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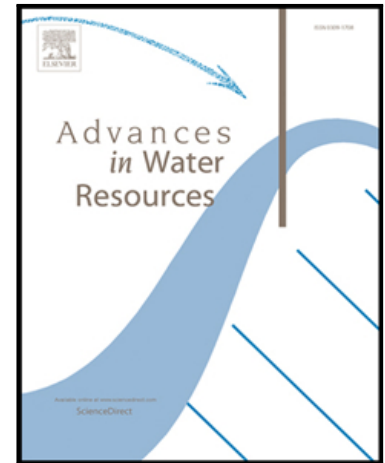
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Highlights

- Porewater from shallow sediment cores from the trans-boundary Lower Jordan River were chemically analyzed.
- Sub-riverine groundwater upwelling that was previously thought to be generally steady is found to vary spatiotemporally.
- Upwelling is seasonally dependent and forced by winter flux, though expressed differently in space and time.
- Given this information groundwater intrusion estimations may be revised especially when they are highly saline or polluted.

Identifying spatiotemporal variations in groundwater-surface water interactions using shallow pore water chemistry in the Lower Jordan River

Noa Hillel¹, Michael L. Wine¹, Jonathan B. Laronne¹, Tobias Licha², Yaron Be'eri-Shlevin³, Christian Siebert⁴

¹Department of Geography and Environmental Development, Ben-Gurion University of the Negev, Be'er-Sheva, Israel

²Geoscience Centre Georg-August-University Göttingen, Dept. Applied Geology, Goettingen, Germany

³Israel Oceanographic and Limnologic Research, Yigal Alon Kinneret Limnologic Laboratory, Migdal, Israel

⁴UFZ - Helmholtz Center for Environmental Research, Dept. Catchment Hydrology, Halle/Saale, Germany

Abstract

Groundwater-surface water interactions as result of in- and effluent conditions along a stream may have a strong impact on the quantity and quality of the river water. These interactions are controlled by river morphology and by transient hydraulic gradients between river and surrounding groundwater. Here we document the existence of spatiotemporal variations in groundwater-surface water interactions in the bed of the Lower Jordan River through pore water analysis of shallow sediment cores using major ions (Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , Br^- , SO_4^{2-}) and stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$). Our results demonstrate that temporal variations are neither spatially uniform nor steady. Upwelling of groundwater is seasonally dependent and forced by a winter pulse of groundwater recharge and by estival low river discharge.

Keywords: Lower Jordan River, pore water, major ions, isotopes, groundwater—surface water interactions

1. Introduction

Groundwater inflow into fluvial, limnic or marine systems as a source of pollutants, nutrients or dissolved salts has been documented to result in eutrophication and salinization of fresh surface water (Schlüter et al., 2004; Santos et al., 2008; Krause et al., 2009). Attempts to estimate groundwater inflow into fluvial systems requires differentiation amongst agricultural return flow, deep groundwater upwelling (Scanlon et al., 2007; Hogan et al., 2007; Gardner et al., 2011; Smerdon et al., 2012; Harrington et al., 2013; Beisner et al., 2018), and hyporheic exchange (Cook, 2012; Gomez-Velez et al., 2014), as well as interactions among these components (Dahm et al., 1998; Harvey & Wagner, 2000). Much research has been carried out in sandy and relatively coarse-grained fluvial environments (e.g., Arntzen et al., 2006; Zimmer & Lautz, 2014). However, water flow through fine-grained silty or clayey riverbeds with considerably lower hydraulic conductivities and consequently reduced matrix permeability (Younger et al., 1993; Boulton et al., 1998) has been less widely examined. Groundwater upwelling, controlled by hydraulic head gradients, may be driven by the formation of brines within artesian aquifers ascending along fractures and faults (Cherubini et al., 2014) or through hydrologic windows (Pepin et al., 2014).

Natural causes for river water salinization, such as saline groundwater infiltration (Hogan et al., 2007) and direct evaporation, are typical of closed drainage basins in semi-arid and arid regions (Williams, 1999; Phillips et al., 2003). River water salinity may also increase due to dissolution of saline deposits accumulated in dry periods by surface runoff (Anker et al., 2009). Anthropogenic induced river salinization due to agricultural return flows, sewage, land-use changes (Scanlon et al., 2007), water

diversion, and river damming (Williams, 1999; Williams, 2001) often occur alongside natural causes (Hogan et al., 2007).

Groundwater inflow may be inferred from monitoring piezometric heads, adjacent to the river, by discharge differences between gauging stations along the stream and by temperature measurements (e.g., Marzadri et al., 2013; Briggs et al., 2016). However, these methods pose considerable uncertainties and require adequate monitoring stations. Alternatively, a variety of chemical and isotopic environmental tracer methodologies have been successfully applied to determine groundwater inflow, e.g., $\delta^{18}\text{O}$, $\delta^2\text{H}$, ^{222}Rn , Cl, Sr, CFCs and ionic ratios (Cook et al., 2003; Negrel et al., 2003; Rodgers et al., 2004; Darling et al., 2010; Gardner et al., 2011; Barthold et al., 2011; Cook, 2012; Shaw et al., 2014; Hillel et al., 2015; Atkins et al., 2016). These approaches are particularly useful to evaluate regional aspects, since the chemical and isotopic composition of a water parcel is the integral of its entire pathways, influenced by both geogenic and/or anthropogenic factors (Kimball et al., 2001).

The Lower Jordan River (LJR) receives water from the confluence of freshwater from Lake Kinneret (TDS: 0.6 g/l) and brackish Yarmouk River (TDS: 2.8 g/l), together with saline springs from the saline diversion channel (SDC - TDS: 4.2 g/l) and treated wastewater (TDS: 1.2 g/l), while it enters the Dead Sea with strongly enhanced and variable salinities of 8-10 g/l (Figure 1). Neither evaporation nor the known saline inflows may cause this high salinity. Excess salinity is most likely supplied by inflowing saline groundwater, which was estimated to amount to 20–80% and 10% of the total flow in the northern and southern segments of the LJR, respectively (Farber et al., 2004; Holtzman et al., 2005). This wide range of estimated saline

groundwater contribution and the strong temporal variations in chemical composition of the LJR (Hillel et al., 2015) indicate chemically distinct temporal contributions of variable solute sources.

The LJR flows through urbanised and intensely exploited agricultural land possessing sources of anthropogenic pollution (sewage, fishpond spills). Additionally, saline springs of the Kinneret basin are diverted to minimize salinization of the Kinneret and enter the LJR via the SDC, thereby contributing to the solute content of the river. The geological setting of the river provides abundant and readily soluble evaporate minerals (gypsum, halite, calcite, aragonite). Finally, deep-seated and pressurized brines ascend (Möller et al., 2012; Starinsky & Katz, 2014), perhaps driven by the pressure from a thick succession of sedimentary rocks (Rosenthal 1988). Though the hydrogeochemistry of saline waters in the Jordan-Dead Sea Rift has been intensely studied (Bentor, 1969; Starinsky, 1974; Salameh, 2001; Farber et al., 2004; Farber et al, 2007; Möller et al., 2007a, Möller et al., 2007b; Möller et al., 2018), including groundwater-surface water interactions (Siebert et al., 2009; Ionescu et al., 2012; Siebert et al., 2014b), none investigated the spatial and temporal variability of groundwater-surface water interactions.

We aim to enhance understanding regarding where and when groundwater from a range of sources having variable composition enters the Lower Jordan River along its course. Therefore, we monitored the seasonal and spatial variability of environmental tracers (Cl^- , SO_4^{2-} , Br^- , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , $\delta^2\text{H}$ and $\delta^{18}\text{O}$) in the interstitial water of the riverbed and in the river water, comparing these hydrogeochemical characteristics with those of previously characterized aquifers. Field measurements to support the present study could be carried out at limited

locations since the river forms a highly restricted international border and security considerations make swaths of the river inaccessible. Nevertheless, our goal was to overcome this challenge and to advance our ability to investigate groundwater-surface water interactions in comparable hydrological systems characterized by very limited data, information and accessibility.

2. Study area

The Lower Jordan River meanders along ~200 km through the Jordan Valley from Lake Kinneret (Sea of Galilee, -210 m MSL, Figure 1) to the Dead Sea (currently -432 m MSL). Along the aerial distance of the river (100 km), climatic conditions change from semi-arid at its origin to hyper-arid at its mouth. Potential evaporation rates vary from 2,100 to 2,400 mm yr⁻¹ from north to south (Salameh, 2001). The wet season occurs between October and April with the majority of precipitation occurring during January and February. The LJR's base flow consists of a small amount of relatively fresh water from (i) Lake Kinneret, (ii) Yarmouk River, (iii) SDC, which diverts springs with varying salinities from the Kinneret and (iv) sewage treated to various degrees (Figure 1). Additionally, fishpond spills, agricultural return flows, and to large degree seasonal floods contribute to the total discharge of the LJR (Hillel et al., 2015). Groundwater sources that may enter the LJR are manifold (Figure 2): (i) pressurized brines, which ascend along faults from deep aquiferous units within the rift fill; (ii) fresh to brackish groundwater hosted in the Mesozoic sandstone complex (Lower Cretaceous and older formations) of the rift margins, consisting of silt-, sand-, lime-, and dolostone; and (iii) fresh and modern groundwater from the Upper Cretaceous Aquifers, composed of cherts, lime-, dolo- and marlstones.

Runoff from the side valleys (Wadis) infiltrating into the wadi deposits and groundwater from all these sources migrate through the Post-Miocene fluvial and lacustrine sediments of the Lower Jordan Valley (LJV) to reach the river. The LJV-deposits possess variable hydraulic conductivities. Aquifer sequences such as the Waqqas and the Dana conglomerates in Jordan and the Samra formation west of the river efficiently transport water, while the covering Plio-Pleistocene laminated aragonite, chalk, gypsum and clay beds of the Lisan formation efficiently act as an aquiclude (Guttman, 2009; Starinsky & Katz, 2014).

3. Methods

At six stations along the LJR and at the outlet of the Lake Kinneret river water was sampled monthly between early 2015 and the end of 2016 (Figure 1). Additionally, at these locations, sediment cores were drilled on three occasions (Dec 2014, Apr 2016 and Aug 2016) to study possible seasonal effects. Since the upper ~10 km of the river is not an international border, station density is higher in this reach relative to the rest of the study area. Location of sampling stations could not be determined purely on scientific preferences. Rather, they were chosen (1) arbitrarily by officials according to administrative considerations and (2) where the river could be accessed without mortal danger.

Sampling: Sediment cores were obtained by manually inserting a 2-inch diameter plastic liner into the streambed. Core lengths vary (Table 1) and were determined by local sediment depth and limitations of the manual method. Immediately after recovery of the liner, it was cut to core-length and sealed with a fitted cap to prevent disturbance and mixing. On the same day sediment was removed from the liner by a

piston. Starting at the sediment water interface, cores were divided into slices of 2 to 3 cm. These subsamples were centrifuged for 15 min at 4,000 rpm. The supernatant water was removed with a syringe. Several slices did not yield enough water for analysis resulting in missing data. SDC and Abdullah stations were not sampled for technical reasons during the December campaign.

Water analysis: Both stream water and extracted pore water were filtered (0.45 μm) and analysed for major ions and water isotopes ($\delta^{18}\text{O}$, δD). Stream water samples were analysed at the University of Goettingen. Anions (Cl^- , Br^- , NO_3^- , SO_4^{2-}) were analysed by IC (Ion Chromatography) Dionex DX-320 and cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) were analysed applying conductometric detection using an IC Dionex DX-500. The analytical error was estimated to be 8%. Major ions in pore water were analysed at the Helmholtz Centre for Environmental Research (UFZ) applying IC (ICS-2000 Dionex for anions and Dionex DX-120 for cations). Bicarbonate and DIC were determined using standard titration technique and a Shimadzu Total Carbon Analyser TOC5000/5050, respectively.

Water isotope analyses were performed at UFZ using a Los Gatos Research Triple Isotope Water Analyser 45-EP with a respective analytical precision of 1.5‰ and 0.4‰ for ^2H and ^{18}O , respectively.

Inverse modelling: The public domain software PhreeqC (Parkhurst 1995) and the Phreeq.dat thermodynamic database were applied to calculate inverse models by which the interpretation of chemical and isotopic composition of pore waters may be supported, but not explained.

Based on hydrogeological considerations we assume that the porewater at each sampling location is the result of mixed known solutions, namely LJR water and local

ground- or reservoir waters, which react with the occurring geological material of the Jordan Valley. In the case of the Lake Kinneret core, lake water replaces the river water component. Generally, at most two waters, which are known to be present in the area of the respective coring location, are considered and mixed with the covering river/lake water during the time and at the location of sampling. These solutions (Table 2) are allowed to be in equilibrium with common and plausible minerals at each location.

The model input consists of field measured pH, temperature and concentration of major ions. Mineral phases (halite, dolomite, aragonite, calcite, anhydrite and gypsum) represent the solid phases in the shallow sediments of the LJV, which either dissolve (+) or precipitate (-) (Table 3). Reactive surfaces MgX_2 , CaX_2 , NaX and KX enable cation exchange and either gain (+) or release (-) Mg^{2+} , Ca^{2+} , Na^+ and K^+ , respectively. CO_2 represents the amount of transferred gaseous CO_2 . $Sum_{residuals}$ represents the sum of the remaining components that could not be attributed by Phreeqc to specific reactions. Phreeqc allows for inaccuracies in the analysis of each solution and for uncertainty of the reaction scheme. The former was attributed by setting uncertainty to 5-10%.

Multiple models of different solutions were inversely modelled for each pore water core and the best model determined from its geochemical plausibility and goodness of fit was selected for each core and presented in Table 3.

To suspend the majority of mathematically correct simulation results and to end up with few models, which best fit the measurements, the following criteria have been applied: (i) phase transfers are coherent to saturation indices, and (ii) the sum of residuals ($Sum_{residual}$) and (iii) the number of mol-transfers are lowest. For each

sample the one fitting best molar Na/Cl ratio of the sampled pore water has been selected as the most plausible solution. Although this process of elimination leads to feasible results, these inverse modelling results are not a unique solution but a plausible answer with an acceptable uncertainty.

4. Results

4.1. Na^+ , Cl^- , Br^- and Mg^{2+} distribution in pore water profiles (Figure 3 a-d)

Two distinct behaviours are observable in the ionic distribution of the pore water profiles that may be mainly attributed to saline sources, such as brines and the dissolution of minerals (Figure 3). First, low concentration pore water profiles that do not vary significantly with depth are derived from Kinneret, SDC, Beit-Zera and Menahamiya stations (Figures 3 a-d) all located in the northern segment of the river, and are henceforth combined to a “northern cluster”. Second, profiles with large variations and enhanced concentrations with depth, sampled at the southerly Tovlan, Baptism and Abdullah sites are henceforth combined to a “southern cluster”. In the northern cluster, Kinneret differs in April, with slightly higher Na^+ , Cl^- , Br^- and Mg^{2+} concentrations along the profile, while Beit-Zera shows increasing concentrations of these ions during December. The southern cluster has distinctly different and site-specific ion concentrations with depth. Both cores in the southernmost Abdullah are characterized by increasing ion concentrations with depth. In the April core, the deepest samples may represent maximum concentration of 180 meq/l and 1.5 meq/l for Cl^- and Br^- at this location, respectively (Figure 3 b-c). During August, enhanced concentrations are reached at shallower depths.

In April ion concentrations at the Baptism site do not vary with depth with the exception of Mg^{2+} (Figure 3d). During August and December a substantial, almost linear increase of ion concentrations with depth is typical of the Baptism site. At Tovlan, concentrations vary only in August, when they continuously increase to a depth of 0.3 m and decline thereafter.

4.2. Distribution of Ca^{2+} and SO_4^{2-} in pore water profiles (Figure 3 e-f)

Except for the Abdullah and Baptism site stations, where concentration profiles of Ca^{2+} and SO_4^{2-} nearly resemble those of Mg^{2+} , all other stations show distinctly different behaviours (Figures 3 e-f). At Tovlan, Ca^{2+} shows a possible concentration maximum at 0.3 m depth during April, while SO_4^{2-} does not vary with depth from the riverbed to 0.35 m, increasing thereafter. Depth-independent concentrations of both these ions are lowest during December. At Kinneret and Menahamiya, their concentrations increase with depth and are lowest in December and highest in August. Contrastingly, no distinct trends are observable at the SDC and Beit-Zera locations.

4.3. The variation with depth of 1000Br/Cl and Na/Cl ratios

Salinity in groundwater of the Jordan Dead Sea Rift is mostly associated with the ascent of either residual seawater brines (e.g., Starinsky, 1974; Rosenthal et al., 1988) or post-halite ablation brines (Flexer et al., 2000), which show an enhanced 1000Br/Cl ratio of 5 and a low Na/Cl ratio of <0.86 (Möller et al., 2018). In contrast, waters with lower 1000Br/Cl ratios and $0.86 < \text{Na/Cl} \leq 1$ refer to halite dissolution by freshwater. $\text{Na/Cl} > 1$ indicates basaltic weathering solutions, where Na^+ is released from plagioclase minerals (Siebert et al., 2014a).

In December and April pore water profiles along the river show average 1000Br/Cl ratios of 5, which, except for Kinneret and Beit-Zera, slightly increase with depth (Figure 4a). During August, ratios increase to >7.5 at Lake Kinneret, Beit-Zera and the Baptism site. Ratios of 1000Br/Cl in pore water samples of Lake Kinneret are persistently elevated relative to lake water, which varies in the range 3–3.8 (Siebert, 2006). At the Baptism and Abdullah sites, 1000Br/Cl ratios in pore water resemble the characteristic distribution of Cl^- and Br^- in the respective cores (Figures 3b-c).

The vertical distribution of Na/Cl ratios within the cores is less distinct. At the Kinneret, ratios vary between 0.7 and 1.05 during the year, with the December core showing the lowest values. In April and August values increase close to and below the water/sediment interface to >1 and decrease downwards (Figure 4b). At SDC, Beit-Zera and Menahamiya, Na/Cl values increase with depth to almost unity. This stands true for Tovlan as well, except for August, when the concentration maxima for Na^+ and Cl^- (Figures 3b; c) result in a minimum Na/Cl of 0.5 at a depth of 0.3 m. At the Baptism site, ratios are highest (0.7–0.9) during December and April, and lowest (0.6–0.7) in August. Unlike the Br/Cl ratios, Na/Cl ratios at Abdullah exhibit no trend, but vary with depth (0.56–0.84).

4.4. Variation of Mg/Ca ratios with depth

The northern cluster, SDC, Beit-Zera and Menahamiya are defined by Mg/Ca equivalent ratios <1, while Kinneret shows ratios <1 only in August. While Kinneret shows no continuous trend during December and April, in August ratios decrease with depth. No significant variations with depth occur at the other northern stations.

At the southern cluster, i.e. Tovlan, Baptism and Abdullah, Mg/Ca ratios are >1 throughout the year. While Tovlan shows lowest values in April, Baptism and Abdulla

show highest ratios at that time. At the Baptism and Abdullah sites ratios increase with depth, while values in Tovlan differ between the seasons, but do not vary considerably with depth.

4.5. Cross plot Equivalent ratios in pore- and river waters

Cross-plots of pore water Na/Cl vs. Mg/Ca form distinct groups: either Ca-dominated in the northern cluster or Mg-dominated in the southern cluster (Figures 5 a-c). This grouping is valid throughout the year for most stations. Only Kinneret pore water vary: whereas they belong to both groups in April (Figure 5a), they are Ca-dominated in August (Figure 5b) and switch to Mg-dominated in December (Figure 5a). Pore waters in the southern cluster have a stronger Mg-dominance with decreasing Na/Cl. In the northern cluster Ca/Mg ratios do not significantly change with changes in Na/Cl.

Cross-plots of Na/Cl versus 1000Br/Cl do not show grouping of pore water (Figure 5 d-f). Pore waters plot mostly right of the mixing line of the Dead Sea Rift Brines (DSRB, Klein-Ben David et al., 2004). In December Br/Cl ratios within the pore waters of each station are similar, resulting in an almost horizontal deviation of samples from the DSRB mixing line and indicating a freshwater component to which DSRB is variably admixed (Figure 5d). River water samples consistently plot close to the DSRB and differ from pore water composition. In April pore water in the southern Baptism and even more in Abdullah sites move up the DSRB line to higher Br/Cl and lower Na/Cl ratios (Figure 5e), which become even more distinct during August (Figure 5f). In August highest Br/Cl and lowest Na/Cl ratios are observable in the southern stations, while the stations in the upper part of the LJR, including the Kinneret, show variable and unsystematic behaviour.

4.6. Stable isotopes of water ($\delta^2\text{H}$; $\delta^{18}\text{O}$) with depth

Variations of seasonal isotopic compositions with depth are different along the river (Figure 6). The only outlier is observable at the Kinneret, where isotopic signatures in pore water are strongly enriched. All year round, values are positive, for both $\delta^2\text{H}$ and $\delta^{18}\text{O}$. Isotopic values of pore water from the river sediments are relatively similar, ca. $\delta^{18}\text{O}$ of -2.5‰ and $\delta^2\text{H}$ of -10‰ . Signatures in SDC, Beit-Zera and Menahamiya do not vary with depth, while in December Tovlan pore water has increasing values with depth, reaching in the lowest part of the core 1‰ and 0‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. The Baptism site shows stable values with depth during April and decreasing with depth during August, while signatures in December are inconsistent (up to -0.3‰ $\delta^{18}\text{O}$ and -4.2‰ $\delta^2\text{H}$). At Abdullah signatures slightly decline with depth in April and August.

The distribution of $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ shows different conditions during the year (Figure 7). At the end of the rainy season (April) all pore water samples except Beit-Zera and Menahamiya plot to the right of the Global Meteoric Water Line (GMWL, Dansgaard, 1964) and the Levantine MWL (Gat, 1971). Furthermore, all pore water samples except Kinneret, plot left of the long-term trend of Kinneret water (Siebert, 2006). At this time of the year pore waters are isotopically light and follow two distinct trends (Figure 7a). The pore water at Beit-Zera and Menahamiya is close to the GMWL and lighter than the contemporaneous river water at the stations. As for the southern cluster, isotope signatures in pore water plot between GMWL and the Kinneret long-term average. They become isotopically lighter with increasing distance downstream from lake Kinneret. In April contemporaneous river water is isotopically heavier than the pore waters. The heaviest samples are derived from

Lake Kinneret surface water and pore water. Trend lines of both clusters have the closest inclination to the Kinneret water line during April (Figure 7a).

Compared with April, trends in both clusters, but particularly in the southern cluster have lower and almost parallel running slopes during August (Figure 7b) and are distinctly separated. During August, the pore water in the southern cluster plots closely to trend line of Lake Kinneret water. Isotopically lightest water is observed in the Baptism core, while the heaviest is derived from the Kinneret pore water.

At the end of the dry season, in December, the trend lines of both clusters are even less inclined than in August (Figure 7c). Except for Beit-Zera and Menahamiya, all pore waters plot to the right of the long-term trend of Kinneret water (Figure 7c). Though the latter two stations are located slightly downstream of the outlet of the isotopically enriched Lake Kinneret, both river and pore waters at Beit-Zera and Menahamiya are isotopically lighter, indicating an origin differing from Lake Kinneret. Pore water samples become enriched along the river course, reaching $\delta^{18}\text{O} > 0$ at Tovlan and are in all cases isotopically heavier than the co-located river water.

5. Discussion

At Lake Kinneret station Cl^- in pore water increases with depth during April; it is an order of magnitude lower during August and December. Similar behaviours are observable for all other ions and particularly for SO_4^{2-} . Decreasing Na/Cl , variable Br/Cl and variable Mg/Ca ratios with depth indicate an upwards-seeping admixture of recently infiltrated groundwater that has dissolved halite and contains traces of residual brines. Indeed, inverse modelling refers to fractions of fresh Judea Group Aquifer water that mixes with Lake Kinneret water and very small portions of

Tiberias type brines (Siebert, 2006) and dissolves about 4-58 mmol halite per litre (Table 3). In contrast to August and December, in April equivalent ratios of $Mg/Ca > 1$ (Figure 4c) and $SO_4/Ca \gg 1$ indicate weathering of basalts and associated oxidation of sulphide minerals.

These results resemble previous general findings of Stiller et al, (1975; 2009), Stiller (1994) and Dror et al. (1999) who described saline groundwater seepage through the lakebed. Increased chloride concentration during April reflects the seasonal behaviour of groundwater systems in Tiberias and Fuliya (at Lake Kinneret), driven by the hibernal pulse of both lake level rise and groundwater recharge, which control the hydraulic gradient between the aquifers and the lake (Rimmer et al., 1999).

South of Lake Kinneret, the LJR results from the confluence of isotopically light saline groundwater channelized by the SDC and the isotopically enriched fresh lake water. This is observable by the enhanced salinity and decreased isotopic composition in the northern stations compared to the lake.

Except from Beit-Zera in December, stations of the northern cluster have consistently similar behaviour. They show little to no increase in chloride concentration and a stable $Mg/Ca < 1$ with depth. The equivalent increase in Ca^{2+} and SO_4^{2-} , indicating gypsum dissolution and Na/Cl ratios, trending with depth towards unity, suggest halite dissolution. Such high Na/Cl have previously been described in pore water at the southern part of Lake Kinneret (Stiller et al., 2009) and might be related to the Zemah halite body, which extends northwards into the Kinneret Basin (Inbar, unpublished data) and is dissolved by groundwater (Möller et al., 2012).

Within the Lower Jordan Valley, two general types of groundwater with low Na/Cl are observed: Ca- and Mg-dominated (Bentor, 1969). They cause a well-described Mg/Ca contrast in different locations along the rift. Plotting Na/Cl versus Mg/Ca and 1000Br/Cl (Figure 5) reveals that pore water at the Kinneret is dominated by Mg^{2+} and lower Na/Cl ratios during the early and late rainy season ($\text{Mg/Ca} > 1$), indicating a brine contribution, similar to that known from the Ha'on region (Möller et al., 2012), while Ca-rich groundwater ($\text{Mg/Ca} < 1$) dictates pore water composition during August. Then, when Ca^{2+} dominates, Na/Cl of about unity indicates increased contribution of halite dissolution water as described for groundwater in the vicinity of the Zemah borehole (Marcus and Slager, 1985; Möller et al., 2012), drilled at the southern end of Lake Kinneret into thick halite bodies.

Following the river further downstream, only pore water of Beit-Zera in December shows an influence by ascending rift brines. That becomes evident due to distinctly decreasing Na/Cl and increasing ion concentrations (except of SO_4^{2-}) with depth. It is further supported by modelling results, which indicate a fraction of about 0.12 Ca-Cl rift brines of Tiberias type admix to 0.88 LJR water (Table 3) and cause these pore waters to plot close to the Dead Sea Rift line (DSR) introduced by Klein-Ben David et al. (2004).

In contrast to the pore waters at SDC, Beit-Zera, and Menahamiya, river water samples at these locations are always close to the DSR (Figures 5d, e, f), mainly resulting from the saline groundwater carrier (SDC), which collects diluted rift brines at Lake Kinneret and releases them to the LJR, rather than of rift brines ascending through the streambed. A similar picture emerges from the pore water signatures of

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ at these stations. They resemble those of the co-located river water, indicating infiltration of river water into the riverbed sediments.

The southern part of the LJR displays a different behaviour. During April, pore water at Tovlan is characterised by fresh groundwater, observable by a low Cl^- pore water, even less than the lowest river water Cl^- concentrations, which occur during the hibernal high-flow season (Figure 8a). At the end of the wet season (April), fresh effluent dominating the pore space in Tovlan, may be caused by shallow fresh groundwater. Fluctuating concentrations of Mg^{2+} , Ca^{2+} and SO_4^{2-} , with higher concentrations at 8 cm and 15–35 cm depth, but unchanged low Na^+ , Cl^- , and Br^- along the core, are interpreted to indicate layered flow of such shallow groundwater. During August, this pattern of layered flow intensifies. Simultaneously, a distinct salinity peak in pore water at a depth of 15–35 cm indicates a contribution of saline groundwater into that horizon. There, and in comparison to April, all ions except SO_4^{2-} show increased concentrations, lower Na/Cl and higher Mg/Ca ratios suggesting a contribution of Mg-Cl brines of type Aqraa. During December pore water is fresh and shows no variations with depth, except for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ which both increase. This unusual behaviour may be explained by leakage from the relatively fresh Tirtsa reservoir located a few hundred meters upstream Tovlan (Figure 1), also supporting the existence of a hydraulic connection between the nearby Graben flank and the LJR at Tovlan. Inverse models support this concept, which denotes a considerable contribution Aqraa brine in August and variable contributions of Tirtsa reservoir water in August and December (Table 3).

The seasonal sampling scheme revealed varying ascending brines rather than a steady mix with fresh groundwater. While freshwater that leaches Pleistocene and

Neogene sediments with high Na/Cl, high SO_4/Ca , and low Mg/Ca ratios predominantly approaches the riverbed during the wet season (December to March; Farber 2007), low groundwater tables allow enhanced admixture of Mg-rich brines during August.

During the wet season the river head rises expected to increase infiltration into the riverbed (Zimmer & Lautz, 2014). At the Baptism site ionic concentrations in April behave similarly to those contemporaneously at Tovlan, with freshwater dictating the geochemical composition. River water is the only component within the riverbed at that time (Table 3). However, even with low groundwater heads and obviously independent from river water discharge (Figure 8b), salinity in pore water increases significantly with depth in August, and more so in December. Here too, low Na/Cl and high Mg/Ca refer to infiltrating Mg-Cl brine of Aqraa type, which is supported by inverse modelling (Table 3). In August, decreasing $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures with depth may relate to a higher contribution of isotopic light saline groundwater (Möller et al., 2006; 2012). However, in December, when pore water composition indicates a saline component with, enhanced $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures. This supports the contribution of saline water, which has experienced considerable evaporation and approaches the river through the subsurface with the first recharge flush (Figure 8b). Such evaporated saline water may originate from the leaking Karameh Dam, located close to the Baptism Site (Fig. 1). In the Karama dam, saline (TDS up to 35 g/L, $1000\text{Br}/\text{Cl} = 9.03$, $\text{Na}/\text{Cl} = 0.57$, $\text{Mg}/\text{Ca} = 1.68$; Salameh, pers. comm., 2018) and highly evaporated ($\delta^{18}\text{O} = 5.49\text{‰}$ and $\delta^2\text{H} = 24.54\text{‰}$; Siebert, unpubl. data) water is characteristic. The concept of different sources supplying salinity to the porewater of the Baptism site during August and December, is supported by inverse modelling,

which refer to fractions of 0.19 Karama Dam water during December, and 0.16 Aqraa type brine in August in the deepest pore waters at the Baptism site (Table 3).

At Abdullah station fluctuations of the LJR water table are characterised by much smaller amplitudes (Figure 8c) and the chemical composition in the upper 0.15 m of the April core constantly resembles low concentrated river water. This feature indicates stream water infiltration into the sediment. However, below this depth, sharply rising concentrations, increasing Br/Cl and Mg/Ca ratios >1 and low Na/Cl ratios indicate a strong contribution of Mg-Cl rift brines at the least during April and August, when groundwater tables in the surrounding sediments are low. Compared to April, the observed behaviour establishes much earlier during August, likely related to slightly lower riverheads during the dry season, facilitating the ascent of brines. Farber et al. (2004) assumed a continuous high contribution of saline groundwater in that region. This is supported by modelling the deepest pore waters at Abdullah station, denoting a fraction of about 0.1 of Aqraa type brines in August and December (Table 3).

The discussion of our findings is condensed in a conceptual summary (Fig. 9) of the main sources in each station and month, plausibility of which is underpinned by inverse modelling.

6. Conclusions

Though the hydrogeochemistry and origin of saline waters in the Jordan Rift Valley has already been widely investigated, past studies have mainly been restricted to springs, wells, and boreholes at Lake Kinneret and the Dead Sea. Only few studies focussed on the hydrogeochemical composition and development of the LJR but did

not directly interrogate groundwater/river water interactions. These studies defined the groundwater source as nearly a steady contributor by which a static mix of brine and saline groundwater enters the river.

Our study is the first to investigate variations in spatiotemporal groundwater/surface water interactions through direct sampling of riverine pore water hydrogeochemical profiles. The data were collected at the beginning and end of the wet season (December and April), and during midsummer (August) to observe spatiotemporal trends and the micro-scale variability in hydrogeochemical profiles of pore water. Our results suggest spatially as well as seasonally variable connection between the LJR and groundwater. Our central finding is based on the interpretation of chemical and isotopic composition of pore waters, which are underpinned by inverse models for selected pore water samples. Applying reasonable criteria for exclusion, the non-uniqueness of modelling results was eliminated and the remaining, most plausible solutions support our interpretation with an acceptable uncertainty.

Where effluent conditions prevail groundwater inflows and their composition vary spatially and seasonally. The most distinct difference along the LJR is the strong N-S zonation of pore water salinity and composition. Effluent groundwaters in the north of the LJR are almost fresh and Ca-dominated, indicating moderate contribution of Ca-Cl brines as known from the western shore of Lake Kinneret. Contrastingly, between Menahamiya and Tovlan and further southwards, the contribution of brines is much higher and its character switches to Mg-Cl.

Generally, two groundwater types interact with each other: (a) shallow, gravity driven fresh or brackish groundwater and (b) pressurized groundwater brines,

ascending along faults and fractures within the Lower Jordan Valley. These components variably mix and enter the river in varying proportions along its course, causing different pore water compositions. This result has strong implications, since the contribution of deep (saline) groundwater varies temporally, instead of being constant as commonly assumed. Our analyses further demonstrate that surface reservoirs on both sides of the LJR interact sporadically with pore water.

The interplay between the two groundwaters and their final composition are obviously independent from river head, but dependent on groundwater tables in the Graben sediments. Temporal changes at single locations (e.g., in Baptism site) result from seasonal groundwater table fluctuations and their response time to the hibernial recharge.

As stated above, the salinity of the LJR cannot be explained by evaporation or a single groundwater source, but rather by a mixture of sources. By confirming spatiotemporal variability, we demonstrate the transient nature of these sources. Our results also demonstrate the importance of spatiotemporal pore water sampling schemes to better understand complex hydraulic and hydrochemical environments such as the LJR. These results will aid in the global challenge of knowledge-based management of river water quality in rivers draining semi-arid basins.

Future directions

Despite the novelty of the present work examining groundwater/surface water interactions in the LJR through the lens of sub-riverine pore water hydrogeochemical profiles, deeper cores are needed to better characterise the endmembers and clarify boundary conditions for numerical modelling purposes. On this basis, modelling

advective and diffusive flow could be realized, which would facilitate an inverse solution of flow rates.

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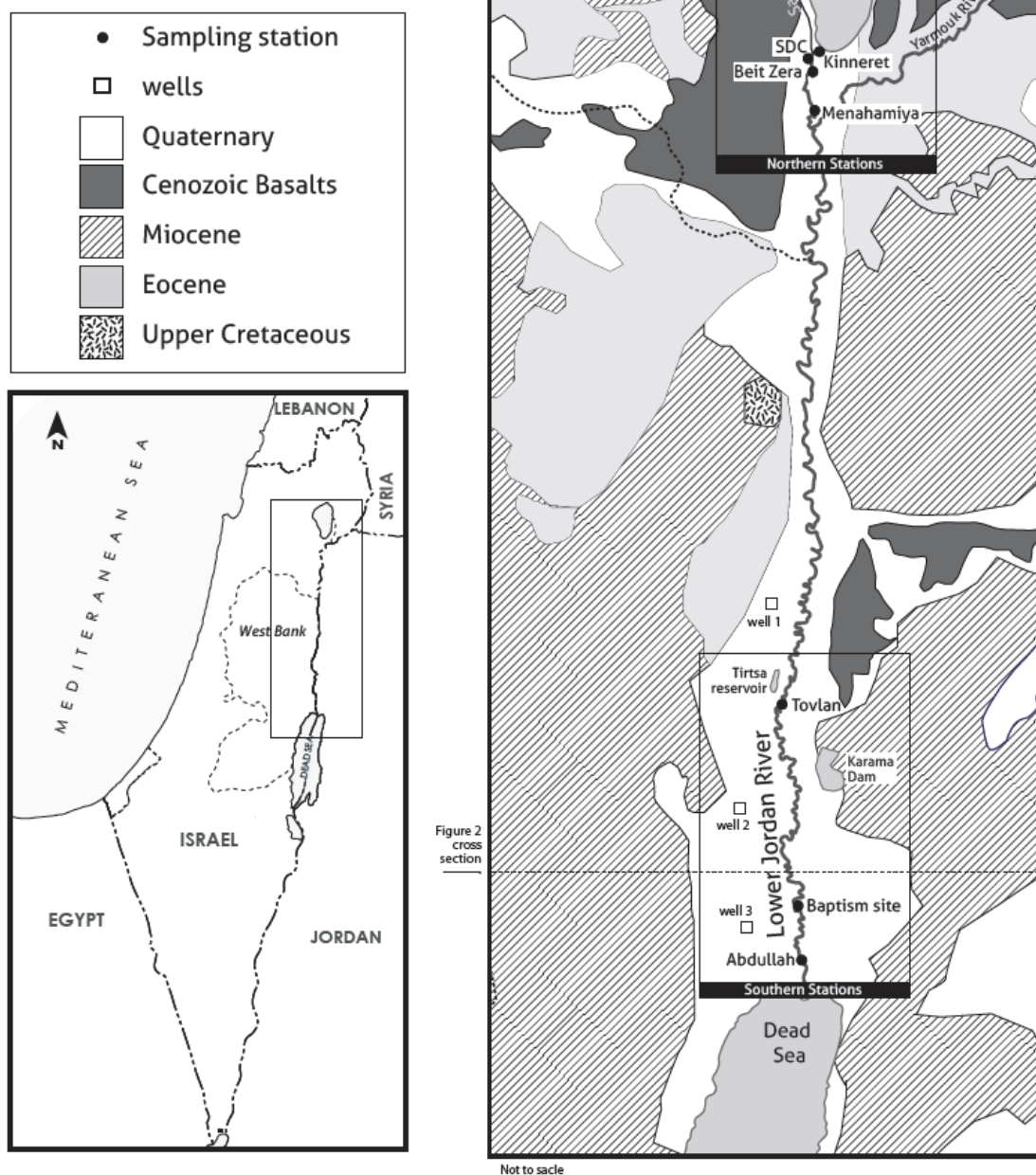


Figure 1: Study area and sampling locations. Division to sections is after the findings of Farber et al., 2004. Adapted from Möller et al., 2007b.

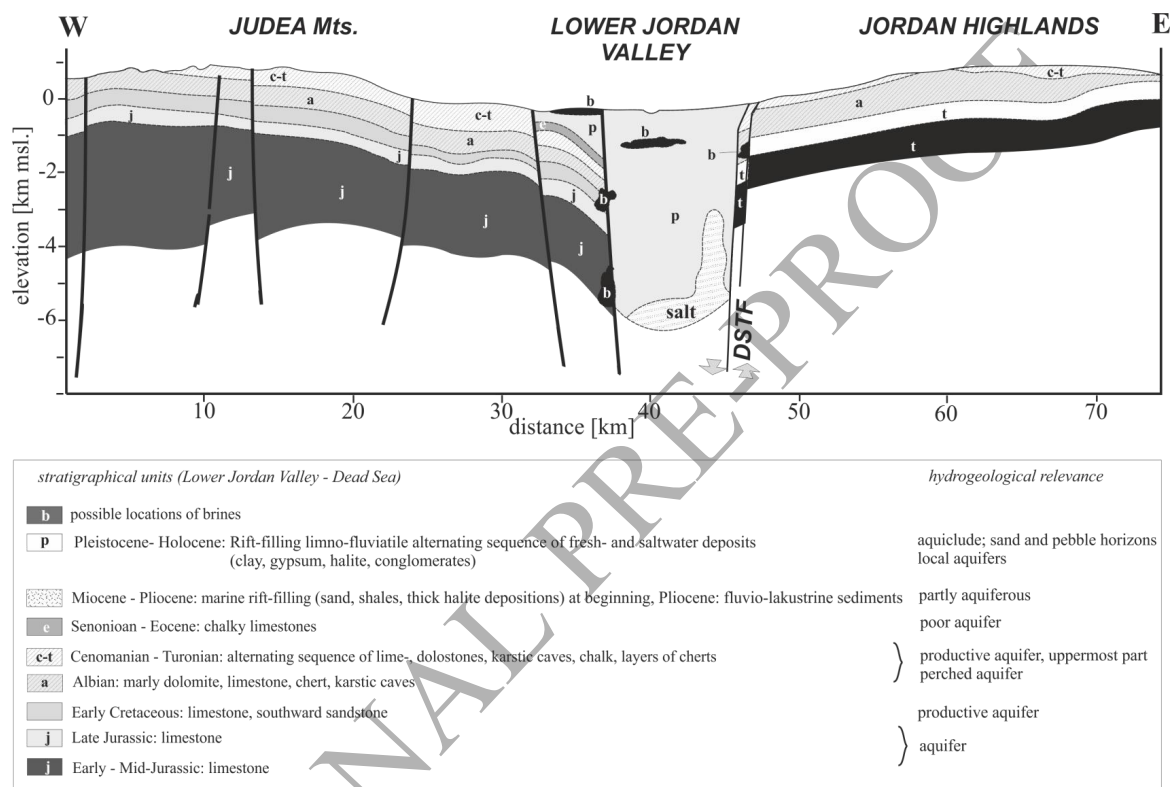


Figure 2: Stratigraphic cross section of the Lower Jordan Valley near Jericho (after Oil exploration 1988). See dashed line in Figure 1 for location.

Table 1: Location and depth of the cores (n.s. refers to “not sampled”).

station	x-coordinate	y-coordinate	Dec 2014	Apr 2016	Aug 2016
	UTM (WGS84; Z36N)			cm	
Kinneret	741454	3622137	17	27	28
SDC	740244	3620947	n.s.	14	20
Beit Zerah	740799	3619876	10	16.5	13
Menahemiya	740895	3615507	14	25	25
Tovlan	737868	3548536	22	46	48
Baptism Site	740992	3525212	14	50	45
Abdullah	741058	3521204	n.s.	33	18

Table 2: Chemical composition of ground-, surface- and pore waters, used as input data for inverse modelling. (PW indicates specific pore water sample; LK - Lake Kinneret, LJR -- Lower Jordan River; THS – Tiberias Hot Spring).

Sample	Date	pH	Na	K	Mg	Ca	Cl	SO4	DIC
[mmol/l]									
Groundwaters									
JGA Kalanit 2 well ³	17.12.00	7.2	0.77	0.05	1.34	1.98	0.83	0.08	8.6
Tiberias Hot Spring (THS) ³	12.12.00	6.0	313	8.52	26.9	85.2	530	8.29	7.5
Haon 1 well ³	17.12.00	6.6	227	11.3	68.2	26.9	445	0.62	11.6
Karameh well ²	-	6.1	324	17.9	88.8	53.0	574	13.5	4.4
Aqraa well ¹	27.02.01	6.0	740	29.4	185	49.2	1078	43.1	4.4
Surface and Pore waters									
Karameh Dam ²	-	8.1	204	11.8	40.8	20.4	252	36.5	6.6
Tirtsa Reservoir ¹	23.05.00	7.0	54.7	2.20	19.5	8.50	75.5	14.0	5.0
Lake Kinneret (LK)	11.04.16	8.0	6.22	0.20	1.44	1.26	8.26	0.63	4.0
LK PW13	11.04.16	7.6	48.1	3.29	24.2	19.9	58.3	31.1	4.0
Lake Kinneret	08.08.16	7.4	6.57	0.21	1.49	1.16	8.35	0.63	4.0
LK PW13	08.08.16	7.6	10.1	0.58	4.78	8.60	12.1	11.4	4.0
LJR Bet Zerah	30.12.14	8.4	31.7	0.97	3.68	7.16	48.8	1.65	4.0
BZ PW5	30.12.14	7.9	72.3	1.96	13.2	16.0	125	1.79	4.0
LJR Tovlan	30.12.14	8.9	40.3	1.54	8.86	5.02	52.8	6.96	5.0
Tovlan PW11	30.12.14	8.1	44.1	1.45	5.20	2.69	49.1	2.74	4.4
LJR Tovlan	08.08.16	7.9	65.9	2.72	15.1	8.17	86.6	12.8	5.0
Tovlan PW15	08.08.16	7.9	101	3.35	37.8	19.6	192	14.9	4.4
LJR Baptism Site	30.12.14	7.9	41.4	1.64	9.60	6.76	55.9	7.65	4.0
Baptism Site PW7	30.12.14	7.0	189	4.71	52.7	21.6	250	29.0	4.0
LJR Baptism Site	11.04.16	8.0	68.9	2.50	17.3	8.09	98.5	12.9	4.0
Baptism Site PW7	11.04.16	7.6	74.1	2.74	26.8	11.1	97.4	20.3	4.0
LJR Baptism Site	08.08.16	7.6	79.8	3.29	20.1	10.6	110	15.4	4.4
Baptism Site PW22	08.08.16	7.5	176	4.40	70.9	30.5	252	34.6	4.4
LJR Abdullah	11.04.16	8.0	72.8	2.71	18.7	8.37	100	13.3	5.0
Abdullah PW17	11.04.16	7.6	147	9.62	48.6	22.3	182	31.5	4.4
LJR Abdullah	08.08.16	7.4	83.6	3.56	22.2	11.9	120	16.1	5.0
Abdullah PW9	08.08.16	7.6	156	7.64	51.6	29.9	211	28.0	4.4

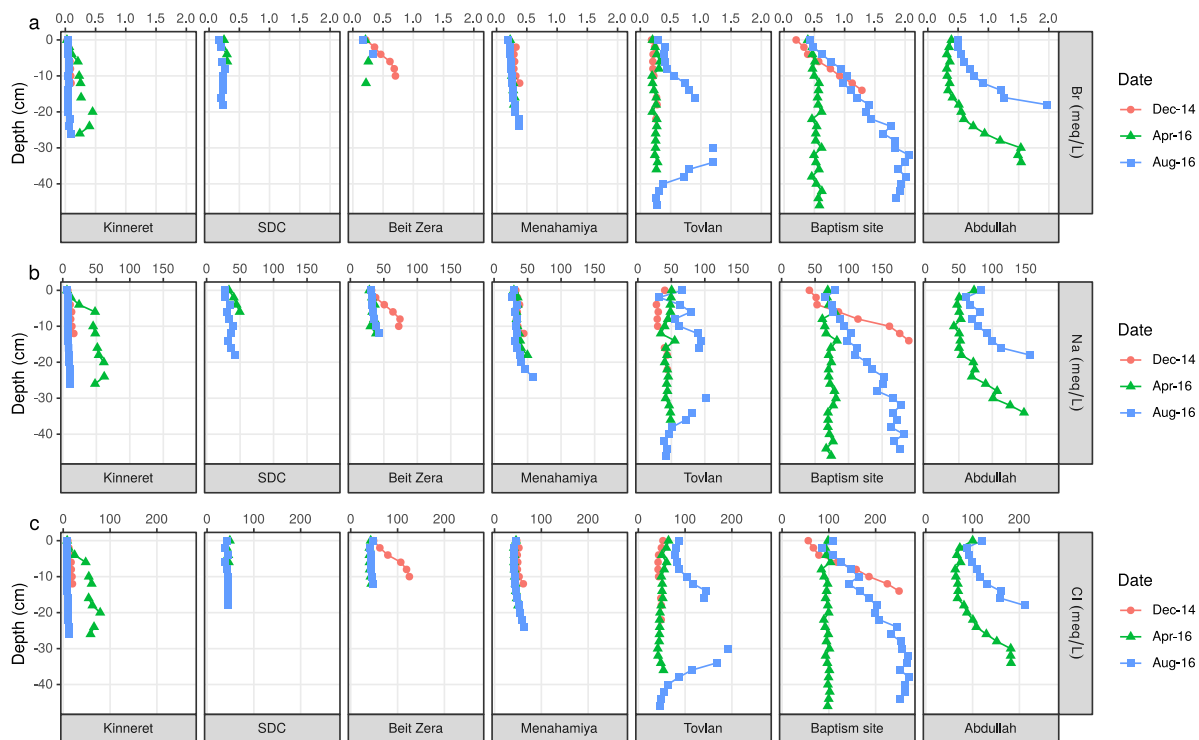
Data taken from ¹ Farber (2005); ² Salameh pers. comm. (2018); ³ Siebert (2006)

Table 3: Plausible inverse models explaining the chemical composition of the final solution (sample). The fractions of Lower Jordan River/Lake Kinneret water (solution 1) and ground- or reservoir waters (solutions 2; 3) are given as well as the mass transfer from the interaction of these mixtures with various geologically available mineral phases and surfaces. Molar Na/Cl ratios are calculated taking composition of initial solutions and their respective fraction and the composition of the final solution (sample).

(Abbreviations: LJR = Lower Jordan River; LK = Lake Kinneret; JGA = Judea Group Aquifer; @ = at location).

Sample	Bet Zerah deep	LK deep (Apr)	LK deep (Aug)	Tovlan deep (Dec)	Tovlan deep (Aug)	BS deep (Aug)	BS deep (Apr)	BS deep (Dec)	Abdullah deep (Aug)	Abdullah deep (Dec)
Solution 1	0.878	0.989	0.2096	0.966	0.9307	0.835	1.000	0.808	0.8879	0.9011
	LJR @Bet Zerah	LK (Apr)	LK (Aug)	LJR @Tovlan (Dec)	LJR @Tovlan (Aug)	LJR @BS (Aug)	LJR @BS (Apr)	LJR @BS (Dec)	LJR @Abdullah (Aug)	LJR @Abdullah (Dec)
Solution 2	0.122	0.011	0.7902	0.034	0.0693	0.165		0.192	0.1121	0.0982
	THS ³	JGA (Kalanit) ³	JGA (Kalanit) ³	Tirtsa Reservoir ¹	Aqraa Brine ¹	Aqraa Brine ¹		Karama Dam ²	Aqraa Brine ¹	Aqraa Brine ¹
Solution 3			0.0002		0.00001					
			THS ³		Tirtsa Reservoir ¹					
Halite	0.020	0.058	0.0042	0.000	0.0285	0.000	0.000	0.179	0.0000	0.0000
Dolomite	0.000	0.000	-0.0006	0.000	0.0000	-0.0001	0.000	0.000	0.0000	0.0000
Aragonite	0.000	0.000	0.0000	0.000	0.0000	0.000	0.000	0.000	0.0000	-0.0004
Anhydrite	-0.001	0.034	-0.0017	0.000	0.0000	0.000	2.227	0.016	0.0106	0.0000
Calcite	0.000	0.000	0.0000	0.000	-0.0004	0.000	0.00018	0.000	-0.0003	0.0000
Gypsum	0.000	0.000	0.0000	-0.005	0.0000	0.014	-2.221	0.000	0.0000	0.0184
CaX2	0.000	-0.015	0.0000	0.003	0.0089	0.000	-0.004	-0.004	0.0005	-0.0087
MgX2	0.007	0.021	0.0000	-0.004	0.0112	0.017	0.009	0.037	0.0065	0.0088
NaX	-0.013	-0.016	0.0000	0.003	-0.0391	-0.030	-0.009	-0.067	-0.0152	-0.0045
KX	0.000	0.003	0.0000	0.000	-0.0013	-0.003	0.000	0.001	0.0011	0.0043
CO2(g)	0.000	0.000	0.0000	0.000	-0.0006	0.000	-0.001	-0.001	-0.0006	-0.0005
Sum_resid	0.109	3.052	3.6404	1.840	0.9789	3.909	2.698	1.810	4.9913	4.6401
Na/Cl (sample)	0.58	0.82	0.83	0.76	0.57	0.70	0.76	0.76	0.74	0.80
Na/Cl (model)	0.61	0.76	0.81	0.76	0.72	0.70	0.70	0.77	0.70	0.71

Data taken from ¹ Farber (2005); ² Salameh pers. comm. (2018); ³ Siebert (2006)



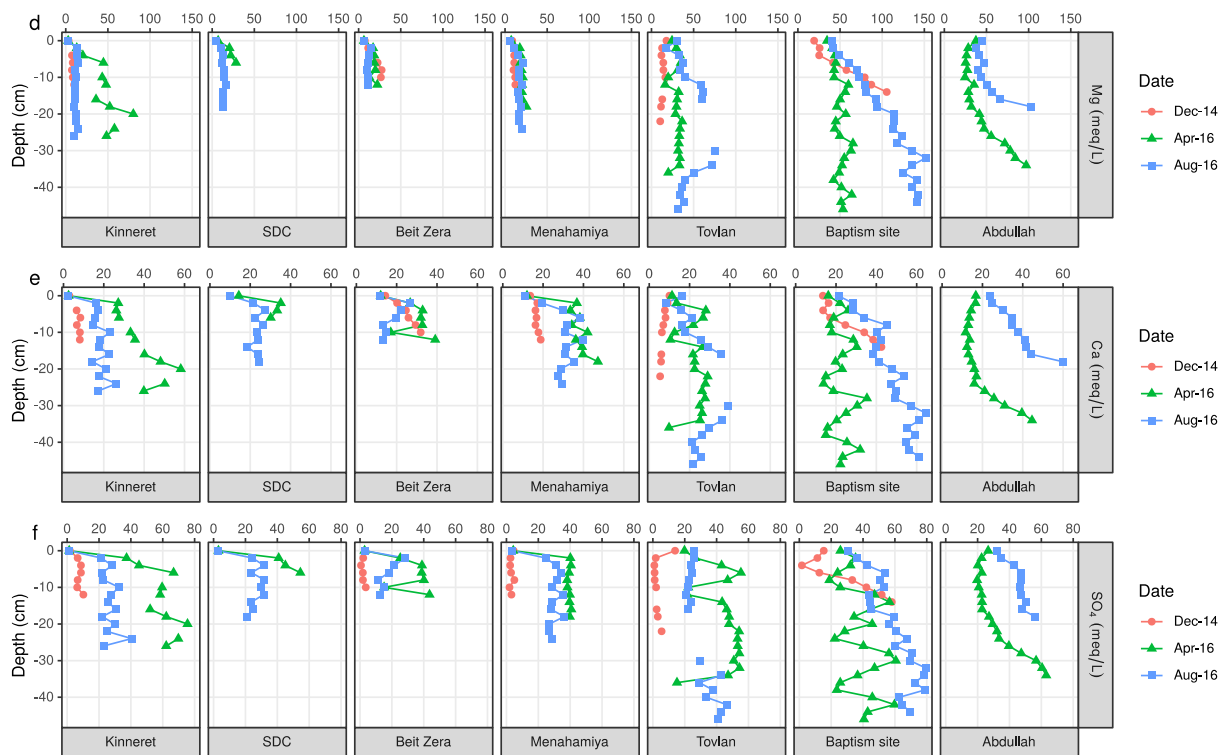


Figure 3 d-f: Variation of Mg^{2+} , Ca^{2+} and SO_4^{2-} concentrations in pore- and river water. Data are given starting with the source (Lake Kinneret station, left) and along the river to the LJR delta at the Dead Sea (Abdullah station, right).

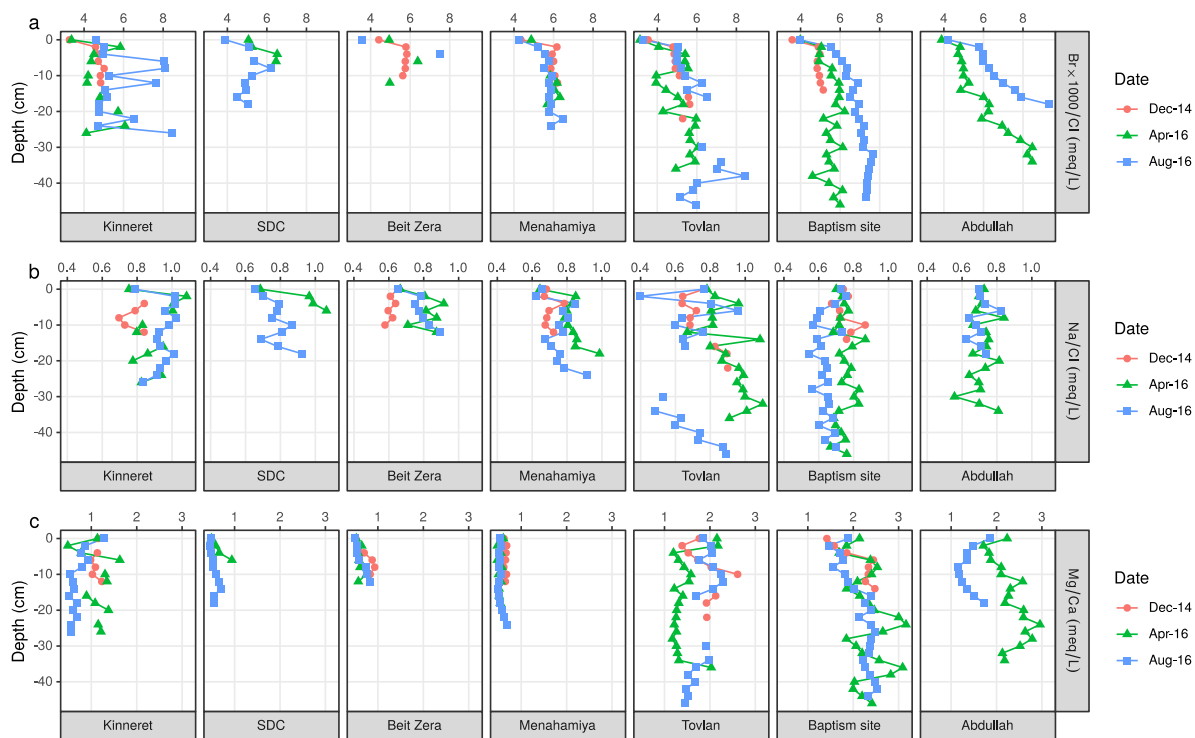


Figure 4: Variation of 1000Br/Cl-, Na/Cl- and Mg/Ca equivalent ratios in pore- and river water. Data are given starting with the source (Lake Kinneret station, left) along the river to the LJR delta at the Dead Sea (Abdullah station, right).

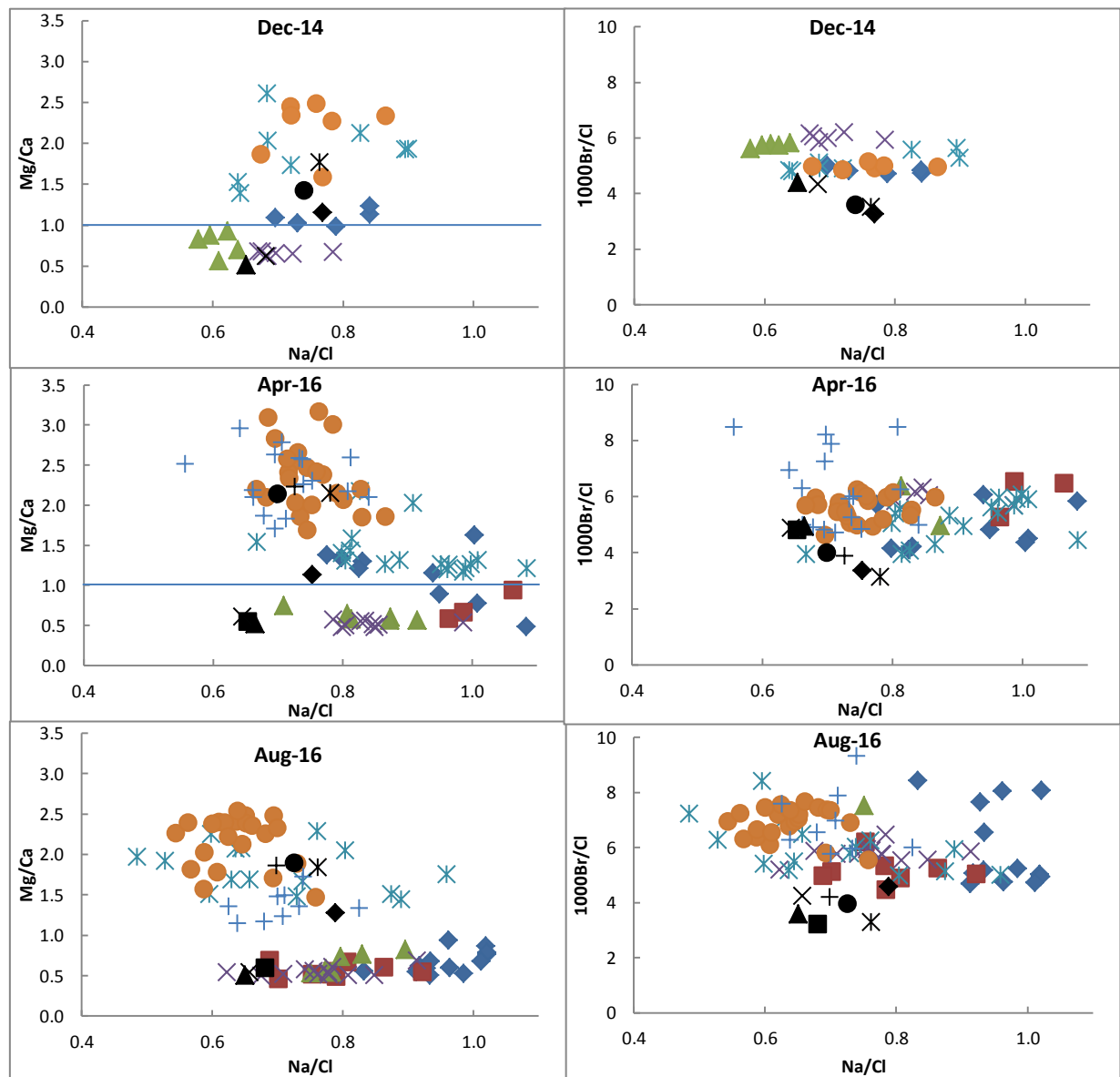


Figure 5: Equivalent ratios of pore- and river water at Lower Jordan River stations, showing Na/Cl ratios vs. Mg/Ca in spring (a), summer (b) and winter (c); Na/Cl vs. 1000Br/Cl in spring (d), summer (e) and winter (f). Blue lines demonstrate the separation to northern and southern groups by the ratio Mg/Ca. The red lines represent the Dead Sea rift brines mixing line after Klein-Ben David et al. (2004).

- ◆ Kinneret
- SDC
- ▲ Beit Zera
- × Menahamiya
- * Tovlan
- Baptism site
- + Abdullah
- ◆ Kinneret w
- SDC w
- ▲ Beit Zera w
- × Menahamiya w
- * Tovlan w
- Baptism site w
- + Abdullah w

*w = river water

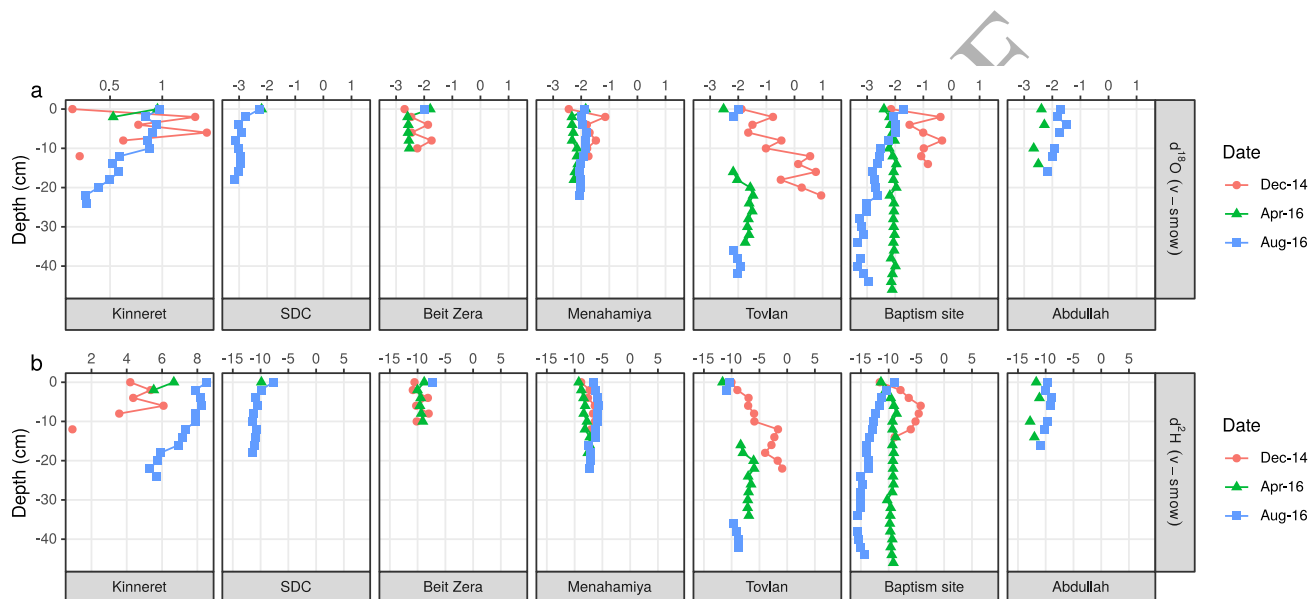


Figure 6: Variation of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures in pore- and river water. Data are given starting with the source (Lake Kinneret station, left) and along the river to the LJR delta at the Dead Sea (Abdullah station, right).

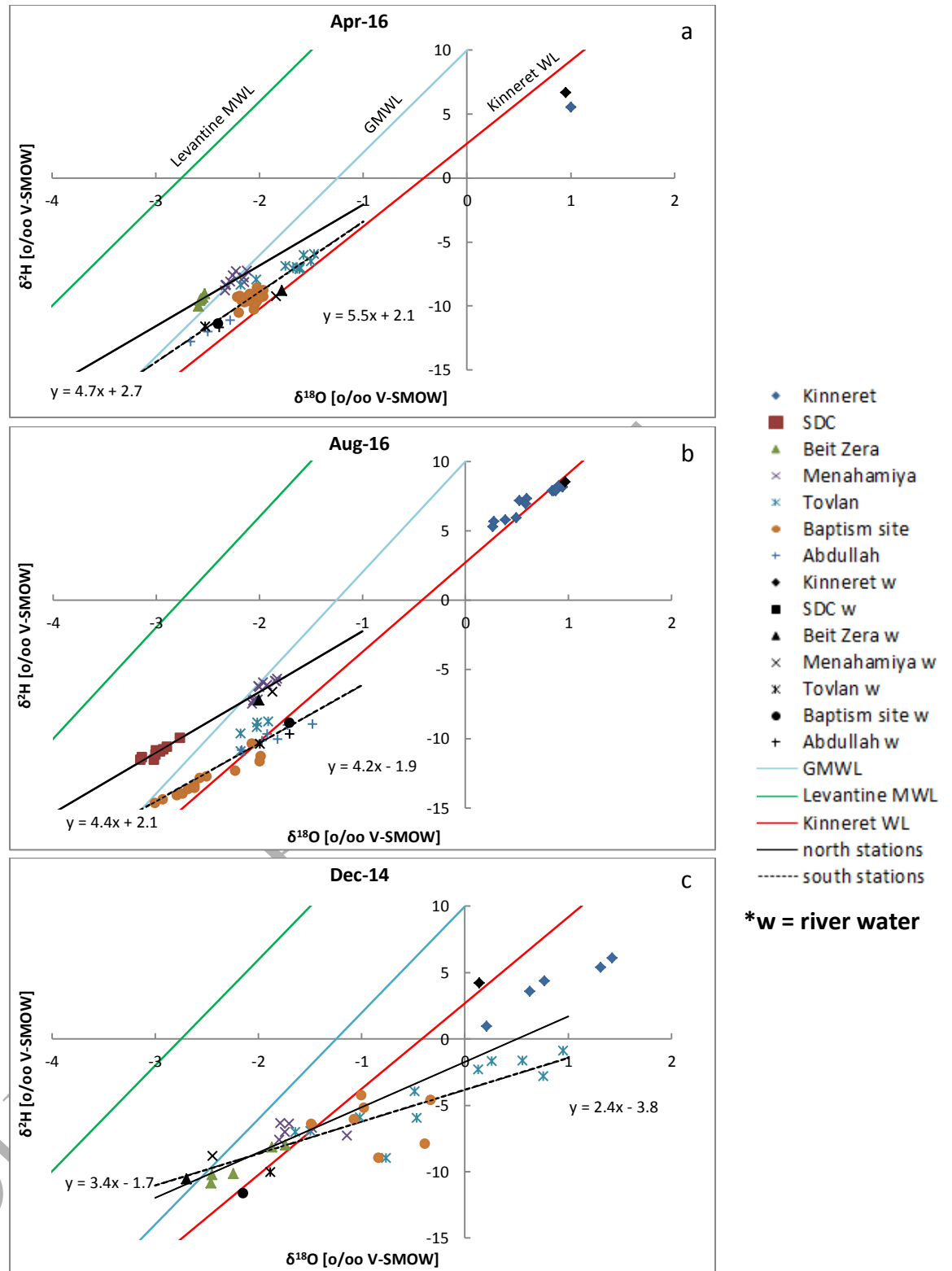


Figure 7: Isotope signatures in porewater- and river water (black marks) samples. For comparison, the Global Meteoric Water Line (GMWL, Craig, 1961), the regional Levantine Meteoric Water Line (Gat, 1971), and the long-term trend for Lake Kinneret (Kinneret WL; Siebert, 2006) are presented.



Figure 8: Temporal variation of Cl concentration of river water and pore water and local well trends at the sampling sites Tovlan (a), Baptism (b) and Abdullah (c). Note that the river level values are arbitrary to fit the scale of wells. Numbers given in a-c indicate order of samples taken from the respective seasonal cores at the given location, starting from 1 at water-sediment interface down to the highest numbers, which represent the deepest samples.

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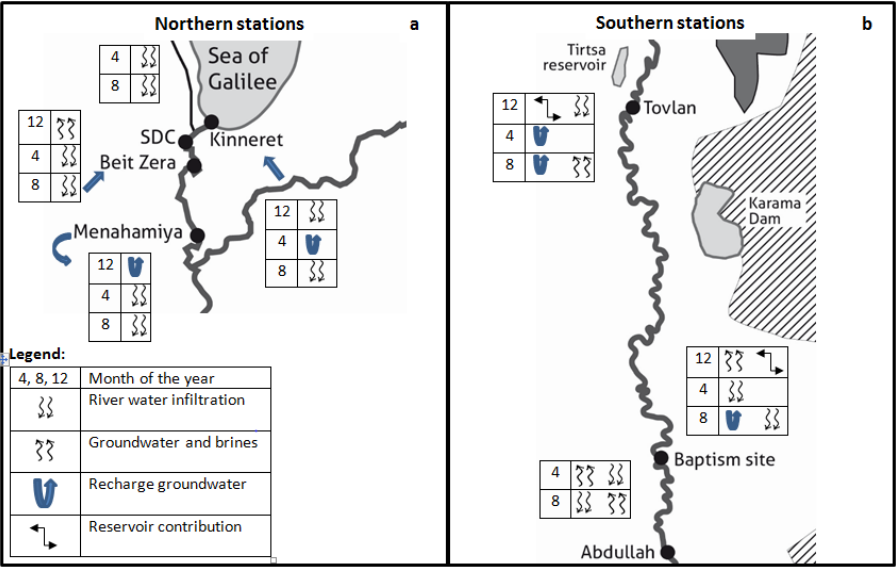


Figure 9: Conceptual model summarizing the main contributors to pore water composition in each station and month in the northern cluster (a) and southern cluster (b). At the northern stations river water signature dominates pore water during April and August, and at the Kinneret during August and December. In the southern stations, pore water composition is variably influenced by infiltrating reservoir-, river- and groundwater throughout the year.