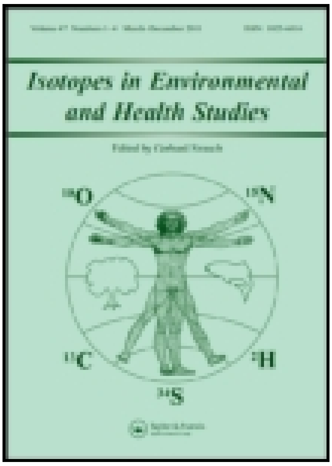

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Spatiotemporal patterns of stable isotopes and hydrochemistry in springs and river flow of the upper Karkheh River Basin, Iran

Khaled Osati[a], Paul Koeniger[b], Ali Salajegheh[c], Mohammad Mahdavi[c], Kamran Chapi[a] & Arash Malekian[c]

[a] College of Natural Resources, University of Kurdistan, Sanandaj, Iran

[b] Federal Institute for Geosciences and Natural Resources (BGR), Geozentrum Hannover, Hannover, Germany

[c] Faculty of Natural Resources, University of Tehran, Karaj, Iran

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Spatiotemporal patterns of stable isotopes and hydrochemistry in springs and river flow of the upper Karkheh River Basin, Iran

Khaled Osati[a], Paul Koeniger[b]*, Ali Salajegheh[c], Mohammad Mahdavi[c], Kamran Chapi[a] and Arash Malekian[c]

[a]*College of Natural Resources, University of Kurdistan, Sanandaj, Iran;* [b]*Federal Institute for Geosciences and Natural Resources (BGR), Geozentrum Hannover, Hannover, Germany;* [c]*Faculty of Natural Resources, University of Tehran, Karaj, Iran*

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Karst springs of the Zagros Mountains contribute a significant amount to agricultural and human water demands of western and south-western Iran. For an adequate management of available water resources in semi-arid and arid regions, sufficient hydrological monitoring is needed, and hydro-chemical and isotope hydrological data provide important additional information. About 350 water samples were collected from precipitation, river water, and karst springs of the upper part of the Karkheh River Basin (20,895 km^2) located between 33°35′ and 34°55′ North and 46°22′ and 49°10′ East with elevations ranging from 928 to 3563 m above sea level. Sampling was conducted in monthly time resolution from August 2011 to July 2012. All samples were analysed for hydro-chemical parameters (pH, electrical conductivity, and major ions) and stable isotopes (deuterium, oxygen-18). Isotope values of precipitation indicate a local meteoric water line (Zagros MWL $\delta^2\text{H} = 6.8\ \delta^{18}\text{O} + 10.1$; $R^2 = 0.99$) situated between the Mediterranean MWL and Global MWL. Spring and river water isotope values vary between −7.1 and −4.1 ‰, and −38 and −25 ‰ for δ^{18}O and δ^2H, respectively, responding to winter snowmelt and evaporation. This work implements stable isotopes and hydro-chemical information of springs and river water to understand hydrological and hydro-geological interrelations in karstic semi-arid areas and helps to improve the current water resources management practices of western Iran.

Keywords: evaporation; hydrogen-2; Iran; karst; oxygen-18; river water; spring water; upper Karkheh Basin

1. Introduction

In semi-arid and arid regions such as the Karkheh Basin in western Iran, water quantity and quality very often provide severe problems because of urbanisation and intense agriculture. For such areas changing discharge patterns either due to enhanced abstraction or climate change challenge authorities to guarantee water and food supply for the society. Additional difficulties arise for karstic formations, where the hydrological output mostly depend on factors such as type of precipitation (e.g. snow, rain), recharge mechanism (allogeneic, diffuse, and internal runoff character), patterns of areal recharge, actual status of the aquifer system (drained or full), overall hydraulic gradient (smooth or rugged topography), storage volume, overall geological setting, and degree of karstification [1–7]. Therefore, the hydrological response of karst formations in

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*Corresponding author. Email: paul.koeniger@bgr.de

heterogeneous arid and semi-arid systems is very often complex, and reliable prognoses on water resources are difficult to establish.

Isotope hydrological methods provide additional information for investigation and management of water resources. Especially, the stable water isotopes (^{2}H and ^{18}O) were extensively used. Novel laser techniques that were recently developed for stable water isotopes allow a higher throughput of samples at lower costs [8]. The stable isotopes allow an estimation of groundwater recharge rates, a delineation of source areas of recharge and an identification of paleo-water systems [9]. Studies on groundwater river water mixing [10–12] and river water infiltration into aquifers [13] were published using stable isotope techniques. In rivers, ^{2}H and ^{18}O primarily reflect the input from precipitation, melt water from snow and glaciers, impacts by evaporation, and very often a time-delayed contribution of groundwater. A global network for monitoring water isotopes in precipitation (GNIP) [14] started in the early 1960s, and only recently attempts were undertaken to include river water monitoring in similar networks [15–17]. Such data sets have the potential to improve our understanding of river–aquifer interactions, impacts of climate change and human activities on river runoff [17]. Continuous sampling of river water isotopes gains information on groundwater contributions especially under different climate conditions as was recently shown for the Euphrates River in Syria [18] or in combination with high resolution sampling of the Danube River in Austria [19] and Serbia [20], the Sava River in Slovenia [21], and the Weser River in Germany [22]. Whereas in arid regions [18], stable isotopes and chloride concentrations were

Table 1. Reports and publications in Persian language.

Author(s); affiliation	Report title	Year
[R1] Haidarizadeh M, Mohammadzadeh H; Mashhad, Iran	Seasonal variation of stable isotope (^{18}O and ^{2}H) in Tehran precipitation and it's relation to climatologic factors, 2012, 1st National Conference of Water Management in Coastal Area, University of Agriculture and Natural Resources of Sari, Sari, Iran, 8–9 December 2010	2010
[R2] Mohammadzadeh H, Ebrahimpoor S; Mashhad, Iran	Application of stable isotope and hydrogeochemistry to investigate the origin and water resources quality variations in Zarivar Lake catchment area. Journal of Water and Soil 26, 1018–1031	2012
[R3] Boomeri M; Zahedan, Iran	Assessment of geothermal energy resources of Taftan volcano by Stable isotope, Geography and development. Spring and summer issue	2005
[R4] MOP Ministry of Power; Tehran, Iran	Assessing hydraulic connection between Karun 3 dam storage and big springs in its downstream, final report	2008
[R5] Raghimi M, Yakhkashi ME; Gorgan, Iran	The origin of thermal water of Ziarat, Gorgan, by hydrochemistry and isotopic studies. Journal of Agriculture Science and Natural Resources 9, 29–40	2002
[R6] Maghsoudi M, Karimi H, Safari F, Charrahi Z; Tehran, Iran	Study of Karst Development Using Recession Coefficient, Spring Death Time and Chemical and Isotope Analysis in Parave–Bistoun Massif (Kermanshah Province-West of Iran), Physical Geography Research Quarterly 41, 51–65	2009
[R7] Mahmoudi F, Maleki A; Tehran, Iran	Karst development and its role in ground water resources of Bistoun–Parave Massive (Kermanshah). Geographical Research Quarterly 40, 93–105	2001
[R8] JAMAB Consulting Engineers in Association with Ministry of Energy; Tehran, Iran	Comprehensive Assessment of National Water Resources: Karkheh River Basin	1999
[R9] Governmental Organization of Water and Electricity of Khuzestan, Ahvaz, Iran	–	2012
[R10] ODMK, Organization of Disaster Management of Khuzestan; Ahvaz, Iran	–	2012
[R11] Saadati H, Sharifi F, Mahdavi M, Ahmadi H, Mohseni Saravi M; Tehran, Iran	Determining origin of groundwater recharge resources, drought and wet periods by isotopic tracers in Hashtgerd plain. Journal of Range and Watershed Management (Iranian Journal of Natural Resources) 62, 49–63	2009

mainly reflecting evaporation influence and groundwater return flow, in more humid climates [19–22]; seasonal variations of stable isotopes in precipitation and river water were useful to investigate water mixing after tributaries and residence time estimations.

In Iran, stable isotopes were implemented for water resources studies [23–27] as well as other works, documented in Persian language or in unpublished reports ([R1, R2]; see Table 1). These studies additionally implement stable isotopes beside other techniques for water sources studies (e.g. hot springs, dam recharge), whereas studies on precipitation, springs, and rivers were conducted rather infrequently. Seasonal variations, high intensity rainfall, and temperature effects on stable isotope compositions [24,26, R1] as well as the influence of evaporation on lake and surface water stable isotope composition in different parts of Iran were described [23,24,27, R2].

Water resources studies of the karstic Zagros Mountain systems that implement stable isotopes are reported [25, R2]. Karimi et al. [25] measured stable isotope compositions of nine karstic springs of the Alvand Basin, in the western part of the upper Karkheh Basin. The authors classified karstic springs using stable isotopes and geochemical parameters by a principal component analysis, and an elevation effect of stable isotopes is visible for their data. They also identify main factors that control the isotopic composition and the seasonal variations of spring discharge such as geology, elevation, and the rate of karst development.

The objective of our contribution is to identify meteorological and hydrological influences on isotope and hydro-chemical patterns in springs and river water of the large-scale upper Karkheh Basin. We discuss our own results in context with the earlier work and aim to present a review on other stable isotope investigations conducted in western Iran.

2. Study site and methods

The Karkheh Basin in western Iran is located in the middle and south-western part of the Zagros Mountains and drains an area of 51,843 km^2. With a mean discharge of 176 m^3 s^{-1} at the Payeh Pole gauging station for the period from 1961 to 2008, Karkheh River is the third largest river in Iran in terms of discharge following the Karun and Dez Rivers [28]. The Karkheh River flows towards the south and reaches the Hoorolazim lagoon at the border to Iraq after about 900 km. Land-use patterns of the Karkheh Basin are dominated by crop farming, and the Karkheh Basin contributes up to 9 % of the total wheat production in Iran which is facilitated by a large irrigation network [29].

The study area that we focus on in this work is the upper part of the Karkheh Basin. It is located in the Zagros Mountains between 33°34′44″ and 34°54′57″ North and 46°22′13″ and 49°10′02″ East. This area covers approximately 20,338 km^2 and reaches over six provinces (i.e. Kermanshah, Hamedan, Lorestan, Kurdistan, Ilam, and Markazi). Elevations of the study site range from 928 m above sea level (a.s.l.) at Holailan, the outlet of the upper Karkheh Basin, to up to 3563 m a.s.l. at the Garin Mountain range, southeast of the study area. About 90 % of the study area range between elevations of 1300 and 2300 m. The average elevation is about 1748 m. Most of the land is used for dry farming (45 %), range lands (28 %), irrigated lands (14 %), and forests (11 %) while cities, saline or bare lands, and open water bodies cover minor parts (3 %). Land-use proportions were extracted from geographical information system (GIS)-based land-use maps of Iran that were prepared by forestry, rangeland, and watershed management organisations of Iran.

In Iran, karst carbonate formations cover about 11 % of the land area, and the Zagros Mountain range was estimated to present 55 % [30]. In the study area, the surface geology is dominated to about 32 % by carbonate formations. Especially, mountain ranges are composed of carbonate formations of Tertiary and Miocene age. The deeper formations of the plains are generally karstic formations which are covered by Quaternary sediments. The extension of the karst system and the related landforms in the study area are neither described nor explored in detail. Karst landforms (e.g. jamas, uvulas, dolines, and caves) in the Parave area, the northeast of Kermanshah, are described by Maghsoodi et al. [R6]. The thickness of the Bistoun carbonate formation in Parave was estimated to be more than 2000 m, partly affected by tectonic activities [R7]. The existence of big karst springs (e.g. Ravansar, Taghbostan, Sahneh, Nilofar, Harsin, Barnaj, Bistoun, Shian, and others) with a mean discharge of up to 2.4 $m^3 s^{-1}$ exemplify the importance of karst water resources and indicate that the development of carbonate aquifers play a major role for the water resources management in this area.

The mean annual precipitation of the Karkheh Basin is about 450 mm, ranging between 150 mm in the south to more than 750 mm in the northern mountain regions of the upper Karkheh Basin [R8]. Kermanshah, the only station in the inner part of the study area with long time series, reports a mean yearly precipitation of 442 mm (168–858 mm) for the period from 1951/1952 to 2011/2012. About 96 % of the yearly precipitation occurs during the period October–May. The mean yearly temperature for Kermanshah is 14.4°C (12.5–17°C) for the period from 1951/1952 to 2011/2012. Mean monthly temperatures range from 2°C in January to 27°C in August. Both precipitation and temperature are highly variable in space and time. Spatial variability in mean yearly precipitation and temperature for the study site was estimated with geo-statistical methods (co-kriging: using elevation as a covariate) from 270 mm and 9°C to more than 840 mm and 18°C. A statistical interpolation was carried out independently for each sub-basin because strong micro-climate effects are dominating, and there were no sufficient stations available.

Streamflow patterns reflect effects of snowmelt and rainfall on flood events during March–May [31]. Extreme droughts, extra-utilisation of ground water resources, and ineffective management cause severe problems for water resources management of the Karkheh Basin. Masih et al. [32] assessed the trends of streamflow in the Karkheh Basin for the period from 1961 to 2001. They highlighted a significant decline during low flow in the upper part of the basin (e.g. for Gharehsoo sub-basin), and a significant positive trend in the Kashkan sub-basin was shown for flood analyses. These have been interpreted as climate-induced changes [33]. For the recent decade, discharge records of the Karkheh Basin highlight a significant decrease in river discharge. During the water year 2011/2012, i.e. from 22 September 2011 to 21 September 2012 following the Jalali Calendar, mean discharge of the Karkheh Basin dropped to 18 % of the long-term mean discharge. As a consequence, the Governmental Organisation of Water and Electricity of Khuzestan stopped all agriculture planting and irrigation activities during summer 2012 in the Karkheh Basin downstream of the plains [R9]. About 70,000 farmers in the plains of Sosangerd, Bostan, Hovaizeh, and Hamideyeh lost incomes from about 38,000 ha of farm land, which was estimated to a loss of about 1 billion US$ for the 2011/2012 growing period [R10]. The upper Karkheh Basin discharge records show declining trends for the last decade as well. The mean discharge for the period of 2002/2003 to 2011/2012 at the Holailan River gauge, the outlet of the upper Karkheh Basin, was calculated to be 41 $m^3 s^{-1}$. This reflects a 40 % decline in comparison to the mean long-term discharge of 69 $m^3 s^{-1}$ (period 1961/1962–2011/2012).

Our field work is focusing on the upstream areas of the Karkheh River Basin which includes the Gharehsoo and Gamasiab sub-basins as well as parts of the Saimareh Miani sub-basin. All streamflow monitoring systems (about 47 stations) were installed and managed by the Ministry of Energy. However, data monitoring was not conducted continuously, and sometimes the series show irregularities. The outlet of the study area is the Holailan River gauge. The flow regime of the upper Karkheh River is influenced by precipitation and snowmelt. Floods usually occur during February till May and dry periods between August and September. Human influences on discharge patterns are mainly caused by water abstraction through pumping for agricultural use during dry periods. There are severe effects on river water quality downstream of the Kermanshah city. Up-stream of the station Pire Solaiman, a dam is under construction which might additionally change the natural conditions in near future. Precipitation and streamflow patterns for the study

Table 2. Catchment characteristics of river (1–6) and spring (18, 19) sampling sites: mean discharge (Q), catchment size (A), elevation (h), distance to outlet at Holailan (x), and number of samples taken in the field (N) within the Karkheh Basin.

Station	Q^a ($m^3 s^{-1}$)	A (km^2)	H (m a.s.l.)	x (km)	N (–)
18, Taghbostan	1.1	n. k.	1345	152	12
19, Ravansar	2.1	n. k.	1343	268	12
1, P. Solaiman	2.8	547	1532	190	12
2, Aran	4.2	1988	1415	211	12
3, Doab	15.4	7770	1410	205	12
4, Haidar Abad	11.8	2070	1284	145	12
5, Faraman	21.0	5406	1264	109	10
6, Holailan	71.3	20,863[b]	928	0	12

Note: n. k., not known.
[a] Period January 1981–December 2005.
[b] Upstream catchment area derived from a digital elevation model.

period are summarised in Figure 2 for Holailan, Ravansar, and Taghbostan. Table 2 presents sub-basin characteristics and mean streamflow data for the period 1981–2005. Unfortunately, there is no discharge data available for the Taghbostan and Ravansar springs after 2005 because no measurements were conducted.

Monthly field sampling campaigns were conducted between August 2011 and July 2012. Precipitation samples were collected as monthly totals at six sites over this period whenever precipitation occurred and were analysed for stable isotopes (A, Pire Solaiman; B, Doab; C, Haidar Abad (Dinavar); D, Kermanshah; E, Ravansar; and F, Holailan). More infrequently samples were taken at four points during event studies (G, Karkhaneh; H, Khosro Abad; I, Pole Jadeh; and H, Mahidasht) (Figure 1). No precipitation was collected before November 2011. For river water, a grab sampler was used to collect an aliquot of water for hydro-chemical and isotope analyses directly from the flow line of the stream. Eight sampling points were continuously collected: 1, Pire Solaiman; 2, Aran; 3, Doab; 4, Haidar Abad (Dinavar); 5, Faraman; 6, Holailan; 18, Taghbostan karst spring; and 19, Ravansar karst spring (Figure 1). During the campaign in April 2012, 10 sampling points on the river network and 1 sample from the Harsin karst spring were collected additionally for an intense campaign characterisation (7–17 and 20–21) (Figure 1). The samples were stored in evaporation tight brown plastic bottles for subsequent shipping and laboratory analyses. Beside weather conditions, the parameters water temperature (T), electrical conductivity (EC), and pH value (pH) were determined in the field using a multi sensor (HI 98129, Hanna Inc.) and coordinates were reported with a global positioning system.

All monthly samples were analysed for the major ions of calcium, magnesium, sodium, potassium, bicarbonate, carbonate, and chloride at the Laboratory for Soil and Water, Department of Rehabilitation of Arid and Mountain Regions at the University of Tehran. Ca^{2+} and Mg^{2+} concentrations were measured by titration with ethylenediaminetetraacetic acid, murexide, and eriochrom black-T as colour indicators. Na and K concentrations were determined by flame photometry (flame photometer PFP7, Jenway). Cl^- was measured by titration with silver nitrate, and potassium chromate as indicators. HCO_3^- and CO_3^{2-} concentrations were determined by titration with sulphuric acid and phenolphthalein and methyl orange as indicators. Uncertainties after ion mass balance calculations were less than 10 % for all samples. All values are expressed in milli equivalent per litre (meq. l^{-1}). The sodium adsorption ratio (SAR), commonly used as an indicator of water suitability for irrigation, is determined using the following equation:

$$\mathrm{SAR} = \frac{[\mathrm{Na}^+]}{\sqrt{\frac{1}{2}([\mathrm{Ca}^{2+}] + [\mathrm{Mg}^{2+}])}} \qquad (1)$$

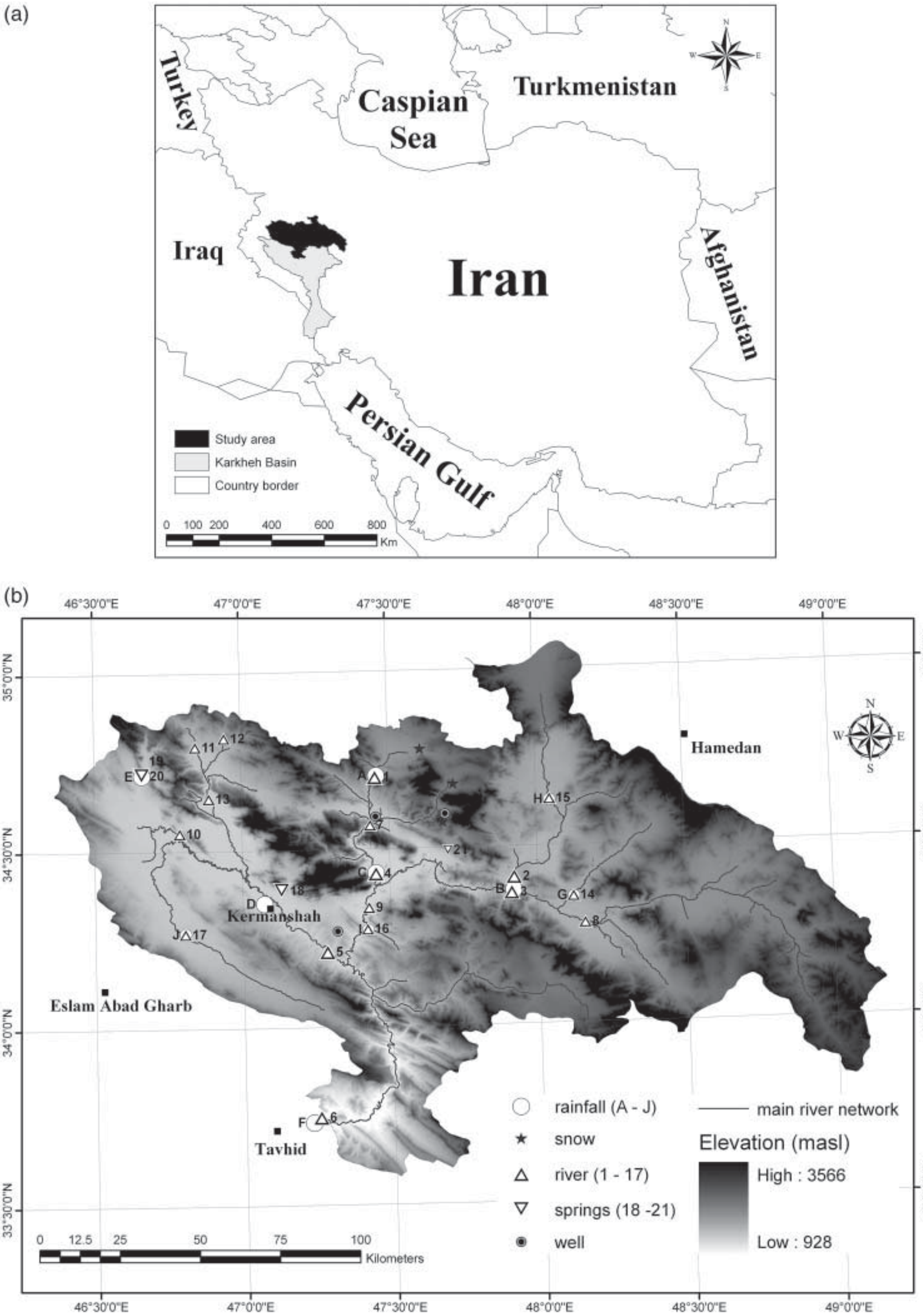

Figure 1. (a): Location of the upper Karkheh Basin in the Zagros Mountain range in western Iran, and (b) meteorological stations, hydrological stations and sampling sites during the field campaigns from August 2011 to July 2012. Rainfall sampling sites are labelled with letters A–J (A, Pire Solaiman; B, Doab; C, Haidar Abad (Dinavar); D, Kermanshah; E, Ravansar; F, Holailan; G, Karkhaneh; H, Khosro Abad (Pole Shekasteh); I, Pole Jadeh; and J, Mahidasht). River sites and springs are labelled with integers 1–21 (1, Pire Solaiman; 2, Aran; 3, Doab; 4, Haidar Abad (Dinavar); 5, Faraman; 6, Holailan; 7, Mianrahan; 8, Sange Sourakh; 9, Pole Cheher; 10, Doab Merek; 11, Alak; 12, Biar; 13, SarAsiab; 14, Karkhaneh; 15, Khosro Abad; 16, Pole Jadeh; 17, Mahidasht; 18, Taghbostan karst spring; 19, Ravansar small karst spring; 20, Ravansar big karst spring; and 21, Sahneh karst spring). Large symbols refer to monthly sampling intervals, small symbols indicate locations where event samples were collected occasionally. Snow samples (stars) and groundwater wells (circles) were collected only once.

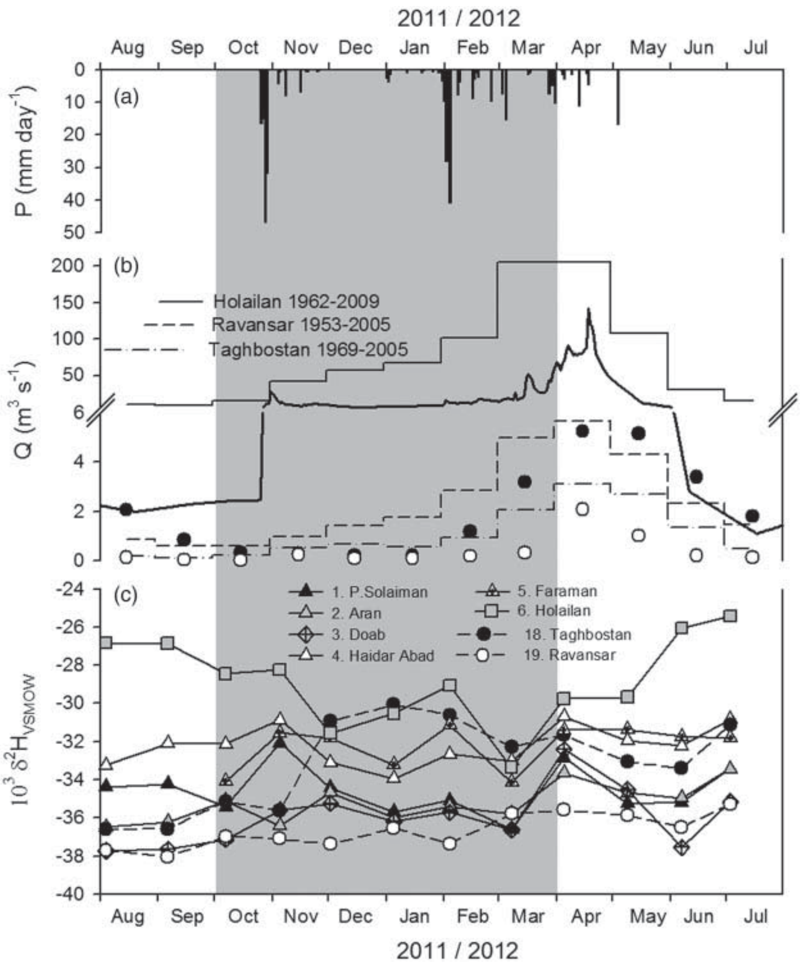

Figure 2. (a) Daily precipitation from Kermanshah station and (b) long-term mean monthly streamflow values, and monitored values during the field campaigns in the study period (August 2011–July 2012) from the outlet of the study site at Holailan and Taghbostan and Ravansar karst springs; (c) time series of δ^2H values for springs and river stations collected in the upper Karkheh Basin. Grey shaded box marks the winter season.

Mean values calculated from all campaigns are given in Table 3 for each sampling point.

Aliquots of all samples were analysed for stable isotopes (^{2}H and ^{18}O) at the Isotope Laboratory of the Federal Institute for Geosciences and Natural Resources in Hannover, Germany. A Picarro L2021-i laser analyser equipped with a vaporiser and autosampler was used. An additional post correction scheme for machine drift was applied following the work of van Geldern and Barth [34]. All values are given as δ values in per mil (‰) against the international standard Vienna standard mean ocean water (V-SMOW, normalised to V-SMOW/SLAP scale) as defined by Equation (2)

$$\delta = \left[\left(\frac{R_{SA}}{R_{ST}}\right) - 1\right] \tag{2}$$

where R_{SA} (–) denotes the isotope ratio of ^{2}H/H or ^{18}O/^{16}O of a sample and R_{ST} (–) of the standard, respectively. For notation of δ values in figures and tables, we follow recommendations given by Coplen [35]. Analytical errors of a quality check sample measured within each run are better than 0.2 ‰ for δ^{18}O and 0.8 ‰ for δ^2H measurements. Deuterium excess (d) values calculated from

Table 3. Long-term mean values of EC, pH, water temperature (T), ion concentration (meq. l^{-1}), and SAR at eight sites within the Karkheh Basin for the study period of August 2011–July 2012.

Station	T (°C)	pH	EC (μS cm^{-1})	Ca^{2+}	Mg^{2+}	CO_3^{2-}	HCO_3^- (meq. l^{-1})	Cl^-	Na^+	K^+	SAR
18, Taghbostan	13	7.8	264	1.9	0.5	0.5	2.3	0.1	0.03	0.02	0.05
19, Ravansar	16	7.6	331	2.1	1.1	0.5	3.1	0.1	0.05	0.02	0.05
1, P. Solaiman	13	7.9	571	3.6	1.4	0.8	4.5	0.6	0.55	0.05	0.48
2, Aran	16	8.1	456	2.5	1.5	0.4	4.0	0.5	3.67	0.05	0.25
3, Doab	16	8.2	478	2.4	2.0	0.9	3.6	0.5	0.55	0.05	0.51
4, Haidar Abad	15	7.8	400	2.4	1.4	0.7	3.2	0.3	0.24	0.03	0.25
5, Faraman	18	7.8	636	2.3	1.7	0.9	4.3	1.0	1.07	0.16	1.04
6, Holailan	16	8.4	473	2.0	1.8	1.1	2.9	0.7	0.91	0.12	0.95

$\delta^{18}O$ and $\delta^{2}H$ values show more consistency than those derived from earlier isotope ratio mass spectrometer measurements, because here both isotopes are measured from one sample at the same time. In this work, d values are better than 1 ‰ for a continuously measured quality check sample. It has to be mentioned that high contents of dissolved organic carbons (DOC) are problematic for laser measurements because of potential interference with the used water absorption bands. Picarro Inc. provides a data correction software called ChemCorrect^{TM} (unaltered factory settings) which flags samples with high DOC interference for repetition or discard.

3. Results

At the end of October 2011 and beginning of February 2012, strong rainfall events of more than 40 mm d^{-1} were monitored at the meteorological station at Kermanshah (Figure 2). The measured accumulated rainfall amount for the period 2011/2012 was 308 mm. No rainfall was recorded between June and the end of October. Streamflow at Holailan, the outlet of the Karkheh Basin, showed response in November (solid line in Figure 2(b)). The observed discharge values, however, are much lower than the mean long-term values for Holailan (step lines in Figure 2(b)). The springs at Ravansar and Taghbostan both show a similar response with Ravansar generally having a larger discharge (Figure 2(b) and Table 2). Hydro-chemical parameters are summarised in Table 3 as mean values over the study period for the two springs and the six river sites (monthly samplings) in the Karkheh Basin. The waters are in general of a Ca/Mg–HCO_3 type as expected for a karstic area. EC as well as Cl^- and Na^+ concentrations of the springs differ clearly from those of the river waters. Pire Solaiman shows the highest Ca^{2+} and HCO_3^- concentrations for river water. At Faraman, the outlet of the Gharehsoo sub-basin, the highest temperature, EC, Cl^-, and Na^+ concentrations were measured most likely due to wastewater contamination of the Kermanshah city. The Gharehsoo sub-basin shows a higher EC than the Gamasiab sub-basin, and accumulated effects appear at Holailan.

Isotope concentrations of precipitation, spring, and river water samples are summarised in $\delta^{18}O$ vs. $\delta^{2}H$ space in Figure 3. The collected samples plot almost between the Mediterranean meteoric water line (MMWL) and the global meteoric water line (GMWL) with some exceptions for river water samples that were collected during summer months. For 36 monthly rain samples collected during the study period of August 2011–July 2012, a local meteoric water line (LMWL) for the Zagros Mountains (ZMWL) was calculated as $\delta^{2}H = 6.8\ \delta^{18}O + 10.1$ with a R^2 factor of 0.99.

The monthly isotope values of springs and river sites are shown in more detail in Figure 3(b). The samples for the two springs plot close to the MMWL, whereas the river sites cluster below the ZMWL, and with increasing flow distance to the outlet at Holailan, the river samples plot closer to the GMWL. Isotope variations are visible for all sampling sites at the time series plot

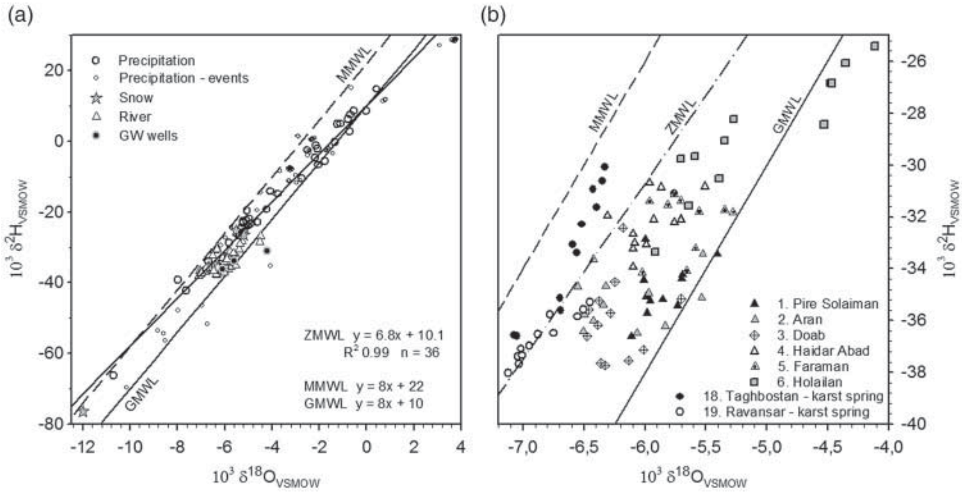

Figure 3. δ^2H vs. δ^{18}O plot of (a) rain and river water samples, MWL and (b) river water samples from 1 to 6 (see Figure caption 1).

Table 4. Long-term mean values of δ^{18}O, δ^2H, and deuterium excess (d) with standard deviation of sampling sites within the Karkheh Basin for the period of August 2011–July 2012.

Station	$10^3\ \delta^{18}$O (−)	$10^3\ \delta^2$H (−)	$10^3\ d$ (−)
18, Taghbostan	-6.54 ± 0.35	-33.1 ± 2.4	19 ± 2
19, Ravansar	-6.84 ± 0.23	-36.7 ± 0.9	18 ± 1
1, P. Solaiman	-5.85 ± 0.20	-34.6 ± 1.3	12 ± 1
2, Aran	-6.17 ± 0.37	-35.2 ± 1.0	14 ± 3
3, Doab	-6.25 ± 0.22	-36.0 ± 1.5	14 ± 2
4, Haidar Abad	-5.95 ± 0.22	-32.2 ± 1.0	15 ± 1
5, Faraman	-5.67 ± 0.24	-32.2 ± 1.1	13 ± 2
6, Holailan	-5.07 ± 0.63	-28.8 ± 2.3	12 ± 3

(Figure 2(c)) and also for the summary plot in Figure 3(b), which can either be explained by the seasonal variation of the isotope input signal or evaporative enrichment during warmer periods. The highest values occur at Holailan and tend to be more depleted during the winter months (grey shaded box in Figure 2(c)). For the Ravansar spring isotope, values tend to rise rather slowly and reflect a dampened constant signal, whereas the Taghbostan spring isotope values show a sharp increase in December 2011. Mean values of the monthly series (12-month period) are summarised in Table 4. The most depleted values were observed for the Ravansar and Taghbostan springs, and waters from downstream river sites are more enriched in heavy isotopes in comparison to those. Deuterium excess (d) values tend to be highest for the springs (18 and 19 ‰) and are between 15 and 12 ‰ for the river water samples.

Correlation analyses of δ^2H values of monthly samples of precipitation, river water and event samples collected in April 2012 during an intense field campaign with elevation and distance to outlet are presented in Figure 4. The correlation with elevation is shown on the left-hand side, and with distance to outlet of the upper Karkheh Basin at Holailan is shown on the right-hand side. The derived regression equations are indicated as well in Figure 4. The derived correlation factors (R^2 values) vary between 0.22 and 0.71 for precipitation and between 0.56 and 0.95 for river water samples plotted in relation to elevation and distance to outlet. For the correlation of the event sampling campaign, the spring samples were not considered.

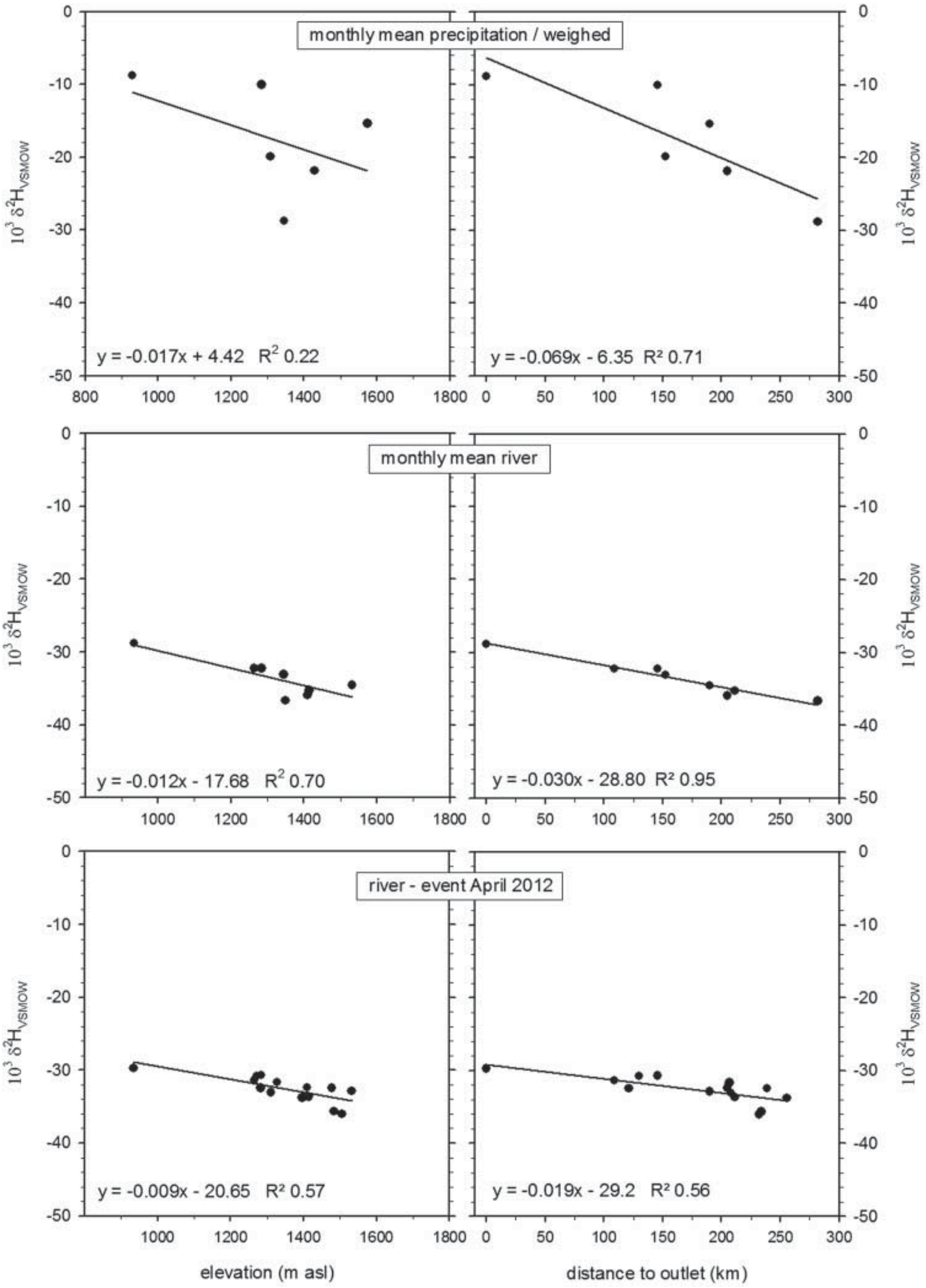

Figure 4. Correlation of δ^2H values of precipitation, mean monthly samples of springs and river sites, and samples collected during an event sampling campaign in April 2012 with elevation (left-hand side) and distance to outlet (right-hand side).

4. Discussion

With a total of 308 mm precipitation and a mean daily temperature of 15.3°C, the study period (water year 2011/2012) was rather dry but not exceptional different from other years. The mean discharge at Holailan, however, was much lower than the long-term mean discharge (Figure 2(b)). Considering a continuous trend of decreasing discharge of up to 40 % for Holailan and new profound water regulation projects in this area, conflicts and problems will increase and challenge communities in the Karkheh Basin. Just one indication might be that currently more than 14 decrepit dams and dam projects in development exist alone in the Kermanshah province. EC and SAR values are generally increasing with flow length with Pire Solaiman as an exception. This is indicating a decreasing water quality and suitability for agriculture, although the values for EC and SAR are still in acceptable ranges. Samples collected at Pire Solaiman show the highest Ca^{2+} and HCO_3^- concentrations for all river water samples. Karst formations cover less than 20 % of the Jamishan watershed mostly at the ridge close to outlet of the sub-basin. Therefore, current karst development conditions seem to explain the hydro-chemical patterns. In our study, hydro-chemical parameters are difficult to use for an observation of groundwater influence or an estimation of residence times, because river water quality downstream of Kermanshah and evaporation effects alter river water chemistry in addition to a rather complex response due to the geological formations. The facts that the study area is large and partly karstified and that groundwater contributes from different aquifers with varying quality and residence time makes it difficult to appropriately apply mass balance methods for a quantitative analysis of groundwater contribution. Chemical mass balance methods are applicable when the sources from aquifers and rivers are quantitatively available, or in other words when it is possible to cross-check all components.

Isotope hydrological observations of precipitation conducted over a whole year period in the upper Karkheh region led to a local ZMWL with a slope of 6.8 and an intercept of 10.1. This is in good agreement with some other studies that were conducted in this area. Tehran, the capital of Iran, is the only city where isotope series in precipitation were reported over a longer time period (1200 m a.s.l.; Tehran-East 1350 m a.s.l). This data set is available at the WISER-GNIP database [14]. The location of Tehran station is about 360 km northeast of the Karkheh Basin. Climate and topography are considerably different for both sites. Other studies that established LMWLs in the larger vicinity that are of interest for the upper Karkheh Basin are compiled in Table 5 (see also, [24,36,37, R2, R11]).

More elaborated GIS-based calculations using GNIP data sets provided on the water isotopes website [38] led to a LMWL of $\delta^2H = 6.5\ \delta^{18}O + 4.2$ for Kermanshah (34°N, 47°E, 1390 m a.s.l.) which is not well confirmed by our field studies for 2011/2012. Strong temperature and rainfall gradients mainly caused by local topography influence local climate and isotope patterns. Temperature has a large influence on isotope fractionation, and it is generally more pronounced at lower temperatures. Therefore, seasonal patterns of isotopes in precipitation correspond with

Table 5. Compilation of parameters of LMWLs in closer vicinity of the Karkheh Basin.

Station (distance to study site)	Time period	Slope	Intercept	R^2	*N*	Reference
ZMWL (–)	8/2011–7/2012	6.8	10.1	0.99	36	
Tehran (300 km NE)	1/1960–12/1987	6.6	2.7	0.95	137	[14]
Tehran-East (300 km NE)	1/2000–12/2004	7.7	12.5	0.97	19	[14]
Senyurt/Turkey (600 km NW)	1/1990–2/1993	7.6	11.7	0.93	28	[14]
Marivan (190 km NW)	12/2010–1/2011	7.5	9.0	n.k.	16[a]	[R2]
Hashtgerd (320 km NE)	12/2005–6/2006	7.8	1.0	0.91	6[a]	[R11]
Isfahan (400 km SE)	4/1994–3/1996	7.1	12.3	0.98	8[a]	[24]
Rafsanjan (900 km SE)	11/1999–9/2001	5.9	16	0.96	8[a]	[37]
Mashhad (1000 km NE)	2008–2009	7.2	11.2	0.95	n. k.	[37]
Kermanshah (–)	mean monthly	6.5	4.2	0.99	12	[38]

Note: n.k., not known.
[a] Event samples instead of monthly precipitation weighed samples.

seasonal temperature changes at vapour source. Isotope elevation effects are also connected to changes in temperature because vapour cools during upward lifting of air masses at mountain systems [39]. The influence of micro-climate and spatial variability of topography and rainfall on isotope patterns has to be studied in more detail during future work. Such information might then allow using end member mixing approaches for event studies or more sophisticated isotope balance approaches if isotope concentrations of water vapour are available. The mountain ranges of Parave and Bistoun northeast of Kermanshah are the main influencing topographical regions of the study area that overprint usually expected regional temperature and rainfall gradients. Therefore, it is difficult to spatially interpolate variables into unknown areas.

Unfortunately, it was not possible to collect sufficient rain event data during this study. A sampling of monthly totals of precipitation was favoured for an overall classification of isotope hydrological conditions. Future isotope studies might also focus on a comparison of isotope patterns from rain events and imprints on flood events in the Karkheh River system. We were just able to collect snow samples infrequently because we were focusing on a larger region and it was not possible to include snow campaigns into the field work schedule.

Our results suggest that springs show a different time response to input for isotope values. Whereas the Taghbostan spring shows a rather quick response to rainfall even in winter months, the response of the Ravansar spring is rather damped. In early spring isotope, values of Ravansar tend to respond slowly as well (white circles in Figure 2(c)). Taghbostan (black circles) exposes a step shift to enriched values in December 2011 and just slowly returns to more depleted values after winter. This response might most likely reflect karst pathways but it is difficult to apply residence time modelling approaches because an input function is not available and interpolation would include large errors. The Ravansar spring exhibits more depleted isotope values than the Taghbostan spring and therefore indicates a higher mean catchment elevation. A detailed interpretation of mean catchment elevations of the springs would afford a good isotope elevation effect for precipitation, which is currently missing for this area. In north-western Iran, Maghsoodi et al. [R6] studied isotopes, hydrochemistry, recession coefficients, and dynamic storage of springs in the Parave–Bistoun massif (Barnaj, Bistoun, and Tagh-e-Bostan) as well as in the Zagros Mountains (Shian and Niloufar springs). The Shian and Niloufar springs are located close to the Kermanshah city, in the inner part of the upper Karkheh Basin. The authors discussed reasons for low mineralisation of the Taghbostan spring and argue that rapid flow and a high degree of canalisation of the recharge system causes minimal interaction of water with the geological substrate. This assumption was supported by death time and recession coefficient analyses of the springs (Parave–Bistoun springs) that the authors interpreted with a high level of karstification and well-developed conduits and channelling feeding system for the springs. The fast response of the Taghbostan spring is also reflected by a step change of isotope concentrations at the beginning of the winter season.

Holailan at the outlet of the upper Karkheh River exploits the largest seasonal isotope variations with depleted values during the winter and most enriched values during the summer months (Figure 2(c)) in correspondence with the higher and lower flow seasons, respectively. The other river sites show isotope variations in response to precipitation events. The mean values over the study period reflect highest correlation with distance to basin outlet and time for evaporative fractionation. Evaporation influence on river water samples is also reflected by long-term mean deuterium excess values (Table 4). The two springs show relatively high d values reflecting Mediterranean vapour source [40]. The mean values of the river samples are much lower (between 15 and 12 ‰) and indicate evaporative enrichment especially for Pire Solaiman and Holailan. Time series of d values (Figure 5) indicate similar values for the summer months but reflect higher values of winter water input and hence minor evaporation during the winter season. This observations are supported by calculations on potential evaporation, which is about 5.3 times higher (1716 mm in comparison to 328 mm average annual precipitation) for the period of 1989/1990–2010/2011 at the Holailan meteorological station.

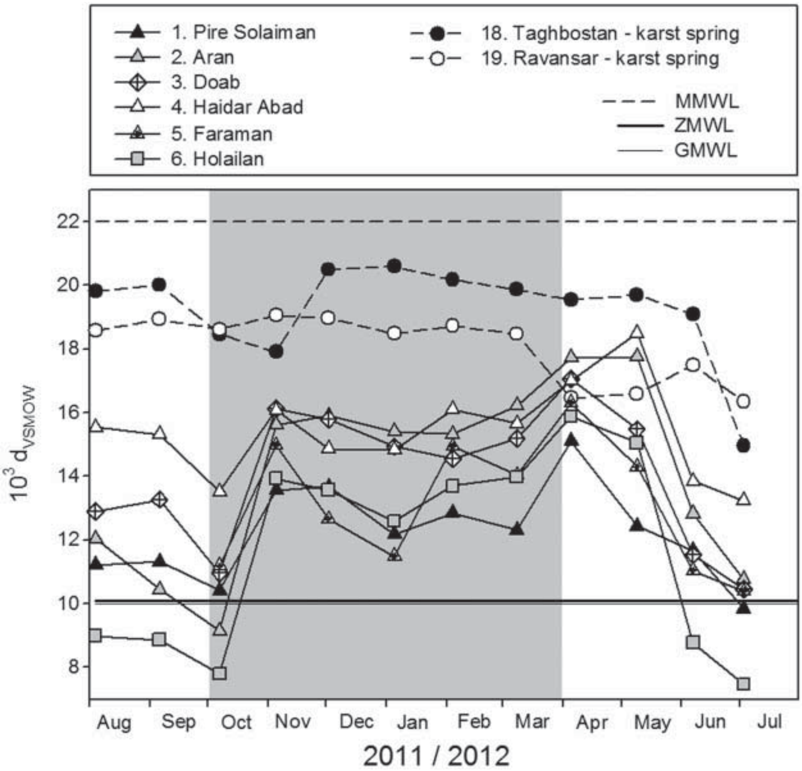

Figure 5. Deuterium excess values for springs and river samples collected in the upper Karkheh Basin during August 2011–July 2012.

Investigations conducted close to our study area at the Lake Zaribar in Kurdistan [R2] show similar effects of evaporation on lake water. Average values of rain, groundwater, and lake water were −8.3, −7.0, and −5.5 ‰ for δ^{18}O, and −53.6, −42.2, and −16.9 ‰ for δ^{2}H. Groundwater was related to meteoric water with minor evaporation loss, whereas the lake water indicates relatively high enrichment and *d* values ranging between 24 and −9 ‰. A LMWL was reported that is close to the one that we propose.

5. Conclusion

Hydro-chemical and isotope data were collected for the first time in the upper Karkheh Basin during 12 intense field campaigns in 2011/2012. The results show that river water isotope patterns are dominated by evaporative enrichment. River water reflects best correlation factors when related to river flow length. Two important karst springs in the area were investigated and show much higher deuterium excess values (18–19 ‰) than river water samples which can be related to Mediterranean vapour source. The larger spring Ravansar exhibits a relatively damped seasonality in comparison to the smaller spring Taghbostan and more depleted isotope values that indicate a higher mean catchment elevation. This work will serve as a base for further investigations on groundwater recharge source areas and groundwater contribution to river water in this area with complex geology. More effort is necessary to find main climatic control on spatial isotope variability, especially a determination of isotope elevation effects, and to calculate the isotope enrichment in river water following evaporation processes. Potentially larger variations of δ^{18}O and δ^{2}H have to be expected in semi-arid climates because the spatiotemporal distribution of rainfall is not as regular as in humid climates. In such cases, it is difficult to relate campaign studies to average values of rain input. With this contribution, we initiate an interpretation of rainfall, river, and spring isotope data in the Karkheh Basin as a basis for future isotope studies in this area.

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