Germany. Major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) content were determined via ion chromatography (IC) using an 850 Professional IC Metrohm with Metrosep C4-150 column and 2 mM dipicolinic acid eluent. The SO_4^{2-}, Cl^- and F^- anion levels were determined with a Metrohm Compact IC Pro 881 and Metrosep A sup 15-150 column was used with 3 mM $NaHCO_3$ and 3.5 mM Na_2CO_3 as eluent. The determination of U, As, Se and Sr (and other elements, not reported here) were done with an ICP-MS XSeries-2 (Thermo Scientific) either in direct mode or using the collision mode. The reproducibility of IC and ICP-MS determinations was around 2% and 5% respectively. The DOC measurement was conducted on a pre-filtered water samples. DOC was analyzed on Elementar Liqui TOC II analyzer with ±5% reproducibility.

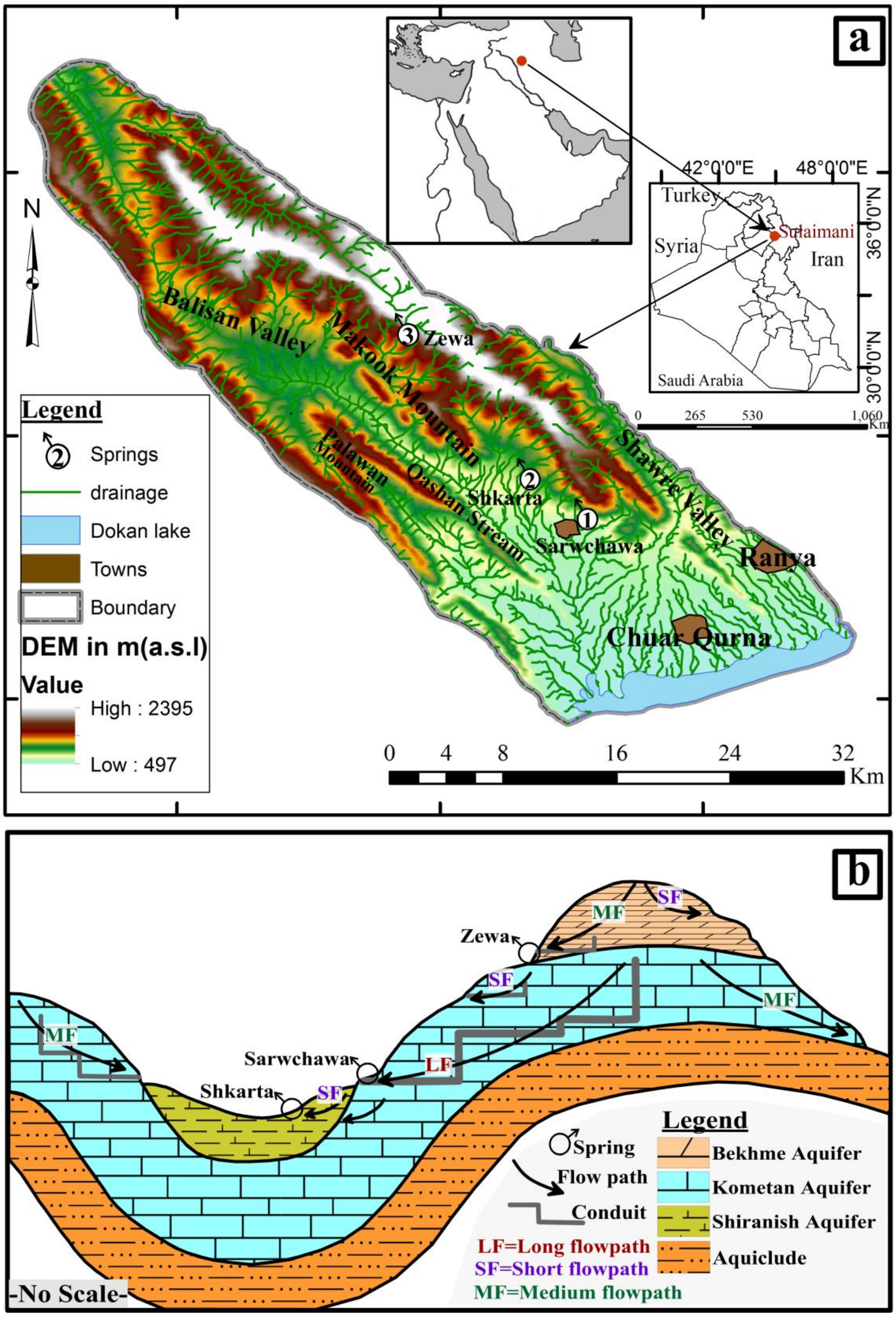

Figure-1: The study area. (a) Location of the studied karst springs (adapted from Mustafa et al., 2015). (b) Conceptual model illustrate the geology and hydrogeology of the study area (adapted from Mustafa and Merkel, 2015).

D. Geochemical Modeling and Statistical Analyses

The data used in this work were subject to various different quality assurance procedures and statistical tests using SPSS software package (Landau and Everitt, 2004). Non-parametric two-tailed correlation analysis (Kendall and Spearman correlations) was performed for the hydrogeochemical and field parameters in addition to basic statistical treatment. The ion balance, partial pressure of CO_2 (P_{CO2}) and saturation index of calcite ($SI_{Calcite}$) and dolomite ($SI_{Dolomite}$) and molar concentration of U(VI), U(IV), Se(IV), Se(VI), As(V), As(III), Sr^{2+} and $SrHCO_3^+$ were calculated by means of PHREEQC (Parkhurst and Appelo, 2013) using the WATEQ4F database.

Results and Discussion

A. Hydrogeochemistry and Dominant Parameters

Field parameters, hydrochemistry and trace element species of the springs are given in *Table: 1, Table: 2,* and *Table: 3*. The relative analytical error (E%) was within an acceptable range of ± 2% (*Table: 1*). Ca^{2+} and Mg^{2+} concentrations range between 41 to 92 mg/L and 17 to 24 mg/L, respectively. Na^+ and K^+ vary between 0.8 to 5.9 mg/L and 0.4 to 2.3 mg/L, respectively. With regard to the major anions, HCO_3^- ranges from 199-280 mg/L, SO_4^{2-} from 17.4 to 86.6 mg/L and Cl^- concentration from 2 to 15.5 mg/L.

Table-1: Physicochemical, modeled hydrogeochemical and flow characteristics of the selected karst springs in the study area

Spring	***Statistics***	***pH***	***pE***	***T (°C)***	***DOC (mg/l)***	***Flow (L/s)***	***PCO_2***	***$SI_{Calcite}$***	***$SI_{Dolomite}$***	***E%***
Sarwchawa	***St.D***	0.2	0.55	3	1.8	762.3	NA	NA	NA	NA
	Min	7.1	5.79	11	2.3	2370	-2.2	-0.25	-1	-1
	Max	7.6	7.34	18.7	7.8	4630	-1.8	0.31	0.3	1
	Mean	7.3	6.56	15.1	5.3	3233	-2	0.02	-0.3	-0.3
Shkarta	***St.D***	0.2	0.53	6.1	1.6	0.4	NA	NA	NA	NA
	Min	7.1	5.66	6	1.3	0.1	7.03	-0.23	-1.1	-4
	Max	7.8	7.28	23.4	6	1.1	7.36	0.43	0.3	0
	Mean	7.4	6.48	17.4	3.4	0.5	6.37	0.006	-0.6	-1
Zewa	***St.D***	0.4	0.58	3.1	1.9	45.9	NA	NA	NA	NA
	Min	7.3	5.47	8	1.8	48	-0.47	-1.3	-1.3	-1
	Max	8.4	7.02	15.2	6.7	165.8	0.71	1.2	1.2	3
	Mean	7.8	6.21	11.6	3.2	109	0.06	-0.2	-0.2	0.7

pE = oxidation reduction potential; ***T*** = water temperature; ***Flow*** = discharge of the springs; DOC = dissolved organic matter measured by TOC analyzer; ***PCO_2,$SI_{Calcite}$*** and ***$SI_{Dolomite}$*** were calculated by PHREEQC; NA = Not available; *E%*= relative analytical error. The statistical tests are based on 6 measurements (***n***) for each springs; The field parameters were measured onsite

Table-2: Hydrogeochemical characteristics of the karstic springs of the study area

Spring	**Statistics**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**Cl^-**	**$SO4^{2-}$**	**HCO_3^-**	**U**	**Se**	**As**	**Sr**
		Concentrations are in mg/L							**Concentrations are in µg/L**			
Sarwchawa	***St.D***	*0.09*	*0.06*	*14.7*	*2.5*	*0.6*	*18.1*	*12*	*0.19*	*0.34*	*0.08*	*211.6*
	Min	*2.32*	*0.7*	*49.9*	*17*	*2*	*39*	*265.7*	*0.36*	*0.08*	*0.14*	*366.2*
	Max	*2.53*	*0.85*	*91.7*	*23.9*	*3.5*	*86.6*	*298.9*	*0.86*	*0.95*	*0.38*	*846.7*
	Mean	*2.41*	*0.77*	*76.1*	*21.5*	*2.6*	*70.4*	*279.3*	*0.72*	*0.60*	*0.3*	*661.1*
Shkarta	***St.D***	*0.82*	*0.25*	*9.9*	*1.5*	*4*	*8.2*	*15*	*0.04*	*0.09*	*0.02*	*55.37*
	Min	*3.59*	*1.48*	*48.2*	*9.6*	*4.8*	*17.4*	*213.7*	*0.24*	*0.32*	*0.31*	*288.4*
	Max	*5.89*	*2.27*	*75.3*	*13.7*	*15.5*	*40.4*	*253.9*	*0.34*	*0.58*	*0.35*	*437.2*
	Mean	*4.36*	*1.84*	*66.5*	*10.7*	*8.3*	*24*	*231.5*	*0.28*	*0.42*	*0.34*	*329*
Zewa	***St.D***	*0.06*	*0.2*	*5.4*	*0.9*	*0.5*	*2*	*4.3*	*0.03*	*0.13*	*0.03*	*9.82*
	Min	*0.79*	*0.41*	*41.4*	*12.9*	*0.9*	*8.4*	*180*	*0.51*	*0.08*	*0.28*	*99.09*
	Max	*0.94*	*0.94*	*56.6*	*15.5*	*2.1*	*13.9*	*192*	*0.59*	*0.37*	*0.36*	*125.2*
	Mean	*0.88*	*0.55*	*47.1*	*14.2*	*1.4*	*10*	*186.1*	*0.56*	*0.27*	*0.33*	*106.9*

Na, K, Ca, Mg, Cl and ***SO_4*** were measured by Ion Chromatography (IC); ***HCO_3*** was measured by Titration; ***U, Se, As*** and ***Sr*** were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS); The statistical tests are based on 6 measurements (***n***) for each spring

Ca^{2+}, Mg^{2+} and HCO_3^- are the most dominant ions indicating carbonate minerals as the major source. Only the Shkarta spring had higher Na^+, K^+ and Cl^- concentrations (*Table: 2*) than all other springs revealing the presence of clay minerals of the Shiranish Formation (marly limestone). Springs that stem from Kometan aquifer (Sarwchawa spring) are characterized by higher concentration (Ca^{2+}, SO_4^{2-}, Sr^{2+}, HCO_3^- and DOC) compared to springs that drained from dolomites of Bekhme aquifer (Zewa, Qala Saida and Gullan springs). Therefore, it can be concluded that water chemistry of the springs allows identification of feeding aquifers.

The Sarwchawa spring (Kometan aquifer) has the highest flow rates (2370 and 4630 L/s in dry and rainy seasons, respectively) and represents the most developed karst in the Makook karst system. On the other hand, the Shkarta spring (Shiranish aquifer) represents slightly or not karstified aquifer with an average low flow rate of 0.5 L/s.

Variations of U, Se, As and Sr concentration during the monitoring period in the springs of the Makook karst system are shown in *Table: 3*. The most dominant species of uranium was U(VI) and for selenium was Se(IV). The predominant arsenic species observed in karst waters was As(V) and for strontium was Sr^{2+}.

B. Temporal Variation of different Species

Different patterns for temporal trace element variation were recognized (*Figure: 2*). Concerning Sarwchawa spring (Kometan aquifer), both U(VI) and U(IV) shows increasing during April 2012, while Se(IV) and Se(VI) shows different responses (*Figure: 2a, b*). In difference, Shkarta spring (Shiranish aquifer) shows smooth pattern for uranium species till the November 2012, which shows a rising (*Figure: 2c*). During December 2011- January 2012 a falling in Se was recognized (*Figure:2d*). Relating to Zewa spring (Bekhme aquifer), both U(VI) and U(IV) shows nearly the same pattern, except in April 2012 U(VI) was rapidly increased (*Figure: 2e*), and this is not the case in species of Se, because they shows different temporal pattern (*Figur: 2f*). Taking uranium and Se species as examples, it can be concluded that springs of different aquifers shows different patterns, which helps in recognition of different karst waters. The temporal variation of U, Se, As and Sr species in some cases is due to groundwater recharge, and other factors like water-rock interaction processes could have an impact as well.

Table-3: Species of U, Se, As and Sr in karst springs of the study area

Spring	Statistics	U(IV)	U(VI)	Se(VI)	Se(IV)	As(III)	As(V)	Sr^{2+}	$SrHCO_3^+$
Sarwchawa	***St.D***	*5.50E-20*	*1.70E-15*	*4.10E-11*	*2.90E-10*	*1.10E-20*	*8.40E-15*	*1.80E-06*	*7.30E-08*
	Min	*5.30E-22*	*1.90E-16*	*6.10E-14*	*9.70E-11*	*1.20E-24*	*1.70E-15*	*4.80E-06*	*1.40E-07*
	Max	*1.50E-19*	*5.10E-15*	*1.00E-10*	*9.40E-10*	*2.60E-20*	*2.70E-14*	*9.50E-06*	*3.40E-07*
	Mean	*4.00E-20*	*2.30E-15*	*2.40E-11*	*5.80E-10*	*5.20E-21*	*1.30E-14*	*7.90E-06*	*2.70E-07*
Shkarta	***St.D***	*6.01E-20*	*6.72E-16*	*2.76E-11*	*2.06E-10*	*4.34E-20*	*9.22E-15*	*6.08E-07*	*1.10E-08*
	Min	*3.11E-22*	*5.76E-17*	*2.61E-14*	*2.18E-10*	*1.26E-24*	*1.98E-15*	*3.13E-06*	*1.01E-07*
	Max	*1.52E-19*	*2.02E-15*	*6.12E-11*	*8.20E-10*	*1.07E-19*	*2.96E-14*	*4.76E-06*	*1.31E-07*
	Mean	*2.95E-20*	*7.99E-16*	*1.80E-11*	*4.98E-10*	*1.86E-20*	*1.30E-14*	*3.58E-06*	*1.11E-07*
Zewa	***St.D***	*3.06E-19*	*2.68E-15*	*1.26E-09*	*2.78E-10*	*7.96E-20*	*6.52E-15*	*1.21E-07*	*4.51E-09*
	Min	*2.01E-23*	*7.08E-18*	*6.46E-15*	*2.09E-10*	*2.55E-27*	*1.44E-16*	*1.10E-06*	*2.17E-08*
	Max	*7.72E-19*	*6.60E-15*	*3.09E-09*	*8.60E-10*	*1.96E-19*	*1.46E-14*	*1.42E-06*	*3.36E-08*
	Mean	*1.49E-19*	*1.93E-15*	*5.22E-10*	*4.76E-10*	*3.35E-20*	*5.68E-15*	*1.20E-06*	*2.58E-08*

Concentration of species are in mole and calculated by PHREEQC; ***St.D*** = standard deviation; ***Min*** = minimum; ***Max*** = maximum; The statistical tests are based on 6 measurements (***n***) for each springs

C. Factors affecting speciation of U, Se, As and Sr

In order to investigate the factors that affect the hydrogeochemistry in karst waters a two tailed ≤ 0.05 Pearson correlation analysis was applied.

On a temporal scale, U(VI) in Sarwchawa spring is inversely correlated with pH value (*Figure: 3a*), and this indicates the dependency of uranium speciation on the pH variation. Although, refers to slightly oxidizing environment in Kometan aquifer's water. The relation between U(VI) and pH in Shkarta and Zewa springs are inverse but they are not correlated, reflecting no direct influence of pH on the speciation of uranium in Shiranish and Bekhme aquifers, respectively.

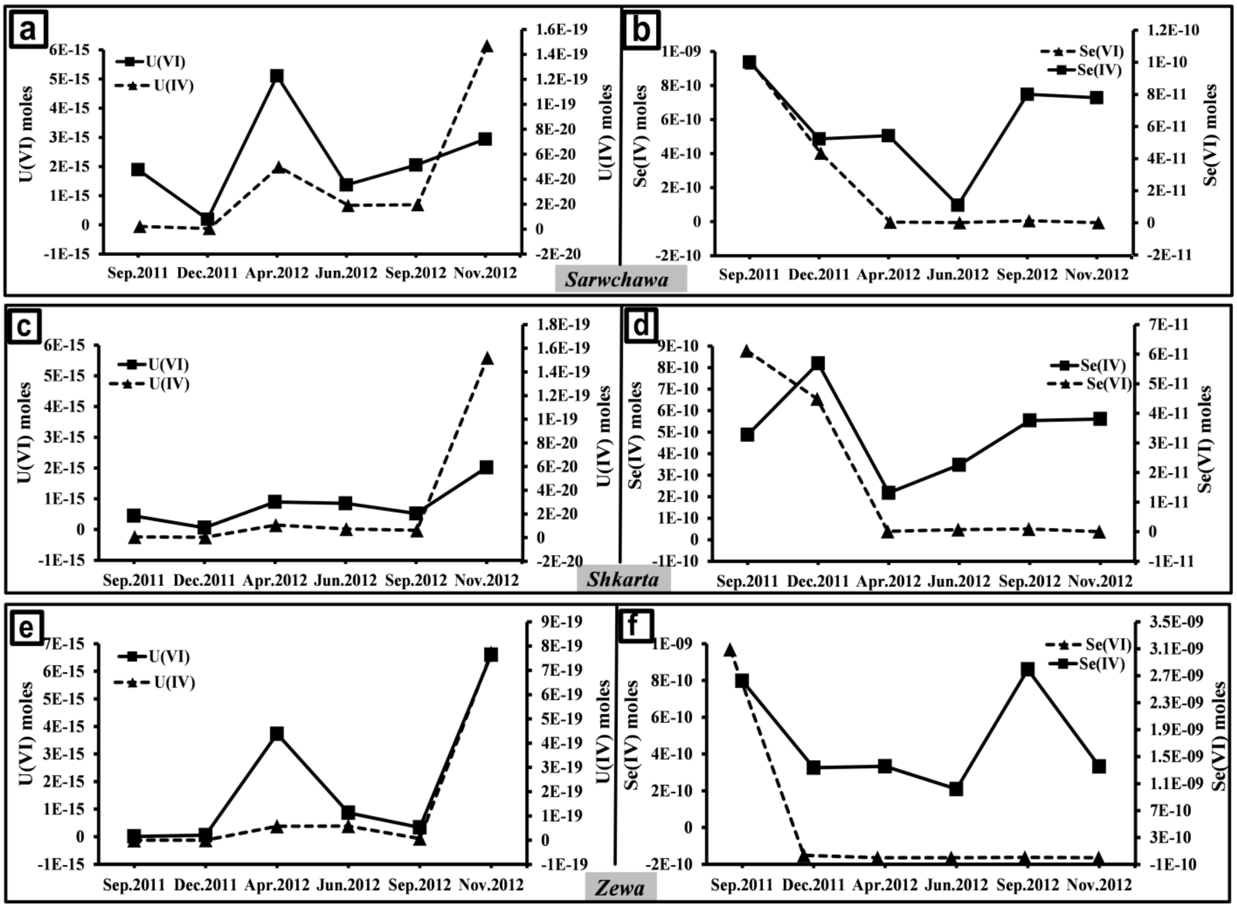

Figure-2: Abundance and temporal variation of U and Se. Concentration of species are in moles; Sarwchawa is representative of Kometan limestone aquifer, Shkarta is for marly limestone Shiranish aquifer and Zewa for Bekhme dolomite aquifer.

Majority of the trace elements are sensitive to redox variation in groundwater, because those elements may retain different redox states, or the redox state controls the concentrations of soluble complexes (Mapoma et al., 2014). Temporal variation of Se(VI) with pE (redox) positively (*Figure: 3*b), could be interpreted as increasing mobilization of the Se species in groundwater, which reported by (Masscheleyn et al., 1990) as well.

Temporal variation water temperature in karst waters of Makook system has an impact on the speciation of U(IV) as well (*Figure: 3c*). Increasing of temperature leads to decreasing of uranium concentration. Dissolution of carbonate minerals increases with increasing of temperature, and this could be an explanation for the inverse correlation between U(IV) and karst water temperature.

Increasing of $SI_{Calcite}$ and $SI_{Dolomite}$ corresponds to decreasing of U(VI) and As(V), respectively (*Figure: 3d, e*). This correlation is significant in case of Sarwchawa (Kometan aquifer) and Zewa springs (Bekhme aquifer), and shows lower correlation coefficient (R^2 = -6) in case of Shkarta spring (Shiranish aquifer). Karst waters which are under-saturated with calcite and dolomite contain higher concentrations of U(VI) and As(V). From this point, it can be concluded that mineralogical content of the host rocks controls the speciation of the studied elements in karst water. Based on mineralogical composition and hierarchical cluster analysis, three principal groups of rocks were recognized: Limestone in Kometan aquifer, dolomite in Bekhme aquifer and marly carbonate in Shiranish aquifer (Mustafa and Merkel, 2015b).

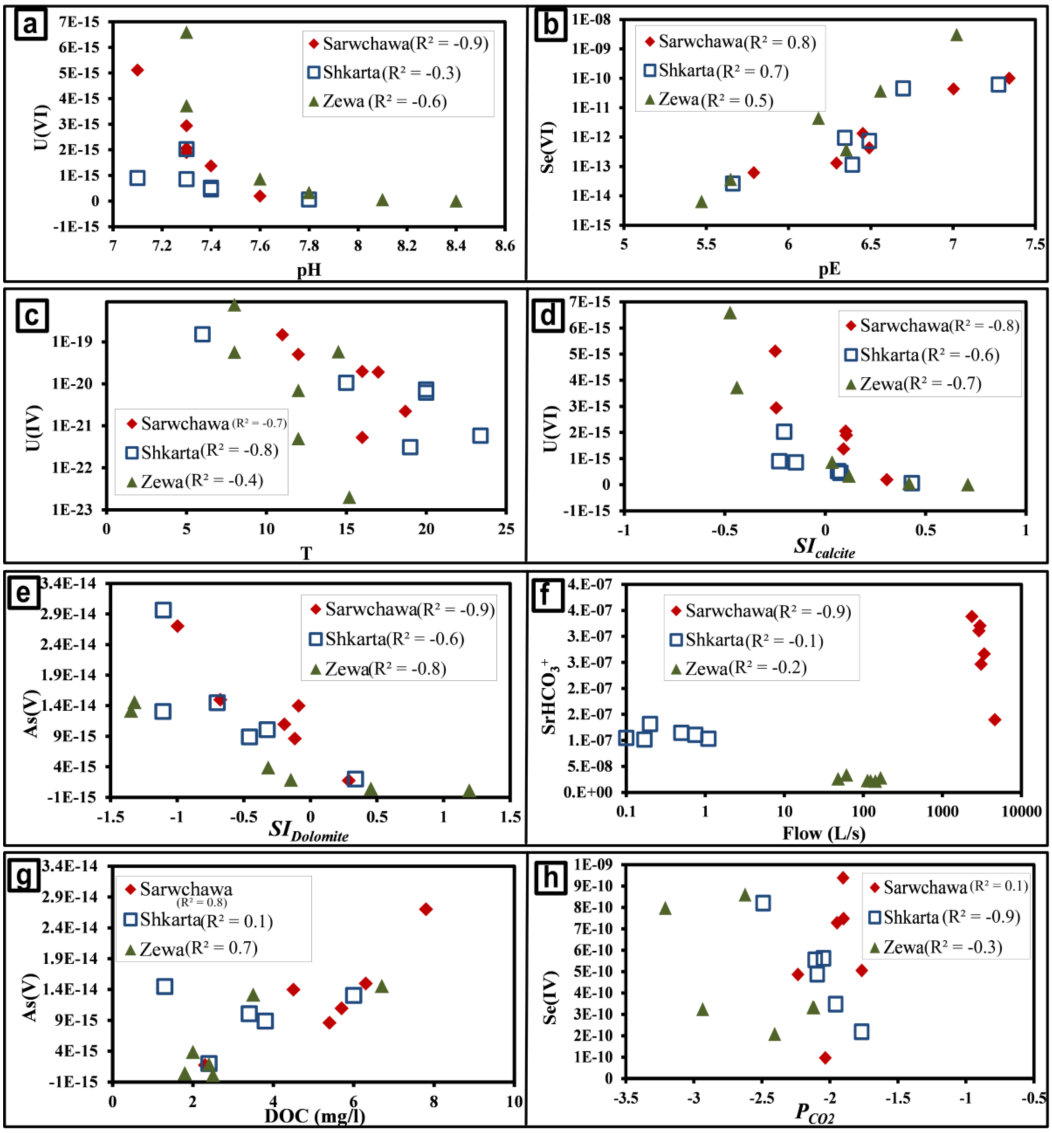

Figure-3: Factors affecting the speciation of U, Se, As and Sr. Concentration of species are in moles; R^2= is the correlation coefficient of the scatter plot.

Age of water and its flow regime within the aquifer ensures mineralization of groundwater through contact with underlying aquifer materials (Mapoma et al., 2014). The temporal variations of Sr-carbonate species are controlled by the flow of the springs (*Figure: 3*f). In Sarwchawa spring increasing of flow is accompanied by decrease in $SrHCO_3^+$ concentration (R^2 = -0.9, n = 6, p = 0.001). This can be interpreted by less time for water to react with aquifer rocks in high flow periods compared to the low flow periods (Mustafa and Merkel, 2015a).

The higher concentration of As(V) is corresponds to the higher DOC content and this correlation is significant in case of Sarwchawa and Zewa springs. The As(V)-DOC is not correlated in case Shkarta spring(*Figure: 3g*).

In Shkarta spring P_{CO2} is correlates inversely with Se(IV) (n = 6, p <0.001), and this could be interpreted as decreasing of Se(IV) with increasing partial pressure of CO_2. In case of Sarwchawa and Zewa springs, no correlations are shown; therefore, P_{CO2} affects differently on Se speciation in different aquifers (*Figure: 3*h).

Conclusions

The results of this paper enhanced the impact of different factors on the speciation of trace elements in karst waters. Uranium and Selenium speciation are influenced by pH and pE, respectively. Temperature and dissolution of calcite and dolomite in karst waters corresponds to decreasing of uranium species and As(V) concentrations. As a result of less time for karst water to interact with rock material, a decrease in $SrHCO_3^+$ concentration is observed during high flow. Increasing of DOC in karst waters drained from limestone and dolomite aquifers is accompanied by increasing of some trace element like As(V). Increasing of partial pressure of CO_2 leads to decrease in Se(IV) concentration in marly carbonate aquifer.

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