Assessment of water quality and quantity of springs at a pilot-scale: Applications in semi-arid Mediterranean areas in Lebanon

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November 22, 2022

Abstract

This work presents an integrated methodology for the assessment of threats on spring quality and quantity in poorly investigated Mediterranean semi-arid karst catchments in Lebanon. Pilot investigations, including 1) high-resolution monitoring of spring water and climate, 2) artificial tracer experiments, and 3) analysis of micropollutants in surface water, groundwater, and wastewater samples were conducted to assess flow and transport in three karst catchments of El Qachqouch, El Assal, and Laban springs. First, the high-resolution in-situ spring data allows the quantification of available water volumes, as well as their seasonal and yearly variability in addition to shortages and floodwaters. Moreover, the statistical analysis of hydrographs and chemographs helps assess the karst typology, spring type and hydrodynamic behavior (storage versus fast flow). Furthermore, a series of artificial tracer experiments provides information about key-transport parameters related to the intrinsic vulnerability of the pilot springs, while the analysis of micropollutants gives insight into the specific types of point source pollution as well as contaminant types and loads. On the one hand, the tracer experiments reveal that any potential contamination occurring in snow-governed areas can be observed at the spring for an extensive time due to its intermittent release by gradual snowmelt, even with enough dilution effect. On the other hand, the assessment of persistent wastewater indicators shows that springs in the lower catchment (including El Qachqouch) are highly vulnerable to a wide range of pollutants from point source (dolines and river) and diffuse percolation. Such contaminants breakthrough is challenging to predict because of the heterogenous duality of infiltration and flow, typical of karst systems. Finally, this set of investigations is essential for the proper characterization of poorly studied systems in developing areas, whereby results can be integrated into conceptual and numerical models to be used by decision-makers as support tools in science-evidenced management plans.

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Keywords

Karst methods, springs, tracer experiment, monitoring, micropollutants, Mediterranean

Abstract

This work presents an integrated methodology for the assessment of threats on spring quality and quantity in poorly investigated Mediterranean semi-arid karst catchments in Lebanon. Pilot investigations, including 1) high-resolution monitoring of spring water and climate, 2) artificial tracer experiments, and 3) analysis of micropollutants in surface water, groundwater, and wastewater samples were conducted to assess flow and transport in three karst catchments of El Qachqouch, El Assal, and Laban springs. First, the high-resolution in-situ spring data allows the quantification of available water volumes, as well as their seasonal and yearly variability in addition to shortages and floodwaters. Moreover, the statistical analysis of hydrographs and chemographs helps assess the karst typology, spring type and hydrodynamic behavior (storage versus fast flow). Furthermore, a series of artificial tracer experiments provides information about key-transport parameters related to the intrinsic vulnerability of the pilot springs, while the analysis of micropollutants gives insight into the specific types of point source pollution as well

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1. Introduction

Freshwater, notably groundwater is presently under tremendous stresses due to climate change and variability in addition to the increase of urbanization, contamination, water needs, and demands (Hou et al., 2013, Jongman, 2014, Kløve et al., 2014, Van Loon et al., 2017, Luo et al., 2020). The Mediterranean region has been identified as one of the most vulnerable areas in terms of increase in forecasted air temperatures and precipitation (Diffenbaugh and Giorgi, 2012, Goderniaux et al., 2015, Nerantzaki and Nikolaidis, 2020), expected to affect drastically water resources in semi-arid regions (Iglesias et al., 2007, Doummar et al., 2018b, Dubois et al., 2020, Marin et al., 2021, Sivelle et al., 2021). Karst aquifers predominant in the Mediterranean (Chen et al., 2017) provide about 25% of the water supply worldwide (Ford and Williams, 2007, Stevanovic, 2019a). Mediterranean karst catchment areas characterized by limited surface runoff and high infiltration rates reaching 70% are drained by one or multiple springs (Doummar et al., 2012a, 2018, Hartmann et al., 2014,2015). Due to the duality of flow and heterogeneities in karst systems, flow and transport occur in highly permeable conduits draining a low permeability matrix (Geyer et al., 2008, Mudarra et al., 2010). Generally, the breakthrough of contaminants in karst springs varies according to the dynamic conditions in the aquifer (Doummar et al., 2018a) and the type of pollutant (Hillebrand et al., 2012, Doummar et al., 2014, Doummar and Aoun 2018b). While transport may occur rapidly because of fast flow velocities (Pronk et al. 2006, Bailly-Comte et al. 2010), the flow rates increasing exponentially during a short period as a response to high rain events will induce a high dilution, thus reducing the concentration of contaminants in the spring (Chang et al., 2020). Given this complexity, the spring responsive behavior, often highly variable to climatic conditions and hydraulic properties of the aquifer, is very difficult to predict in the long and short-run (Sivelle et al., 2021). Chen et al., 2018 show that the total flow rates of a karst spring in an Alpine setting will substantially decrease under the different climatic scenarios mostly because of the shift in snowmelt patterns. Nerantzaki and Nikolaidis, (2020) found that multi-year droughts are expected after 2059, for three investigated springs in Greece under all varying climatic scenarios. Moreover, Hartmann et al., (2012) show that a 10 to 30% decrease in flowrate is expected in a large karst spring in the West Bank after 2068. Furthermore, in Lebanon, it is expected under forecasted climatic scenarios (2020-2100; e.g., IPSL_CM5; GCM; RCP, 6.0) to witness a high variability of spring flow rates with more pronounced extremes and periods of droughts (Doummar et al., 2018b) in snow-governed mountainous areas. Additionally, sensitivity studies show the high influence of varying climatic factors (notably precipitation) on spring hydrographs (Dubois et al., 2020, Sivelle et al., 2021) and water availability.

Karst springs are an important component of the groundwater systems and play a significant role in the development of civilizations (Luo, et al., 2020, Stevanović 2019b). Particularly, springs have been investigated as vital resources for social and economic development (Andreo et al., 2006, He and Wu., 2019) in many areas around the world, such as Jinan Springs (Gao et al., 2020), Gallusquelle Spring in the Swabian Alps (Sauter 1992, Heinz et al., 2009, Doummar et al., 2012a), and notably around the Mediterranean area (Nerantzaki and Nikolaidis, 2020). In these semi-arid environments where water scarcity is rapidly increasing (Hartmann et al., 2014a), springs have been regarded as important resources for large to small scale local water supply such as El Gran Sasso springs in Italy (Barbieri et al., 2005, Pettita, et al., 2020), the Lez spring in southern France for Montpellier (Fleury et al., 2009, Marechal et al., 2013, Sivelle et al. 2021); the Eastern Ronda Springs and Ubrique spring for Malaga Province in Southern Spain (Barbera and Andreo, 2012, Hartmann et al., 2013, Marin et al., 2021). In these areas, the continuous monitoring of spring quality and quantity is performed to ensure sustainability in the supply and the preservation of the water quality at the source. The increasing urbanization, especially in areas that lack waste-water treatment plants (mostly in rural developing countries) has resulted in a growing level of unpredictable contamination (Gao et al., 2020). Furthermore, a sturdy understanding of the hydrological processes and the factors influencing groundwater dynamics including climatic ones are needed to develop well-informed water management tools and policies (Luo et al., 2020, Stevanović and Stevanović, 2021). Numerical models have been proposed as successful decision support tools for water management in karst (Sivelle et al., 2021). Flow in these systems has been simulated using lumped and distributed approaches depending on the level of surface and subsurface characterization (Worthington, 1999, Doummar et al., 2012a, Hartmann et al., 2013b, Duran and Gill, 2021). However, the suitability of the model highly relies on the amount and quality of the available data and its temporal extent (Hartmann et al., 2017). In some instances, robust sensitivity analysis allows decreasing the uncertainty in the model output (Hartmann et al., 2013c, Chen et al., 2014, Mazilli et al., 2017, Dubois et al., 2020). To overcome the challenges of transport assessment in karst, even with a calibrated and validated flow model, the analysis of spring responses provides insights into the dynamics of a karst system. Firstly, the breakthrough of conservative (or reactive) contaminants and/or spring signatures (stable isotopes) have been used in spring high-resolution time series to understand the dynamic response of springs to a variation in input and extent of dilution (Frank et al., 2018, Hillebrand et al, 2015, Wang et al., 2020, Ahmed et al., 2021). Moreover, tracer experiments have been implemented to assess the connection between karst springs and a contamination point source and estimate transport velocities and dispersivity (Goeppert and Goldscheider, 2008, Marin et al., 2015, Doummar et al., 2018a, Benischke, 2021) in the aquifer and its intrinsic vulnerability to contamination (Epting et al., 2018). Additionally, emerging micropollutants (MPs) such as pharmaceuticals and personal care products were revealed to be suitable transport indicators for persistent and degradable contamination of different origins (Hillebrand et al., 2012, Doummar et al., 2014, Zirlewagen et al., 2016, Stange and Tiehm, 2020). They can be detected to various extents in raw wastewater and treated wastewater, if persistent, or in groundwater and surface water, notably in areas lacking proper wastewater treatment systems (Gasser et al., 2010, Schmidt et al., 2013, Doummar and Aoun, 2018a, Clemens et al., 2020).

Lebanon counts more than 409 springs with discharges ranging between 0.001 m^3/s to more than 10 m^3/s on average (ElGhawi et al., 2021). Some are used for local supply, while others may serve as an alternative decentralized water source for selected villages to overcome the forecasted water scarcity. The high urbanization and lack of an effective wastewater system in Lebanon (Massoud et al., 2010), pose a significant contamination risk on springs located below 1600 m above sea level even in rural settings. Therefore, there is a need for thorough investigations on selected potential springs, to understand their vulnerability against contamination events or climatic parameters (Epting et al., 2018). The latter can be only achieved with a robust monitoring network, the collection of high-resolution data, the analysis of representative temporal and spatial water quality samples, and the assessment of contamination indicators (Torresan et al., 2020). The objective of this work is to highlight some of the important methods used for the conceptualization of flow and transport in pilot karst springs and the identification of their inherent resilience to contamination hazards and potential future threats in a rural groundwater catchment in Lebanon. The proposed methodology can be applied to other case studies in poorly investigated spring catchment areas. The results are further discussed in terms of policy enforcement and drafting of guidelines and laws to ensure sustainable protection of spring water resources (Fleury, 2009).

2. Field site

The investigated springs are located in the Middle East- Lebanon, north of the capital Beirut in a Mediterranean semi-arid snow-governed climatic region (Figure 1, Table 1). They belong to the Nahr El Kalb River rural catchment (Figure 1). The catchment extends from sea level to an elevation of 2600 m above sea level and is characterized by karstified Jurassic and Cretaceous rock sequences disturbed by complex structural deformations (Bakalowicz, 2015). The catchment is drained by important springs heavily relied upon for water supply; for instance, the Jeita spring with mean flowrates of 8 m^3/s is used as a water supply source for the capital Beirut (1.5 million inhabitants; Doummar et al., 2014, Koeniger et al., 2017).

Based on two recording stations, the total precipitation recorded on the catchment area varies between 800 mm (closer to the coast) and 1800 mm as snow in the mountains (Fayad et al., 2017; Koeniger et al., 2017, Doummar et al., 2018b, Dubois et al., 2020). The Qachqouch Spring located at 64 m above sea level, emerges from Jurassic age rocks, composed of fractured limestone and basalts. During low flow periods, the spring is used to complement the water deficit in the capital city Beirut and surrounding areas. Its total yearly discharge reaches 35-55 Mm^3 based on high-resolution monitoring of the spring (2014-ongoing; Dubois et al., 2020). Flow maxima reach a value of 10 m^3/s for short periods following flood events; it is about 2 m^3/s during high flow periods and 0.2 m^3/s during recession periods. On the other hand, Laban and Assal Springs are located in the highlands of Nahr El Kalb catchment, at respective altitudes of 1552 and 1600 m above sea level. The main source of recharge is the snowmelt over a total groundwater basin of about 25 km^2. They partially drain the Albian-Cenomanian rock formations composed of limestone and dolostones. The upper catchment area is a plateau characterized by a high-density doline distribution (exceeding 19 dolines/km^2), which enable relatively fast infiltration of snowmelt and rain. The dolines mapped during various campaigns (2012, by the BGR: BundesAnstalt Fuer Geowissenschaften and Rohstoffe; by AUB 2015 and AUB 2020-21 are buried ones with non- discernable 20-50 cm swallets buried by rock debris. Fast infiltration of rain or snowmelt can occur in the buried holes within the doline while diffuse infiltration happens within the soil depending on the rock facies in the Cenomanian rock sequence. The thickness of the soil in the dolines may exceed 5 m as portrayed by representative auger excavations. The Assal spring has an annual volume of 22-30 Mm^3 (Doummar et al., 2018b) is used locally for water supply 24,000 m^3/day while water from the Laban spring, with a total annual volume of 20-25 Mm^3, is conveyed to the Chabrouh Dam in Faraya (Figure 1). The overflow from both springs feeds the two tributaries of the Dog River (Nahr El Kalb) in the highlands (Doummar and Aoun 2018a), while that of Qachqouch spring is discharged into the River closer to the coast. The highest observed volumes in the three springs are recorded during the high flow periods (December to April) exceed the water demand and supply, while available water volumes drop substantially during low flow periods extending from May till November where water supply is mostly needed. Therefore the three karst springs are currently not exploited to their full potential, due to the presence of alternative resources and the natural deficit in water availability during low flow owing to their karstic nature. The Qachqouch spring is a karst spring characterized by a duality of flow in a low permeability matrix and high permeability phreatic conduit system (Dubois et al., 2020). As such, it is highly reactive to rain events with a recession coefficient ranging between 0.005 and 0.1 depending on the event responses (Dubois et al., 2020). Assal spring is less responsive to snowmelt and is characterized by a storage capacity that allows it to sustain a flow rate of 240 l/s during the dry season (August till October). The Laban spring is highly reactive to snowmelt due to its higher level of karstification and has a limited storage capacity, thus it runs almost dry during the summer period (August-October). Wastewater treatment plants are absent in most areas in Lebanon, especially in rural areas because of the difficulty of continuous operation and maintenance (Karnib, 2014). Additionally, wastewater effluents and solid waste may be disposed of directly on the river flanks, or in bottomless septic tanks in areas that are not connected to the public wastewater network (Massoud et al., 2010). Furthermore, outdated generic groundwater protection guidelines or laws (for wells, springs, and River) are not reinforced or rigorous enough to ensure the protection of spring catchment areas. As a consequence, land use and cover expand in highly vulnerable areas of spring recharge without proper mitigation measures (Korfali and Jurdi, 2009). The major threats faced by the investigated springs are related to intrinsic or anthropogenic factors influencing both the pristine spring water quality and quantityyielding an increase in the karst disturbance factor (van Beynen and Townsend, 2005, North et al., 2009). Such threats can decrease the available water of good quality for supply over the short- and long-term scale (especially in countries that have adhered to the United Nations Sustainable Developmental goals (SDG VI). On the other hand, the opportunities are infrastructural, technological, or policy-making changes that can enhance the sustainable supply of water quantity over time, mitigate the contamination risk, and achieve a potential recovery of the pristine status of the spring.

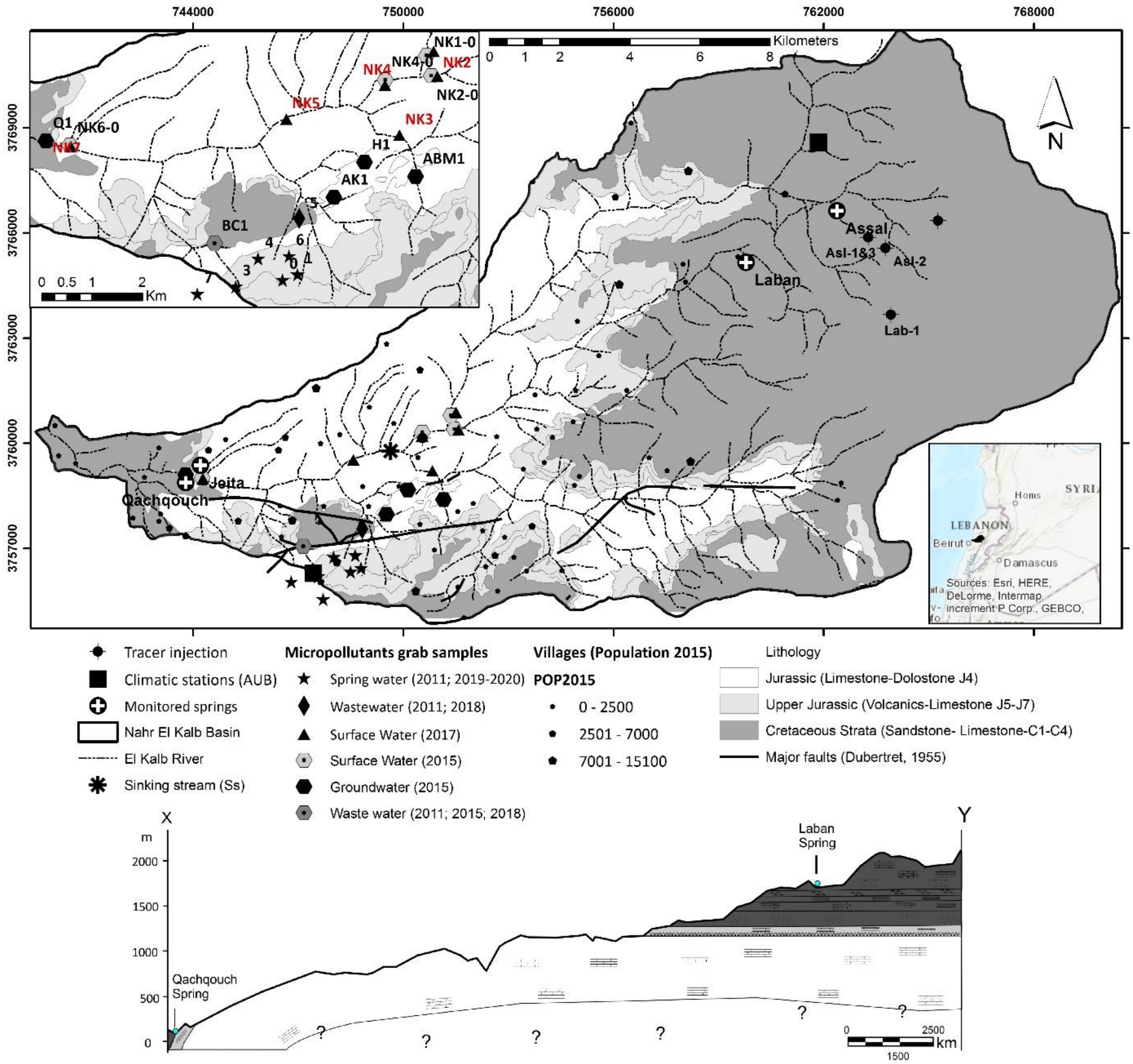

Figure 1. Geological map showing the location of the three investigated springs and the location of collected samples on the Nahr El Kalb Catchment. A conceptual cross section shows the different lithologies and thicknesses of the main aquifers

Table 1 Geological and hydrogeological characteristics of the three investigated springs

Spring	X Y Z (m above sea level) (WGS, 1984)	Formation	Major threats	Major opportunities
Qachqouch	33.943985°N 35.637690°E 64 m	Jurassic limestone, Aquifer highly	Water contamination from	Floodwaters to be used for managed aquifer recharge or to

<table>
<tr><th>Spring</th><th>X
Y
Z (m above sea level)
(WGS, 1984)</th><th>Formation</th><th>Major threats</th><th>Major opportunities</th></tr>
<tr><td></td><td></td><td>karstified and responsive to rain events (the flow rates increase shortly following precipitation events,
Low to moderate storage</td><td>waste water effluents surface-water Interaction (Doummar ad Aoun, 2018 a, b)</td><td>compensate for the water shortage</td></tr>
<tr><td>Assal</td><td>34.009710° N
35.838760°E
1552 m</td><td>Cenomanian dolostones and limestone, medium karstified high storage capacity, Reactive to snowmelt events</td><td rowspan="2">Increasing waste water contamination
Climate change, snow cover decrease, longer recession period because of earlier snowmelt and increasing temperatures (Doummar et al., 2018 b)</td><td rowspan="2">Limited land use/landcover leading to limited contamination
Snowmelt ensures a longer-lasting recession, springs can be used to compensate low flow shortages at lower altitudes</td></tr>
<tr><td>Laban</td><td>33.994961°N
35.828203°E
1662 m</td><td>Cenomanian limestone, Highly karstified, Low storage capacity, Reactive to snowmelt</td></tr>
</table>

3. Investigation Methods

Extensive hydrogeological studies are performed on spring water, including 1) high-resolution monitoring to analyze flow dynamics and hydro-chemical variations (Gao et al., 2020), 2) Assessment of intrinsic transport from tracer experiments, 3) Evaluation of specific transport of selected micropollutants. These methods aims at collecting sufficient data about water quality and quantity, and at constructing conceptual models that feed into process- based numerical models to be calibrated based on continuous data acquisition and system characterizations. Such models if validated can be used for prediction purposes (Hartmann et al., 2014b, 2020), ultimately to anticipate the forthcoming threats on existing springs.

3.1 High-resolution data collection

A rigorous monitoring network in groundwater basins is lacking in Lebanon due to the high cost of maintenance and operation. Therefore, since 2014, a monitoring network was set up to collect high-resolution data on a pilot catchment area (in the framework of international research projects). This constant monitoring of spring flow and quality allows quantifying the water volumes, the flow rates, and their variation during the hydrological regimes (Mudarra et al., 2012) and consequently ensure the evidence-supported protection of the investigated springs in terms of quality and quantity. The collected mmonitoring data in the three springs and catchment consists of automatic data, grab samples, and automatic sampling entailing climate and flow data, as well as physico-chemical data. The rate and frequency of sampling along with the type of data is directly linked to the information required for spring characterization (Table 2).

Table 2 Information provided by the measured parameters/ experiments on springs used for spring characterization and construction of conceptual models

Spring Parameters and frequency of measurements	**Indicator for spring response used as input for conceptual and numerical models**	**Selected literature**
Flow rates/ Water level 2014-ongoing	Time series correlative analysis and statistical correlation between input and output Evaluation of aquifer type, storage, and recession Insights into aquifer geometry Analysis of snow melt on volume and spring dependence of climate variability and change Applications: Water availability and alternatives	Lu and Liu, 2020 Olarinoye et al., 2020 Dubois et al., 2020
Bacteriological analysis, Turbidity and Particle distribution	Indicative of potential bacteriological contamination	Pronk et al., 2006, Stedmon et al., 2011, Frank et al., 2018

Spring Parameters and frequency of measurements	**Indicator for spring response used as input for conceptual and numerical models**	**Selected literature**
Periodically 2019-ongoing Occasionally or event based prior to 2019	Application in early warning systems and contamination indicator	
Electrical conductivity Temperature 2014- ongoing	Indicative of fast infiltrated water from point source origin and snow component Degree of karstification	Lu and Liu, 2020 Wang et al., 2020 Torresan et al., 2020, Ahmed et al., 2021
Chemical analysis Periodically 2019-ongoing Occasionally or event based prior to 2019	Insights into water-rock interaction, Identification and estimation of anthropogenic contamination indicator	Gasser et al., 2010 Schmidt et al., 2013
Micropollutants (Pharmaceuticals and Personal Care Products; PPCPs) Occasionally or event based	Origin of contaminants Transport and persistence of compounds in the matrix Type of infiltration (diffuse versus point source) Specific vulnerability	Einsiedl et al., 2010 Doummar et al., 2014 Doummar and Aoun 2018a and b, Warner et al., 2019
Artificial tracer experiments Occasionally or event based. Constant monitoring with field fluorometer	Intrinsic vulnerability Spring protection Contaminant outbreak management	Geyer et al., 2007, Goeppert and Goldscheider, 2008, Doummar et al., 2018a Beniscke et al., 2021
Stable Isotopes (Oxygen and Hydrogen) Since 2019 Occasionally or event based prior to 2019	Recharge assessment (quantification of fast infiltration, elevation etc.)	Perrin et al., 2003 Barbieri et al., 2005 Koeniger et al., 2017 Rusjan et al., 2019

1. Climatic stations (HOBO and alpine Campbell brands) for the measurement of precipitation (including snow), humidity, wind direction and magnitude, temperature, and radiation at two different altitudes (950 and 1700 m above sea level). The data is used for the assessment of potential evapotranspiration and input precipitation (frequency of 15 -60 min) and snowmelt based on temperature variation.

2. Flow monitoring in the River and springs is done using pressure transducers for water level measurement. Discharge is estimated using rating curves based on the monthly measurements

of discharge. Where and when accessibility to both spring and River is constrained, uncertainties in high flow periods may lead to an overestimation of the annual budget, and consequently the quantities of water available for supply in addition to the calculation of contaminant/tracer masses. The error in flood flowrates can be reduced or quantified based on the analysis of a longer time-series data set due to the high variability and seasonality of flow in addition to a statistical analysis of numerical modelling output. However, these errors are not detrimental to the conceptualization of flow and early numerical modelling calibration.

3. In situ physico-chemical parameters are measured with a periodically calibrated (when needed) multi-parameter probe (Aquatroll 600- Insitu) for Electrical Conductivity (EC), Temperature (T), Turbidity (TU), and pH, as well as Dissolved Oxygen (DO) installed on the spring.

4. Two automatic samplers are scheduled every 3 days to collect samples for the analysis of indicator parameters in spring water (El Qachqouch) for the following analysis:

    - Stable Isotopes (Oxygen and Deuterium) collected in glass bottles analysed using a PICARRO isotopic analyzer L2130-i cavity ring-down spectrometer (CRDS) with a VAP A0211 vaporizer and automatic sampler. The standards for oxygen and hydrogen used for calibration and routine checking of the measurements, are well preserved standards of known isotopic composition (values versus VSMOW for $\delta^{18}O$: 0.3, -20.6, -29.6 ‰, and for $\delta^{2}H$: 1.8, -159, and -235.0 ‰,)

    - Major ions for water types and pollution assessment collected occasionally to weekly analyzed using Ion Chromatography (IC) with the appropriate concentration standards for the respective measured ions.

- Particle size distribution for the assessment of suspended particles leading to turbidity using a Coulter counter (Multi-sizer 4e, Brand Beckman) with different apertures used according to the grain size measurements (ranging from 2µm- 2000 µm)

5. Field fluorometers (GGUN-FL30-Albilia) are installed at each spring for the measurements of natural fluorescence in pristine waters and tracer experiments conducted on injection points on the catchment area. The fluorometers were calibrated in the field following each experiments with the injected tracer and the spring water.

6. Bacteriological analysis *(fecal and total coliform, pseudomonas aeruginosa and enterococci*) analyzed occasionally) at a local certified bacteriological laboratory to detect the variation of fecal indicators in the spring and associate it with continuous point-source contamination on the catchment.

3.2 Tracer experiments and identification of transport parameters

3.2.1 Tracer experiments

Tracer experiments were undertaken on the catchment area, whereby artificial dyes (uranine; sodium fluorescein and occasionally amidorhodamine-G), considered conservative and nontoxic to humans and the environment (Käss, 1998) were injected in the River (Qachqouch catchment) and specific dolines on the catchment of the Laban and Assal springs. Tracer concentrations were simultaneously monitored and recorded every 15 min in the spring using a field fluorometer (GGUN-FL30; Schnegg, 2002) that was calibrated for the applied tracers. Discharge measurements were estimated based on the recorded water level and rating curve under different flow conditions (high flow, low flow, snowmelt, and medium flow). Restitution of the tracer allows identifying a connection between the injection point, considered as a vulnerable contribution point of the recharge area, and the spring (Benischke, 2021). Furthermore, the transport parameters such as mean velocity and dispersivity can be estimated for conservative pollutants based on the analysis of the breakthrough curve using a 1-D transport model (Toride et al., 1999; Geyer et al. 2007, Goeppert et al. 2020, Sivelle et al., 2020). Tracer experiments reflect the intrinsic vulnerability of a spring system as well as the transport mechanisms of a conservative pollutant from different origins (fast preferential flow; doline, or a sinking allochthonous stream; River). While the duration of tracer recovery provides insights into the duration of the breakthrough of a non-reactive pollutant, the observed tracer concentration is indicative of the intensity of the contamination above admissible limits for a certain contaminant load (Doummar et al., 2018a).

3.2.2 Micropollutant analysis

Micropollutants (MPs) were analyzed in 75 grab samples collected from surface water, wastewater, wells, and springs in 2015-2019 to characterize the point source contaminants existing on the catchment area. Additional limited samples collected and analyzed in 2011 (Doummar et al., 2012b) serve for comparison purposes of the variation of MPs over the last decade. The selected micropollutants span from pharmaceuticals to personal care products present in domestic, industrial, and hospital wastewater effluents such as nonsteroidal anti-inflammatory drug (ibuprofen), lipid regulators (gemfibrozil), artificial sweeteners (sucralose, and acesulfame-K), epileptic drugs (carbamazepine), bronchodilators (albuterol), hospital contrast media (iohexol), detergents (nonylphenol), dyes manufacturing (quinoline) and others (metformin, and caffeine). Furthermore, these pharmaceuticals were also monitored in one of the springs to detect the variations in concentrations and loads in spring water (Zuccato et al., 2005, Hillebrand et al., 2012). Moreover, the breakthrough of MPs loads and concentrations in the spring was related to the origin of effluents (surface water or point source infiltration) according to the flow dynamics based on binary mixing models (Buerge et al, 2009, Gasser et al., 2010, Doummar et al., 2014, Mawhinney et al, 2011, Oppenheimer et al, 2011, Wolf et al, 2012, van Stempvoort et al, 2013, Liu et al, 2014, Nödler et al, 2016). The MPs that are revealed to be persistent and least degradable in the system independent of recharge are the ones that can be used as viable wastewater indicators (Oppenheimer et. Al., 2011) and can be of threat to the spring water quality if they exceed the maximum admissible limits (MAL). Additionally, the distribution and evolution of MPs concentrations can provide insights into the type of wastewater and water usage on the rural catchment (Werner et al., 2019).

A correlation between easily monitored parameters at the spring, for example, turbidity and electrical conductivity with the breakthrough of these emerging micropollutants such as Ibuprofen, sucralose and acesulfame-K, and carbamazepine), gemfibrozil was used to assess the contamination arrival at the spring with easily measured indicator parameters (Doummar et al., 2018b). Binary and ternary mixing models (based on mass-fluxes of chloride, micropollutants, and stable isotopes) are used to identify the percentage of wastewater inflow into pristine groundwater (from wastewater effluents discarded on the catchment and in the River; Gasser et al., 2010, Schmidt et al., 2013, Doummar and Aoun 2018a). The analysis of the breakthrough curve of micropollutants with other measured parameters (electrical conductivity, chloride and calcium, etc.) allows identifying mass fluxes of these persistent pharmaceuticals (Doummar et al., 2014, Doummar and Aoun, 2018b).

4. Discussion and results

4.1 High-resolution data as insight to systems hydrodynamics

The high-resolution data (until 2018) from the three existing springs was partially included in the global data set on karst springs (Olarinoye et al., 2020). The three springs shows an uneven distribution of flowrates during the year indicating a shortage in the summer time following the hydrograph recession. The total water volumes throughout the six years show a high variability from dry to intermediate to wet years, typical of semi-arid regions, which adds to the lack of predictability in water availability for supply (Figure 2, Table 3). The Qachqouch spring is characterized by flood waters that can reach up to 50 Mm^3 during high flow periods in wet years (the discharge rates exceeding its average discharge during low flow periods as recorded in July-October).

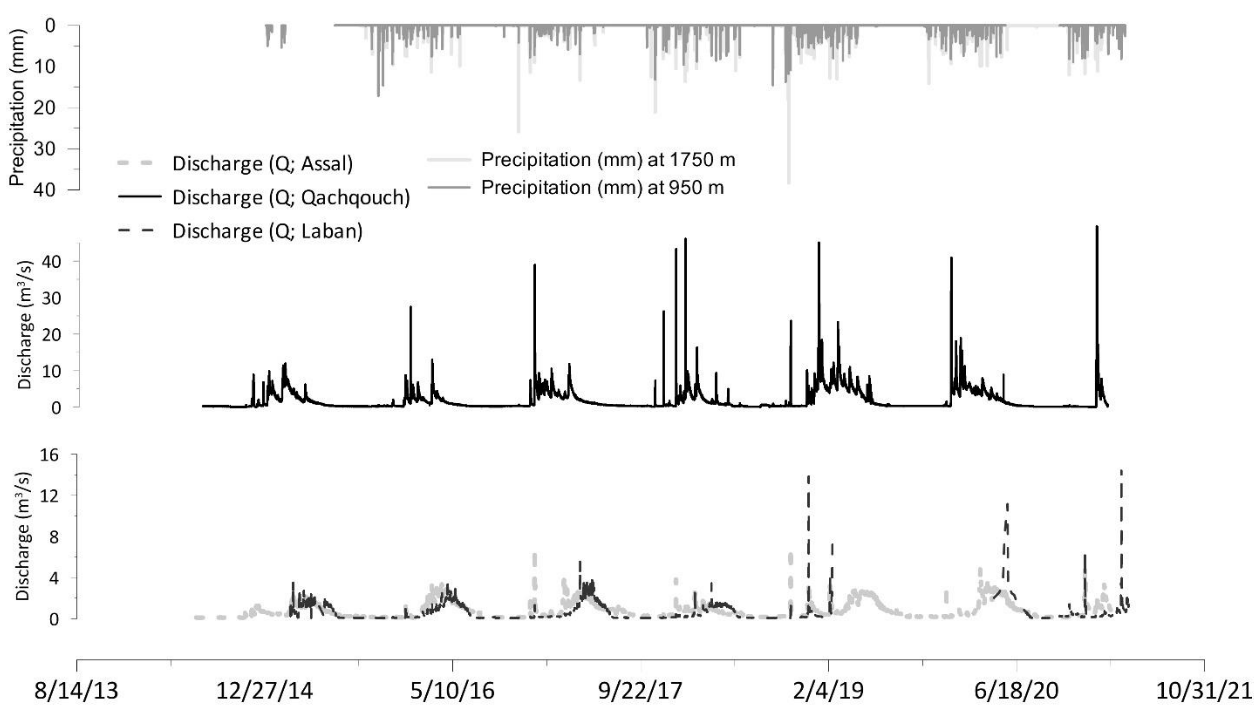

Figure 2 Spring hydrographs for the three monitored springs illustrating the variation in discharge for along with total amount of precipitation (snow and rain)

Table 3 Spring volumes illustrating the variation from wet (2018-2020), intermediate (2016-2017) and dry years (2014-2017 and 207-2018). Spring type and coefficient estimated from spring hydrographs.

	2014-15	**2015-16**	**2016-17**	**2017-18**	**2018-19**	**2019-20**	**Spring type *(k, i)**
Precipitation (950 m)	NA	921.6	1034	1090	1764	1319	
Precipitation (1700 m)	NA	1110	1005	1084	1838	1405	
V Qachqouch (Mm^3)	49.80	35.80	61.50	43.40	100.1	69.20	**Type 1 (0.11, 0.77)
V Laban (Mm^3)	NA	16.10	18.90	12.50	NA	20.00	***Type 2 (0.09, 0.24)
V Assal (Mm^3)	NA	24.20	24.60	16.90	30.90	27.10	***Type 3 (0.4, 0.44)

*After Mangin, 1975; k: characterizes the extent of the phreatic zone and its regulating capacity; its storage and discharge of fast infiltrated water (k>0.5 is characteristic of porous aquifer), i close to 0 implies a fast infiltration, compared to a value closer to 1.

**from Dubois et al., 2020

*** Calculated based on time series following the method by Mangin, 1975 in Dubois et al., 2020

Detailed correlative analysis of time series reveals information about the geometry and the parametrization of a subsurface karst system (Mangin, 1975, Dubois et al., 2020,). For instance, the number of groundwater reservoirs and the spring recession coefficients are inferred from statistical analysis of time series (discharge, electrical conductivity, precipitation). Furthermore, the analysis of the flow time series can yield a classification of the spring typology (Mangin, 1975, El Hakim et al., 2007, Stevanovic, 2015), which unravel the type of flow, indicative of the behavioral response of the spring, its reactivity versus storage capacity, and its porosity type (equivalent porous, versus dual and triple porosity). Additionally, the springs response (discharge and other monitored parameters) to rain or snowmelt events provides valuable information about the total volume of fast point source infiltration (such as dolines). In the Qachqouch spring, the correlation of electrical conductivity, stable isotopes, and chloride along with flow show that the newly recharged water range between 10 and 70 % of the total volume per event. The latter being highly dependent on the saturation of the system. On the other hand, the Assal spring is classified as type 3, characterized by a slow infiltration and a higher storage. The discharge curve displays a fluctuation indicative of diurnal snowmelt and nocturnal freezing. The volume of freshly infiltrated snowmelt directly related to the number of dolines on the catchment is also estimated daily based on the high-resolution data series. The relevance of newly infiltrated water or snow has an important implication if it is closely related to a point source contamination (Jodar et al., 2020). On the other hand, the Laban spring located 2 km away from El Assal spring within the same aquifer, displays a different hydrodynamic behavior, as shown from a k value closer to 1, and an I value closer to 0. The latter can be attributed to the variation of facies within the Cenomanian aquifer (lower dolomitic member versus the upper more karstified limestone member).

4.2 Assessment of spring intrinsic vulnerability

4.2.1 Qachqouch Spring

The tracer breakthrough curve (BTC) recorded at the Qachqouch spring reveals a connection between the River and the spring (Figure 3, Table 4). the breakthrough curve was characterized by one main peak and other minor peaks or discontinuous recovery of the tracer for a longer period. The first peak in May and November dyes appear as a composite peak, which may be due to a considerable longitudinal dispersion in the River before infiltration occurs during snow melt and low flow periods. The injected uranine was first detected at the spring between 5 to 20 hours after injection, which corresponds to maximum transport velocities of 0.07 m/s, 0.17 m/s, 0.25 m/s, and 0.77 m/s in, May, November, June, and February respectively (Figure 3). The mean velocities and dispersivities are estimated for the first main peak of the BTC based on 1-D analytical solutions for transport Two-Region Non-equilibrium model (2NREM) depending on the extent of tailing and shape of the BTC (Figure 3).

Table 4 Characteristics of the tracer experiments, results of the graphical interpretation and estimation of transport parameters based on BTC analysis and inverse modeling

Name		May Dye			Feb Dye			November Dye	June Dye	Asl-1	Asl-2	Asl-3	Lab-1
Injection points		Sinking stream (Nahr El Kalb)								Doline			Doline
Observation point		Qachqouch spring								Assal			Laban
Date		05/08/16			02/19/17			11/24/17	06/04/20	07/01/14	06/01/16	05/01/15	07/01/20
Type of BTC		Multi peak (3 peaks)			Multi peak (3 peaks)			One major peak	One major peak	One major peak	One major peak	One major peak	One major peak
Tracer type		SF			AR			SF	SF	SF	SF	AR	SF
M	g	3000			2000			5000	3883	400	2000	1500	2408
x	m	8920			8700			8920	8920	1330	2330	1330	3140
M_R	g	71			150			58	213	112	360	135	241
M_R	%	2%			8%			1%	5%	28%	18%	9%	10%
Break-through peaks (P)		P1	P2	P3	P1	P2	P3	P1	P1	P1	P1	P1	P1
Qmean	m^3/s	0.78	0.65	0.62	4.86	3.16	3.98	0.37	0.72	0.25	0.31	1.05	0.27
Cp	[µg/l]	0.2	0.12	0.16	0.09	0.03	0.04	1.07	1.36	1.5	2	0.9	5
Tf	[h]	35	242	461	3	480	768	15	10	288.0	175.2	21.0	65.4
tcp	[h]	87	293	500	22	604	829	42	15	336.0	197.0	29.0	87.0
vf	m/h	255	37	19	2788	18	11	595	893	4.62	13.30	63.30	48.00
vf	m/s	0.07	0.01	0.01	0.77	0.01	0.00	0.17	0.25	0.0013	0.0037	0.0176	0.0133
Duration BTC	hours	112	233	81	55	226	121	156	110	182	71	>220	535
	days	4.68	9.73	3.36	2.29	9.42	5.04	6.50	4.58	8	2.95	>10	22.3
Model		2NRE			2RNE			2RNE	2RNE	AD	AD	AD	AD
v_m	[m/h]	66			241			140	421	3.8	11.4	45.7	34.4
v_m	[m/s]	0.018			0.067			0.039	0.117	0.001	0.003	0.013	0.010
D_m	$[m^2/h]$	27000			188000			50000	16600	24	79	300	458
D	$[m^2/s]$	8	NA		52	NA		14	5	0.007	0.022	0.083	0.127
tm	[h]	135			36			64	21	1.40	7.38	16.88	30.00
α	[m]	408			780			357	39	6.32	6.89	6.56	13.31
ϕ	m	3.66			4.80			1.74	1.40	0.55	1.10	3.91	1.71

The dispersivities ranging between 39 and 780 m are indicative of transport in karst (Doummar et al., 2018a) and imply the duration of recovery of a tracer and a potential conservative contaminant from the River.

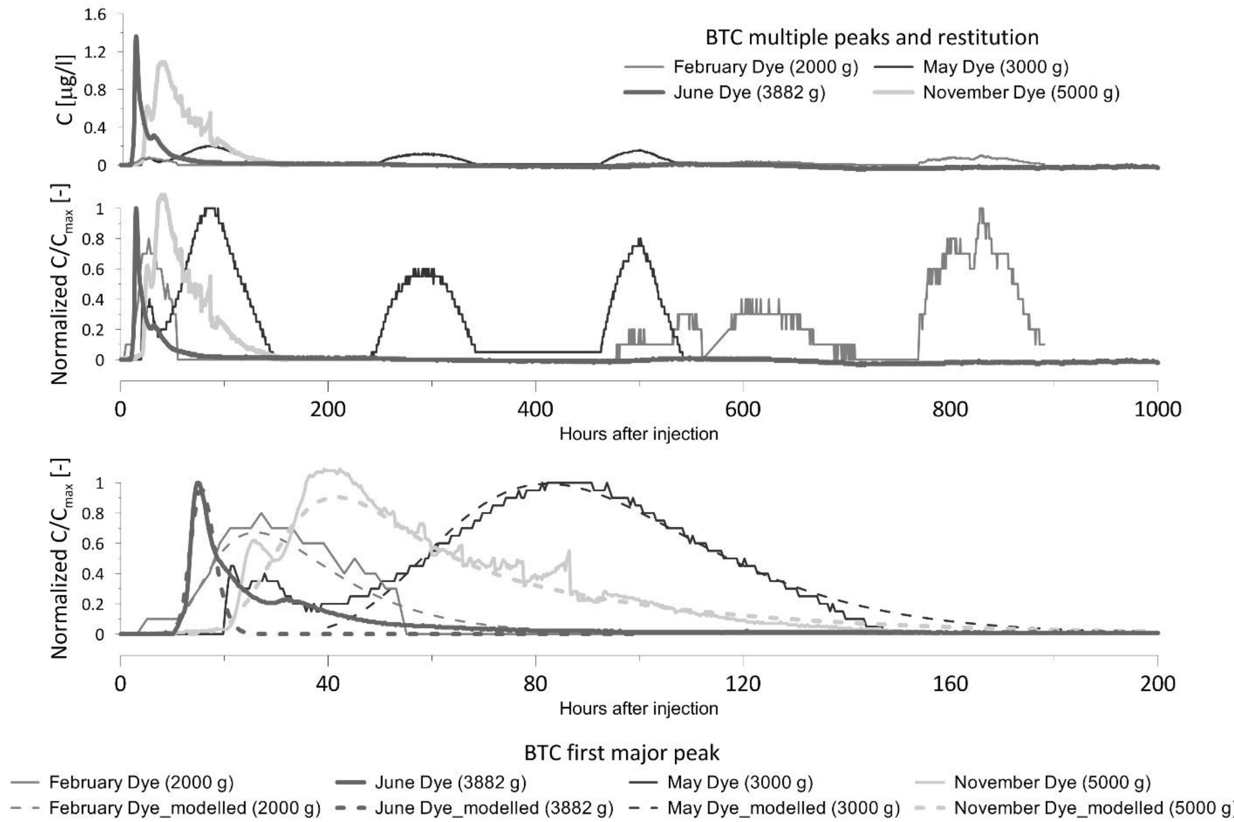

Figure 3 Tracer breakthrough curves (BTC) recorded at Qachqouch springs from four injections in the Nahr El Kalb sinking stream (2016-2020). First peaks in the BTCs are modelled using 2NRE model to account for the tailing effect.

The tracer experiment indicates a relationship between the heavily polluted River and the spring under different flow conditions. During high flow conditions, as the base level in the River is higher, infiltration through fast flow pathways along the river (sinking streams and karst flooding) is more prominent (Gutierrez et al., 2014), as indicated by the higher mass recovery during February (8% compared to 1 % during the lowest flow). Despite a highest infiltration of River water in the spring during February, the dilution attenuates the maximum concentration of the BTC. On the other hand, in November, the observed concentrations of conservative contaminants are expected to be highest despite the limited mass loads from the River. The first peak in the BTC recovered in the Qachqouch lasts between 2.5-6.5 days, while the tracer continues to appear in the spring for more than 40 days. The duration and number of peaks depend on the tracer injection and mass, as well as on the flow regimes in both the River and the spring. On the one hand, the relatively long duration of breakthrough indicates the lingering effect of a contaminant transport between the River and the spring (Figure 3). The multi-peak BTC shows that the River and the Spring are linked by continuous infiltration or through multiple conduits or multiple sinking streams. On the other hand, phreatic diameters calculated based on the total volume of water during the mean transit time of the first BTC peak provide information about the subsurface conduit dimensions and revealed to range between 1.4 and 4.8 m under varying flow periods (Table 4). Moreover, the subsurface complexity and heterogeneity can be further assessed with a more advanced modeling of the multiple-peak BTC using a convolution of a multiple-step input breakthrough curves (Siirila-Woodburn et al., 2015).

4.2.2 Upper Catchment springs

Springs located above 1500 m, namely Laban and Assal springs, are mostly governed by snowmelt and show a high vulnerability both in terms of quantity and quality. The mean transport velocities in Assal range between 0.001 and 0.003 m/s during low flow periods (Figure 4). The BTCs recorded at the Assal and Laban springs during a snowmelt event (May 2015 and July 2020 respectively) were modeled using a simple advection dispersion model (ADM), since the tailing effect is due to a superposition of various melting signals. A more advanced model is being implemented to illustrate the convolved tracer arrival with subsequent melting events. Since the tailing was not prominent in the BTCs recorded in low flow periods (June 2014 and 2016) are also modeled using the ADM for comparison purposes among tracer results. Tracer experiments undertaken under snow melt conditions in both spring catchments reveals velocities of 0.01-0.013 m/s, indicating a fast response during snow melt. The tracer experiment breakthrough curve is restituted for a duration exceeding 500 hours (or 21 days), because of the reactivation of the tracer in the saturated zone during daily snow melt events, therefore any conservative contamination occurring at the catchment areas in the investigated dolines will result in a relatively long breakthrough at the spring, which will require subsequent treatment if the catchment area is not well protected. Moreover, the melting of the snow highly affects the discharge at the spring, therefore these springs can be considered highly vulnerable to climate variability, as they are highly responsive to daily snowmelt events. Longitudinal dispersivities for both Laban and Assal systems calculated based on longitudinal dispersion and mean velocities are 6.5 m and 13.3 m, respectively (Table 4). Phreatic diameters between injection points and springs range between 0.55-3.91 m for Assal spring and 1.71 m for Laban spring depending on the flow period.

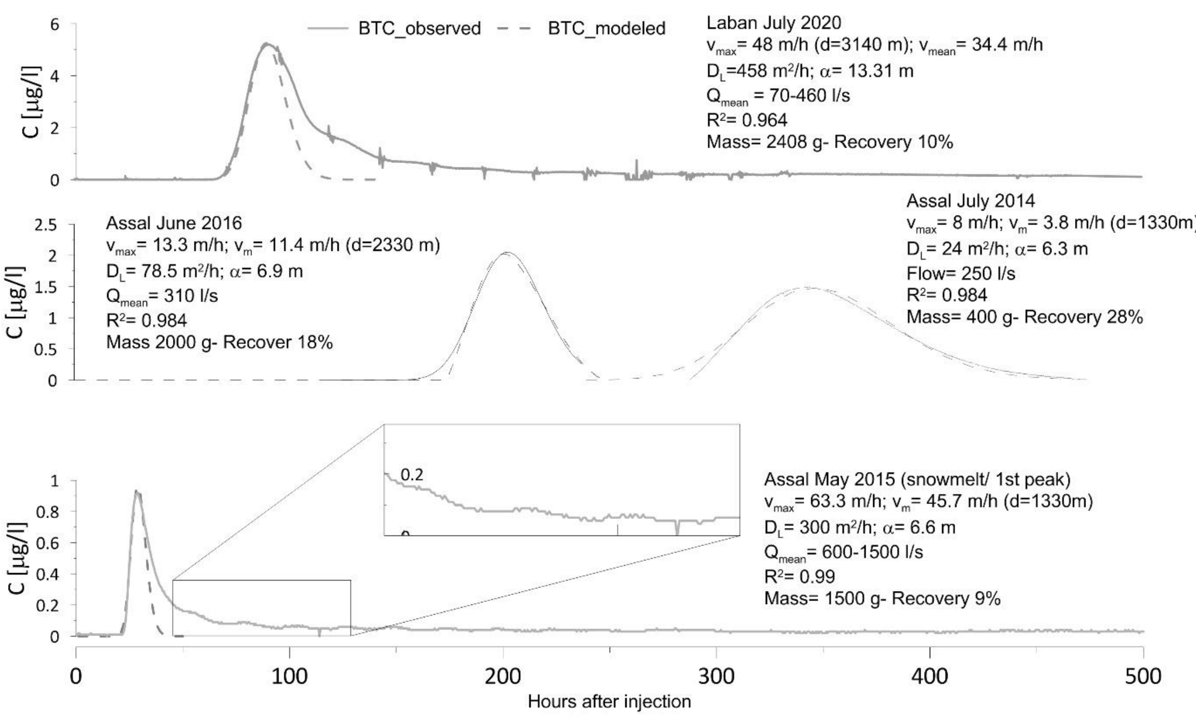

Figure 4 Tracer breakthrough curves (BTC) recorded at Assal and Laban springs from four injections in dolines on their respective catchment areas (2014-2020).

4.3 Assessment of spring specific vulnerability

The concentrations of pharmaceuticals in the springs were below toxic limits in the range of nanograms per liters (Chiffre et al., 2016, Doummar et al., 2018 a and b). Even if not considered of a great threat to human consumption, the identified micropollutants can serve as an indicator for the different type of pollution on the catchment area and of the vulnerability of the springs depending on their source of recharge, and their hydrodynamic characteristics (Werner et al., 2019). On the one hand, three types of pollution sources were identified on the catchment of each spring, the predominant one being related to domestic wastewater effluents (Caffeine, diclofenac, gemfibrozil, artificial sweeteners, carbamazepine, Cotinine). Minor ones related to industrial (Quinoline), hospital (Iohexol), or agricultural practices were also detected, where lipid regulators are used in poultry farms (Doummar and Aoun, 2018a) on the Qachqouch catchment. On the other hand, the raw wastewater collected on the catchment show a similar composition, to the exception of Quinoline used in rural industrial zones (BIK sample). Table 5 displays the range of concentrations for different MPs. The MPs found in the Qachqouch spring water samples are infiltrating via various pathways 1) surface water infiltration, 2) fast infiltration point source such as doline, as well as 3) diffuse infiltration (Doummar and Aoun, 2018b). The most persistent are the ones that are found in the spring during periods where the River is dry and no recharge occurs, such as Carbamazepine and Gemfibrozil. Therefore, these two micropollutants can be used as waste water indicators (Doummar et al., 2014). Mass loads of MPs estimated from flow rates and concentrations allow the backtrack calculations of used drugs and number of users and loads of wastewater on the catchment (Zuccato et al., 2005 for cocaine). For instance, daily mass loads of carbamazepine (CBZ) used on a smaller sub-catchment (small scale springs including three villages) vary between 0.26 and 81 mg/l, while this load increases to 63-5075 mg/l per day in the Qachqouch spring because of the inflow of additional point source contamination infiltrating to the spring from the entire catchment.

In the upper springs, only caffeine was detected, implying a rather limited amount of contamination due to the lack of urbanization in the highlands of the area (two mountain huts, restricted settlements mostly above Laban spring, and the ski resort). Additionally, the *fecal coliform and enterococci are* also limited (Assal: 0-12 CFU/100ml and 0-130 CFU/100 ml), in samples collected during baseflow (July 2020- February 2021) depending on the sampling time, and show a lower level of fecal contamination in the Upper catchment springs. However, it is expected that breakthrough of contaminants occurs from wastewater stored in bottomless pits from mountain huts. The latter require further high-resolution monitoring and tracer experiments in specific locations to test the contribution of such point-sources of pollution.

Table 5 Concentrations of micropollutants (ng/l) and bacteriological analysis in surface water, spring, well, and wastewater samples collected on the Nahr El Kalb catchment

Type of sample	Surface water					Groundwater (Springs and wells)							Upper catchment springs				Waste water		
Name	Nahr El Kalb					Spring Qachqouch					Other springs	Wells	Laban		Assal		BC1		BIK
Approximate discharge range (l/s)	NA	NA	250-1810	1097-4800	2000	NA	NA	700	300-7500	290	0.14-1.06	NA	NA				0.1-2		
Bacteriological analysis																			
Date (Bacteriological)	November 2019-Feb 2021					November 2019-Feb 2021					Apr-17	NA	July 2020- February 2021				NA		
Number of samples	**12**					**13**					**7**		**5**		**6**				
Fecal coliform (CFU/100ml)	4303-100000					102-3783					3-80		2-500		0-40				
Total Coliform (CFU/100ml)	1686-9799					0-968					NA		0-130		0-12				
Enterococci (CFU/100ml)	450-2500					6-255							0-33		0-3				
Micropollutant analysis																			
Date (Mps)	3/1	9/1	5/1	4/1	6/1	3/1	9/1	5/1	1/1	6/20	4/1	5/1	3/1	9/1	3/1	9/1	3/1	5/1	4/1
Number of samples (81)	**5**	**1**	**4**	**7**	**3**	**1**	**1**	**1**	**20**	**19**	**7**	**2**	**2**	**1**	**2**	**2**	**1**	**1**	**1**
Gemfibrozil (lipid regulators)	21	-	17	47	NA	-	4.6	0	5.2-38	NA	NA	0	-	-	-	-	1424	3500	780
Iohexal (contrast Media)	-	-	10	33	NA	-	-	12	19-47	NA	NA	0-13	-	-	-	-	-	290	0
Acesulfame-K (Artificial sweetener)	NA	NA	85	80	NA	NA	NA	170	s	NA	NA	180-640	-	-	-	-		210000	10000
Ibuprofen (nonsteroidal anti-inflammatory drug)	24	-	13	64	NA	-	-	-	-	NA	NA	0	-	-	-	-	>7500	2100	3000
Diclofenac (Analgesic)	-	-	7	5	NA	-	-	-	-	NA	-	0	-	-	-	-	45	-	310
Caffeine (Stimulants)	297	190	304	330	22-120	17	9.9	-	-	15-54	14-380	-	6.0	10	0	246	>17000	-	81000
Cotinine (nocotine metabolite)	16	-	23	47	20-23	-	-	-	NA	-		-	-	-	-	-	1255	7100	1900
Carbamazepine (Anticonvulsants)	5	25	NA	8	8.1-15	13	43	16.0	NA	16-38	11-890	-	-	-	-	-	227	370	710
Metformin (Blood sugar control)	NA	NA	NA	NA	NA	NA	NA	NA	NA	-	6-11	NA	-	-	-	-		NA	360
Quinoline (manufacturing dyes)	NA	NA	14	-	NA	NA	NA	-	NA	-	7.6-12	-	-	-	-	-		-	330
Atenolol (Antihypertensive agent)	10	-	6	13	-	-	-	-	0.0	-	19	-	-	-	-	-	0	0	500

A value of - implies BMRL= Below Mean Reporting Limit

NA = not analyzed

4.4 From conceptual to numerical models

Conceptual and process-based numerical models are developed based on the synthesis of field experiments and statistical correlative analysis of the time series collected on the spring catchment areas (Mudarra et al., 2019, Dubois et al., 2020). Additionally, insights into the intrinsic and specific vulnerability allow for understanding the recharge mechanisms and point source potential pollution. First, a semi-distributed linear reservoir numerical model has been parameterized and constructed for the complex catchment of Qachqouch spring and further calibrated based on the continuous analysis of field and time-series data (Dubois et al., 2020). a lumped model was selected for the Qachqouch Spring catchment, following the detailed statistical and correlative time- series analysis and spring classification as complex Jurassic highly karstified aquifer. Such high variability of flow and response to rain events, and karst heterogeneity, complex dynamics could not be simulated using an equivalent porous medium continuum model. On the other hand, , a integrated distributed process-based flow model (DFM) was constructed with Mike she (DHI, 2017) for the less karstified Cenomanian aquifer of El Assal spring (using an equivalent porous approach with a bypass function along dolines for fast infiltration; Doummar et al., 2018b). Similarly, a 2-D variable saturated flow (VSF) model was developed by Koohbor et al., (2020) to simulate flow in El Assal spring while accounting for discrete fractures. Both models were used to simulate future flowrates to forecasted climate change scenarios and show a drastic change in water availability after 2070 and a high variability between wet, dry, and intermediate years after 2030 with a steady increase of recession duration of 5.5 days per decade. The VSF model shows that neglecting the fractures leads to an overestimation of the flow. However, the integrated distributed model (DFM) can still serve in the case of El Assal spring to simulate peak and recession flow and help in the understanding of spring response to snow-melt for future management purposes. Furthermore, these models allow to quantify the water availability for supply with some degree of uncertainties based on predicted future flow under various climate conditions and identify water resources alternatives (Hartmann et al., 2012, Doummar et al., 2018b, Sivelle et al., 2021). The results have shown a highest sensitivity of the model output (mean and minimum discharge) to temperature in the snow-governed springs, while a decreasing precipitation will mostly impact the availability of flood waters in the Qachqouch spring at lower elevation. While, these numerical models can be further validated and potentially upscaled to aquifers of similar reservoir characteristics, with a collection of additional data, they can act as a decision support tool to test the response and sensitivity of the springs to a variation in input (temperature, rain, snowmelt) or contamination

(Kresic and Stevanović, 2010, Parise et al., 2015). Nonetheless, the selection of the most suitable model depends not only on the type and available data, but also on the degree of heterogeneity of the system and on the model's efficiency of portraying complex karst processes (Scanlon et al., 2003). To overcome this challenge and select the proper modelling approach (lumped, distributed, semi distributed models), it is primordial to achieve a quantitative conceptualization of the karst system in space and time based on a proper long-term hydrogeological assessment and monitoring.

5. Conclusions

This work illustrates a selection of methods used in karst catchments for the proper characterization of spring systems in poorly studied semi-arid regions facing a high risk of water scarcity and pollution. On the one hand, the characterization of flow and transport in these pilot springs allows gathering scientific evidence to support changes in policy and for the establishment of guidelines for the protection of the sustainable quantity and quality of these valuable resources (Fleury, 2013; Parise et al., 2018). For instance, the relationship established from tracer experiments between the River and the spring and the occurrence of indicator micropollutants implies the need for the protection of the El Kalb River against pollution and potential contamination from point source domestic, industrial, and hospital wastewater effluents. Additionally, the groundwater catchment is also characterized by point source contamination as portrayed by the persistent pharmaceuticals detected in the sampled upstream springs and wells. On the other hand, the response of the spring to contamination is not homogenous throughout the year, as it highly depends on the saturation of the system, the intensity of the precipitation event, the discharge of the River, and the type and frequency of effluents. Therefore, guidelines for spring protection should account for the variability of the vulnerability and resilience of the karst spring.

The investigation at the pilot scale is essential for upscaling purposes, where the integration of field data into similar and/or regional scale models can allow for a better management of spring water resources at a larger scale. In the future, the water deficit typical of these semi-arid regions, will be exacerbated as forecasted by forward-flow simulations because of climate change constraints. Therefore, the high-resolution monitoring yields a quantification of yearly volumes of floodwaters that can be used for potential managed recharge (storage and recovery; ASR;) during the high flow to decrease shortage during low flow periods. Additionally, the identification of indicator parameters and spring response to different types of contamination hazards can be used in the development of Early Warning Systems to be implemented for water treatment and supply. The investigation of the pilot karst springs since 2014 allowed the classification of the springs, and the identification of potential threats, while providing models to act as support tools for decision-makers to alleviate the risks and ensure the sustainable exploitation of spring water or the identification of alternative water resources. This study highlights the importance of setting up monitoring networks and collecting high-resolution data in poorly studied spring catchments to understand karst systems, calibrate and validate models, and predict potential spring responses to variable input (recharge or contamination).

6. Acknowledgments

This work was funded by multiple grants and awards since 2014; USAID and National Academy of Science (Peer Science; project award: 102881; Cycle 3), UNICEF (Award# 103924; Project# 25778), AUB; University Research Board (Award# 103951; Project# 25512) and KARMA project (L-CNRS in the framework of the PRIMA program; Award# 103895; Project# 25713).

Moreover, Beirut and Mount Lebanon Water Establishment and The Litani Water Authority are thanked to facilitate the installation of instruments and access to field sites. Prof. Jason J. Gurdak is thanked for his contribution to the work. Michele Citton, Fouad Andari, and Emmanuel Dubois are thanked for field data collection. Additionally, the committee members of the municipalities of Sakiet El Misk- Bhersaf, Bikfaya-Mhaidseh, Ballouneh and Kfardebbiane among others are acknowledged for their kind collaboration.

7. Author contribution

Joanna Doummar: Approach and methodology, funding, flow and transport simulations, and writing; **Marwan Fahs**: Numerical simulations and review, **Michel Aoun**: Transport simulations, field acquisition, writing; **Assaad Kassem**: Data processing and flow simulations, writing; **Reda ElGhawi**: Field acquisition and data collection; **Jihad Othman and Mohamad Alali**: Field acquisition and data processing.

8. Competing interests

No competing interests.

9. References

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