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Spatial and temporal variability of groundwater quality of an Algerian aquifer: the case of Soummam Wadi

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ABSTRACT

Five-year monitoring of physicochemical parameters was performed with two campaigns in low and high water periods of the Lower Soummam catchment. Data from 18 wells were processed by multivariate statistical tools in order to identify the principal factors influencing groundwater chemistry. Two matrices of 14 and 8 physicochemical parameters with 18 groundwater samples collected in wells were obtained. The correlation matrix showed strong associations between nine variables: K^+, Ca^{2+}, Na^+, $SO_4{}^{2-}$, Cl^-, Mg^{2+}, $NO_2{}^-$, Zn^{2+} and Sr^{2+}. Principal component analysis and factor analysis showed that the cumulated variance of high and low water periods was of 83.19% and 78.55%, respectively. The variables assigned to the mineralization effect or to pollution indicators were presented by the factor analysis. The bivariate plots confirmed a mineralization model, ascribed to dissolution of geological materials, and to high levels of saline contamination attributed to leakages from sanitary systems. They also showed an increase "upstream to downstream" of the mineralization, visualization of temporal variations, and a dilution process identification of the natural mineralization during the recharge of the aquifer.

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1 Introduction

In the current world economic paradigms, sustainable socio-economic development of every community depends greatly on the available water resources (Belkhiri *et al.* 2010). Over recent years, Mediterranean regions, including North Africa, have been confronted by a significant decrease and important pollution of water resources. Since 1990/91, this region has experienced severe drought and increasing human pressure (Margat and Vallee 1999). The area depends heavily on groundwater as a water resource. This water is used for various purposes such as agricultural water, domestic water and industrial water. The population has increased greatly. Rapid urbanization has modified land-use patterns and increased water demands. To increase agricultural production, there is intense use, in all agricultural areas, of pesticides and fertilizers that infiltrate deeply. Such large demands on groundwater have affected water quality and caused the contamination of groundwater, hence, becoming an important issue for urban groundwater supply (Jeong 2001a).

The concept of groundwater quality seems to be clear; however, its study and evaluation are still complicated (Chenini and Khemiri 2009). The quality requirement of groundwater depends on its different uses, such as drinking, industrial and irrigation waters. The chemical quality of the groundwater is indispensable as a factor enabling its utilization for the different uses mentioned above (Tathy *et al.* 2011). From the chemical composition of groundwater, it is not easy to distinguish between contributions due to natural weathering and/or anthropogenic input (Murray 1996, Rosen and Jones 1998, Jeong 2001b).

According to many authors (Hem 1985, Bricker and Jones 1995), water chemical composition is controlled by many factors, which include composition of precipitation (Dzhamalov and Zlobina 1995), mineralogy of river basins (Oyarzûn *et al.* 2013), aquifers (Kortelainen and Karhu 2009), climate (Okkonen and Kløve 2012) and topography (Ielpo *et al.* 2012). Those factors may combine to create various types of water with a change in composition over space and time (Yidana 2008). The chemical composition of groundwater is a function of the chemical composition of the aquifer host rocks, flow conditions and residence time in the aquifer (Back and Hanshaw 1971). The spatial variability is frequently determined by the intensity and diversity of anthropic activities (Shil'Krot and Yasinski 2002, Shrestha and Kazama 2007). The use of the major ions as natural tracers has become a common methodology to delineate flow paths in aquifers (Back 1966, Eberts and George 2000, Plummer and Sprinkle 2001, André 2002, Güler and Thyne 2004, Belkhiri *et al.* 2010).

In the literature, many different methodologies have been applied to study, evaluate and characterize the sources of variation in groundwater geochemistry. Among these methods, the multivariate techniques have been used to resolve hydrological factors such as aquifer boundaries, groundwater flow paths and hydrochemical parameters (Seyhan *et al.* 1985, Razack and Dazy 1990, Join *et al.* 1997, Ochsenkühn *et al.* 1997, Wang *et al.* 2001,

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Locsey and Cox 2003, Yidana and Yidana 2010). Several techniques have been used to assess water quality, based mainly on correlation of chemical ions, and some ion ratios can predict mineralization origin (Locsey and Cox 2003, Pulido-Leboeuf *et al.* 2003, Bennetts *et al.* 2006). Chemometric analyses have been performed to distinguish between water samples based on composition and origin (Singh *et al.* 2005).

This study attempts to gain more information on the items that limited existing information. The main objectives in the study are assessment of groundwater chemistry, determination of the anthropogenic factors that presently affect the water chemistry in the region, and identification of the main geochemical processes controlling the groundwater. To this end, water chemistry characteristics and processes involved in groundwater mineralization are scrutinized (Yidana *et al.* 2010). Two large data matrices, corresponding to 10 measurement campaigns realized during high and low water periods were obtained during a 5-year monitoring program (2002–2006). In this study, 18 wells (measurement points) were monitored. Data were subjected to different multivariate statistical techniques for extracting information about similarities or dissimilarities between sampling sites of the lower Soummam catchment. Principal component analysis (PCA) and factors analysis (FA) were used to analyse and interpret the overall data structure (Caillez and Pages 1976, Bouroche and Saporta 1980, Lefebvre 1983, Cloutier *et al.* 2008).

2 Study area description

2.1 Land-use pattern and urbanization

Geographically, the study area is situated in northeastern Algeria. The groundwater sampling sites were localized in the catchment of the Soummam valley (950 km^2), situated between 4°30′ and 5°10′ east and 36°20′ and 36°50′ north, and are within the great catchment of Soummam (9125 km^2) (Fig. 1). Considered as the third main river in Algeria, the Soummam Wadi receives many important flow tributaries, in particular from the high Akfadou–Taourirt Ighil mountains (Remila Wadi) in the west, the Gouraya–Aghbalou mountains (El-Kseur Wadi, Ghir Wadi) in the north, and the Babors mountains (Amassine Wadi, Amizour Wadi) in the south (Saou *et al.* 2012) (Fig. 1). The Soummam Wadi is characterized by a wet climate and average precipitation and temperature of about 750 mm year^{-1} and 18°C, respectively (Saou *et al.* 2012). The lower Soummam plain contains a strategic alluvial aquifer of vital importance. Its water has significant socio-economic interest. The plain is used for feeding the local population but is poorly protected against pollution originating from the surface (Maane-Messai *et al.* 2010). This water can be affected by surface activity and can act as a vector of pollution between sources and valuable surface water resources. Generally, the land is mainly used for agricultural and industrial activities. Being part of the Mediterranean Basin, the study area has undergone important agricultural and industrial development since 1990. In the past decade, the Soummam valley, whose primary activity is food processing, has experienced important industrial development, with the consequences of plentiful untreated discharges in the area. Figure 1 illustrates the main human activities in the study area, as well as the significant discharges, which may constitute a source of groundwater contamination. In this area, planting of fruit trees induces great use of fertilizers and pesticides. The industrial activities are often accompanied by accidental metal waste and hydrocarbon discharges. In addition, demographic

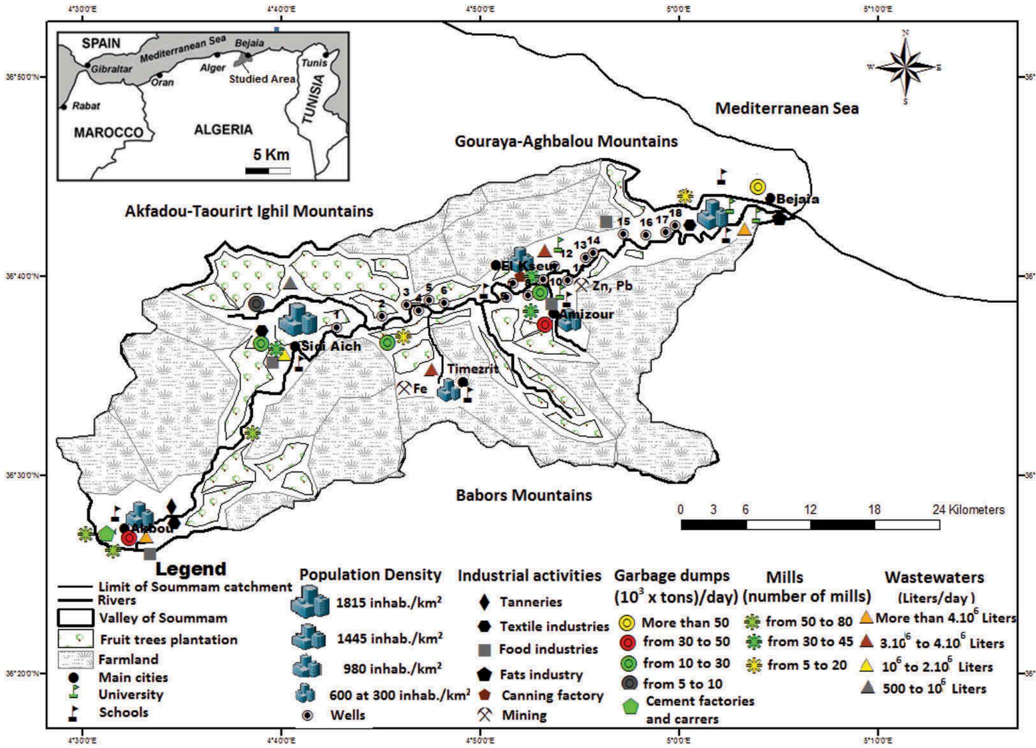

Figure 1. Location of the study site and the groundwater sampling location. Important human activities (industrial and agricultural) are situated around the main urban centres. The abandoned lead–zinc and iron mines are also indicated.

expansion has created an important water demand and, therefore, a significant release of wastewater. The population significantly increased from 490 423 inhabitants in 2006 to 924 279 inhabitants in 2009 (density of 250–1814 inhabitants km^{-2}) of which more than a half is concentrated along the valley (DPAT 2010). The fast increase of the population and the urbanization have modified land-use patterns and have accentuated water demands. The groundwater wells receive pollution load from point and non-point sources and the water runoff of farmlands from the area directly or via a draining flux. In fact, the downstream area produces important amounts of untreated water discharges due to urban and industrial concentrations. On the other hand, the upstream area is generally under irrigation, with subterranean water drawn from wells with water of fairly good quality. Ultimately, these waters are intended to be mixed with groundwater after infiltration, carrying the fertilizer. In contrast, waters of the highly polluted Soummam Wadi irrigate the downstream zones, and this pollution degrades the groundwater quality much more. Two sources of pollution are found in wells: the pollution engendered by both the use of fertilizers and the return of irrigation waters to groundwater, and pollution caused by the direct input of sewage.

As part of a programme inventorying the groundwater quality in the study area, this contribution aims to solve the problem of aquifers in the Soummam region and to contribute to a better understanding of the alluvial hydrogeology in the context of climate changes. To the best of our knowledge, this contribution is the first study that shows the spatial and temporal variability of groundwater quality in northeast Algeria.

2.2 Local geology and hydrogeology

According to many authors (Betier *et al.* 1951, Duplan 1952, Duplan and Gravelle 1960, Clinckx 1973, Lekine *et al.* 1981, Saou *et al.* 2012), the plain of the lower Soummam is an alluvial depression located between the northern and the southern Tell. It is of great complexity due to the superposition of geological units that characterizes the geology of northern Algeria. The area of the Soummam catchment is composed of Oligocene formations crossed by Lower Cretaceous. The downstream portion is of Miocene formations. Except for the Sidi Aïch region, the rest of the Soummam Wadi is composed of alluvial terraces. The right side of the Soummam catchment is mostly composed of Lower Cretaceous deposits. The soil is generally impervious, containing Oligocene argillaceous sandstones, Albo-Aptian schist and Cretaceous marl limestones (Fig. 2) (Duplan 1952). The geological section to the south of El Kseur city shows that Quaternary alluvium and Miocene conglomerates have a thickness ranging from 40 m to over 45 m at the level of the D13 drilling (Fig. 3) (Duplan 1952). In the south, Jurassic and Cretaceous formations are mainly observed in the Babors Mountains. In the north, these formations are observed in the Gouraya–Aghbalou and Akfadou–Taourirth Ighil Mountains. The Jurassic formation is composed of limestone, dolomite, shale and marl. The Mio-Pliocene formation consists of limestone, sandstone, clay and conglomerates (Fig. 3). A piezometric survey shows a flow direction from west to east towards the Mediterranean Sea, which constitutes the main outlet of the Soummam aquifer. Generally, the aquifer has good hydrodynamic characteristics (Clinckx 1973). The highest permeability value, reaching 5.1×10^{-4} m s^{-1}, is found in the western zone. Lower values are found in the eastern zone. The transmissivity varies from upstream to downstream, ranging from 1.98×10^{-1} to 10^{-2} m^{2}s^{-1} (Saou *et al.* 2012).

3 Materials and methods

3.1 Water sampling and analytical methods

The sampling locations of the wells (18 groundwater monitoring points) are illustrated in Figure 1. The wells are located at various sites: schools and universities, parks, industrial companies, public institutes, private residential houses and other public

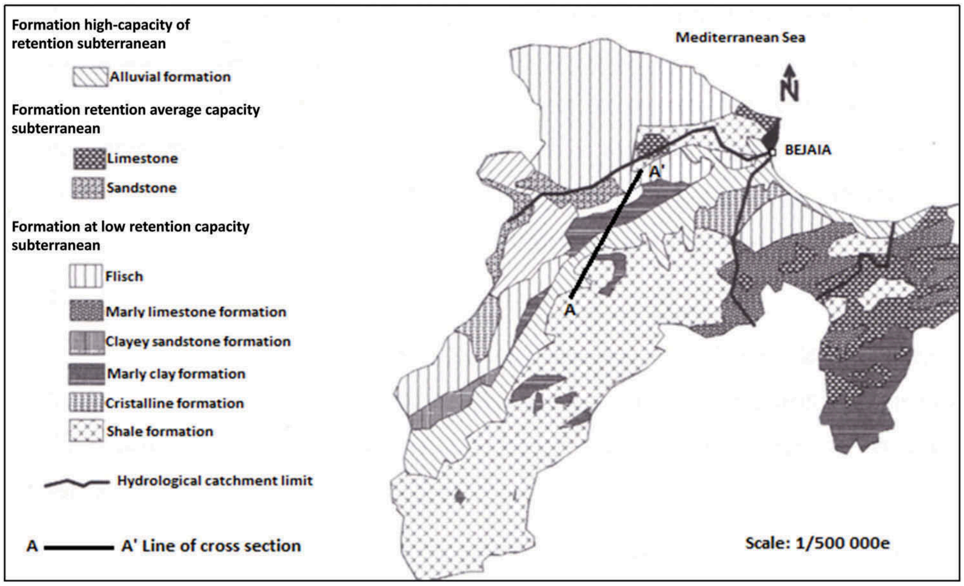

Figure 2. Hydrogeological map of the alluvial aquifer of the lower Soummam (Clinckx 1973) showing the cross-section AA′ which allowed the drawing of Figure 3.

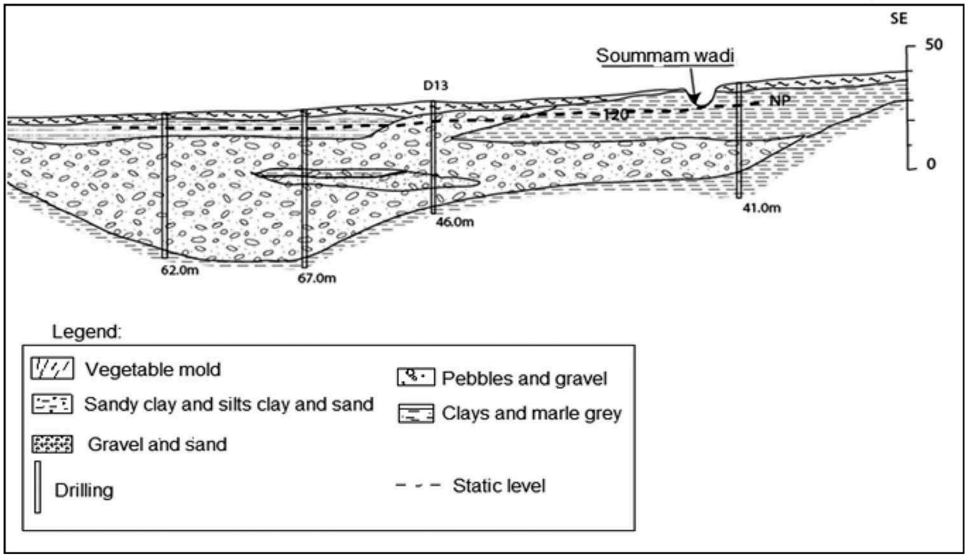

Figure 3. Southeast lithological cross-section through the study area. The location of the cross-section is indicated on Figure 2.

places. The coordinates of each station were determined using the Global Positioning System (GPS) and are depicted in Table 1. The wells currently in use were selected based on a preliminary field survey, taking into account the overall distribution of various types of wells in the study area compared to the diversity of human activities. The wells were also chosen according to multi-parametric criteria: groundwater level, electrical conductivity and their location relative to wastewater discharges. Most of these wells supply water for drinking, irrigation and industrial uses. Most of the groundwater wells are situated in the immediate vicinity of streams. The depths of these wells vary from 5 to 65 m and the elevation of the water table closely follows the land surface topography (Fig. 3). The existing aquifer is mainly recharged through runoff events. Samples were collected following a 10-minute pumping until the electrical conductivity (EC) and pH values had stabilized.

The sampling process was carried out during the 2002–2006 period according to two sampling campaigns per year; that is, January–February (high water period) and April–May (low water period). The analyses were performed on 14 ions: K^+, NO_3^-, NO_2^-, Ca^{2+}, HCO_3^-, Na^+, Cl^-, SO_4^{2-}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Fe^{2+} and Sr^{2+}, corresponding to the high water period and 8 ions: K^+, NO_3^-, Ca^{2+}, HCO_3^-, Na^+, Cl^-, SO_4^{2-} and Mg^{2+}, corresponding to the low water period. The difference between the numbers of aforementioned measured ions is justified by the fact that at low and high water periods an ion's dissolution in groundwater is affected during periods of high water corresponding to aquifer recharge. The elevated water velocity during flooding will cause re-suspension of previously deposited ions. During this period, a dilution process takes place. Furthermore, the undetected concentrations of some ions, in the low water period, were below the detection limit (noted b.d.l. in Tables 3 and 4) of the measurement devices. Analytical methods used in this study are summarized in Table 2. For each analysed parameter, the mean values of the temperature, pH, electrical conductivity, dissolved oxygen, 5-days biological oxygen demand (BOD_5), and chemical oxygen demand (COD) parameters are presented in Table 3. Two extreme values (minimum and maximum), the average values and the standard deviations of chemical parameters are given in Table 4. It seems clear from the field measurements and laboratory analysis that physical values and concentrations of major elements do not undergo significant change over the 5 years of monitoring (2002–2006). For this reason, the results of the five campaigns of high water period and the five campaigns of low water period were combined into one.

Table 1. Sampling stations (wells) in lower Soummam.

Sampling station	Relative location	Longitude (UTM*)	Latitude (UTM*)
1	HM20 REMILA	653300	4054200
2	Q7 VSA	656700	4055300
3	T8 ABANE	658700	4056400
4	ADEKAR (275)	659700	4055900
5	W2/3	660200	4056400
6	BC9 MAOUCHI	661300	4056300
7	F6 BARBACHA	666000	4057200
8	DE3 EL KSEUR	667600	4057400
9	G5 ROMPEAU	666400	4058500
10	I2/3 DECAILLET	669000	4058700
11	L5 LARBAA	670500	4059200
12	PUITS N°3	669500	4059800
13	HM 24	672000	4061300
14	F6 MOUSTACHE	672400	4061500
15	PUITS GH7	674600	4063300
16	PUITS KHEIRDDINE	676300	4063200
17	CEVITAL 1	678300	4063400
18	CEVITAL 2	678600	4063600

*UTM: Universal Transverse of Mercator.

3.2 *Multivariate statistical analyses*

In general, PCA and FA are useful tools and have been widely used for groundwater quality exploration (Usunoff and Guzman-Guzman 1989, Laaksoharju *et al.* 1999, Suk and Lee 1999, Anazawa *et al.* 2003, Güler and Thyne 2004, Anazawa and Ohmori 2005, Sing *et al.* 2005, Venugopal *et al.* 2009). PCA/FA seeks to establish combinations of variables capable of describing the principal tendencies observed

Table 2. Groundwater quality parameters, units and methods of analysis (water temperature, pH and EC measurements were performed *in situ*).

Symbol	Units	Test parameter	Analytical method
WT DD	°C	Water temperature	Mercury thermometer
pH	pH unit	pH	pH-meter
EC	$\mu S\ cm^{-1}$	Electrical conductivity	Electrometric
DO	$mg\ L^{-1}$	Dissolved oxygen	Winkler azide method
BOD_5	$mg\ L^{-1}$	Biochemical oxygen demand	Winkler azide method
COD	$mg\ L^{-1}$	Chemical oxygen demand	Dichromate reflex method
K^+	$mg\ L^{-1}$	Potassium	Flame AAS
NO_3^-	$mg\ L^{-1}$	Nitrate nitrogen	Spectrophotometric
NO_2^-	$mg\ L^{-1}$	Nitrite	Spectrophotometric
Ca^{2+}	$mg\ L^{-1}$	Calcium	Flame AAS
Na^+	$mg\ L^{-1}$	Sodium	Flame photometer
HCO_3^-	$mg\ L^{-1}$	Bicarbonate	Titrimetric
Cl^-	$mg\ L^{-1}$	Chloride	Spectrophotometric
SO_4^{2-}	$mg\ L^{-1}$	Sulphate	Spectrophotometric
Mg^{2+}	$mg\ L^{-1}$	Magnesium	Flame AAS
Cd^{2+}	$mg\ L^{-1}$	Cadmium	Inductively coupled plasma mass spectrometry
Pb^{2+}	$mg\ L^{-1}$	Lead	Inductively coupled plasma mass spectrometry
Zn^{2+}	$mg\ L^{-1}$	Zinc	Inductively coupled plasma-mass spectrometry
Fe^{3+}	$mg\ L^{-1}$	Iron	Inductively coupled plasma mass spectrometry
Sr^{2+}	$mg\ L^{-1}$	Strontium	Inductively coupled plasma mass spectrometry

Table 3. Average hydrochemical data from 18 groundwater monitoring wells in lower Soummam for the periods of high (HW) and low (LW) water (average over 5 years from 2002 to 2006).

Sample no.	*T* initial (°C)		pH		EC ($\mu S\ cm^{-1}$)		Dissolved O_2 ($mg\ L^{-1}$)		BOD_5 ($mg\ L^{-1}$)										COD ($mg\ L^{-1}$)	
									1 day		2 days		3 days		4 days		5 days			
	< 25°C		6.5–9		<2800 ($\mu S\ cm^{-1}$)		> 5 ($mg\ L^{-1}$)		25 ($mg\ L^{-1}$)										20 ($mg\ L^{-1}$)	
Standards	HW	LW	HW	LW	HW	LW	HW	LW	HW	LW	HW	LW	HW	LW	HW	LW	HW	LW	HW	LW
1	20.1	21.2	7.21	7.04	3220	3160	8.04	9.01	14	16	14	16	14	16	14	16	**14**	**16**	43	57
2	21.2	22.3	7.24	7.21	3010	2900	**9.60**	**9.98**	4	6	4	6	4	6	4	6	6	8	30	28
3	20.3	20.3	7.05	**6.98**	3050	2900	7.42	7.61	4	6	4	6	4	6	4	6	4	6	45	53
4	21.2	20.2	7.32	7.04	2645	2470	8.12	8.26	2	4	2	4	2	6	4	6	4	4	38	49
5	21.0	21.1	7.24	7.01	3420	3310	7.65	7.74	8	10	8	10	8	10	10	12	10	12	42	43
6	22.2	21.2	7.12	7.08	3942	3740	8.56	8.95	2	2	2	2	2	4	2	4	2	4	**04**	**06**
7	20.4	19.3	7.20	7.80	**3970**	**3960**	9.01	9.30	4	6	4	6	4	6	4	6	4	6	20	b.d.l.
8	20.5	21.3	7.08	7.06	3030	2900	7.75	7.83	4	6	4	6	6	6	6	6	6	6	23	b.d.l.
9	21.2	22.0	7.05	7.01	2450	2310	7.24	7.45	4	4	4	4	4	4	4	4	4	4	24	28
10	**22.4**	22.0	**7.01**	6.99	1920	1843	7.14	7.24	4	6	4	6	4	6	4	6	6	8	22	25
11	20.6	21.6	7.20	7.10	2396	2180	8.68	8.77	8	8	8	8	8	8	8	8	8	8	**68**	**72**
12	21.2	19.4	7.11	7.05	**1453**	1332	6.98	7.04	8	6	8	8	8	8	8	8	8	8	34	38
13	20.5	21.6	7.17	7.07	1657	1546	**6.13**	**6.48**	2	4	2	4	2	4	2	4	2	6	18	20
14	21.3	21.2	7.30	7.20	2865	2750	6.96	7.03	2	4	2	4	2	4	4	6	6	6	24	29
15	20.2	**19.1**	7.14	7.08	1934	1830	7.01	7.16	4	6	6	6	4	6	4	6	6	6	20	22
16	**19.5**	19.2	7.16	7.11	2430	2140	6.42	6.62	2	4	4	4	2	4	4	6	6	6	33	38
17	22.2	**23.9**	**7.43**	**7.32**	2328	2220	8.02	8.22	2	4	2	4	2	4	2	4	4	6	17	b.d.l.
18	22.3	22.1	7.25	7.03	1931	3150	8.07	8.19	2	4	4	4	4	4	4	4	6	6	31	23

The values of all variables are in $mg\ L^{-1}$ except for *T* (temperature), EC (electrical conductivity) and pH, which are measured in degrees Celsius, microsiemens per centimetre and pH units.

Underlined and bold values represent the maximal and minimal results.

b.d.l.: In general, values below detection limit.

while studying a given matrix (Jackson 1991, Jeong 2001a, Bengraine and Marhaba 2003, Farnham *et al.* 2003). The technique is extracting the eigenvalues and eigenvectors from the covariance matrix of original variables (Brown 1998). The principal components (PCs) are the uncorrelated (orthogonal) variables obtained by multiplying the original correlated variables by the eigenvectors (loadings or weightings).The participation of the original variables in the PCs is given by the loadings, and the individual transformations are called scores (Sabater *et al.* 1990, Reed *et al.* 1998, Hoffman and Lieberman 2000). The factor loading can be used to determine the relative importance of a variable as compared to other variables in a component. Positive values for each component are related to important contributions and the negative values correspond to minor contributions. To reduce the overlap of original variables over each principal component, a varimax rotation was conducted (Helena *et al.* 2000). The Kaiser criterion (Kaiser 1960) was applied to determine the total number of factors for each dataset in this analysis. Following the criteria of Cattell and Jaspers (Huntley *et al.* 1995), only factors with eigenvalues greater than or equal to 1 will be accepted as possible sources of variance in the data, with the highest priority ascribed to the factor that has the greatest eigenvector sum (cumulative variance). According to

Table 4. Statistical summary of average hydrochemical parameters of groundwater for periods of high (HW) and low (LW) water (average values over 5 years from 2002 to 2006 and 18 wells).

Variables	Standards	Observation	Obs. without missing data	Minimum		Maximum		Mean		Standard deviation	
				HW	LW	HW	LW	HW	LW	HW	LW
K^+(mg L^{-1})	12 (mg L^{-1})	18 × 5	18 × 5	3.20	5.60	10.300	12.60	6.889 ^{a*}	8.361 ^{b*}	1.883	2.057
NO_3^-(mg L^{-1})	50 (mg L^{-1})	18 × 5	18 × 5	0.000	0.00	72.000	30.00	9.878 ^{a*}	5.765 ^{b*}	20.289	10.319
NO_2^-(mg L^{-1})	0.1 (mg L^{-1})	18 × 5	18 × 5	0.000	b.d.l.	0.011	b.d.l.	0.002 ^{a*}	b.d.l.	0.03	b.d.l.
Ca^{2+}(mg L^{-1})	75 (mg L^{-1})	18 × 5	18 × 5	92.980	200.40	264.520	298.19	188.637 ^{a*}	240.531 ^{ab*}	43.516	33.950
Na^+(mg L^{-1})	200 (mg L^{-1})	18 × 5	18 × 5	72.390	66.47	310.200	386.40	150.098 ^{a*}	216.159 ^{ab*}	77.273	98.013
HCO_3^-(mg L^{-1})	180 (mg L^{-1})	18 × 5	18 × 5	219.600	311.10	451.400	506.30	349.593 ^{ab*}	371.382 ^{ab*}	58.106	54.587
Cl^-(mg L^{-1})	250 (mg L^{-1})	18 × 5	18 × 5	134.900	177.50	340.800	340.80	287.944 ^{ab*}	308.224 ^{ab*}	59.289	43.046
SO_4^{2-}- (mg L^{-1})	250 (mg L^{-1})	18 × 5	18 × 5	205.500	230.00	1278.000	1210.00	600.725 ^{a*}	657.647 ^{a*}	290.825	304.716
Mg^{2+}(mg L^{-1})	50 (mg L^{-1})	18 × 5	18 × 5	7.680	57.36	95.880	145.68	59.673 ^{b*}	82.566 ^{b*}	23.926	25.410
Cd^{2+}(mg L^{-1})	0.003 (mg L^{-1})	18 × 5	18 × 5	0.084	b.d.l.	0.106	b.d.l.	0.093 ^{b*}	b.d.l.	0.006	b.d.l.
Pb^{2+}(mg L^{-1})	0.01 (mg L^{-1})	18 × 5	18 × 5	0.232	b.d.l.	0.819	b.d.l.	0.625 ^{b*}	b.d.l.	0.159	b.d.l.
Zn^{2+}(mg L^{-1})	3 (mg L^{-1})	18 × 5	18 × 5	0.001	b.d.l.	0.055	b.d.l.	0.013 ^{b*}	b.d.l.	0.012	b.d.l.
Fe^{3+}(mg L^{-1})	0.2 (mg L^{-1})	18 × 5	18 × 5	0.242	b.d.l.	0.548	b.d.l.	0.390 ^{b*}	b.d.l.	0.093	b.d.l.
Sr^{2+}(mg L^{-1})	–	18 × 5	18 × 5	0.130	b.d.l.	1.630	b.d.l.	0.875 ^{b*}	b.d.l.	0.384	b.d.l.

*Levels not connected by same letter are significantly different (comparisons for all pairs using Tukey-Kramer HSD; HW: $q^* = 3.66041$ and $\alpha = 0.05$, LW: $q^* = 3.46212$ and $\alpha = 0.05$)

Obs.: Observations

b.d.l.: In general, values below detection limit.

Liu *et al.* (2003), factor loadings were classified as "strong", "moderate", and "weak" corresponding to absolute loading values of >0.75, 0.50–0.75, and 0.30–0.50, respectively.

PCA/FA was conducted taking into account the 14 and 8 hydrochemical variables cited above and measured, respectively, for the high and low water periods. Before the PCA/FA analysis, the Kaiser–Meyer–Olkin method (KMO) and Bartlett's test were performed on the dataset (Sabater *et al.* 1990). PCA/FA, followed by a *post-hoc* analysis (Tukey HSD) to compare means, was applied in order to recognize and classify groundwater. Relationships between the considered variables were tested using Pearson's coefficient as a non-parametric measure with statistical significance set *a priori* at $p < 0.05$ (Alkarkhi *et al.* 2008, Li *et al.* 2008). Analysis of variance (ANOVA) was used to classify and test the significance ($p < 0.05$, least-significant difference, LSD) of the systematic factors that are statistically responsible for the dataset's variability. FA of chemical data was used to quantify the contributions of natural chemical weathering and anthropogenic contributions to the chemical composition of groundwater in the lower Soummam catchment.

All mathematical and statistical calculations were implemented using Statistica 8 software. For the Tukey–Kramer HSD (honestly significant difference) test, JMP7 software was used, and for Piper diagram and hydrochemistry parameters, Diagrammes 5.8 software (chemistry multilanguage, Roland Simler, Laboratory of Hydrogeology, Avignon) was used.

4 Results and discussion

4.1 Exploratory analysis of hydrochemical data

Table 3 shows the mean measurements and results of chemical analyses performed on samples in 18 wells during the 2002–2006 period. Table 4 summarizes the mean, minimum, and maximum values with the standard deviations for both the 14 and the 8 hydrochemical variables measured at the same wells. Multiple comparisons, using the Tukey–HSD method, revealed the means for major ions, including $K^+, NO_3^-, Ca^{2+}, Na^+$, which show a very high variance, and were significantly different at $p < 0.05$ among the groundwaters during the 5 years. All results were compared to World Health Organization limits (WHO 1998, 2000) which are also used as drinking water standards in Algeria. The results reflect the fact that hydrochemical data are affected by the diversity of natural and anthropogenic factors.

4.1.1 pH

The examined groundwater was in the alkaline pH range, with negligible variations. All pH values are in the range of WHO limits (WHO 1998, 2000) for drinking water. In comparison, for a given well, pH values in low water were found to be smaller than those of high water, in which the maximum values are 7.32 and 7.43 for low water and high water periods, respectively. It should be noted that these two values were given by the same well (well 17), whilst the minimum pH values were recorded in two different wells (well 10 for HW and well 3 for LW). The pH variations and dissolved oxygen (DO) levels simultaneously regulate most of the chemical reactions affecting water composition.

4.1.2 Electrical conductivity

The EC measurement provides an indication of ion concentration. As in the case of pH, a similar trend was observed. The highest values were found in well 7 in low and high water periods (3960 and 3970 µS cm^{-1}), whereas the lowest values were obtained in well 12 (1332 and 1453 µS cm^{-1}). Figure 4(a) and (b) illustrates this spatial distribution in the study area. The highest values of EC (>2800 µS cm^{-1}) are for locations at the upstream of the lower Soummam catchment. In contrast, the values of EC in the downstream decreased slightly. About 45% of the values were above the standard (2800 µS cm^{-1}). Similar behaviour exists in low and high water periods, where 11% of samples are in the range of 750–1750 µS cm^{-1} and are therefore of good quality. Over 88% of samples have high EC (>1750 µS cm^{-1}). According to Nisbet and Verneaux (1970), the values that show strong mineralization are due to residual

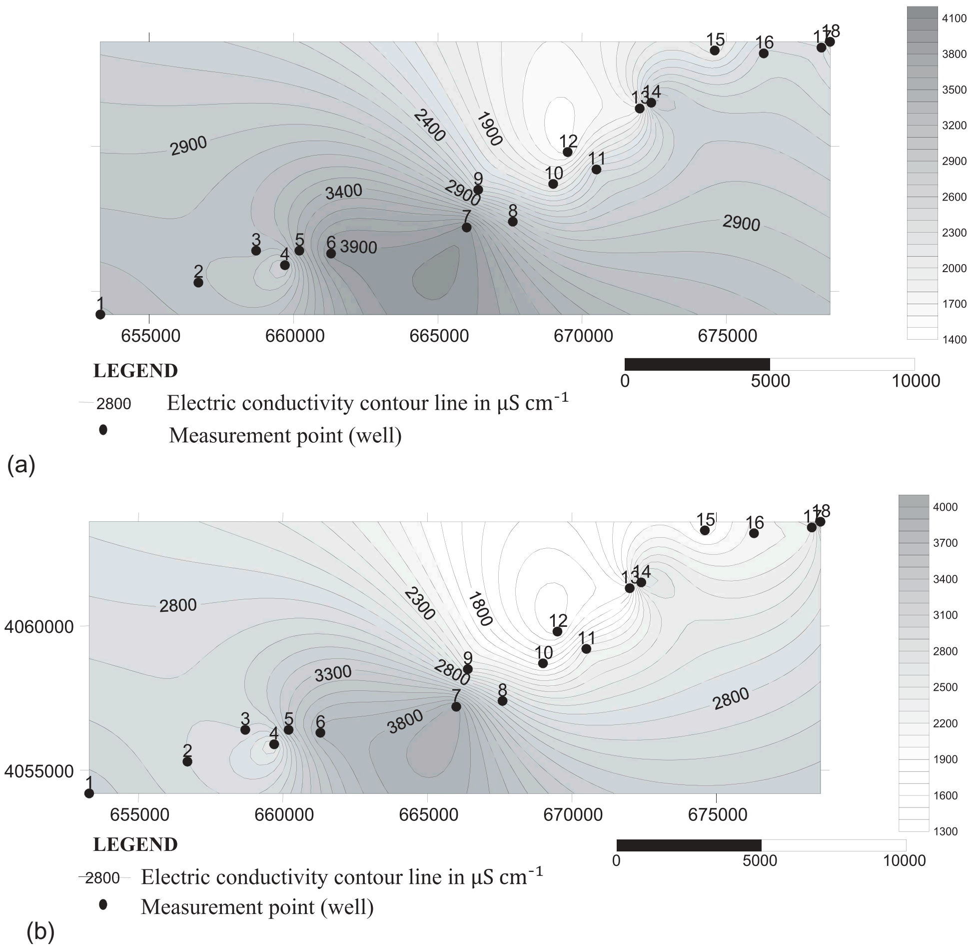

Figure 4. Spatial distribution of average EC (µS cm^{-1}) for high (a) and low (b) water periods.

wastewater rich in artificial fertilizers from industrial activities and by the strong mineralization of organic load. Indeed, the upper catchment is experiencing high mineralization due to organic load from intense human activity (dairy and derivatives industry).

4.1.3 *Dissolved oxygen*

The DO is the most important component of groundwater that initiates self-purification processes. The DO concentration varied from 6.13 to 9.60 mg L^{-1} and 6.48 to 9.98 mg L^{-1} in high and low water periods, respectively. The DO concentrations of more than 5 mg L^{-1} indicate an oxygenated groundwater environment. The DO in the examined groundwater showed large variations. These variations are spatial rather than temporal. Lower values were recorded during the warm periods. From upstream to downstream, all values are high and above the standard.

4.1.4 *Organic loading*

The BOD$_5$ levels were found to be low in all groundwater samples. In contrast, the COD values indicated another distribution, showing high values in most analysed samples, and exceeding the allowable standard of 20 mg L^{-1}. More than 80% of samples exceeded the standard. The values are in the range of 6 to 72 mg L^{-1} at the low water period and from 4 to 68 mg L^{-1} at high water period. These values decreased from upstream to downstream. The calculated ratio of COD/BOD$_5$ gave values ranging between 1.5 and 12.25. Samples containing biodegradable effluents had a COD/BOD$_5$ ratio less than 2.95. They represent only 5–6% of all samples. Ninety-four per cent of samples had a ratio greater than 3, indicating that the effluent is hardly biodegradable. The values above the standards were recorded during the campaigns carried out at the low water period and situated in the downstream of the catchment.

4.1.5 *Speciation of nitrogen*

In nearly all monitoring sites, NO_3^- is the dominant soluble form of nitrogen. Mean values of nitrates were lower than the standard (Meybeck 1982, 1998). Nevertheless, all mean concentrations were lower than the maximum permissible concentration for drinking water, and thus they could be classified as unpolluted groundwater (Jarvie *et al.* 1998). A high mean nitrate concentration was observed in the two wells 7 and 16 with 57 and 72 mg L^{-1}, respectively. In this study area, the industrial and agricultural activities are intense. Wastewater discharges produced by these activities are carried by infiltration during the groundwater recharge of the aquifer at times of high water (Chapman and Kimstach 1996). Chemical fluctuations in shallow groundwater typically result from different cumulative effects such as land use and associated chemical concentration in the topsoil, net vertical recharge (affected by leaching rainfall), local depth to groundwater, and lateral recharge from ground or surface water sources (Munoz-Carpena *et al.* 2005).

4.1.6 Major cations and anions

The analytical results present the abundance of the major cations in the following order $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$, and in all samples Ca^{2+} exceeded the admissible limit for drinking water (75 mg L^{-1}) (Fig. 5(a)). However, Mg^{2+}exceeded the admissible limit (50 mg L^{-1}) in 67% of samples (Fig. 5(b)). Only Ca^{2+} concentrations are about three times higher than that of Mg^{2+} in the low Soummam groundwater. This is because the major element chemistry of Soummam is mainly controlled by rock weathering, with Ca^{2+} dominating the major ion composition. Calcium is one of the major carbonate rock elements (limestone [$CaCO_3$], dolomite [$(Ca, Mg)CO_3$] and chalk [$CaCO_3$]). It is also abundant in other types of sedimentary rocks such as gypsum [$CaSO_4{\cdot}2(H_2O)$].

The Na^{+} concentrations in groundwater samples in the lower Soummam were of the order of 72.4–66.5 mg L^{-1} and 310.2–386.4 mg L^{-1} in high and low water periods, respectively. The highest concentration (300 mg L^{-1}) was observed in well 6 and the lowest one (75 mg L^{-1}) in well 12 (Fig. 5(c)). Sources for these ions are likely to be related to human activities, effluent from industrial facilities, leachate from municipal landfills, and some agricultural chemicals. Natural sources included rock–water interactions.

From a chemical standpoint, magnesium is similar to calcium. It is often present in carbonate rocks (dolomitic limestone, dolomite), evaporite rocks (magnesium salts [$MgSO_4$]), and magmatic rocks. The magnesium minerals are less soluble than calcium-containing minerals.

The analytical results present the abundance of the major anions in the following order: $SO_4^{2-} > HCO_3^{-} > Cl^{-}$; and in all samples, SO_4^{2-}(Fig. 5(d)) and HCO_3^{-} (Fig. 5(e)) exceeded the admissible limit of 250 mg L^{-1} and 180 mg L^{-1}, respectively, whereas Cl^{-} exceeded the admissible limit of 200 mg L^{-1} in 89% of samples (Fig. 5(f)). The potential sources of SO_4^{2-} include atmospheric sulfur deposition, the dissolution of sulfate mineral such as gypsum ($CaSO_4{\cdot}2(H_2O)$) and the oxidation of sulfide minerals (Jeong 2001b). In this case, the sulfate content is very high. Figure 6(a) and (b) illustrates the spatio-temporal variation of the sulfate content in the periods of high and low water, respectively. All values are above the standard. However, the change is important from one site to another. Values change very little between high and low water periods. However, from upstream to downstream, the sulfate concentrations are higher than those of the 2005 and 2006 periods. These two years were particularly wet. In general, the high values were localized downstream of industrial activities. In addition, high values are likely to be related to either the populated urban centres or geological features of the soil.

The bicarbonate ions are formed from the dissolution of carbonate minerals by meteoric waters that load CO_2 during their percolation through the soil. Whatever the lithology, chloride levels are generally low in groundwater.

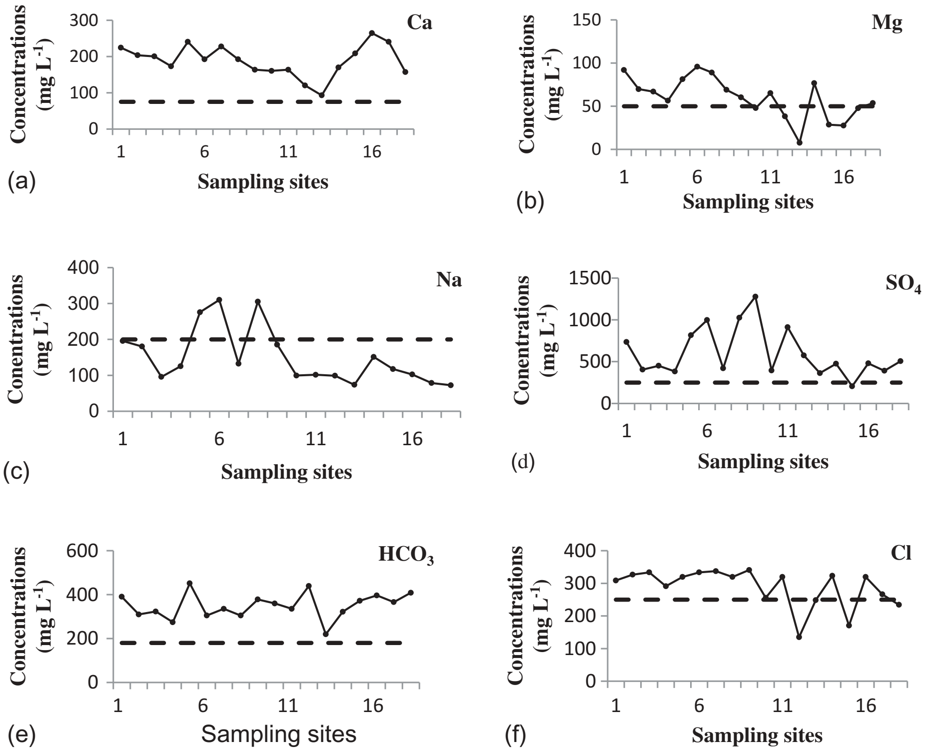

Figure 5. Spatial variations of some mean original variables (—) associated with groundwater pollution compared to standard (----): (a) calcium, (b) magnesium, (c) sodium, (d) chloride, (e) bicarbonate, (f) sulfate.

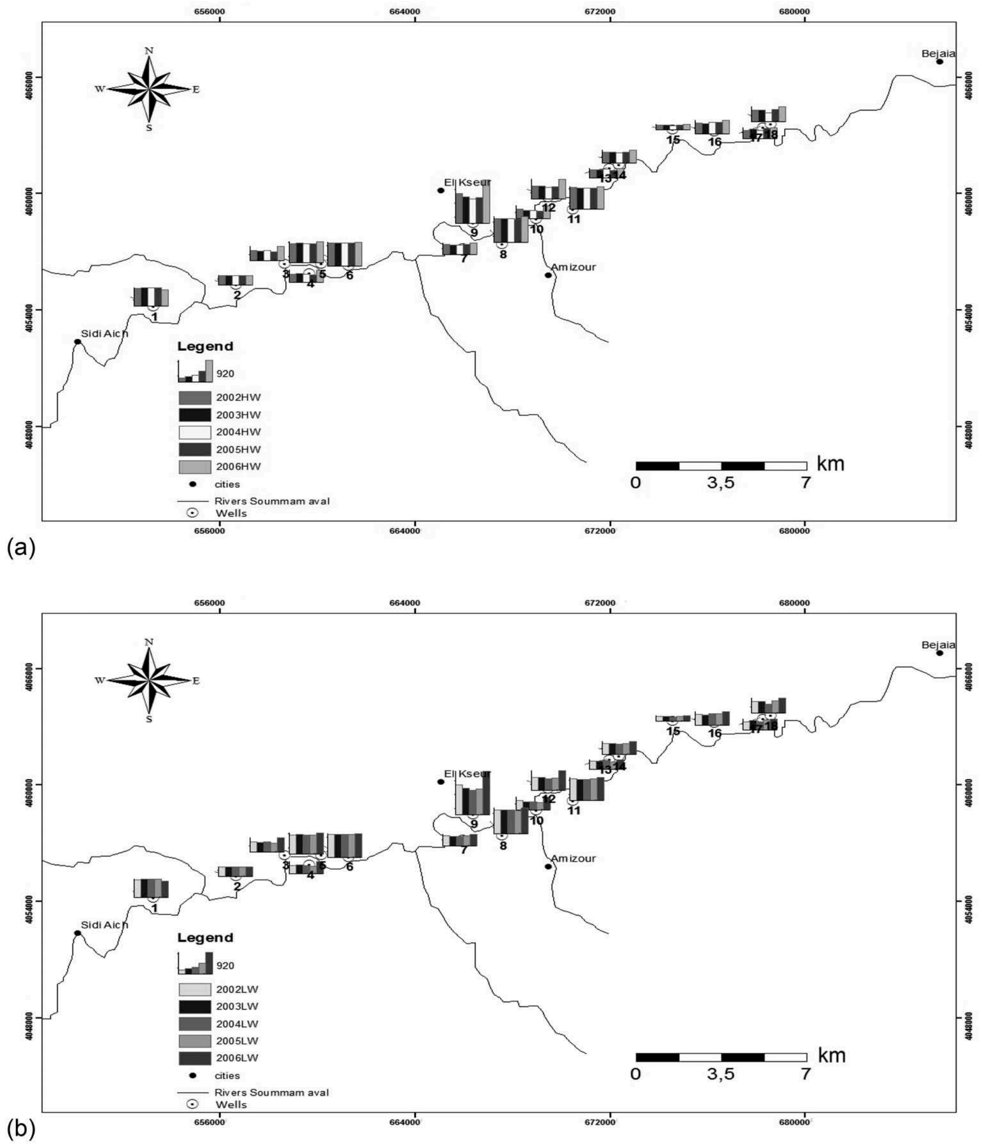

Figure 6. Column diagram showing the spatio-temporal variability of SO_4^{2-} ions (mg L^{-1}) during high (a) and low (b) water periods.

The relatively high concentrations of Cl^- in groundwater reflect inflow of surface water into the aquifer or anthropogenic effects, derived from application of chemical fertilizers and manure for cultivation mainly along the stream (Lee *et al.* 2005). Hamamo *et al.* (1995) showed that Cl^- concentrations in super phosphate and triple super phosphate fertilizers ranged from <50 mg kg^{-1} to 6.18% (by weight) in the solid phase, with a median concentration of 112 mg kg^{-1}. Such large concentrations of chlorine in the fertilizer may be partly responsible for the increase of Cl^- in tile drainage from agricultural fields. The dissolution of halite (NaCl) or the presence of a salt intrusion (coastal aquifer) can eventually lead to high levels of chlorides.

All the above-mentioned geological formations (conglomerate, clay and marl, limestone, carbonate and marl, carbonate and sandstone, sandstone and marl, carbonate, marl, evaporite) are present in the lower Soummam catchment (Fig. 2) and may explain the presence of the ions Ca^{2+}, $Na^+, Mg^{2+}, SO_4^{2-}, HCO_3^-$ and Cl^-. There were large variations in the major-elements contents in the groundwater. The curves of $Ca^{2+}, Na^+, Mg^{2+}, SO_4^{2-}, HCO_3^-$ and Cl^- concentrations show that (i) high concentrations were measured between wells 1 to 12; (ii) concentrations of these elements decreased until well 12 and then increased again until the estuary. This spatial distribution reflects water–rock interactions.

4.1.7 Heavy metals

The mean concentrations of some heavy metals $Cd^{2+}, Pb^{2+}, Zn^{2+}$, Fe^{2+} and Sr^{2+} show significant variation between all monitoring sites. As observed, the curve of Cd^{2+} (Fig. 7(a)) was high but relatively stable. By contrast, the curve of Pb^{2+} (Fig. 7(b)) increased in all sites. High values of Cd^{2+}, Pb^{2+}, Fe^{2+} and Sr^{2+}, exceeding accepted standards for drinking water (WHO 1998, 2000), were observed in almost all wells. The mean concentrations of Zn^{2+} showed little variation between different monitoring sites and were below the acceptable standard. The concentrations increased from upstream to downstream until the estuary, suggesting a more important influence of geological

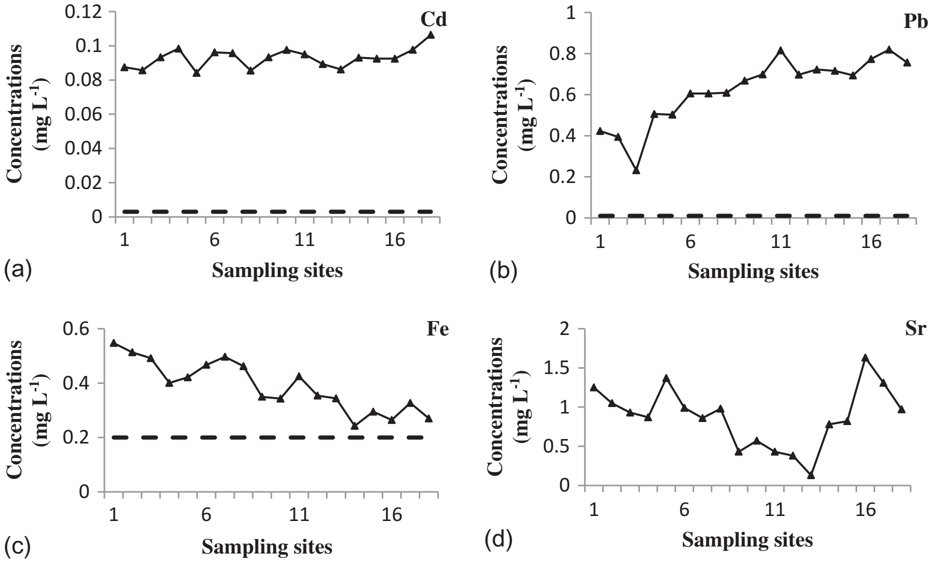

Figure 7. Spatial variations of some mean original variables (—) associated with groundwater pollution compared to standard (----): (a) cadmium, (b) lead, (c) iron, (d) strontium (standard unregulated for Sr).

deposits than pollution point sources. Being an element often associated with evaporates, strontium may originate from strontianite ($SrCO_3$) dissolution (Carré 1975) or from celestite ($SrSO_4$), a mineral commonly associated with gypsum (Saou *et al.* 2012). According to Carré (1975), strontium is not commonly discussed because the available data are scarce. Indeed, it does not appear in any list of elements of risk and is not subject to any concern. However, according to Hem (1985), the strontium concentration in natural waters (surface and groundwater) is of the order of 100 μg L^{-1}, although there are cases where it exceeds 1 mg L^{-1}. A maximum of 52 mg L^{-1} for drinking water has been documented in the United States (Hem 1985).

The high concentration of Fe^{2+} (Fig. 7(c)) in sampled waters cannot be due exclusively to anthropogenic activities, but may also have a natural origin.

Except for Zn^{2+} (Fig. 7(d)), all concentrations of heavy metals were observed only after flood events in the high water period. It is worth highlighting that, except for the present analyses, no work has been done on wastewater discharges in industrial and agricultural activities in the Soummam valley. The concentrations of major elements did not undergo significant variation during the 10 seasons (2002–2006). For this reason, the 10 sampling campaigns were merged into one.

4.2 Classification of main hydrochemical facies using the Piper diagram

The chemical nature of the studied groundwater is shown in the Piper diagram (Piper 1944) (Fig. 8(a) and (b)) which is based on the relative concentrations of the main anions and cations measured during the high and low water periods. The Piper trilinear diagram for the study area shows that there were two types of water with variable concentrations of major ions. These are $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ type water and $SO_4^{2-} > HCO_3^{-} > Cl^{-}$ type water, with relatively high concentrations of nitrate, sulfide and chloride. Four hydrochemical facies in groundwater have been identified, namely:

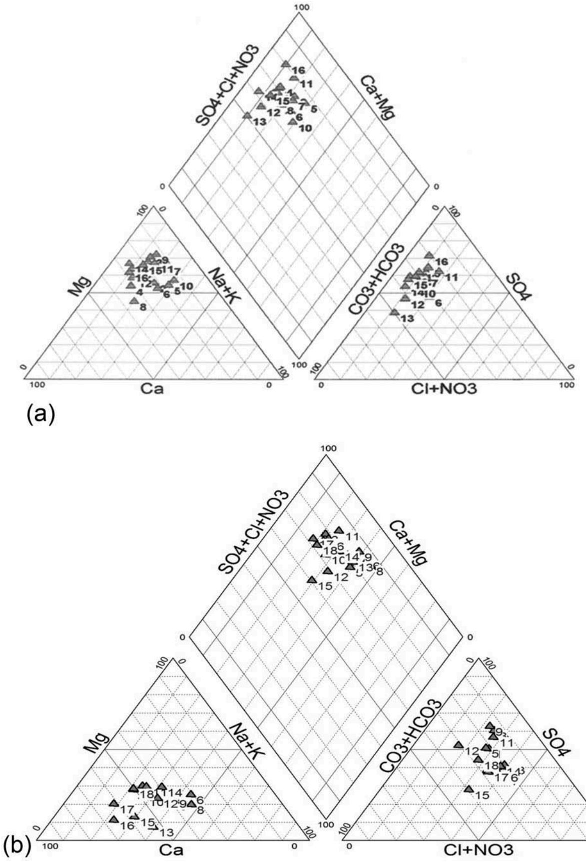

Figure 8. Piper plot showing all the groundwater samples from the dataset grouped according to their subtype in the lower Soummam catchment for the low (a) and high (b) water periods.

- The calcium bicarbonate facies has been localized at the upstream of the catchment;
- The calcium sulfate facies has been localized only in the northeast of the aquifer, near Jebel Aghbalou–Gouraya where evaporitic formations are absent;

- The sodium chloride facies has been found in the centre of the aquifer (El Kseur zone);
- The calcium chloride facies has been found near the aquifer downstream boundaries.

4.3 Correlations between variables

The relationships between variables of two periods (high and low water) were analysed by using the Pearson correlation matrix method. Because the 5-year monitoring sampling stations were combined to calculate the correlation matrix, the correlation coefficients should be interpreted with caution as they are simultaneously affected by spatial and temporal variations. The results are shown in Table 5 (a) and (b). Only results showing correlation values higher than 0.50 were considered (underlined values). The chemical element concentrations in groundwater do not interact with each other. On the contrary, they are often more or less correlated for physical or chemical reasons (Blum *et al.* 2001). The high degree of correlation between element concentrations suggests either a common or similar geochemical behavioural origin (Kucuksezgin *et al.* 2008). From Table 5a, corresponding to the high water period, it can be observed that there are strong relationships between zinc and potassium (0.87), strontium and potassium (−0.88), calcium and nitrite (0.93), strontium and sodium (0.9), and strontium and zinc (−0.73). For the low water period (Table 5b), high correlations exist between magnesium and calcium (0.79), sulfate and calcium (0.74), magnesium and sulfate (0.87), potassium and sodium (0.86), sulfate and sodium (0.89), sulfate and potassium (0.80), and finally sodium and chloride (0.67). Hakanson and Jansson (1983) suggested that even metals with quite different chemical properties "measured in laboratory" might appear with similar distribution patterns in nature. From the above results, it can be seen that the correlations between the elements are stronger in low waters in which the number of analysed parameters is less than that of high waters. Correlations between sulfate and calcium, on the one hand, and chlorides and bicarbonates, on the other hand, indicate that salinity could arise from saline formations such as gypsum. The absence of a strong correlation between other elements suggests that concentrations are not controlled by a single factor (Jain *et al.* 2005).

5 Origin of the spatio-temporal variability of the groundwater quality using PCA/FA

The KMO results of 0.730 and 1310.5 for the Bartlett chi-square statistic indicate that the degree of intercorrelation between variables and appropriateness of FA is middling. Table 6(a) and (b) summarizes the PCA results after rotation, including loadings, eigenvalues and the amount of variance. In these tables, the highest loadings, explaining the participation of each chemical component to each VF, are underlined. For the high water period, the output results for the chemical data are given in Table 6(a). In this analysis,

Table 5. Correlation matrix of the 14 and 8 physico-chemical parameters determined for periods of (a) high and (b) low water.

(a)

Parameter	K^+	NO_3^-	NO_2^-	Ca^{2+}	Na^+	HCO_3^-	Cl^-	SO_4^{2-}	Mg^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Fe^{3+}	Sr^{2+}
K^+	1													
NO_3^-	−0.409	1												
NO_2^-	0.168	−0.475	1											
Ca^{2+}	0.173	−0.386	0.934	1										
Na^+	−0.168	−0.057	0.530	0.396	1									
HCO_3^-	−0.517	0.630	−0.093	−0.088	0.355	1								
Cl^-	0.191	0.074	0.149	0.121	0.426	0.459	1							
SO_4^{2-}	−0.497	0.172	0.221	0.163	−0.030	0.662	0.149	1						
Mg^{2+}	−0.259	0.649	−0.160	−0.095	0.379	0.643	0.091	0.445	1					
Cd^{2+}	−0.631	0.450	−0.059	−0.170	−0.063	−0.451	0.057	0.631	0.459	1				
Pb^{2+}	0.423	−0.188	0.041	−0.016	−0.222	−0.328	0.125	−0.106	−0.186	−0.020	1			
Zn^{2+}	0.869	−0.168	0.179	0.217	−0.229	−0.398	−0.011	−0.364	0.005	−0.470	0.358	1		
Fe^{3+}	0.427	−0.313	−0.024	−0.024	0.219	0.475	−0.200	−0.275	−0.280	−0.361	0.284	0.521	1	
Sr^{2+}	−0.884	0.461	0.406	−0.175	0.901	0.292	0.370	0.452	0.281	0.638	−0.386	−0.727	−0.410	1

(b)

Parameter	Ca^{2+}	Mg^{2+}	Na^+	K^+	NO_3^-	HCO_3^-	Cl^-	SO_4^{2-}
Ca^{2+}	1							
Mg^{2+}	0.787	1						
Na^+	0.440	0.612	1					
K^+	0.590	0.605	0.857	1				
NO_3^-	0.515	0.590	0.591	0.659	1			
HCO_3^-	0.098	0.057	0.051	0.239	0.331	1		
Cl^-	0.352	0.407	0.668	0.637	0.317	−0.471	1	
SO_4^{2-}	0.734	0.868	0.891	0.799	0.610	0.025	0.569	1

Underlined values represent relevant correlations:
"Strong" correlation coefficient >0.75 (underlined values: statistically significant at the 0.05 level),
"Moderate" correlation coefficient 0.75–0.50,
"Weak" correlation coefficient 0.50–0.36.

Table 6. Initial eigenvalues greater than one, their percentage of variance explained by each other and cumulative percentage of variance (%CV) in the FA, determined from hydrochemical data (rotated component matrix) for the (a) high and (b) low water periods.

(a)

Hydrochemical item	VF1	VF2	VF3	VF4	VF5	Initial communalities	Final communalities	Specific variance
K^+	$\underline{0.653}$	−0.402	0.308	−0.143	−0.023	0.940	0.704	0.296
NO_3^-	−0.162	$\underline{0.899}$	0.141	0.248	−0.262	0.987	0.984	0.016
NO_2^-	−0.232	$\underline{0.775}$	0.254	0.232	−0.354	0.978	0.898	0.102
Ca^{2+}	0.401	$\underline{0.827}$	−0.100	−0.266	0.271	0.947	1.000	0.000
Na^+	$\underline{0.794}$	−0.050	0.303	−0.091	−0.077	0.960	0.739	0.261
HCO_3^-	$\underline{0.081}$	0.307	0.222	$\underline{-0.523}$	0.003	0.950	0.423	0.577
Cl^-	$\underline{0.616}$	0.267	0.045	$\underline{0.527}$	0.185	0.959	0.764	0.236
SO_4^{2-}	$\underline{0.599}$	−0.209	$\underline{0.669}$	0.079	−0.038	0.959	0.858	0.142
Mg^{2+}	$\underline{0.808}$	0.069	0.012	0.171	0.268	0.954	0.759	0.241
Cd^{2+}	−0.314	0.148	0.032	0.297	0.484	0.806	0.444	0.556
Pb^{2+}	$\underline{-0.632}$	0.061	$\underline{0.664}$	−0.044	0.206	0.953	0.888	0.112
Zn^{2+}	$\underline{-0.561}$	−0.080	0.130	0.032	0.320	0.781	0.441	0.559
Fe^{3+}	$\underline{0.728}$	−0.120	−0.287	0.168	−0.104	0.969	0.666	0.334
Sr^{2+}	0.420	$\underline{0.714}$	−0.155	−0.331	0.170	0.950	0.849	0.151
Eigenvalue	5.181	3.091	1.739	1.325	1.141			
% variance	34.543	20.609	11.595	8.836	7.604			
% CV	34.543	55.152	66.747	75.583	83.187			

(b)

Hydrochemical item	VF1	VF2	Initial communalities	Final communalities	Specific variance
Ca^{2+}	$\underline{0.653}$	−0.402	0.765	0.131	0.531
Mg^{2+}	−0.162	$\underline{0.899}$	0.849	0.074	0.420
Na^+	−0.232	$\underline{0.775}$	0.884	0.114	0.347
K^+	0.401	$\underline{0.827}$	0.898	0.069	0.311
NO_3^-	$\underline{0.794}$	−0.050	0.744	0.352	0.141
HCO_3^-	$\underline{0.081}$	0.307	0.090	0.942	0.221
Cl^-	$\underline{0.616}$	0.267	0.661	0.652	0.220
SO_4^{2-}	$\underline{0.599}$	−0.209	0.956	0.041	0.097
Eigenvalue	4.806	1.478			
% variance	60.072	18.478			
% CV	60.072	78.551			

Underlined values represent relevant correlations.

VF1 explains 34.5% of the variance, where $K^+, Na^+, Cl^-, SO_4^{2-}, Mg^{2+}, Pb^{2+}, Zn^{2+}$ and Fe^{2+} have an important contribution. Except for metals, all elements are positively correlated with factor 1 weighting. Thus, factor 1 represents the degree of overall mineralization of the groundwater. Such a fraction of the explained variance may partially imply the effect of water mineral reactions and anthropogenic activities (Pb^{2+}). Lead (Pb^{2+}) does not originate from one source only. It can be seen as a representation of "anthropogenic-toxic" pollution issuing from either metal activities or industrial effluents. This anthropogenic pollution might come from the heavy traffic of motor vehicles using the road lying alongside the river. Already, the low Soummam region harbours a high population density while being a tourist area. Each summer, the region receives 4 to 5 million tourists coming from other Algerian regions and abroad (DPAT 2010). Therefore, car traffic is important during that period. Lead could come from exhaust fumes, atmospheric deposition and transport by storm water runoff from upstream. Also, the lead may originate from abandoned mining works in the hills of the Amizour region, as indicated in Figure 1. It is noteworthy that both Pb^{2+} and Zn^{2+} had high loads in VF1, indicating that anthropogenic pollution and mineral rock erosion are probably their sources. In addition, the high contents of these metals found in some samples confirmed a point source. However, VF2, which explained 20.7% of the variance, describes the human pressure referred to previously (see Section 2), including NO_3^-, NO_2^-, Ca^{2+} and Sr^{2+} with high average concentrations that would be contained in untreated wastewater. This nutrient-type component may be interpreted as originating from agricultural and urban runoff. Calcium and strontium have a geological origin. VF1 and VF2 explain the major geochemical processes. Clearly, the principal process controlling groundwater hydrochemistry is the dissolution of chlorides, dolomite and evaporite in salt-rich zones. Domestic wastes are also a process that might contribute to the concentrations of these ions in groundwater. VF3 showed high loadings for SO_4^{2-} and Pb^{2+}; whereas VF4 showed high loadings for HCO_3^- and Cl^-, with variance of 11.6 and 8.8%, respectively. However, the fifth factor (VF5) does not constitute a source of explained variance in the groundwater hydrochemistry since it had no loading greater than 0.50; therefore, it was eliminated and only four factors were retained for varimax rotation. These four factors are assumed to represent adequately the overall variance of the data set.

For the low water period, the analysis results for the chemical data are given in Table 6(b). Only two factors (VF1 and VF2) had an eigenvalue more than 1, while the other factors contributed slightly to the explanation of the total variance. Both accounted for 78.55% of the total variance and have a high loading for VF1, which explains 60.07% of the variance, where Ca^{2+}, NO_3^-, Cl^- and SO_4^{2-} have an important contribution. VF2 explains 18.5% of variance and has a high loading for $Mg^{2+}, Na^+ and K^+$. The same chemical elements as those of the high water period are observed during the low water period, but in much smaller number because other elements not mentioned are below the detection limit. Their origins could be similar. The low water period corresponds to an evaporation phase. Therefore, high values of these constituents are most probably due to evaporation. All are positively correlated with VF1. Thus, VF1 represents the degree of groundwater mineralization. This, in turn, is affected by mineral dissolution and evaporation. Evaporation is believed to be the most important factor during the low water period. Both NO_3^- and Cl^- are the most significant contaminants associated with domestic wastewater. VF2 explained 18.5% of the total variance and had a high loading of Mg^{2+}, Na^+ and K^+. It may reflect the initial dissolution of minerals by groundwater.

5.1 Spatio-temporal characterization during the high water period

The graphic representation of observations (18 wells) and variables (14 elements) on the same factorial axis (Fig. 9) shows that axes 1 and 2 explained 55.15% of total variance (Table 6(a)). The first factorial axis represents 34.54% of total inertia. Table 7(a) summarizes the explanations of spatio-temporal characterization during high water periods. The ionic constituents $Cd^{2+}, Pb^{2+}, Mg^{2+}, Ca^{2+}, HCO_3^-, Sr^{2+}, Cl^-, NO_3^-, NO_2^-, Zn^{2+}, Na^+, K^+, Fe^{2+}$and SO_4^{2-} show a strong water mineralization. Among them, NO_3^-, NO_2^-, K^+ and SO_4^{2-} determine urban pollution, and Cd^{2+}, Pb^{2+}, Sr^{2+}, Fe^{2+}, $Cl^-$and Zn^{2+} determine water–rock interactions. Calcium and strontium, whose origins may be in calcite dissolution, represented facing the first pole, are another family of elements responsible for high groundwater mineralization. This calcite dissolution arises from bicarbonate formations exposed along the right bank of the Soummam Wadi. As regards the presence of elements such as Cl^-, Mg^{2+}, SO_4^{2-} and K^+, this is probably due to the dissolution of the gypsum and evaporitic formations lying along the left bank of the wadi. The first principal axis divides the sampled wells in two separate areas: (i) the first area corresponding to upstream of the catchment that contains the wells numbered from 1 to 9, and (ii) the second area where the wells numbered from 10 to18 are located. These two areas are separated by the El-Kseur region, representing the aquifer centre. Water wells situated upstream of the catchment are well oxygenated, highly mineralized, and rich in Cl^-, SO_4^{2-}, K^+, Ca^{2+} and Mg^{2+}. The presence of SO_4^{2-} and K^+, whose origin is anthropogenic, might be related to industrial wastewater and to garbage dumps loaded with sulfates. Potassium likely originates from the use of agricultural fertilizers (NPK). In contrast, water wells located downstream are not very oxygenated and are rich in organic matter, $NO_3^-$and metals Cd^{2+}, Pb^{2+} and Sr^{2+}. The elements Mg^{2+}, Ca^{2+}, Sr^{2+}, NO_3^- and Pb^{2+} are located on the positive side with respect to the second factorial axis (Fig. 9). This axis brings together elements responsible for natural mineralization of waters (rock origins) and elements coming from the highly polluted surface waters (Maane-Messai *et al.* 2010) crossing the zone unprotected by geological coverage.

5.2 Spatio-temporal characterization during the low water period

Observations and variables projected on the same factorial axis (Fig. 10) show that axes 1 and 2 explain 78.75% of the total variance (Table 6(b)). The first one represents 60.07% of the total inertia. Table 7(b) summarizes the explanations of the spatio-temporal characterization during low water periods. This axis demonstrates good relationships between Ca^{2+}, NO_3^-, Mg^{2+}, K^+, SO_4^{2-}, Cl^- and Na^+, whose origins are probably the dissolved geological formations. These ions constitute a family of elements responsible for strong water mineralization and are eventually of anthropogenic origin

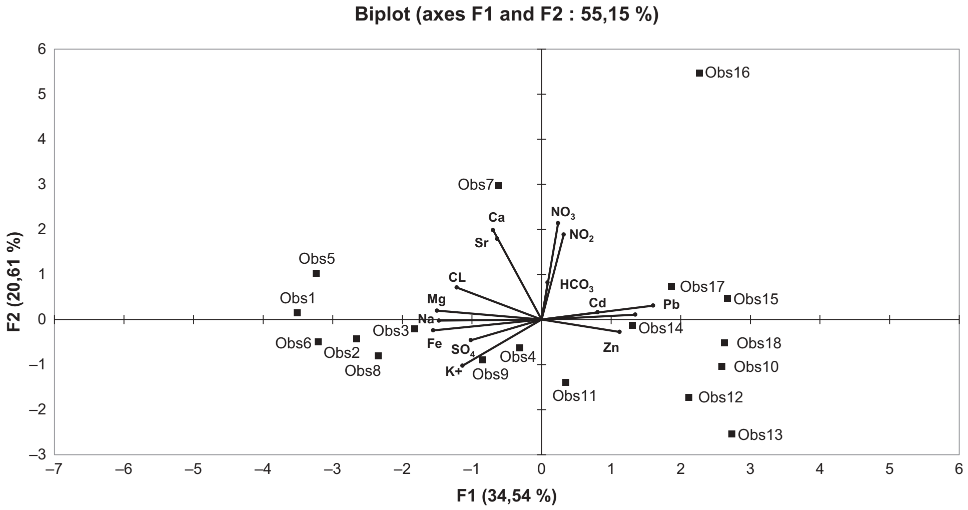

Figure 9. Plot of scores and loadings of 18 groundwater samples (noted obs.) characterized by 14 chemical parameters ($K^+, NO_3^-, NO_2^-, Ca^{2+}, HCO_3^-, Na^+, Cl^-, SO_4^{2-}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Fe^{2+}, Sr^{2+}$) for the high water period.

Table 7. Explanations of the spatio-temporal characterization during high (a) and low (b) water periods.

(a) High water period					
First factorial axis 34.54%					
Positive coordinates (or Positive side)			Negative coordinates (or Negative side)		
Observations* (number of wells)	Variables	Probable causes of contamination	Observations* (number of wells)	Variables	Probable causes of contamination
16, 15, 17, 14, 18, 11, 12, 13, 10	Cd^{2+}, Pb^{2+}, Zn^{2+} Mg^{2+}, HCO_3^-, NO_3^-, NO_2^-	-Natural mineralization and human activities for Cd^{2+}, Pb^{2+}, Zn^{2+} -Dissolution of carbonate rocks (limestone and dolomite) for Mg^{2+}, HCO_3^- -Agricultural (fertilizer leaching) and domestic or industrial waste for NO_3^-, NO_2^-	7, 5, 1, 8, 2, 4, 9, 6, 3	Ca^{2+}, Sr^{2+}, Cl^-, Mg^{2+}, SO_4^{2-}, Fe^{2+}, K^+, Na^+	-Dissolution of carbonate rocks (marly limestone, gypsum, calcite dissolution) for Ca^{2+}, Mg^{2+}, SO_4^{2-} and/or anthropogenic (fertilizers leaching) for SO_4^{2-} -Sedimentary rocks (evaporite: sylvite) or fertilizer application for K^+ -Crystalline formation for (halite dissolution) and salt intrusion for (coastal aquifer) Na^+ Cl^- -Geological (bedrock weathering) for Sr^{2+} -Dissolution of carbonate rocks (abandoned mining origin) for Fe^{2+}
Second factorial axis 20.61%					
Observations* (number of wells)	Variables	Probable causes of contamination	Observations* (number of wells)	Variables	Probable causes of contamination
1, 5, 7, 15, 16, 17	Cd^{2+}, Pb^{2+}, Sr^{2+} Mg^{2+}, Ca^{2+} NO_3^-, NO_2^-	-Natural and human activities for Cd^{2+}, Pb^{2+}, Sr^{2+} -Dissolution of carbonate rocks (limestone and dolomite) for Mg^{2+}, Ca^{2+} -Agricultural (fertilizer leaching) and domestic or industrial waste for NO_3^-, NO_2^-	18, 10, 14, 12, 13, 11, 8, 2, 6, 4, 3, 9	$Zn^{2+}, Na^+, K^+, SO_4^{2-}$	-Geological and/or anthropogenic for Zn^{2+} -Agricultural input (farming and fertilizing) and sewage effluents for K^+, SO_4^{2-} -Halite dissolution for Na^+
(b) Low water period					
First factorial axis 60.07%					
Positive coordinates (or Positive side)			Negative coordinates (or Negative side)		
Observations* (number of wells)	Variables	Probable causes of contamination	Observations* (number of wells)	Variables	Probable causes of contamination
1, 5, 6, 8, 7, 10	Ca^{2+}, NO_3^-, Mg^{2+} HCO_3^-, Cl^-, Na^+	-Dissolution of carbonate rocks (limestone and dolomite) for $Ca^{2+}, Mg^{2+}, HCO_3^-$ -Agricultural and domestic waste for NO_3^- -Crystalline formation for Na^+ (halite dissolution Na^+Cl^-)	12, 17, 18, 13, 16, 11, 2, 14, 15, 9, 4, 3	None	In low water, there is no contribution of chemicals by leaching. This results in a low groundwater level due to (i) low precipitation, (ii) high evaporation, (iii) excessive use of groundwater resources by pumping
Second factorial axis 18.48%					
Observations* (number of wells)	Variables	Probable causes of contamination	Observations* (number of wells)	Variables	Probable causes of contamination
1, 5, 6, 8, 12, 17, 18, 13, 16	Ca^{2+}, NO_3^-, Mg^{2+}, HCO_3^-, K^+	-Dissolution of carbonate rocks (limestone and dolomite) for $Ca^{2+}, Mg^{2+}, HCO_3^-$ -Agricultural (fertilizer leaching) and domestic or industrial waste for NO_3^-, K^+	7, 10, 11, 2, 14, 9, 4, 3, 15	SO_4^{2-}, Cl^-, Na^+	-Marine water intrusion for Cl^- -Crystalline formation for Na^+ -Agricultural pollution, infiltration of domestic, industrial waste, the gypsum formations and miscellaneous source for SO_4^{2-}

*The presentation order of observations depends on their relative contribution to explaining the variance ranked in descending order.

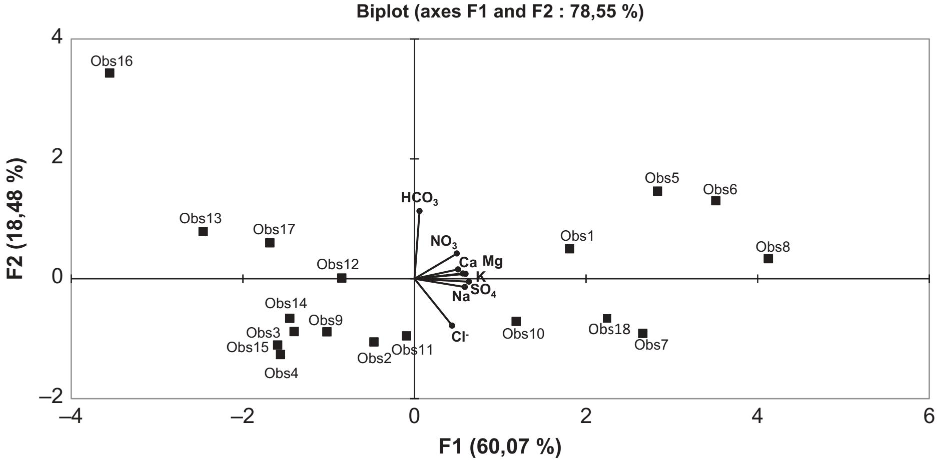

Figure 10. Plot of scores and loadings of 18 groundwater samples (noted obs.) characterized by eight chemical parameters ($K^+, NO_3^-, Ca^{2+}, HCO_3^-, Na^+, Cl^-, SO_4^{2-}, Mg^{2+}$) for the low water period.

for K^+, SO_4^{2-} and NO_3^-. This is a significant decrease of pollution downstream in periods of low water. The increase of the contamination gradient results in a slight enhancement in oxygen and a reduction in COD and nitrates. It is related to the infiltration of products used in agriculture for NO_3^- and to geological formations such as rocks, dolomite and limestone present in the right bank of the Soummam Wadi. As regards SO_4^{2-}, Na^+ and Cl^-, they might be due to the presence of gypsum and halite in the left bank of the wadi. However, none of the analysed chemical elements is represented on the negative side with respect to the first axis. Indeed, on the positive side of the first axis, more than 50% of the variance is explained. The decrease of element concentrations depends on several factors: the decline of the load of water pollutants resulting from self-purification (Bremond and Perrodon 1979), the reduction of floor contamination (bioaccumulation and biodegradation of organic materials), and the frequency of rain which limits the effects of rainfall leaching (Langenbach 2013). Actually, in the dry season, the sampling stations are loaded with organic pollutants. The second axis represents 18.48% of the total inertia. This is dominated on the positive side by HCO_3^- and on the negative side by Cl^-. Both elements may have originated from (i) natural geological formations such as rocks, dolomite and limestone in the right bank and the left bank of the wadi; (ii) the dissolution of evaporite and/or infiltration of fertilizers applied in the form of potash (KCl); (iii) sulfate salts. The Na^+–Cl^-group is more dominant during low water. The Cl^- concentrations are correlated with those of Na^+ (r = 0.7). These concentrations are related to the weathering of rocks rich in Na^+ and Cl^- elements (evaporites) and to the role of leaching rainwater. The evaporitic deposits, which are located at the northeast of the aquifer, show high concentrations of sodium ions through the effects of leaching, evaporation and base exchange. This explains the high concentrations of Na^+, which exceed 386 $mg\,L^{-1}$ in the low water period in the upstream catchment (wells 5, 6 and 8). However, the lowest value is about 72 $mg\,L^{-1}$, recorded downstream of the catchment (well 13) during the high water (Fig. 5c). Concentrations vary widely (SD = 77–98 in high and low water periods, respectively) due to their different origins. For Cl^- concentrations, about 74% of wells exceed the drinking water standards. The chlorides may have several origins: the gypsiferous sandy clays that cover the entire basin, the evaporitic deposits, and the discharge of wastewater into the plain. In fact, salinization detected in the wells located in the vicinity of the wadi was probably caused by infiltration of water through a sandy bed containing salt as the halite. In contrast, the salinization detected in the coastal part (downstream of catchment) is mainly controlled by seawater intrusion. Sulfates are present in significant amounts. The origin of sulfates is probably either the infiltration of domestic, industrial waste or the gypsum formations present in the left bank of the Soummam Wadi. The presence of sulfates in water may relate to the dissolution of gypsum content in the marls and leaching of evaporitic deposits according to equation (1):

$$Ca^{2+}SO_4^{2-} \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O \qquad (1)$$

The lowest values are recorded upstream and near the aquifer boundaries, where the gypsum marls are absent (they appear in the centre and northeast of the aquifer). Potassium probably originates from the marl-clay formations. It is provided from potassium-clayey alteration and the dissolution of chemical fertilizers (NPK), which are frequently used by farmers. The presence of this element could also be related to domestic wastewater discharges in the plain. The bicarbonate reaches a maximum value of 506.3 $mg\,L^{-1}$ and a minimum value of 311.2 $mg\,L^{-1}$ during the high and low water periods, respectively. The origin of bicarbonate is the limestone formation located downstream of the right bank of the wadi. The presence of bicarbonate in water is due to the dissolution of carbonate formations according to the Equation (2):

$$Ca^{2+}CO_3^- + H_2O + CO_2^- = 2HCO_3^- + Ca^{2+} \qquad (2)$$

Apparently, the iron concentration levels are high due to the dissolution of iron from the Timezrit abandoned mine (Fig. 1). Except for Zn^{2+}, the presence of metals with moderately high values is explained by the existence of important industrial and domestic discharges.

6 Conclusion

In the present work, the variables of groundwater quality are identified by PCA/FA and provide a set of original results about the quality of groundwater in the studied area. The statistical approach to the data illustrates alterations that arise from various origins. It is found that natural mineralization and anthropogenic pollution in the alluvial aquifer of the lower Soummam are involved in such alterations. On the other side, the high density of population, with approximately 1800 inhabitants km^{-2} (one of the highest densities in the Mediterranean Basin), and its implications for urban, agricultural and industrial wastes, explains the relatively high values of ion concentrations. Moreover, a ratio above 3 for DCO/DBO$_5$ shows that in 95% of tested wells there is a predominance of non-biodegradable organic matter, which is likely the outcome of emission sources of persistent organic pollutants (fats industry, oil mills, tanneries, and so on). Most of tested wells show relatively high concentrations against standards for inorganic pollution represented by major cations and anions. These dissolved ions in groundwater seem to be due to the simultaneous contributions of natural mineralization (water–rock interactions, salt effect), anthropogenic inputs (fertilizer application, use of unpurified irrigation water, and agricultural pollution), marine water intrusion and miscellaneous sources. Furthermore, the comparison between low and high water periods shows that the dissolution of ions in groundwater is affected during periods of high water. Otherwise, an increasing gradient of dissolved ions from upstream to downstream is observed during the period of low water; whereas a dilution process takes place in the high water period.

Other than for zinc, 65% of tested wells have high heavy metal concentrations compared to standards. These concentrations increase upstream to downstream of the catchment.

The Piper diagram shows that the bicarbonate calcium facies is localized at the upstream of the catchment. The sulfate calcium facies is localized only in the northeast of the aquifer, near Jebel Aghbalou–Gouraya, where evaporitic formations are absent. The sodium chloride facies is found in the centre of the aquifer (El Kseur zone). The calcium chloride facies is found near the aquifer downstream boundaries.

To our knowledge, this study shows that, for the first time, the groundwater of the alluvial aquifer in the lower Soummam is subjected to the threat of organic and inorganic pollution, which may have consequences for public health.

In prospect, monitoring of high-frequency measurements of the studied parameters will clarify the arguments advanced by increasing the number of monitored wells and measured parameters.

Based on our results, and from the perspective of a lead and zinc extraction project, which could be operational in the Amizour region, dam construction would be very important in order to manage water treatment systems and control stream waters, which could come from the mining area. The development of a surface water-monitoring network is a critical element in the assessment, restoration and protection of groundwater quality. The releases from anthropogenic activities must be inspected and treatment of discharged waters from homes and industries should be performed. To this end, in order to avoid the contamination of groundwater and to protect water resources, a comprehensive sanitation network connected to anthropic activities in the area is urgently and highly required.

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