



A systematic approach to derive natural background levels in groundwater: Application to an aquifer in North Lebanon perturbed by various pollution sources

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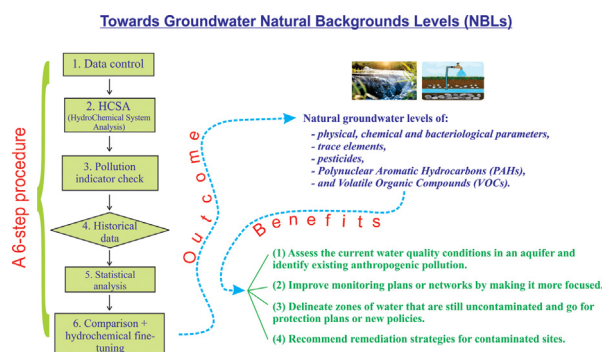
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HIGHLIGHTS

- Deriving baseline groundwater levels is challenging in several hydrological settings.
- A fully comprehensive scheme towards natural background chemistry is formulated.
- Establishing baseline levels fosters robust assessment of anthropogenic perturbations.
- Groundwater composition shifts are tracked for multi-parameters and pollution sources.

GRAPHICAL ABSTRACT



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ABSTRACT

Several efforts have recently emerged to develop methods capable of determining groundwater natural background levels (NBLs) due to their utmost importance in assessing water quality. A recently developed systematic approach to derive NBLs is the Khadra-Stuyfzand (KS) scheme. It has a clear and standardized flow with multi-steps to eliminate biased or contaminated samples, and hence it is capable of dealing with different pollution sources as well as saltwater intrusion. This method was applied to the Koura-Tripoli-Zgharta (KTZ) Miocene aquifer of coastal North Lebanon. It derived baseline conditions for 2 physical, 16 chemical, and 3 bacteriological parameters in addition to 8 trace elements, and 83 pesticides, polynuclear aromatic hydrocarbons, and volatile organic compounds. The results revealed the extent of anthropogenic shift from background levels, and delineated the main contaminated spots. In fact, the established groundwater baseline composition is typical of limestone aquifers with oligohaline-fresh, moderate alkalinity, calcium bicarbonate water, under freshening conditions. Nonetheless, this quality is locally degraded by microbial contamination due to wastewater disposal sites, saltwater intrusion, and minor nutrient loading from agricultural activities and/or urban development. The measured concentrations of major water ions and a variety of drinking water contaminants (e.g. nutrients, pesticides, hydrocarbons, and heavy metals) are below human health benchmarks, but the microbiological content at several spots has exceeded the permissible limits which renders the water unsuitable for domestic use, and calls for prompt mitigation measures.

1. Introduction

Safe water has become a main target requested by most environmental regulations. A major step in studying water quality problems is to define

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natural background levels (NBLs), also known as baseline levels (Edmunds et al., 2003). The EU Groundwater Directive 2006/118/EC define a background value as a “concentration of a substance or the value of an indicator in a body of groundwater corresponding to no, or only very minor, anthropogenic alterations to undisturbed conditions” (European Union, 2006). Defining NBLs has many advantages, for instance to (1) quantitatively assess the current water quality conditions in an aquifer and identify existing anthropogenic pollution, (2) improve monitoring plans or networks by making it more focused, (3) delineate zones of water that are still uncontaminated and go for protection plans or new policies, and (4) recommend remediation strategies for contaminated sites (Edmunds and Shand, 2008).

In recent years, different efforts have emerged to develop methods capable of determining groundwater baseline chemistry; however, there is still no agreement on one standardized approach applicable to all hydrogeological settings. The famous approaches today are: (1) the pre-selection method adopted by the EU project BRIDGE (Hinsby et al., 2008; Gemtzi, 2012; Nakić et al., 2020), (2) statistical and component separation methods (e.g. Edmunds et al., 2003; Wendland et al., 2005; Nakić et al., 2020), (3) hydrogeochemical assessments to derive NBLs based on the lithology of hosting rocks and associated geochemical conditions (e.g. the European HOVER project method; Lions et al., 2021), and (4) an integration of different methods including 2 or more of the aforementioned, for instance the structured approach developed by Khadra and Stuyfzand (2014), hereafter referred to as the Khadra-Stuyfzand (KS) scheme.

The pre-selection method drops biased samples based on a predefined exclusion criterion (e.g. bad charge balance and high nitrate concentration), and then considers the median value or a fixed percentile (e.g. 90th or 95th depending on the size of available data set) of the unbiased data range as a representative NBL (Hinsby et al., 2008). The component separation method is based on separating two statistical distribution functions for (1) natural and (2) influenced components (Wendland et al., 2005). Using, for instance, cumulative distribution graphs, data belonging to background and non-background processes can be separated, and representative mean values are derived (e.g. median \pm 2 mean absolute deviation; Edmunds and Shand, 2008). The probability plot (PP) (Sinclair, 1991) and the Lepeltier method (Lepeltier, 1969) use probability density functions that describe natural processes producing background levels (e.g. Nakić et al., 2020). The PP method traces the differences between probability distribution functions as they correspond to different processes, background and non-background. This distinction can be revealed wherever an inflection point appears on a probability graph, below which the concentrations correspond to background levels (Sinclair, 1991). Similarly, the Lepeltier method draws cumulative frequencies and looks for deviation from the log-normal distribution. Then the background level is the mean of the undisturbed distribution plus two standard deviations (i.e. mean + 2SD). Moreover, deriving NBLs from lithological types is not versatile. It is limited to simplified lithologies, restricted to few parameters, and requires information on anthropogenic pressure and other interfering factors (e.g. conditions of the catchment and surface water shed) (Lions et al., 2021).

All the aforementioned methods have been recently applied and tested separately or in conjunction in different studies (e.g. Muller et al., 2006; Molinari et al., 2014; Sellerino et al., 2019; Lions et al., 2021; Masciale et al., 2021; Voutchkova et al., 2021). An additional method is the KS scheme. It is a structured approach to establish groundwater baseline composition. It is in fact an integration of pre-selection criteria and statistical methods, all organized in clear systematic steps. It incorporates: (1) a robust elimination scheme with multi-steps to scan data for biased or contaminated samples, (2) classification of water bodies based on origin and facies, (3) historical data evaluation, and (4) statistical analyses, all steps based on a process flow of sequential order. It is also capable of dealing with different contamination sources, including saline groundwater in coastal aquifers, a main gap that some of the other methods have (e.g. the statistical methods). Testing the KS scheme on a dolomitic limestone aquifer suffering from salinization and other anthropogenic impacts filtered out the NBLs for 16 main constituents, 64 trace elements, and two isotopes (Khadra and Stuyfzand, 2014).

An updated version of the KS scheme is presented here, and then applied to the Koura-Tripoli-Zgharta (KTZ) Miocene aquifer of coastal North Lebanon (Fig. 1). It is expected that the spread of pollution in the area from agriculture, industry, urbanization, and direct liquid/solid waste disposals have added high concentrations of chemical and biological constituents that pose human health concerns.

2. Material and methods

2.1. The KS scheme

The Khadra-Stuyfzand (KS) scheme is a systematic procedure with clear and standardized steps to derive natural background levels (NBLs) in groundwater. It was initially introduced by Khadra and Stuyfzand (2014) but modified and updated here as all steps were better elaborated, and the selection of representative values was adjusted. The scheme is presented in Fig. 2, and the different steps are explained and detailed below.

- Data control:** This is an initial pre-selection step where erroneous or biased data is eliminated at first based on charge balance checks and the significance of some trace elements:
 - Eliminate samples with a bad charge balance (CB) according to the following criteria: $CB < 4$ if $\Sigma\text{Cations} + \Sigma\text{Anions} > 8$ meq/L, $CB < 6$ if $\Sigma\text{Cations} + \Sigma\text{Anions} = 2-8$ meq/L, and $CB < 10$ if $\Sigma\text{Cations} + \Sigma\text{Anions} < 2$ meq/L, where $CB = 100 (\Sigma\text{Cations} - \Sigma\text{Anions}) / (\Sigma\text{Cations} + \Sigma\text{Anions})$.
 - Discard trace element data if the sample is affected by either filtration bias (inferred from raised Al (≥ 20 $\mu\text{g/L}$)), which testifies of suspended clay for water with $5.5 < \text{pH} < 8.5$ (Stuyfzand, 1987), or well corrosion inputs whether from stainless steel (inferred from Ni > 50 $\mu\text{g/L}$, Mo > 10 $\mu\text{g/L}$, V or Cr > 5 $\mu\text{g/L}$) or brass well screens (inferred from Cu > 50 $\mu\text{g/L}$), both at $\text{pH} > 6.2$.
- Apply HydroChemical System Analysis (HCSA):** HCSA is a classification scheme introduced by Stuyfzand (1999, 2006) and applied by Khadra and Stuyfzand (2014) to discern water bodies based on origin, facies and water types including signs of pollution. The chemical scheme of water type is based on: (1) chlorinity (chloride concentration), (2) alkalinity (as HCO_3^-), (3) dominant ions, and (4) freshening/salinizing tendency, all combined into one code of four divisions like f3CaHCO₃ (Khadra and Stuyfzand, 2014). Chlorinity and alkalinity are designated according to Table 1 Chemical scheme of chlorinity and alkalinity. Dominant ions are represented by the strongest family members (e.g. Ca^{2+} , Mg^{2+} , Na^+ , HCO_3^- , and Cl^-), and a “Mix” is assigned when no anion family > 50 % of anions sum (Stuyfzand, 1989). Finally, the freshening/salinizing tendency is assessed based on the Base Exchange Index (BEX) with either freshened (“+”), salinized (“-”) or equilibrium (“o”) conditions (Stuyfzand, 1986, 2008).

This step provides a clear understanding of water origins and serves three purposes: (1) determining the NBL for each water body separately which is more accurate and representative, (2) excluding mixed samples inferred from mixed redox state based on the major redox sensitive species in water (O_2 , NO_3^- , SO_4^{2-} , Fe-total, Mn-total, NH_4^+ and CH_4) or polluted samples inferred from the Water Pollution Index (WAPI; Stuyfzand and Lüers, 2000; Stuyfzand, 2006) associated with facies determination, and (3) defining the main type of water based on chlorinity. This step is important to fill in the gap that other methods have in dealing with different contamination sources, including saline groundwater in coastal aquifers.

- A second pollution indicator check:** At this step polluted samples are screened further (besides WAPI) with more specific chemical indicators that are used as double checks to define and drop polluted samples, samples with $\text{NO}_3^- > 13$ mg/L, $\text{Cl}^- > 250$ mg/L, and $\text{Cl}^-/\text{Br}^- = 500-600$ are dropped.



Fig. 1. Location map of the Koura-Tripoli-Zgharta (KTZ) area, North Lebanon.

4. **Historical data:** Check historical data for significant hydrochemical trends. In case a significant trend for the sampled location exists, then the minimum (usually the oldest) values represent the natural background levels (NBLs); otherwise (with no significant trend) take the mean of the oldest data. Note that data from pre-pumping periods is preferable, although data prior to excessive pumping might suffice. Caution is required when the minimum values refer to a salinizing tendency as inferred from BEX. BEX definition is included in the HCSA (step 2) as part of the facies or chemical water type determination. In this case further elimination is needed (e.g. clustering analysis to rule out distinctive samples or statistical analysis as indicated in step 5, and then select the lowest values (minimum) as the NBLs). Expert judgment is needed as well to check for possible natural shifts in background chemistry due to, for instance, (1) natural shifts in coastline position as a result of sea level fluctuations with an impact on baseline levels for atmospheric Cl^- , Na^+ and Mg^{2+} , and (2) natural vegetation succession which impacts the evapo-concentration factor.
5. **Statistical analysis:** If historical data is missing and inferences from step 4 is not possible, then go for statistical analyses of the available, even if recent, data. This includes two steps:
 - a. Further screening to discern more subfacies: Correlation matrix, cluster analysis, or frequency distribution can answer four main questions: (1) are there other sample clusters within the previously discerned facies, indicating a subfacies for which a separate natural background composition (NBC) is needed? (2) are there any anomalous clusters with significantly elevated concentrations of major ions compared to the others and need further elimination? (3) are there any outliers? (4) are there any good correlations between Cl^- , SO_4^{2-} or NO_3^- (as pollution indicators) and other parameters? If yes, then finding the natural background level of one of them could help in extrapolating for the other (e.g. knowing Na^+ would help in extrapolating for Cl^- based on Na-Cl relationship).

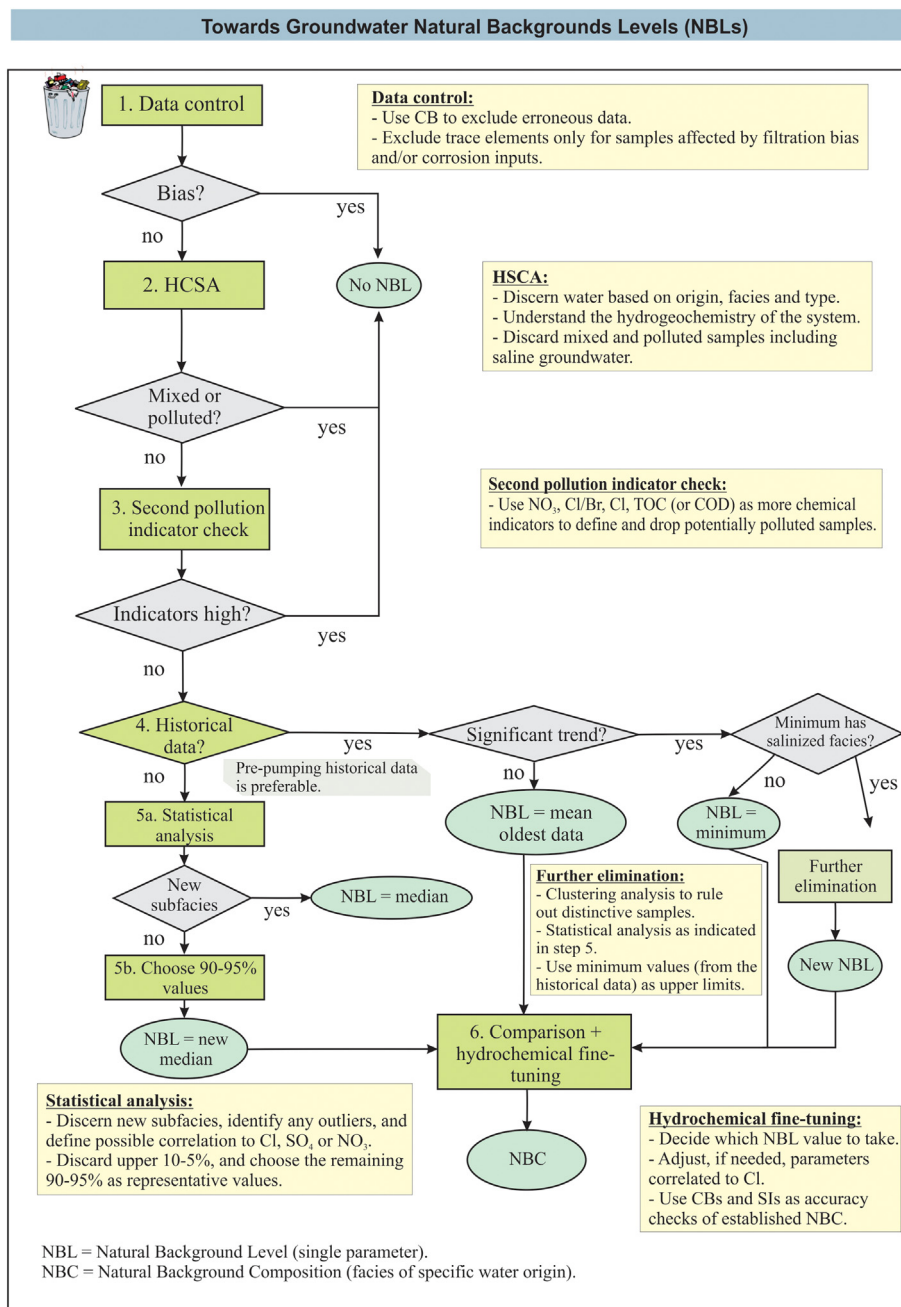


Fig. 2. The KS scheme (modified after Khadra and Stuyfzand, 2014).

- b. Selection of representative values: After all elimination steps are completed, discard the upper 5 % or 10 % of the frequency distribution, so that the values below the 95th or the 90th percentile, respectively, are unbiased and represent natural conditions, then take their median value as the natural background level (NBL) or the maximum (i.e. the 95th or 90th percentile) as the highest possible baseline value. Note that the exact percentage number to select is a matter of dispute and cannot be set a priori, but a common practice is to choose 95th percentile if the number of samples (N) > 30, 90th percentile if $20 < N < 30$ or highly skewed data; otherwise a lower percentile is preferred (e.g. the 70th percentile) (Nakić et al., 2020).

Care is needed when dealing with (deeply) anoxic environments where some parameters like Fe, Mn, NH_4 and CH_4 are mobilized, and hence their concentration is decreased, for instance in response to an anthropogenic

NO_3^- intrusion or a lowering of groundwater tables by pumping. In this case, the higher values could better represent the NBLs.

Substances with concentrations below limit of quantification (LOQ) are assigned provisional NBLs less than LOQ or just LOQ/2. This assumption is becoming safe as lab technologies are evolving fast towards lower detection limits.

6. **Hydrochemical fine tuning:** The previous steps are capable of giving the NBL values; however, some final checks are still needed: (1) check whether the parameters that strongly correlate to Cl^- need to be adjusted, and (2) glue together all NBLs into a natural background composition (NBC) for a specific facies. This requires an accuracy check to ensure that the resulting composition (NBC) shows a correct CB and a pH in accordance with the dominant mineral saturation index (SI_{MIN}) for the aquifer system. If not, then fine tune the major constituents with least confidence via CB, and adjust the pH to obtain the right SI_{MIN} .

Table 1
Chemical scheme of chlorinity and alkalinity.

Code	Parameter	Description/criterion
<i>Chlorinity</i>		
g	Oligohaline-fresh	Chloride concentration in sampled water [mg/L]
F	Fresh	5–30
f	Fresh-brackish	30–150
B	Brackish	150–300
b	Brackish-salt	300–1000
S	Salt	1000–10,000
H	Hypersaline	10,000–20,000
<i>Alkalinity</i>		
*	Very low	Alkalinity as HCO ₃ ⁻ [mg/L]
0	Low	<31
1	Moderately low	31–61
2	Moderate	61–122
3	Moderately high	122–244
4	High	244–488

2.2. Study area

The Koura-Tripoli-Zgharta (KTZ) Miocene aquifer is a major hydrogeological basin in North Lebanon spanning an area of 194 km² east of Tripoli city. It supplies nearly 800,000 citizens in Tripoli and surrounding villages with groundwater extracted artificially by wells or discharged naturally in springs.

The major geological units outcropping in the study area are the sedimentary carbonate and siliclastic rocks of the Miocene, Pliocene and Quaternary deposits (Fig. 3). The lower Miocene is missing in most of Lebanon

including the KTZ area as a result of vast regional stratigraphic hiatus (Wetzel and Dubertret, 1951; Hawie et al., 2013). Only the middle and upper Miocene outcrop around Tripoli and the Koura region. They are represented by sedimentary rocks subdivided into two major units and their corresponding subdivisions: (1) the Langhian to Tortonian (previously referred to as “Vindobonian”) M2, and (2) the Upper-Tortonian to Messinian (previously known as “Pontian”) ML units. The Vindobonian is a marine unit, made of two subunits: the lower Vindobonian which is mainly karstic limestone, with some marly sandy limestone, sand and marl levels especially towards its base, and the upper Vindobonian with marls and marly limestone layers. The Pontian is essentially a continental unit overlying the Vindobonian sequence with a lower marly unit (ML) rich in fine-grained clastic deposits and lacustrine limestone, and an upper unit (ML1), essentially conglomeratic (Mcg) made of alternations of sandstones, conglomerates, and red detrital clay layers. The Pliocene (PI) then outcrops in the northern part of the area. It is made of sandy marl changing laterally to grayish clay and reefal limestone. Finally, a significant areal portion is covered by few meters thick of Quaternary deposits (Q) which are mostly pebbles and sand.

The lower Vindobonian has been identified as the principal aquifer due to its karstic nature. It is confined in some parts of the basin due to the overlying marl layers of the upper Vindobonian and the Pontian units, while it is unconfined where it directly outcrops at the surface.

2.3. Data collection

The groundwater quality data was acquired from [BTD \(2021\)](#). It was collected as part of a series of hydrogeological studies for Lebanon funded

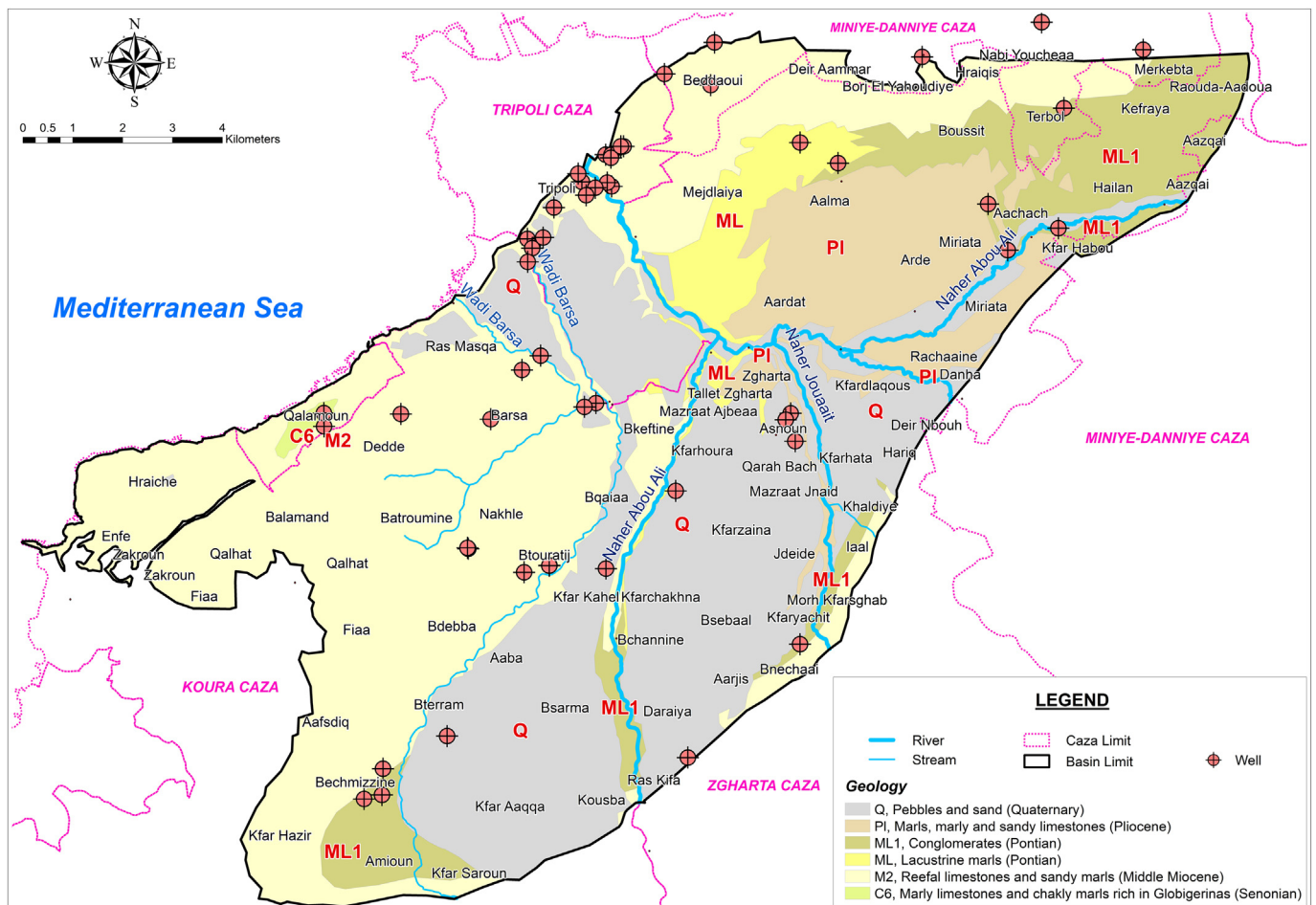


Fig. 3. Geological map of the KTZ Basin, and locations of groundwater samples collected during the May–June 2021 sampling campaign.

by the United Nations International Children's Emergency Fund (UNICEF) and requested by the Ministry of Energy and Water (MoEW). A campaign between mid-May to mid-June 2021 collected 52 water samples from public-supply and private wells, most wells are >100 m deep tapping the Miocene aquifer (Fig. 3). The sampling sites were selected carefully targeting most accessible wells to provide a reasonable representation of the study area, and build a reliable homogeneous hydrochemical database covering a wide range of parameters including physical, chemical and bacteriological parameters, metals, pesticides, Polynuclear Aromatic Hydrocarbons (PAHs), and Volatile Organic Compounds (VOCs). All wells were pumped for enough time to ensure proper purging, requiring the evacuation of more than three standing volumes and a stable electrical conductivity (EC).

Different sets of bottles were used to collect water samples for separate analyses: 1-liter sealed bottles for bacteriological testing, 4 l for major components, metals, hydrocarbons, and pesticides, and 2 bottles (40 mL each) with special preservatives for VOCs. All samples were preserved at around 4–8 °C till delivery to the lab.

The samples were analyzed for: (1) EC, pH, temperature, and turbidity in situ (27 % of the samples had their turbidity exceptionally measured in the lab), (2) Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe, Mn, As, Cd, Cr, Cu, Hg, Ni, Pb, Zn (by ICP-MS), Cl^- and HCO_3^- (by titration), SO_4^{2-} , PO_4^{3-} , NO_3^- , NO_2^- , and NH_4^+ (by spectrophotometry), 68 organic micropollutants (OMPs; including benzene and toluene, PAHs, chloroform and trichloroethene; a detailed list is shown in the *supplementary material*), and 15 pesticides (including the most hazardous and recently banned; a detailed list is shown in the *supplementary material*) in the American University of Beirut labs (LEAF; Laboratories for the Environment, Agriculture, and Food), and (3) microbiology (colony counts at 22 °C, intestinal enterococci, and *Escherichia coli* (*E. coli*)) in the Chamber of Commerce, Industry and Agriculture at Tripoli and North Lebanon (CCIAT) lab. O_2 was measured in situ using a dissolved oxygen (DO) meter (Sanxin SX726) for 41 % of the samples, and their average (4.5 mg/L) was assigned to the other samples that missed the DO measurement due to technical reasons. The presumed oxic condition of the groundwater samples is in line with the measured values of major redox sensitive species (NO_3^- , SO_4^{2-} , Fe-total, Mn-total, and NH_4^+).

Quality control measures showed good results. A sample duplicate and another spike were run for each 10 samples. A blank and a standard were also analyzed for each test to ensure instrument accuracy. For metals, a standard curve including a blank was read each day before the samples were run on the ICP-MS. The % recovery averaged around 110 % for major ions and trace elements, and all labs quality assurance and quality control programs met the ISO/IEC 17025:2017 standard requirements. In addition, all samples were checked for the accuracy of major ions, and they maintained an excellent charge (ionic) balances.

Another 19 samples collected in 2020 from the western part of study area were also added to the database, most of them were sampled twice from the same wells of 2021 campaign except for three wells that were not sampled in 2021. This sums up to a total of 55 wells included in the database. However, the 2020 set included the major ions only.

3. Results

3.1. Chemical water types

The dominating chemical water type in the study area is oligohaline-fresh to fresh, moderate to moderately high alkalinity, calcium bicarbonate, with freshening trend ($\text{g}2\text{CaHCO}_3 + \text{to } \text{F}3\text{CaHCO}_3 +$) (Fig. 4). It is initially $\text{g}3\text{CaHCO}_3$, as it appears eastward in, for instance, Zgharta, Asnoun, Miryata and Merkebta. BEX is at equilibrium, $\text{SI}_{\text{Calcite}}$ is close to zero, $\text{Ca}^{2+}/\text{Mg}^{2+} > 5$, $\text{HCO}_3^-/\text{Ca}^{2+} > 1.5$, and $\text{HCO}_3^-/\Sigma_{\text{Anions}} > 0.4$, which all typify pristine water hosted by calcium carbonate rocks. The pH of all samples range between 7 and 8, which is typical of baseline conditions, and testifies of calcareous water where CaCO_3 and HCO_3^- are the principal acid buffers. This also points to low mobility of heavy metals (e.g. Zn, Cd, Cu and Ni) (Khadra et al., 2017).

In contrast, closer to the sea in Haddadine, Qobbe and Deir Aammam, groundwater samples show brackish conditions ($\text{Cl}^- > 250 \text{ mg/L}$, $\text{Cl}^-/\text{Na}^+ > 2.6$), with moderately high alkalinity. Calcium chloride is the main chemical water type dictated from an occasional salinizing trend as discerned by a negative base exchange index BEX ($\text{B}3\text{CaCl}$). Some samples have BEX at equilibrium ($\text{B}3\text{CaCl}$). This is probably due to the fact that the water samples were collected in May, i.e. after a recent freshening flux due to the recharge period. For example, one sample in Qobbe has sodium chloride as the strongest ion pair and a positive BEX ($\text{B}3\text{NaCl} +$); this points to the replacement of Na^+ for Ca^{2+} during freshening periods.

It is worth noting that the chemical water type and freshening/salinizing tendency are expected to vary with space and time, depending on proximity to the sea, pumping rates, and season (wet versus dry). For instance, a salinizing trend with a negative BEX is expected to re-occur in the dry season where Ca^{2+} could replace Na^+ , and render the water type CaCl_2 .

3.2. Establishing natural background levels

Following the KS scheme, 14 samples out of 71 were initially eliminated due to bad charge balance. No signs of well corrosion inputs were recorded as inferred from Ni and Cu. Filtration bias was not checked due to absence of Al concentrations in the dataset. The HCSA showed 3 samples with mixed redox, and 18 samples polluted according to WAPI, which were all discarded. Further pollution checks eliminated 16 more samples with $\text{NO}_3^- > 13 \text{ mg/L}$.

Historical data is missing and inferences of NBLs from hydrochemical trends is not possible. Hence, the NBL derivation assessment relied on the recent data only. At this step, statistical analysis covered the rest of the data (20 samples) that passed the previous elimination checks. Hierarchical cluster analysis using Ward's method and squared Euclidean Distance revealed two clusters. The anomalous cluster (having 9 samples) with higher Na^+ , Ca^{2+} and Cl^- was dropped. The samples were also checked for outliers, but those having significant variations (e.g. in Na^+ , Ca^{2+} , K^+ , Cl^- , or HCO_3^-) turned out to be inclusive of the eliminated anomalous cluster, which called for no further action.

The upper 30 % of the frequency distribution of the remaining 11 samples was discarded, and the median of the 70th percentile was taken as the natural background level (Table 2). Checking the major ions for accuracy showed good charge balance after a slight raise of Mg from 7.9 mg/L to 10 mg/L. The pH was in accordance with the dominant mineral saturation index ($\text{SI}_{\text{Calcite}} = -0.05$) for the aquifer system, so it necessitated no special action.

3.3. Shifts from groundwater baseline levels

The shift of groundwater main constituents from natural baseline levels is quantified based on the Major Ions Shift Index (MISI).

$$\text{MISI} = \left(\frac{\text{Ca}^{2+}_M/\text{Ca}^{2+}_B + \text{Mg}^{2+}_M/\text{Mg}^{2+}_B + \text{Na}^+_M/\text{Na}^+_B + \text{K}^+_M/\text{K}^+_B + \text{HCO}_3^-_M/\text{HCO}_3^-_B + \text{Cl}^-_M/\text{Cl}^-_B + \text{SO}_4^{2-}_M/\text{SO}_4^{2-}_B + \text{NO}_3^-_M/\text{NO}_3^-_B}{8} \right) \quad (1)$$

where X_M and X_B are the ions measured and baseline concentrations, respectively.

MISI is the *unweighted mean scores* of the ratio of major ions measured values to natural background levels. A value of ≤ 1 means that the overall water quality is below the background level whereas a value > 1 indicates a shift from baseline levels. For instance, a value of 3 means three times more concentration than the background level.

The MISI map (Fig. 5) shows that pristine water is found in few spots only (north of Aalma, north of Nabi Youchaa, and south of Nakhle) whereas the groundwater at other spots is shifted from natural background levels. Three wells concentrated at one spot Haddadine-Qobbe-Beddaoui show significant shift from baseline levels. They have $> 300 \text{ mg Cl/L}$ (i.e. brackish water) and on average around 1 % seawater volume (1 % is enough to make

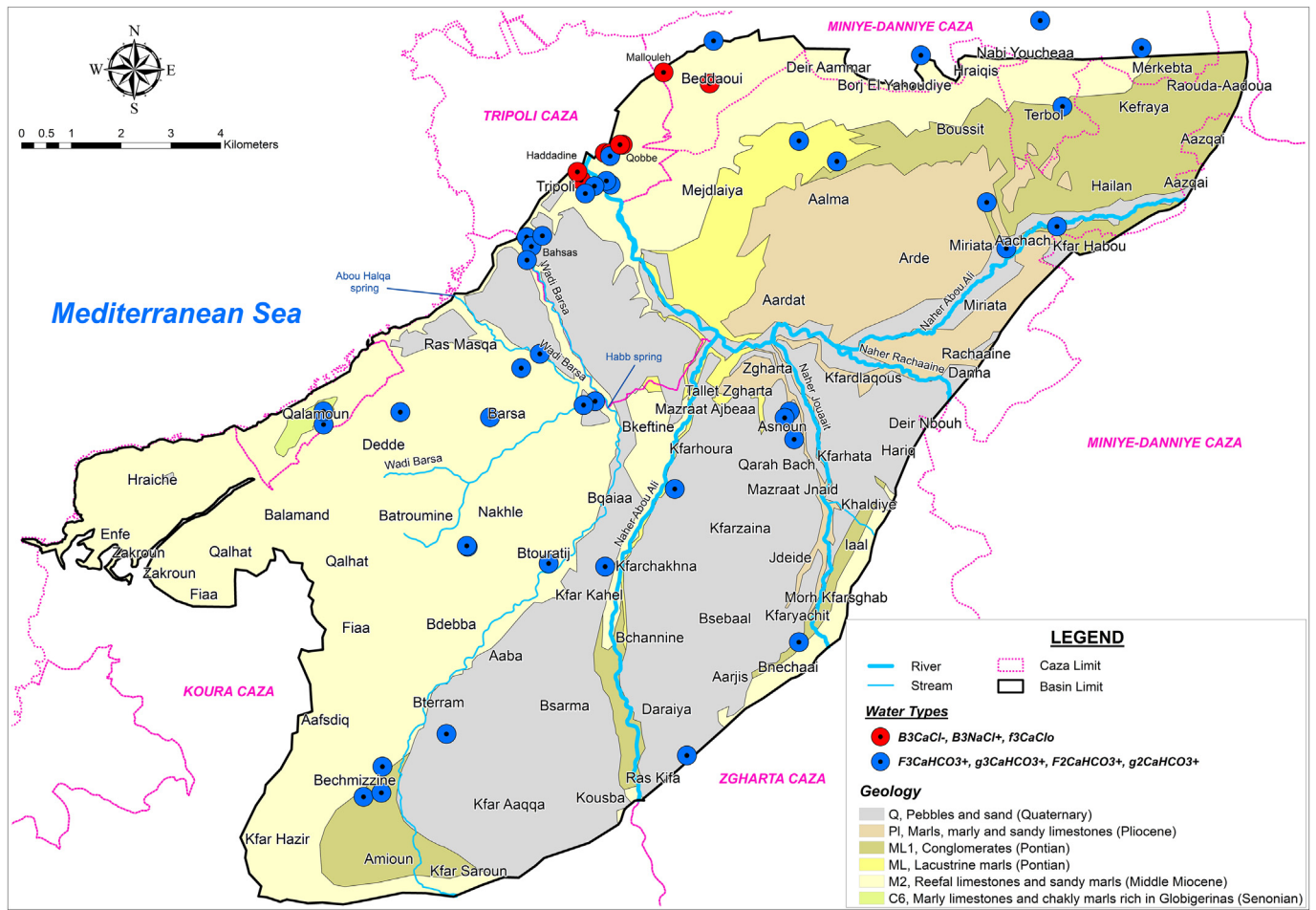


Fig. 4. The spatial distribution of chemical water types in the KTZ basin. Data acquired in Mid-May to Mid-June 2021.

Table 2

Established groundwater natural background levels for the KTZ aquifer.

No. of samples	Chemical water type	EC 20 °C	Turbidity	pH	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	NO ₃ ⁻	NO ₂ ⁻	PO ₄ ³⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	
		[μS/cm]	[NTU]	-	[mg/L]										
71	g2CaHCO ₃ +	375	0.5	7.32	20.4	13.3	223	2.2	0.082	0.05	11.2	2.9	56.6	10	
	Fe Mn NH ₄ ⁺ DO	22 °C colony counts		Intestinal Enterococci		E. coli		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	[mg/L]	[CFU/L]						[μg/L]							
	0.025 0.003 0.084 4.5	24,500		0		0		<1	<1	2	<5	<1	<5	<1	<20

Acenaphthene, Acephthylene, Anthracene, Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(g,h,i,b)perylene, Pyrene, Chrysene, Dibenzo(a,h)anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, and Phenanthrene (each one) < 1 μg/L.

Benzene, Bromobenzene, Bromochloromethane, Bromodichloromethane, Bromoform, n-Butyl Benzene, tert Butyl Benzene, sec Butyl Benzene, Carbon tetrachloride, Chlorobenzene, Chloroform, 4-Chlorotoluene, 2-Chlorotoluene, 1,2-Dibromo-3-chloropropane, Dibromochloromethane, 1,2-Dibromoethane, Dibromomethane, 1,3-Dichlorobenzene, 1,2-Dichlorobenzene, 1,4-Dichlorobenzene, 1,1-Dichloroethane, 1,2-Dichloroethane, cis-1,2-Dichloroethene, trans-1,2-Dichloroethene, 1,1-Dichloroethene, and 1,2-Dichloropropane (each one) < 1 μg/L.

1,3-Dichloropropane, 1,1-Dichloropropene, cis-1,3-Dichloro-1-propene, trans-1,3-Dichloro-1-propene, Ethylbenzene, Isopropylbenzene, p-Isopropyltoluene, Methylene Chloride, Naphtalene, n-Propyl Benzene, Styrene, 1,1,1,2-Tetrachloroethane, 1,1,2,2-Tetrachloroethane, Tetrachloroethene, Toluene, 1,2,3-Trichlorobenzene, 1,2,4-Trichlorobenzene, 1,1,1-Trichloroethane, 1,1,2-Trichloroethane, Trichloroethene, 1,2,3-Trichloropropane, 1,2,4-Trimethylbenzene, 1,3,5-Trimethylbenzene, o-Xylene, m-Xylene, and p-Xylene (each one) < 1 μg/L.

Alpha-BHC, Gamma-BHC (Lindane), Beta-BHC, Heptachlor, Aldrin, and Heptachlor Epoxide (each one) < 0.01 μg/L.

Endosulfan I, 4,4'DDE, Dieldrin, Endrin, and Endosulfan II (each one) < 0.02 μg/L.

4,4'DDD, 4,4'DDT, Endrin Aldehyde, and Endosulfan Sulfate (each one) < 0.06 μg/L.

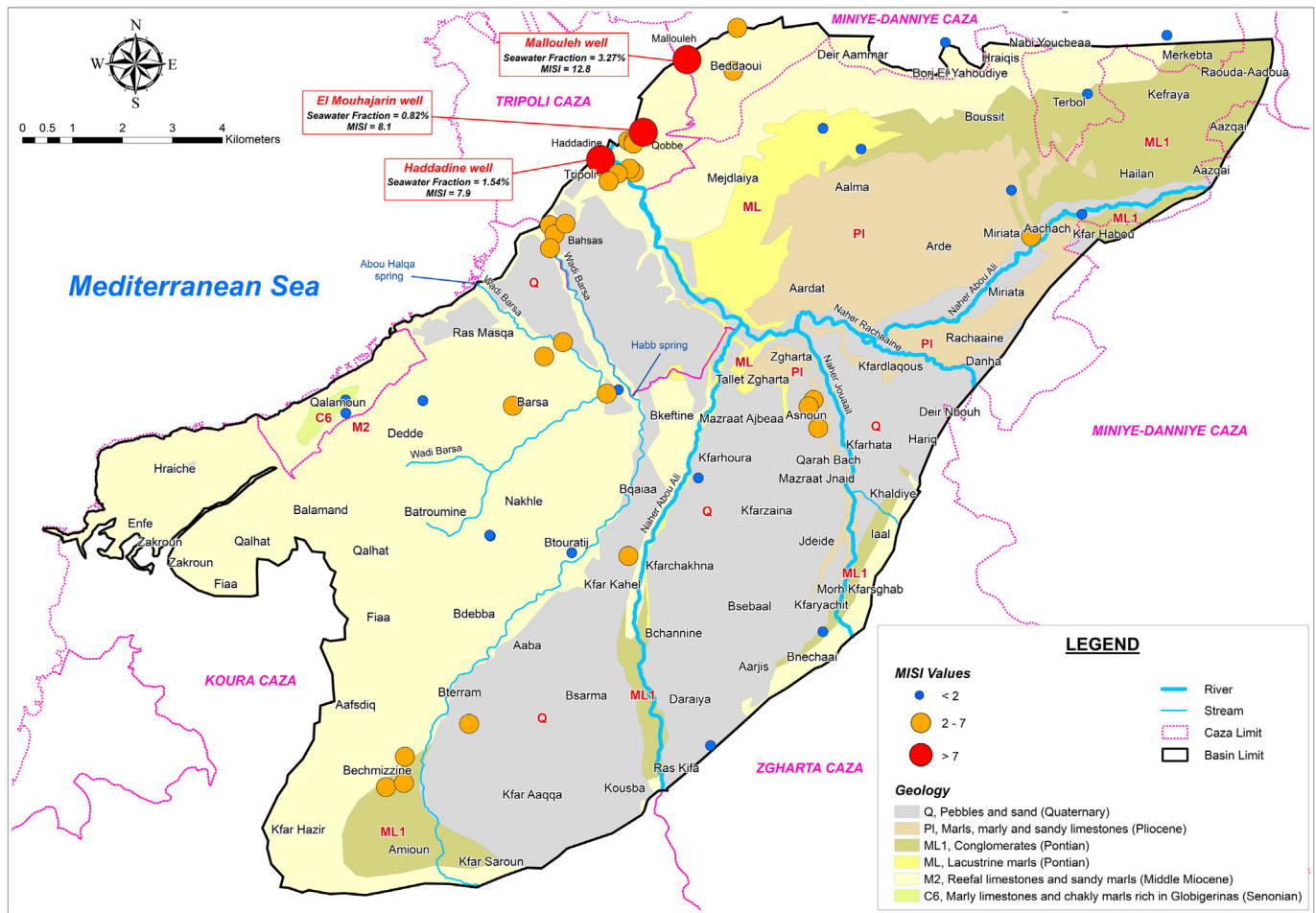


Fig. 5. Shift of groundwater main constituents from natural baseline levels as inferred from the Major Ions Shift Index (MISI) of sampled wells in the study area. Data acquired in Mid-May to Mid-June 2021.

freshwater undrinkable). The maximum salinization is recorded at Mallouleh well (seawater fraction = 3.27 %; MISI = 12.8), Haddadine Well (seawater fraction = 1.54 %; MISI = 7.9), and El Mouhajarin well (seawater fraction = 0.82 %; MISI = 8.1).

Following a similar approach, the Microbiological Constituents Shift Index (MCSI) can quantify the extent of shift from baseline conditions.

$$MCSI = \left(\frac{[Colony\ counts_{22^\circ C}]}{baseline\ value} + \frac{[Intestinal\ Enterococci]}{baseline\ value} + \frac{[E.coli]}{baseline\ value} \right) / 3 [all\ in\ CFU/L] \tag{2}$$

This index is similar to the Water Pollution Index for microbiology (WAPI-J) (Stuyfzand and Lüers, 2000; Stuyfzand, 2006). It is more conservative as it uses the derived baseline values of the aquifer rather than using a general permissible value (e.g. 100,000 CFU/L, 10 CFU/L, and 10 CFU/L for colony counts, intestinal enterococci and *E. coli*, respectively).

$$WAPI - J = \left(\frac{[Colony\ counts_{22^\circ C}]}{100,000} + \frac{[Intestinal\ Enterococci]}{10} + \frac{[E.coli]}{10} \right) / 3 [all\ in\ CFU/L] \tag{3}$$

According to MCSI, many wells showed clear shift from baseline conditions (Fig. 6) testifying of microbial sources of contamination, for instance the highest shifts were recorded at Merkebta well, MCSI = 472; Lebanese University well, MCSI = 400; Kfaryachit well, MCSI = 242; El

Jisr well, MCSI = 228; Saadoun well, MCSI = 221; and El Mouhajarin well, MCSI = 162.

E. coli and/or intestinal enterococci are present in 40 % of the collected samples. This fecal composition is a strong indicator of microbial pathogens, and a clear signal of wastewater contribution overloaded by humans and animal waste. Total colony counts also exceeded the permissible standard (100,000 CFU/L) for another 31 % of the samples that has no *E. coli* or intestinal enterococci. This pollution is expected to be even higher in interconnected rivers due to absence of geo-purification. Pathogenic loading poses a direct threat to human health, and may cause water borne diseases such as diarrhea and gastrointestinal illness.

4. Discussion

4.1. Nutrient loading, organic and inorganic micropollutants

Nitrite (NO_2^-) was not detected in any sample. Ammonium (NH_4^+) was detected in 2 samples only at an average concentration of 0.36 mg/L. Orthophosphate (PO_4^{3-}) was detected in 17 samples where it slightly exceeded the natural backgrounds (average = 0.34 mg/L). Based on phosphate and total inorganic nitrogen ($TIN = NO_3^- + NO_2^- + NH_4^+$), the highest nutrient load is recorded at one well in Abu Samra. Such load usually originates from agricultural sources (e.g. nitrogen based fertilizers or manures), but in the current case and based on pollution sources (BTD, 2021) it is most probably due to urban contaminants (e.g. from wastewater effluents).

The heavy metals As, Cd, Cr, Cu, Hg, Ni, Pb and Zn are trace elements that belong to the environmentally hazardous inorganic micropollutants.

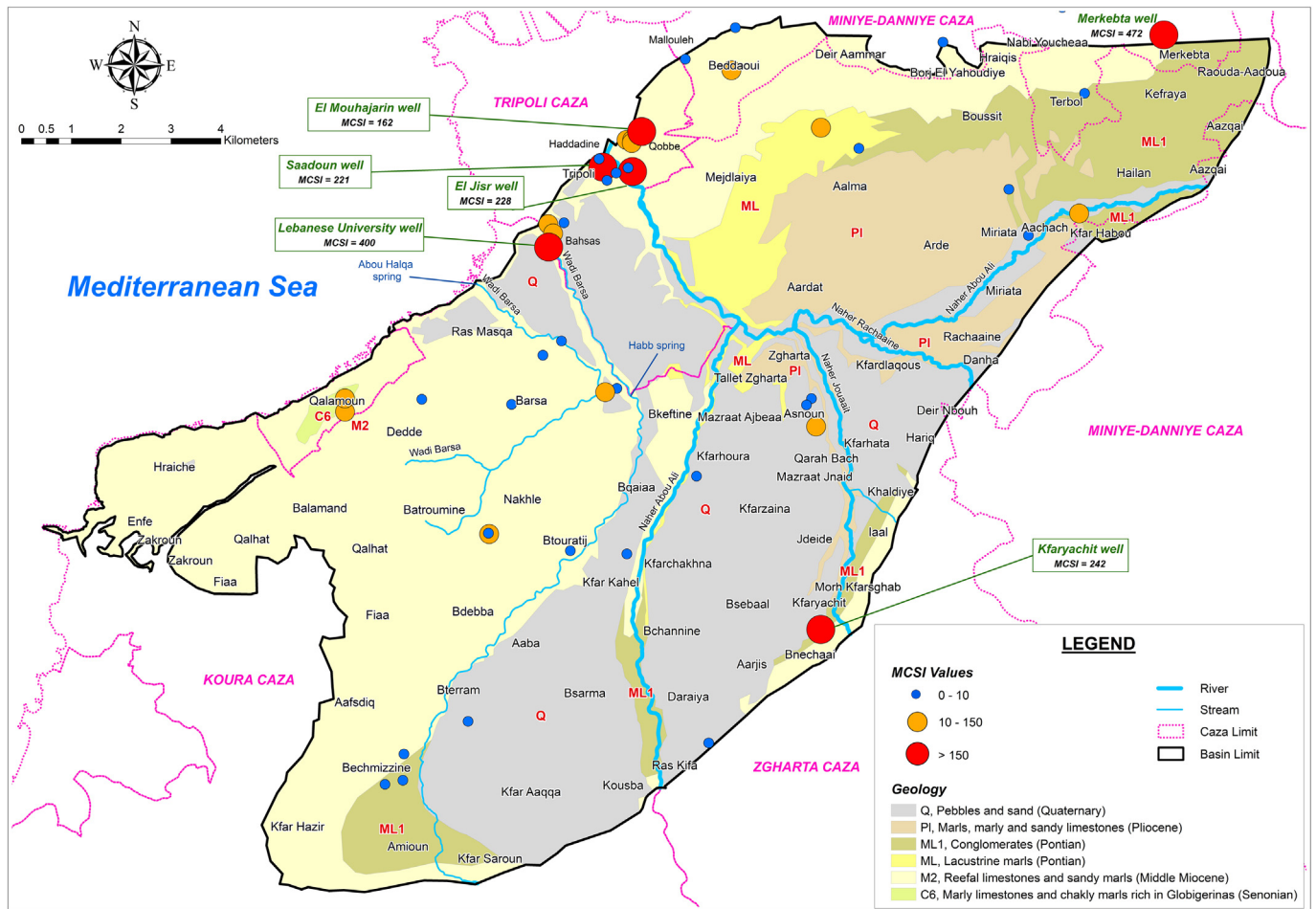


Fig. 6. Shift of groundwater microbiological constituents from natural baseline levels as inferred from the Microbiological Constituents Shift Index (MCSI) of sampled wells in the study area. Data acquired in Mid-May to Mid-June 2021.

They were all barely present although tested at a detection limit of 1–5 $\mu\text{g/L}$. This means that heavy metals are within natural levels and excludes the role of industrial effluents as a potential source of contamination. The highest values were detected at the well in Mallouleh but they remained below background levels ($\text{As} = 3 \mu\text{g/L}$, $\text{Cu} = 16 \mu\text{g/L}$), while one well showed exceptionally high Zn (528 $\mu\text{g/L}$). Based on expert judgment the high zinc in the collected sample is probably just a matter of bias as it corrodes from the well itself due to old galvanized iron pipes.

The NBLs for all major elements and analyzed trace elements (Table 2) are significantly below permissible drinking water levels in accordance to the best recognized standards (European Union, 2020; WHO, 2022) (Table A.4, supplementary material).

All samples showed no presence of any of the tested organic micropollutants (a complete list is shown in the supplementary material) although analyzed at a detection limit of 1 $\mu\text{g/L}$. Their absence excludes industrial point sources and urban runoff as major pollution sources. Significant leaks from gas stations or fuel tanks are eliminated as well due to absence of PAHs and VOCs (e.g. benzene, toluene, ethylbenzene, xylene, trimethylbenzene, and naphthalene). Note that PAHs have high affinity to adsorb to organic matter in the soil, which reduces the chance to reach groundwater unless there is heavy contamination. Also oxic conditions facilitate easier degradation reactions and hence lower the chemical concentrations.

In terms of pesticides none of the tested compounds (e.g. aldrin, alpha-HCH, beta-HCH, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, gamma-HCH, heptachlor, heptachlor epoxide, 4,4'DDD, 4,4'DDE, and 4,4'DDT) were detected at a minimum level of 1 $\mu\text{g/L}$. This means that all groundwater samples are free of these hazardous

pesticides. It is either due to their banned use or high adsorption and hence chemical attenuation in the vadose zone.

4.2. Delineation of main contaminated zones

Based on the hydrochemical and biological shifts of the groundwater constituents from natural background levels it is possible to divide the study area into different zones of contamination: (1) Qalamoun-Ras Masqa-Bahsas-Habb (western side of study area), (2) Haddadine-Qobbe-Beddaoui (northwestern part of study area), (3) Merkebtá (northeast), and (4) Kfaryachit (southeast).

Zone 1 is known for major water potentials, the most notable are the Habb and Abou Halqa springs. Besides raised pollution levels in Bahsas (Fig. 6) due to local pollution sources or in vicinity (e.g. wastewater disposal sites exist eastward) (BTD, 2021). In addition, the wells in Bahsas show minor signs of early salinization ($\text{Cl}^- > 70 \text{ mg/L}$ and $\text{EC}_{200\text{C}} > 700 \mu\text{S/cm}$), which indicates susceptibility to saltwater intrusion.

Zone 2 encompasses Haddadine, Qobbe and Beddaoui in the northwest of the study area. This area is crowded and highly urbanized, and hence characterized by low recharge and intensive pumping. The relatively high salt content ($\text{Cl}^- > 150 \text{ mg/L}$ and $\text{EC}_{200\text{C}} > 1100 \mu\text{S/cm}$ in most wells) testifies of saltwater intrusion. There is possible presence of industrial effluents; however, it occurs in minor traces only as confirmed by the absence of heavy metals and OMPs. Some wells have high microbial contamination attributed to wastewater disposal sites located to south, east and northeast (BTD, 2021). It was noticeable that some wells had no presence of *E. coli* and intestinal enterococci but showed extremely high levels of total colony counts ($>300,000 \text{ CFU/L}$ at 22 °C and hence low MCSI value).

Zone 3 includes Merkebt village. Although one well is not enough to derive signals, it gives an overview of the anticipated conditions. This single well has low MISI (1.7) indicating baseline conditions for major ions but high MCSI (472) indicating high levels of fecal pollution ($E. coli = 1210$ CFU/L) mainly due to wastewater discharge.

Zone 4 encompasses Kfaryachit village. Data is also limited to one well, which only gives an overview of the pollution state. Microbiology is solely responsible for the current pollution state of groundwater. It has high levels of fecal pollution (MCSI = 242) which is mainly due to intestinal enterococci (720 CFU/L). This indicates domestic sewage or human/animal wastes. In fact, part of Kfaryachit still relies on cesspits, and there is a local wastewater discharge point in vicinity.

4.3. Comparison with baseline levels elsewhere

The natural background levels of the KTZ aquifer were compared to the Damour coastal aquifer since it is the only aquifer in Lebanon with established NBLs (Khadra and Stuyfzand, 2014). The groundwater baseline concentrations of major ions between the two aquifers are comparable except for minor changes mainly due to lithological differences (Fig. 7). The Damour aquifer has significantly higher Mg^{2+} due to its dolomitic limestone hosting rocks with $Ca_{0.70}Mg_{0.30}CO_3$ chemical composition (Khadra et al., 2017), and the relatively higher Ca^{2+} and HCO_3^- is probably dictated from lower pH (7.13 for the Damour aquifer) which facilitates calcium carbonate dissolution. In contrast, the elevated potassium in the KTZ groundwater compared to the Damour might be linked to more clayey minerals (e.g. illite) in the former, a scenario that needs further investigation to confirm.

5. Conclusions

The Khadra-Stuyfzand (KS) scheme is a systematic approach to derive natural background levels (NBLs) in groundwater by following clear and standardized steps. It has multi-steps to eliminate biased or contaminated samples, and hence it is capable of dealing with different pollution sources. In addition, when the KS scheme is fully incorporated with the HydroChemical System Analysis (not done here due to lack of data), it is capable of determining the NBLs for groundwater bodies of different origins and their subsequent facies rather than considering the whole aquifer as one lumped volume. Here it is demonstrated that the KS scheme is capable of dealing with groundwater samples dataset affected by multiple pollution sources leading to the estimation of the NBLs for various elements and properties.

Applied to the Koura-Tripoli-Zgharta (KTZ) Miocene aquifer of coastal North Lebanon, the KS scheme derived the NBLs for 2 physical, 16 chemical

(including major ions) and 3 bacteriological parameters in addition to 8 trace elements and 83 pesticides, Polynuclear Aromatic Hydrocarbons (PAHs), and Volatile Organic Compounds (VOCs). The established baseline composition is typical for limestone aquifers with oligohaline-fresh, moderate alkalinity, calcium bicarbonate water under freshening conditions (g_2CaHCO_3+). This quality is locally degraded by microbial contamination due to wastewater disposal sites. In fact, the partially karstic nature of the hosting limestone suppresses the role of natural purification and chemical attenuation of contaminants including microorganisms, and warns of further spreading of pollution in the future. Protection plans are urgent to keep anthropogenic inputs low, and save the present uncontaminated zones.

Of less importance are the rise in salinity due to saltwater intrusion, and the nutrient loading from agricultural activities and/or urban development. The salinity signals detected in the coastal zone at Haddadine and Qobbe (east of Tripoli) point to an early stage of salinization, yet the worse may come and the citizens will find it hard to use salinized water for domestic needs. It is thus recommended that new wells be banned there in order to avoid further deterioration of groundwater quality. The extraction rates should be also lowered at wells currently showing very high salinity (e.g. Mallouleh well) in order to reduce their impact or any possible upconing where saltwater rises vertically below the well pump.

It is true that the measured concentrations of major water constituents and a variety of drinking water contaminants (e.g. nutrients, pesticides, hydrocarbons, and heavy metals) are below human health benchmarks, but the microbiological content of many groundwater samples have exceeded the drinking water permissible limits. This has generally rendered the water unsuitable for drinking or domestic use. It is therefore advised to regularly monitor the general characteristics of water (e.g. pH, DO, EC, NO_3^- , PO_4^{3-} , Cl^- , heavy metals, and microbiology) as proxies to future changes in groundwater composition. With the established baseline levels, the identification of hot spots with clear shifts in the groundwater properties is more evident, even if the various levels of degradation proxies did not reach the usual alarming levels set by the generally permissible levels. This offers the possibility to better select monitoring sites based on the shifts or no shifts from baseline levels.

CRedit authorship contribution statement

Wisam M. Khadra – Conceptualization; Methodology; Formal analysis; Investigation; Data curation; Writing - original draft; Writing - review & editing; Visualization; Supervision.

Ata R. Elias – Conceptualization; Investigation; Resources; Writing - review & editing; Supervision.

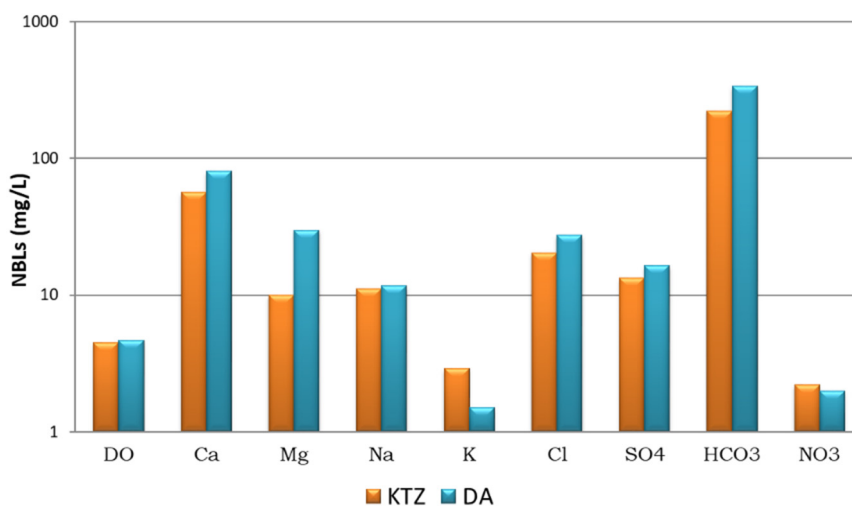


Fig. 7. Comparison of groundwater major constituents NBLs between the Koura-Tripoli-Zgharta (KTZ) and the Damour (DA) aquifers in Lebanon.

Michel A. Majdalani – Resources; Supervision; Project administration; Funding acquisition; Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.157586>.

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