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HYDROCHEMICAL DIVERSITY OF A LARGE ALLUVIAL AQUIFER IN AN ARID ZONE (DRAA RIVER, S MOROCCO)

ZRÓŻNICOWANIE CHEMICZNE WÓD ALUWIALNYCH DUŻYCH RZEK STREFY SUCHEJ NA PRZYKŁADZIE RZEKI DRAA, OAZA MHAMID (PŁD MAROKO)

Abstract: In arid areas, with rivers functioning episodically, alluvial resources are the main source of water. Considering the intensified regulation of discharge in montane catchments, supplying the intermittent rivers, in the nearest future alluvial aquifers will gain key importance for the functioning of people in arid zones. The research aimed to investigate the diversified chemistry of alluvial waters typical of large intermittent river valleys in hot arid zones as well as to analyse processes determining the water chemistry and affecting its diversity. The detailed study, carried out in October 2015, covered the Draa river valley (1100 km total length) in the region of the Mhamid Oasis. The examined water was sampled from all wells found in the study area. Concentrations of the main cations: Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+ , and Li^+ , anions: Cl^- , SO_4^{2-} , HCO_3^- , and NO_3^- , as well as trace elements: Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, and Zn, were identified. Results were analysed with statistical, hydrochemical, and geochemical modelling methods. Alluvial waters of the eastern and western part of the oasis differed in concentrations of numerous components, what resulted from the regulation of irrigation. Specific electrical conductivity showed a 3.5-fold increase, from 3800 to 13800 $\mu\text{S}/\text{cm}$, consistent with the direction of water flow in the oasis, from east to west. Even a greater rise was observed for ions: Cl^- (6x), Na^+ (5.5x), Mg^{2+} (5.0x), Ca^{2+} , and SO_4^{2-} (3.5x). Such a composition indicated multiionic hydrochemical type of waters dominated by Na^+ and Cl^- . Additionally, high Pearson correlation coefficients were recorded for Na^+ and Cl^- (0.98) as well as Mg^{2+} and Cl^- (0.97). The saturation index suggested that the main water components originated from dissolving of minerals such as halite, anhydrite, sylvite, and gypsum. Groundwater chemistry in the Mhamid Oasis was determined mainly by geogenic processes, such as dissolving of evaporates, precipitation of carbonate minerals, and ion exchange.

Keywords: hydrochemistry, alluvial aquifer, salinity, arid zone, intermittent river

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Introduction

The groundwater chemistry is determined mainly by geogenic substances, namely ones originating from the rock medium. Water-bearing levels are also supplied by anthropogenic substances, affecting water chemistry to a various extent, both in a local and regional scale.

However, not only man-made substances discharged to waters can be harmful to human organism, natural ones impose such a threat as well. This issue is of particular importance in hot arid areas, groundwater of which shows high salinity resulting from geogenic processes [1, 2]. An increasing number of studies also points to high nitrate concentration caused by human activity [3-7]. Therefore, it is crucial to investigate the variations, often observed even on small areas, in the chemistry of waters to assess their suitability for irrigation [5, 6, 8, 9] and drinking purposes [5, 10]. Such analyses are most important for regions with strongly limited resources of high-quality waters [11-13], where human impact, including intensive exploitation of waters [14], should involve protection of the groundwater threatened with contamination.

Hydrochemistry of the Draa river catchment area has been previously studied i.a. by [15, 16], who already noticed that its water salinity increases from north to south, according to the direction of river flow. Similarly as in other Moroccan catchments, catchment area of the Draa river is also marked by high concentration of nitrates, locally exceeding the allowable limit set for drinking water by WHO (World Health Organization) at 50 mg/dm^3 [16]. According to [16], the three most distant oases, Fezouata, Ktaoua, and Mhamid, located in the lower part of the middle Draa river, are particularly affected by implications of high water salinity. The decrease in water resources of this region is strictly associated not only with droughts, recorded here during the last several years, but also with regulation of water outflow and its storage in reservoir Mansour Ed Dahbi in the upper part of the river. Considering the environmental vulnerability index [14] classifying this region as prone to climate changes and anthropogenic action, emphasized the lack of sustainable water and agriculture management in the area, resulting in lower water quality and crop yield and consequently worse life conditions for local residents.

The present paper aimed to present the diversified chemistry of alluvial waters typical of large intermittent rivers in hot arid zones, as observed in small scale, as well as to investigate processes determining water chemistry and influencing its diversity.

Study area

The study was carried out in the Mhamid Oasis (Coude du Draa region), the southernmost of 6 oases of the Middle Draa valley (Fig. 1). The Draa is Morocco's longest river, 1100 km and the drainage basin covers 13500 km^2 . This intermittent river is formed by the confluence of two large rivers: Imini Ouarzazate and Dades, supplied by rain and meltwater flowing from the High Atlas Mountains. Since building the Mansour Ed Dahbi dam in 1972, water flow in the Draa river has been regulated. At the time of construction, the total volume of the reservoir was $560 \cdot 10^6 \text{ m}^3$ but decreased to $460 \cdot 10^6 \text{ m}^3$ in 1998 [17]. The reservoir covers an area of 5 ha. The maximum depth varies from 63 to 70 m. On average, inflows into the reservoir amount to approximately $340 \cdot 10^6 \text{ m}^3/\text{year}$, whereas average releases are $225 \cdot 10^6 \text{ m}^3/\text{year}$ [17]. Both have a large variability and the annual trend of inflows and outflows is declining during the last years. However, during floods, release may reach $300 \cdot 10^6 \text{ m}^3/\text{year}$ [15]. Evaporation above the surface of the reservoir varies according to meteorological conditions but on average is $63 \cdot 10^6 \text{ m}^3/\text{year}$. Surface

water is the largest resource for water use in the Middle Draa valley. Only one tenth of the total exploitable resource is provided by groundwater in normal years.

The hot arid climate of the Middle Draa valley is typified by mean annual air temperature of 22.8 °C. Maximum temperature, recorded in July, attains 50.2 °C, while minimum temperature, recorded in January amounts to -5.2 °C (Tagounite meteorological station - southernmost station in the region, nearest to the research area). The annual amount of rainfall attains a mean of ca. 117 mm at Ouarzazate near the reservoir, 60 mm at Zagora and 50 mm at Tagounite. However, in the highest meteorological station in the Draa river basin (Tichka pass - 2100 m a.s.l.) the rainfall attains a mean of ca. 562.5 mm/year. The highest monthly precipitations are noted in November and December. The second maximum is noted in February and March. Evaporation is estimated between 2000 and 3500 mm/year [18].

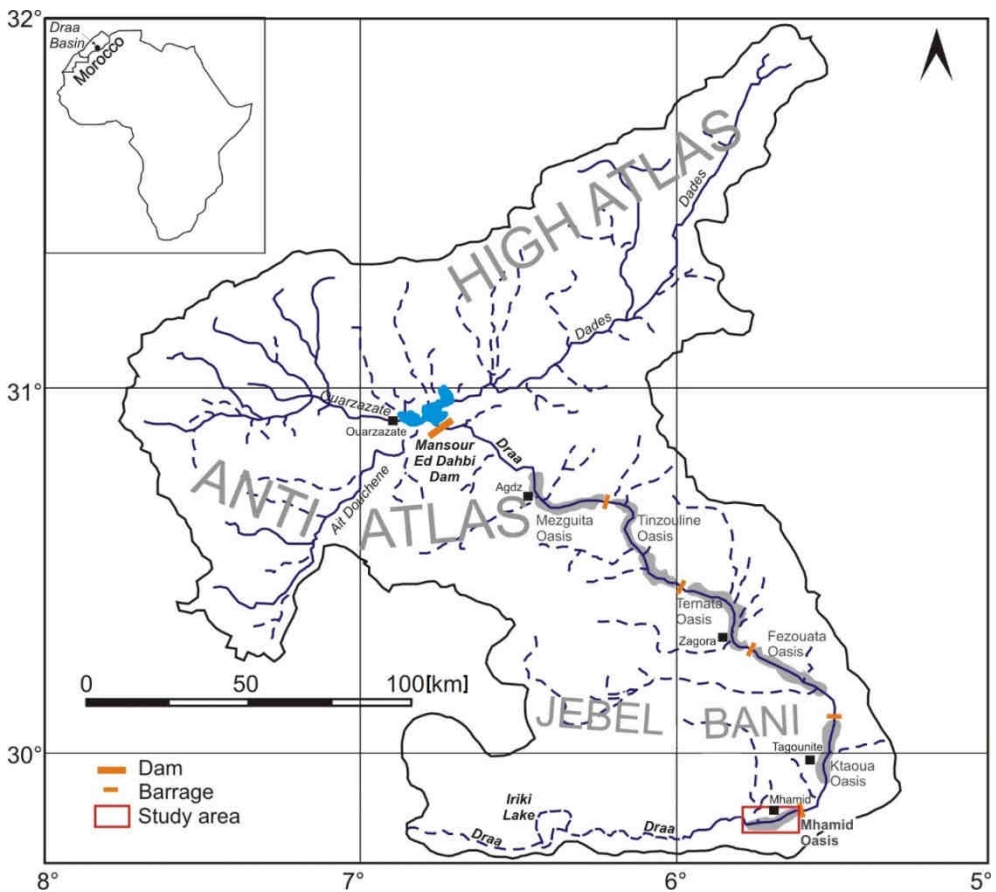


Fig. 1. Location map of the Draa river and Mhamid Oasis (study area) in Morocco. Adapted from the map of Ouarzazate, 1:500 000

Mhamid is the southernmost oasis in the Middle Draa valley, ca. 200 km to the south of Mansour Eddahbi reservoir. It has an area of 3305 ha, but among them only 2231 ha are

cultivated. Approximately 131 000 date palms grow in the Mhamid Oasis. The oasis is situated in a large latitudinal depression between Jebel Bani in the North and Hamada du Draa in the South. The depression is filled by five levels of Quaternary alluvial fans, recent alluvial deposits, lacustrine deposits and sand dune deposits [19]. The study is conducted on a flat lower river terrace in the Mhamid Oasis. The terrace is composed of alluvial deposits, dominated by gravels and cobbles, which origin from various igneous (granite, rhyolite), metamorphic (gneiss, schist) and sedimentary rocks (sandstones, quartzite sandstones, limestone). Water discharged from Mansour Eddahbi reservoir flows 4-5 times a year, primarily to the Mhamid Oasis. It is retained at the Bounou dam above the oasis where it is distributed for irrigation through a major open channel system called *seguias*. The main channels of the system are concrete, whereas subsidiaries are mainly mud channels. The remaining waters (about 50 %) supply the alluvia filling the Draa river channel. Water, infiltrating the alluvia, supplies wells within the Mhamid Oasis. The total area of the aquifers in the Mhamid part of the Middle Draa valley is 70 km². The aquifers store 16.8 Mm³ of natural water reserves. Roughly 60 wells with motor pumps are located within the oasis, however due to economic reasons more than half of them are not in use.

Research methods

Fieldwork was carried out in October 2015 in the area of the Mhamid Oasis, situated in the Draa river valley. All 47 (Fig. 2) wells of the oasis were subjected to measurements of the depth of groundwater level and well bottom. Basic physicochemical parameters of groundwater, such as temperature, T , specific electrical conductivity, EC , and pH, were measured in situ. EC and T were measured with a conductivity meter (CC-401, Elmetron), with automatic compensation to a reference temperature of 25 °C and accuracy of ± 1 % and ± 1 °C, respectively. The pH was measured with a pH meter (CP-411, Elmetron), with an accuracy of 0.01 pH units. From active wells, 42 water samples were taken for further laboratory analyses. All the samples were collected in tight capped polyethylene bottles and stored under low T conditions.

Prior to analyses, the samples were filtered through the Whatman glass microfiber filter (filter size: 25 mm, pore size: 0.45 μm). Cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+ , and Li) and anions (Cl^- , SO_4^{2-} , and NO_3^-) were identified by ion chromatography with ICS 3000 (Dionex), including 3 x 250 mm IonPac CS16 and 2x250 mm IonPac AS18 analytical columns for cations and anions, respectively. Trace elements (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, and Zn) were determined by inductively coupled plasma time-of-flight mass spectrometry (ICP-MS-TOF) with GBC OptiMass 9500. Bicarbonates (HCO_3^-) were analysed by titration. Detection limits amounted to: 0.4 mg/dm³ for Ca^{2+} , 0.2 mg/dm³ for Mg^{2+} , Na^+ , NH_4^+ , and Li^+ , 0.1 mg/dm³ for K^+ , and 0.01 $\mu\text{g}/\text{dm}^3$ for trace elements.

Hydrochemical results for all samples were statistically analysed [20, 21] with the STATISTICA 9.0 software. Since the data showed normal distribution, the Pearson linear correlation coefficient (r) was calculated to evaluate correlations between the variables. Cluster analysis was used to search for patterns in the data set by grouping the (multivariate) observations into clusters. The goal is to find an optimal grouping for which the observations or objects within each cluster are similar, but the clusters are dissimilar to each other. Clustering was based on the Ward method and Euclidean distance. Structures and factors affecting the chemistry of waters were identified with the exploratory factor analysis (EFA).

The water quality of each sample was plotted on a classical Piper diagram, referring to the concentrations [meq/dm³] of hydrochemical components [22]. This diagram provides a convenient method to classify and compare water types based on the ionic composition of different water samples [23].

The saturation index, *SI*, for the measured chemical composition of water samples was calculated using PHREEQC Interactive (USGS, 3.3.3-10424) as $SI = \log (IAP/Ks)$, where *IAP* is the ionic activity product and *Ks* is the mineral solubility equilibrium constant [24]. The calculation of *SI* was carried out to understand the thermodynamic equilibrium between the dissolved and solid phases in the groundwater. Equilibrium is indicated when $SI = 0$. If $SI > 0$, groundwater is considered supersaturated, and if $SI < 0$, groundwater is undersaturated. Due to analytical errors and natural diversity in mineral properties, the water-phase equilibrium is assumed for *SI* values oscillating around $SI = 0$, most commonly $\pm 5\% \log Ks$.

To validate the possibility of using the water for irrigation, the sodium adsorption ratio (*SAR*) was calculated, with the following formula:

$$SAR = \frac{Na}{\sqrt{\frac{(Ca + Mg)}{2}}} \quad (1)$$

where chemical concentrations are reported in [meq/dm³] [25].

Hydrochemical indices were used to indirectly evaluate processes affecting the groundwater. Proportions between the ions result from processes determining the chemistry of waters, depending on their origin and reactions accompanying water flow. The following hydrochemical indices (ratios in [mval/dm³]) were analysed:

$$\frac{rHCO_3^-}{rCl^-}, \frac{rNa^+}{rCl^-}, \frac{rCa^{2+}}{rMg^{2+}}, \frac{rNa^+}{rK^+}, \frac{rNa^+ + rK^+}{rCl^-}, \frac{rSO_4^{2-} \cdot 100}{rCl^-} \quad (2)$$

Below stated mass relationships between the ions were established as well:

$$\frac{Na^+}{K^+}, \frac{Ca^{2+}}{Mg^{2+}}, \frac{SO_4^{2-}}{Cl^-}, \frac{Fe}{Mn} \quad (3)$$

The type of ion exchange was deduced from the base exchange index (*BEI*), given by the following formula: $BEI = ([Cl] - [Na+K])/[Cl]$ [meq/dm³]. $BEI < 0$ indicates fixation of Ca²⁺ and Mg²⁺ and solubilisation of Na⁺ and K⁺. $BEI > 0$ indicates fixation of Na⁺ and K⁺ and solubilisation of Ca²⁺ and Mg²⁺.

Quality assurance and control

The ionic (charge) balance error, expressed as the difference between cation and anion charges divided by their sum and multiplied by 100 %, did not exceed 10 %.

Table 1 presents concentrations of heavy metals determined in the CLMS-2AN certified reference material (SPEX CertiPrep, USA) with the ICP-MS-TOF mass spectrometer. Table 2 includes concentrations of main ions identified in the KEIJM-02 certified material (Environment Canada) with the ICS 3000 (Dionex) ion chromatograph.

Table 1

Comparison of measured and certified concentrations in CLMS-2AN

Analyte	Certified		Obtained		Diff.
	Concentration	±Uncertainty	Concentration	±SD	
	[µg/dm ³]				[%]
Mn	10.1	0.05	9.91	2.3	-1.9
Fe	10.1	0.05	9.79	1.1	-0.4
Cu	10.1	0.05	9.85	1.5	-2.5
Zn	10.1	0.05	9.88	1.1	-2.2
Cd	10.1	0.05	9.89	0.9	-2.1
Pb	10.1	0.05	9.91	1.4	-2.1
Cr	10.2	0.05	10.41	2.1	3.0
Co	10.1	0.05	9.93	0.4	-1.7
Ni	9.98	0.05	10.21	1.9	1.1
As	10.1	0.05	9.88	2.1	-2.2
Sr	10.1	0.05	10.22	1.7	1.2

SD - standard deviation, Diff. - relative difference between measured and certified concentration; $100\% \cdot (c_m - c_c) / c_c$

Table 2

Comparison of measured and certified concentrations in KEIJM-02

Analyte	Certified		Obtained		Diff.
	Concentration	±Uncertainty	Concentration	±SD	
	[mg/dm ³]				[%]
Ca	0.852	0.085	0.812	1.4	-4.9
Mg	0.467	0.038	0.458	1.1	-2.0
K	0.224	0.032	0.234	0.9	4.3
Na	3.800	0.321	3.720	1.3	-2.2
Cl	5.790	0.411	5.680	0.8	-1.9
SO ₄	2.420	0.038	2.350	2.2	-3.0

SD - standard deviation, Diff. - relative difference between measured and certified concentration; $100\% \cdot (c_m - c_c) / c_c$

Results

Results obtained in the study showed that the groundwater level varied between 6.5 and 14.0 m below ground level. Height of the water column in wells ranged from 0.5 to 11.0 m, attaining a mean of 3.0 m. Different values were obtained for the newly drilled well No. 57, with a 15.0 m high water column and groundwater level recorded at the greatest depth of 17.0 m below ground level. Groundwater temperature in wells, amounting to 24.2 °C on average, was similar to the mean air temperature in the region, as recorded in October, 23.5 °C, and annually, 22.8 °C.

Descriptive statistics for physicochemical variables investigated in the study area were provided in Table 3 while the spatial distribution of selected parameters within the Mhamid Oasis was presented in Figure 2. For most parameters, concentration increased according to the direction of water flow in alluvia (see Fig. 1), from east to west. Only occasionally, when the channel was filled with water, the flow became east to south-west oriented. The concentration increased with the direction of water flow for cations of calcium (3.5x), magnesium (5.0x) and sodium (5.5x), anions of chloride (6.0x) and sulphate (3.5x), as well as trace elements such as copper and lithium (3.0x), iron and nickel (5.0x), arsenic (6.0x), strontium (8.0x), cobalt (20.0x), and chromium (35.0x).

Table 3

Descriptive statistics for physicochemical variables of groundwater samples ($n = 42$)

Parameter	Unit	Min.	Max	Mean	SD
Water temperature	[°C]	20.2	26.3	24.2	1.2
EC	[μS/cm]	3 800	13 766	7 988	2 741
pH	[-]	6.8	7.9	7.3	0.3
TDS	[mg/dm ³]	1 900	6 883	3 994	1 370
Na ⁺	[mg/dm ³]	459	2438	1182	500
Ca ²⁺	[mg/dm ³]	313	908	560	168
Mg ²⁺	[mg/dm ³]	162	528	321	99
K ⁺	[mg/dm ³]	4	55	14	10
NH ₄ ⁺	[mg/dm ³]	<i>bdl</i>	20.8	1.7	3.4
SO ₄ ²⁻	[mg/dm ³]	946	3487	2088	686
Cl ⁻	[mg/dm ³]	734	3313	1739	727
HCO ₃ ⁻	[mg/dm ³]	215	769	394	109
NO ₃ ⁻	[mg/dm ³]	0.1	41.3	5.8	8.8
Al	[μg/dm ³]	<i>bdl</i>	6.46	0.15	0.99
As	[μg/dm ³]	12	70	34	16
Cd	[μg/dm ³]	<i>bdl</i>	0.32	0.05	0.09
Co	[μg/dm ³]	0.08	2.03	0.77	0.46
Cr	[μg/dm ³]	0.57	21.12	10.10	6.30
Cu	[μg/dm ³]	11	32	20	6
Fe	[μg/dm ³]	637	3365	1744	744
Li	[μg/dm ³]	57	263	131	50
Mn	[μg/dm ³]	<i>bdl</i>	191	33	49
Ni	[μg/dm ³]	6	27	16	7
Pb	[μg/dm ³]	<i>bdl</i>	1.67	0.33	0.30
Sr	[μg/dm ³]	306	2427	1060	595
Zn	[μg/dm ³]	16	321	64	72

SD - standard deviation, EC - electrical conductivity compensated at 25 °C, TDS - total dissolved solids, *bdl* - below detection limit (0.2 mg/dm³ for NH₄⁺, 0.01 μg/dm³ for Al, Cd, Mn, and Pb)

Other parameters displayed a mosaic distribution and were recorded in higher concentrations only in several wells. Such an observation was made mainly for trace elements, such as cadmium, zinc, lead, and manganese, as well as nitrogen forms, namely ammonium ions and nitrates. The greatest concentrations of manganese, potassium, lead, and zinc, amounting to 0.2 mg/dm³, 55.0 mg/dm³, 1.7 μg/dm³, and 321 μg/dm³, respectively, were determined in the centre of the oasis, while the highest content of ammonium nitrogen, up to 21.0 mg/dm³, was reported for the eastern part. Nitrates attained highest concentrations, up to 41 mg/dm³, in the south-western and central areas of the oasis.

Water pH values, falling within the range of 6.8-7.9, indicated neutral to weak alkaline reaction. Specific electrical conductivity of the examined waters varied between 3800 to 13766 μS/cm, pointing to salt water, with a 3.5-fold increase in salinity from the eastern to western part of the oasis (Fig. 3).

The calculated hydrochemical indices: $(rNa^{+}+rK^{+})/rCl^{-}$ and $rSO_{4}^{2-} \cdot 100/rCl^{-}$, amounted respectively to 0.9-1.2 and 66-166, therefore waters supplying the wells most likely originated from shallow circulation. The rNa^{+}/rK^{+} ratio, ranging between 76 and 566, was also typical to shallow groundwater, however in several wells (19, 49, and 57) did not exceed 70, what may evidence limited inflow of alluvial waters to these sites.

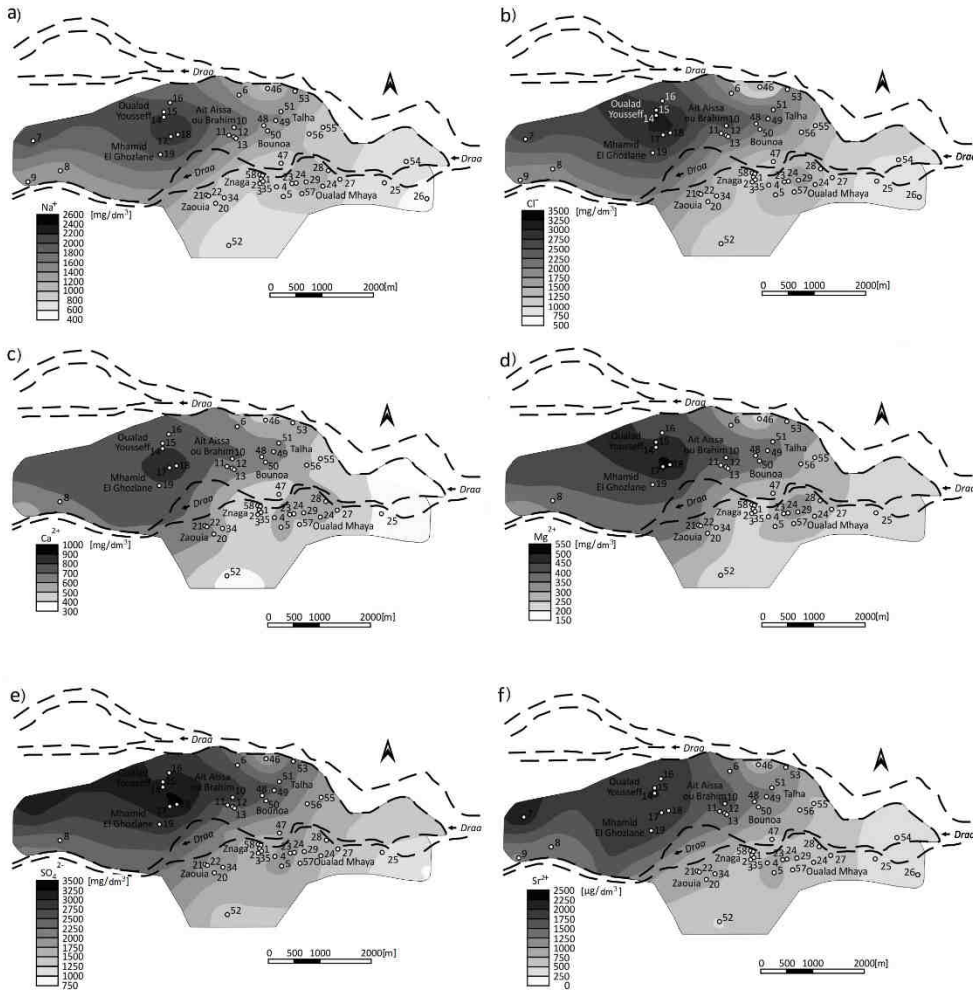


Fig. 2. Spatial distribution of chemical elements concentrations in the study area. a) sodium, b) chloride, c) calcium, d) magnesium, e) sulphur, f) strontium. Numbers refer to studied wells

The saturation index calculated for selected minerals in particular wells (Table 4) attained the following values: $0.4 < SI < 1.4$ for calcite, $0.8 < SI < 2.9$ for dolomite, $0.2 < SI < 1.3$ for aragonite, $-0.5 < SI < 0.1$ for gypsum, $-0.8 < SI < -0.2$ for anhydrite, $-5.1 < SI < -3.9$ for halite, and $-6.7 < SI < -5.2$ for sylvite. Such values of the saturation index indicate dissolving of minerals with chemical composition including sodium chloride, potassium chloride, and calcium sulphate, as well as precipitation of minerals comprising calcium and magnesium carbonates.

Table 4

Saturation index calculated for groundwater samples from the alluvial aquifer (Mhamid Oasis)

Well No.*	Aragonite	Calcite	Dolomite	Anhydrite	Gypsum	Halite	Sylvite
1	0.27	0.41	0.94	-0.70	-0.39	-4.84	-6.27
2	0.29	0.43	0.95	-0.68	-0.37	-4.85	-6.32
3	0.26	0.40	0.89	-0.64	-0.34	-4.74	-6.23
4	0.77	0.91	1.82	-0.49	-0.15	-4.62	-6.13
5	0.79	0.94	1.88	-0.50	-0.18	-4.61	-6.08
6	0.25	0.39	0.85	-0.36	-0.07	-4.33	-6.26
7	0.60	0.74	1.57	-0.26	0.05	-4.01	-5.94
8	1.15	1.29	2.63	-0.44	-0.08	-4.39	-5.87
9	0.74	0.89	1.82	-0.50	-0.15	-4.43	-6.05
10	0.27	0.41	0.95	-0.26	0.04	-3.95	-5.94
11	0.47	0.62	1.30	-0.46	-0.13	-4.41	-5.95
12	0.48	0.62	1.34	-0.42	-0.11	-4.29	-5.85
13	0.66	0.80	1.68	-0.32	-0.01	-4.15	-5.70
14	0.47	0.61	1.34	-0.24	0.07	-3.88	-5.74
15	0.83	0.98	2.10	-0.40	-0.09	-4.08	-5.81
16	0.41	0.55	1.23	-0.29	0.01	-4.06	-5.99
17	0.52	0.67	1.41	-0.23	0.07	-3.99	-5.22
18	0.77	0.92	1.94	-0.25	0.07	-3.86	-5.65
19	0.51	0.66	1.37	-0.28	0.02	-4.04	-5.16
20	0.55	0.69	1.42	-0.43	-0.13	-4.60	-6.19
21	0.88	1.03	2.08	-0.41	-0.09	-4.50	-6.04
22	0.49	0.64	1.39	-0.50	-0.19	-4.57	-5.88
23	1.30	1.44	2.90	-0.45	-0.13	-4.56	-5.81
24	1.21	1.35	2.76	-0.60	-0.29	-4.54	-5.92
25	0.55	0.69	1.50	-0.74	-0.42	-4.89	-6.25
26	0.41	0.56	1.15	-0.82	-0.50	-5.14	-6.41
27	0.82	0.96	1.92	-0.56	-0.25	-4.79	-6.30
28	0.67	0.81	1.70	-0.52	-0.22	-4.61	-6.14
29	0.57	0.71	1.54	-0.53	-0.22	-4.24	-5.74
34	0.26	0.40	0.89	-0.51	-0.22	-4.65	-6.19
35	0.29	0.43	0.97	-0.71	-0.40	-4.80	-6.19
46	0.24	0.39	0.89	-0.71	-0.42	-4.84	-6.68
47	0.22	0.36	0.83	-0.60	-0.30	-4.76	-6.39
48	0.36	0.50	1.09	-0.36	-0.06	-4.26	-6.02
49	0.73	0.87	1.82	-0.34	-0.01	-4.13	-5.33
50	0.66	0.81	1.70	-0.39	-0.09	-4.38	-5.91
52	0.86	1.00	2.12	-0.69	-0.40	-4.92	-6.58
53	0.56	0.71	1.55	-0.40	-0.11	-4.29	-6.42
54	0.55	0.70	1.51	-0.70	-0.41	-4.81	-6.26
55	0.68	0.83	1.78	-0.61	-0.30	-4.7	-6.19
57	0.76	0.91	1.89	-0.60	-0.30	-4.76	-5.94
58	0.62	0.76	1.64	-0.63	-0.32	-4.67	-6.12
*Well No. corresponds to Figure 1							

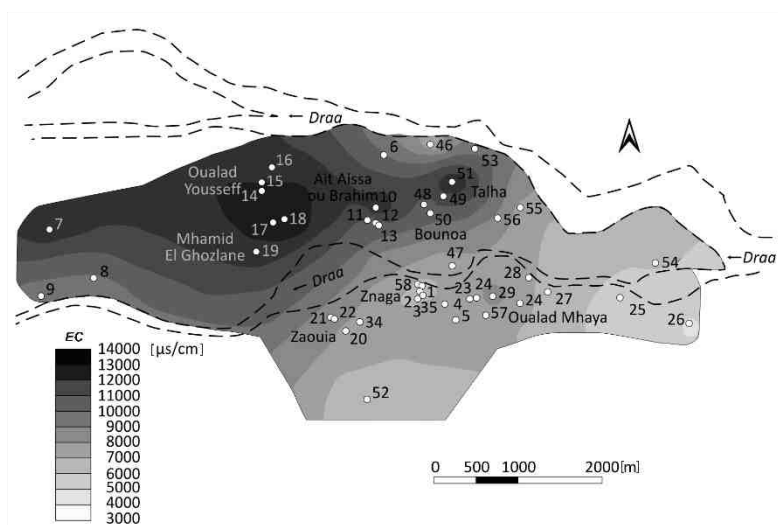


Fig. 3. Spatial distribution of groundwater EC in the study area

The calculated R coefficients (Table 5) showed strong correlations between the main water components, with highest values obtained for Na^+ and Cl^- or SO_4^{2-} (0.98 and 0.94, respectively), Mg^{2+} and Ca^{2+} , SO_4^{2-} , or Cl^- (0.92, 0.95, and 0.97, respectively), as well as SO_4^{2-} and Ca^{2+} or Cl^- (0.94 in both cases).

Table 5
Correlation coefficient matrix for particular ions identified in groundwater samples from the alluvial aquifer (Mhamid Oasis)

	Li	Na^+	Mg^{2+}	K^+	Ca^{2+}	Cl^-	SO_4^{2-}	Pb	Cr	Co	Cu	Mn	Ni	Sr	As	Fe
HCO_3^-	0.51	0.69	0.72	0.54	0.68	0.71	0.62	0.60	0.63	0.51	0.66		0.61	0.64	0.72	0.61
Li		0.80	0.80		0.84	0.76	0.87			0.66	0.68		0.71	0.83	0.76	0.76
Na^+			0.97		0.88	0.98	0.95		0.63	0.70	0.85		0.78	0.91	0.92	0.82
Mg^{2+}					0.92	0.97	0.95		0.60	0.71	0.85		0.80	0.90	0.90	0.83
Ca^{2+}						0.89	0.95		0.57	0.76	0.84		0.88	0.90	0.84	0.89
Cl^-							0.94		0.65	0.72	0.87		0.82	0.94	0.95	0.84
SO_4^{2-}									0.61	0.76	0.87		0.86	0.94	0.89	0.90
Cr										0.78	0.83		0.79	0.75	0.76	0.83
Co											0.78	0.53	0.87	0.83	0.75	0.88
Cu													0.93	0.91	0.90	0.94
Ni														0.91	0.84	0.97
Sr															0.94	0.95
As																0.87

Correlation coefficients below 0.50 were omitted; the highest coefficients were highlighted

Significant correlations were also recorded for trace elements. However, concentrations of HCO_3^- , NO_3^- , NH_4^+ , K^+ , Pb, Cd, Mn, Zn, Al, Li, and Co were independent from each other, what was additionally confirmed by exploratory factor analysis (Fig. 4).

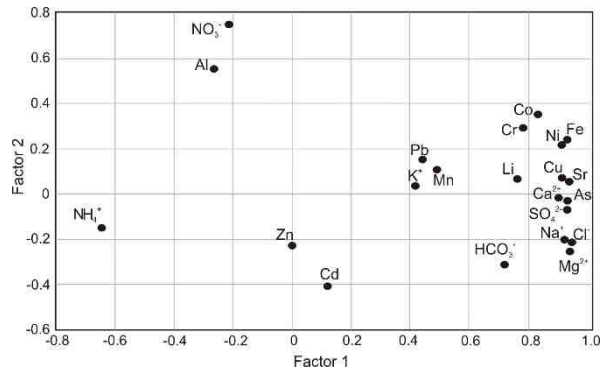


Fig. 4. Exploratory factor analysis for groundwater components in the Mhamid Oasis

Discussion

Groundwater chemistry

The Pearson correlation coefficient calculated for samples collected in the oasis was very high and ranged between $R = 0.94$ and $R = 0.99$. The chemical composition of waters was not clearly dominated by any ions and included several macrocomponents: Na^+ , Ca^{2+} , and Mg^{2+} as well as Cl^- and SO_4^{2-} . Therefore, the hydrochemical type of water [23], presented in the Piper diagram (Fig. 5), can be described as multiionic with Na-Ca-Mg-Cl-SO₄ dominance. Waters comprising macrocomponents in nearly equal proportions were also recorded in other alluvial aquifers of arid and semi-arid zones [2, 5, 8]. Multiionic hydrochemistry results from several processes affecting the chemical composition of waters. One of most important factors determining the groundwater chemistry in arid climate is evaporation [26, 27], particularly capillary evaporation. Groundwater rises towards the surface through pore spaces and evaporates, leading to precipitation of salts, afterwards dissolved by alluvial waters supplying the wells.

Processes proceeding between the water and rock medium and therefore influencing groundwater chemistry can be deduced from the saturation index (Table 4). *SI* values obtained in geochemical modelling evidence that the groundwater was undersaturated with respect to minerals such as halite, gypsum, and anhydrite. However, when considering gypsum and anhydrite, numerous samples were in a near-equilibrium state (*SI* between -0.5 and 0.5). *SI* values recorded for halite displayed a trend pointing to this mineral as the principal source of Na^+ and Cl^- supplied to groundwater. The mainly halite-dissolution origin of these ions in alluvial waters was also reported by [7] and [16]. Chloride ions may have also derived from dissolving of sylvite, evidenced by $SI < 0$, or weathering of carbonate and clay rocks. Another ion determining the hydrochemical type of water was sodium. For the examined samples, its origin also can be linked to dissolving of evaporates, primarily halite. The $r\text{Na}^+ + r\text{Cl}^-$ hydrochemical index, ranging from 1.0 to 1.2 in 91 % of samples, as well as *BEI* below 0 in 69 % of samples served as evidence of ion exchange of Ca^{2+} to Na^+ . Replacement of calcium by sodium cations is typical of shallow circulation waters, i.e. the zone of active exchange in groundwater.

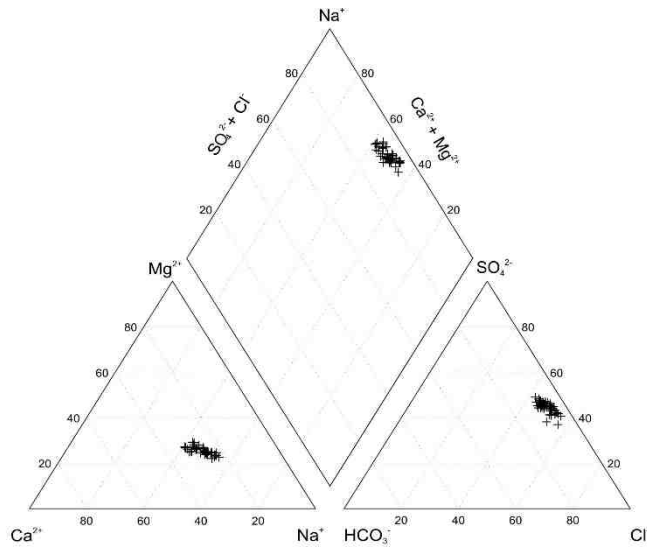


Fig. 5. Piper diagram presenting the composition of sampled groundwater

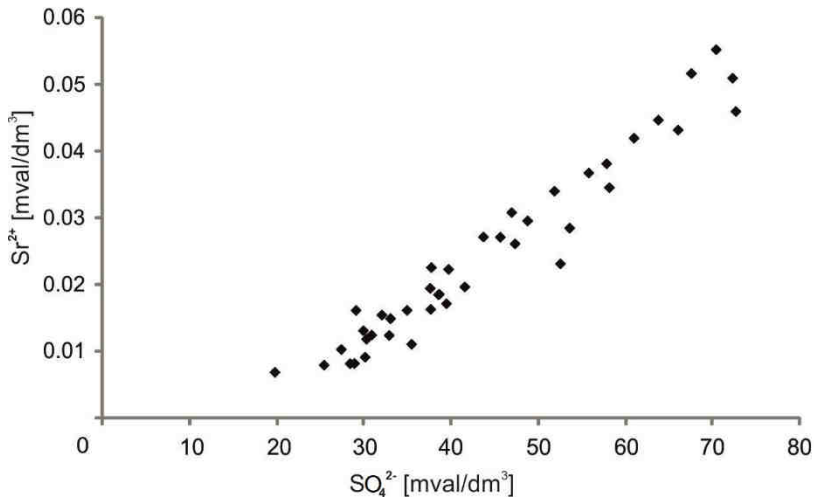


Fig. 6. Strontium versus sulphate concentrations, $R = 0.97$

The investigated alluvial waters were also abundant in calcium and magnesium cations, provided to groundwater by dissolving of sulphate and carbonate minerals. According to geochemical modelling, Ca^{2+} was supplied by gypsum and anhydrite, both being also the source of SO_4^{2-} . Dissolving of evaporates as the process giving origin to SO_4^{2-} ions was also supported by the strong correlation (0.97) between SO_4^{2-} and Sr^{2+} (Fig. 6). In evaporates, strontium is frequently found as the celestine mineral (SrSO_4), accompanying gypsum deposits. Following [28], molar concentration of $r\text{Sr}^{2+}/r\text{Ca}^{2+}$ greater

than or equal to 0.001 evidences evaporate-dissolution origin of SO_4^{2-} . The value of 0.001, confirming the assumptions by [28], was recorded in 95 % of the examined water samples (40 wells). Such a source of sulphates and mean $r\text{Sr}^{2+}/r\text{Ca}^{2+}$ value of 0.0038 was also observed by [29] in alluvial waters of the Maider catchment, ca. 200 km to the east of the study area.

Similar concentrations of macrocomponents in groundwater were also established for other Moroccan areas [3, 6, 30]. However, the values recorded in alluvial waters of the Draa river were higher than in Oman [31] or Tunisia [7].

Diversity of groundwater chemistry

The study results showed that concentrations of the considered parameters varied within the oasis area. What is most important, the content of ions determining the hydrochemical type of water increased according to the main direction of flow in the Draa river channel, from the east to west. This observation was supported by data on electrical conductivity, highest value of which (nearly 14000 $\mu\text{S}/\text{cm}$), recorded in the western part of the Mhamid Oasis, was nearly 3.5-fold greater than in the eastern part. Salinity increased primarily due to supply of sodium, chloride and sulphate ions (Fig. 7), originating, as already mentioned, from dissolving of halite and gypsum. However, although the ions were provided to alluvial waters of the Mhamid Oasis by geogenic processes, the spatial variation in concentrations should be linked to regulation of flow in the Draa river channel. High *EC* values recorded in the Mhamid Oasis resulted from the fact that this most distant among six oases in the middle Draa river valley was also the first one to receive waters discharged from reservoir Mansour Ed Dahbi. Table 6 presents minimum and maximum *EC* measured in the area of all the oases and in reservoir Mansour Ed Dahbi, following [16]. In relation to the reservoir, *EC* of alluvial waters displayed a 3-4-fold increase in the first three oases, Mezguita, Tinzouline, and Ternata, and a 12-15-fold increase in the last three oases, Fezouata, Ktaoua, and Mhamid.

Alluvial waters were supplied due to infiltration by waters flowing in the Draa river channel, during water discharge from reservoir Mansour Ed Dahbi. At discharge, the waters were easily enriched with salts, originating from dissolving of evaporates precipitated in the unsaturated zone. The evaporates were formed in periods of drying out of the channel, each time the regulated flow was ceased. Waters flowing in the Draa river channel could be additionally enriched with salts due to lateral flow of external saline surface tributaries and/or adjacent groundwater [16]. Such processes were observed in the ca. 300 km long river segment between reservoir Mansour Ed Dahbi and the Mhamid Oasis. Consequently, waters reaching the dam closing the channel above the Mhamid Oasis showed very high conductivity, up to 14000 $\mu\text{S}/\text{cm}$, and included Na^+ , Cl^- , SO_4^{2-} , Ca^{2+} , and Mg^{2+} as main components [32]. The waters supplied the alluvial groundwater of the Mhamid Oasis down to its western end, consistently with the main, east to west oriented direction of flow. In the entire oasis area, water flew only in the alluvia, as surface flow was blocked by the dam above the oasis. Several hours after discharge, when most salts were already washed out from the channel, waters reaching the dam above the Mhamid Oasis displayed lower *EC*, ca. 2500 $\mu\text{S}/\text{cm}$. The lowest recorded values attained ca. 1100 $\mu\text{S}/\text{cm}$ and were close to ones reported for reservoir Mansour Ed Dahbi [16]. Low salinity waters coming after the high salinity ones did not reach the western part of the oasis. This may have resulted from the fact that the flow of low salinity waters lasted for a shorter time or was limited by the presence of high salinity waters, with higher density.

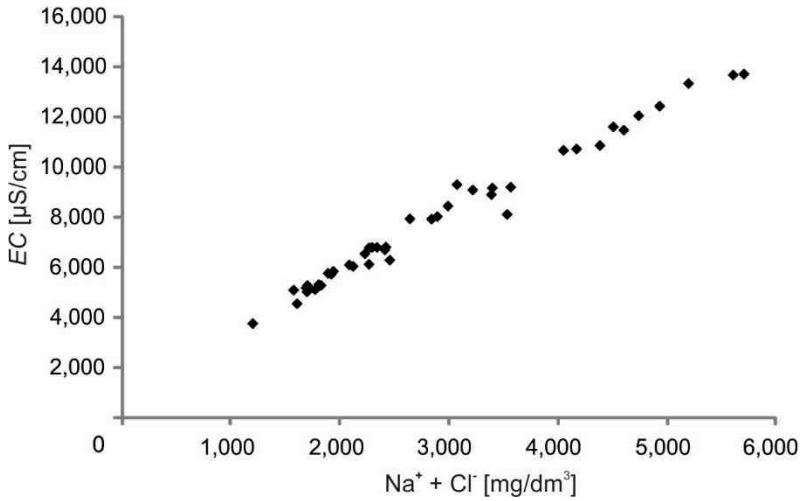


Fig. 7. Variation of $\text{Na}^+ + \text{Cl}^-$ concentration versus EC, $R = 0.98$

Waters discharged from the reservoir flew to the alluvial waters for ca. 4-7 days. After this supply was stopped, groundwater chemistry within the oasis was determined primarily by geogenic processes. The chemistry was rather not affected by the lateral flow from the Jebel Bani area, surrounding the Draa river valley from the north, as the chemical composition of alluvial waters was very similar within the Mhamid Oasis, however different from groundwater supplied from Jebel Bani (Fig. 8).

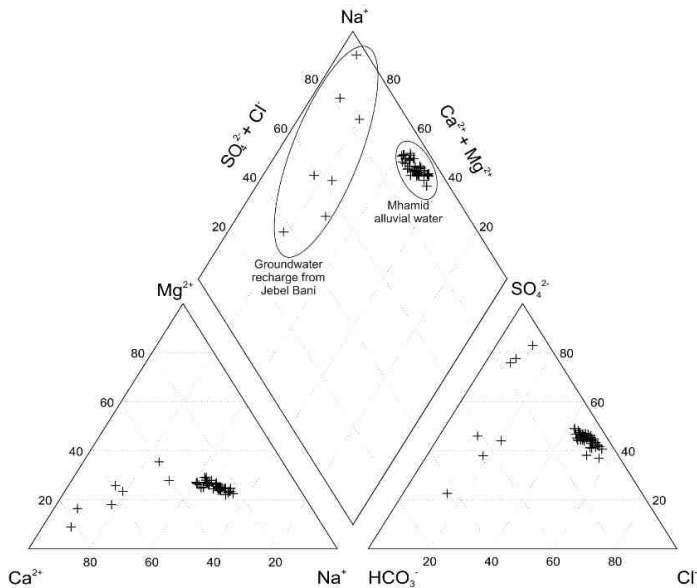


Fig. 8. Piper diagram presenting the composition of sampled groundwater from the Mhamid Oasis and Jebel Bani area

Table 6

Electrical conductivity measured in reservoir Mansour Ed Dahbi and groundwater of oases located in the Draa river valley (following [16])

Reservoir Mansour Ed Dahbi (RME)	Specific electrical conductivity [$\mu\text{S/cm}$]		
	1100		
Oasis	Min.	Max	Increase in relation to RME
1. Mezquita	710	5460	4x
2. Tinzouline	460	4280	3x
3. Ternata	750	4600	3x
4. Fezouata	2210	12430	10x
5. Ktaoua	1085	16700	14x
6. Mhamid	2500	11600	10x

Chemometric analysis indicated that concentrations of HCO_3^- and K^+ differed from other macrocomponents (Fig. 4). Correlation coefficient between the parameters attained 0.54 and both were not significantly correlated with other water components. Content of HCO_3^- , varying between particular areas and also recorded in alluvial waters of western Morocco by [5], points to lack of a universal carbonate buffer system (Fig. 9). Such waters may be prone to pH changes and consequently, due to poor buffering capacity, vulnerable to contamination. Bicarbonates found in groundwater originated primarily from leaching of carbonate rocks and dissolving of atmospheric and soil carbon dioxide in water. Occurrence of the ions usually results from a natural factor [2, 33, 34].

Presence of potassium (Fig. 10) in waters also should be linked to natural factors. In arid climate, the ion may be released by leaching of evaporates, particularly sylvite (KCl), being an easily soluble potassium salt, as evidenced by its saturation index (-6.0 on average).

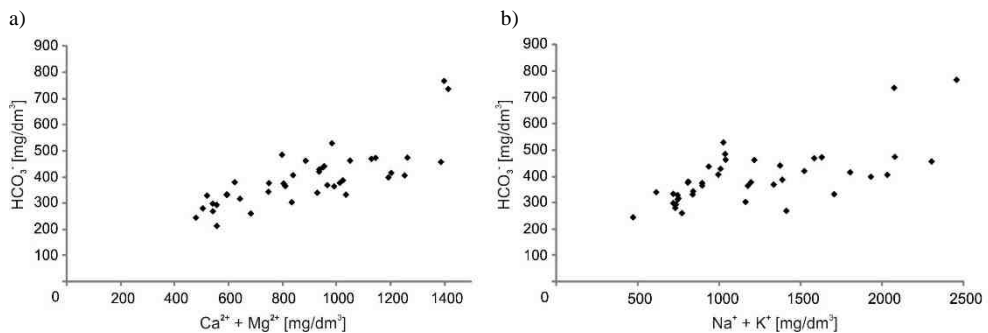


Fig. 9. Variation of: a) $(\text{Ca}^{2+} + \text{Mg}^{2+})$, $R = 0.58$, and b) $(\text{Na}^+ + \text{K}^+)$, $R = 0.43$, versus HCO_3^- concentrations. The spread of points indicates lack of carbonate equilibrium in groundwater

Groundwater may be supplied not only by substances from the water-bearing level but also by ones introduced in human activity. In the study area, the potential influx of agricultural and household contaminants to the water-bearing level was strongly limited due to intensive evaporation and infiltration of waters from the surface area only to the depth of ca. 0.5 m. Nevertheless, despite of hindered infiltration of the water-bearing level, several wells in the oasis displayed elevated concentrations of potassium, ammonium ion, and

nitrites. The mean potassium content in shallow groundwater of the terrestrial saline zone is assumed at 18.4 mg/dm^3 . In 12 % of wells in the oasis, this value was exceeded.

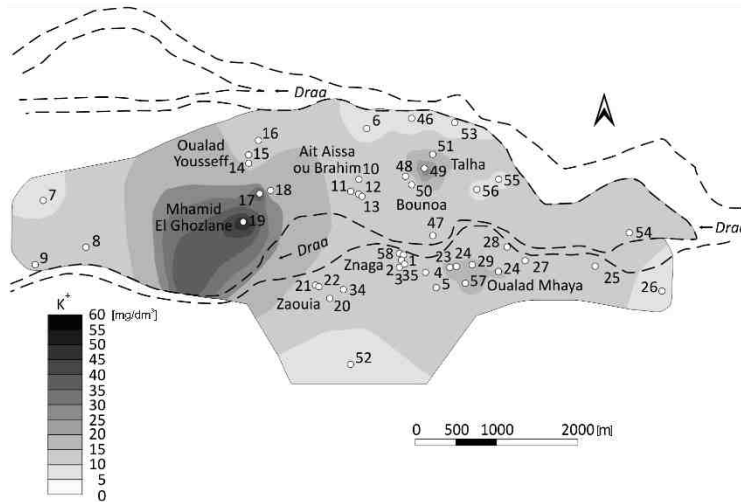


Fig. 10. Distribution of potassium in the Draa river alluvial waters

Additionally, increased concentrations of NH_4^+ and NO_3^- were recorded in some of the wells, however strongly varied (up to 200 and 152 % for NH_4^+ and NO_3^- , respectively). Diversified concentrations of nitrates in groundwater, resulting from agricultural activity and penetration of household contaminants, were already documented in numerous Moroccan regions, e.g. the Essaouira Basin [35], the Triffa Plain [6], the Ziz Basin [3], and the Figuig Oasis [36]. However, in the Mhamid Oasis wells showing high concentrations of K^+ , NH_4^+ , and NO_3^- may have been directly contaminated as the oasis does not have a sewage system.

When considering trace elements, the greatest variability was observed for (in descending order): cadmium, zinc, and lead. The elements were recorded in low concentrations in groundwater as their migration to waters was limited by intensive sorption to clay minerals and low permeability of clay rocks in the study area (filtration coefficient of 10^{-8} - 10^{-6} m/s).

Assessment of water suitability for irrigation and drinking

Assessment of water suitability for irrigation

Suitability of alluvial waters for irrigation purposes was assessed with the sodium adsorption ratio (SAR), an index commonly used for such evaluation in semi-arid and arid areas [8, 37]. Results of analysis carried out for alluvial waters in the Mhamid Oasis were presented in Figure 11. Similarly as in other Moroccan regions [5, 29], the waters displayed high and very high level of salinity for the plants and most samples presented an alkali hazard to the soil. The highest SAR value (16) was recorded in the northern, while the lowest (5) in the southern and eastern parts of the Mhamid Oasis. Much lower SAR (0.6-1.9) was observed in waters flowing from the Jebel Bani area, located ca. 10 km to the north of the Mhamid Oasis.

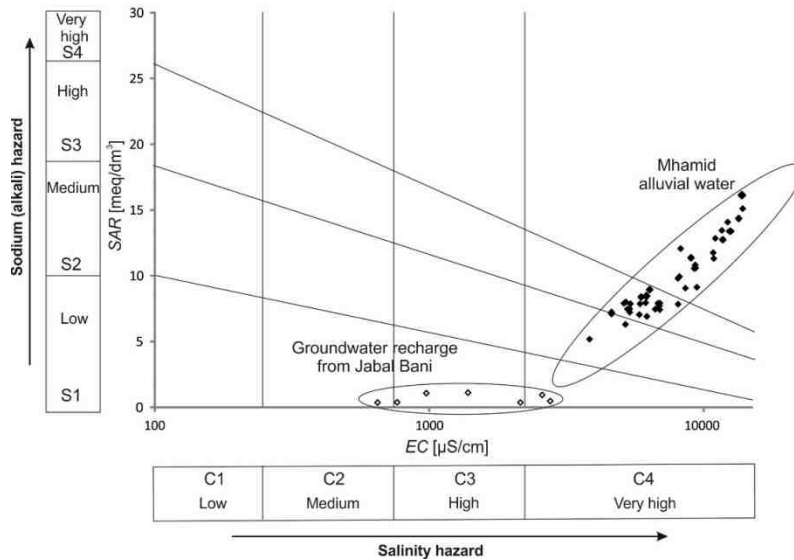


Fig. 11. Wilcox plot of salinity and alkalinity hazard for water in the Mhamid Oasis

According to the SAR versus *EC* plot, alluvial waters of the Mhamid Oasis should not be used for irrigation, particularly of plants intolerant to highly saline waters. These types of waters are suitable only for salt tolerant crops. Another issue arises from the fact that if irrigation water with high salinity hazard is applied to soil for years, sodium from the water can displace calcium and magnesium in the soil. This decreases the ability of soil to form stable aggregates and therefore causes loss of soil structure and tilth. The consequent decrease in soil infiltration and permeability to water leads to problems with crop production [38]. Although according to the SAR classification [39] 62 % of the waters can be recognized as excellent and 38 % as good for irrigation, considering the *EC* values, attaining a mean of 7 988 $\mu\text{S}/\text{cm}$, 100 % of the waters should be categorized as poor for irrigation purposes.

Assessment of water suitability for drinking

Assessment of oasis waters suitability for drinking purposes should consider the time variability of their particular components [40, 41]. Table 7 shows the percentage number of samples with exceeded allowable limits set for drinking water by the World Health Organization (WHO) and European Union (EU) in its directive.

The obtained results indicate that groundwater of the Mhamid Oasis does not meet the requirements defined by the WHO and/or EU for drinking water. The limits were exceeded in 100 % of samples for parameters such as *EC*, Ca^{2+} , Na^+ , Mg^{2+} , Cl^- , SO_4^{2-} , Fe, and As, as well as in 36 % of samples in case of Ni (EU standard). Although this contamination is of geogenic origin, the waters are not suitable for consumption by people, what has been also emphasized by e.g. [1]. The allowable limit for NH_4^+ was exceeded in 64 % of samples, indicating local anthropogenic water pollution, restricted to several wells. However, oasis groundwater was not typified by overnormative concentrations of NO_3^- , frequently observed in other regions of Morocco [3-5, 42].

Table 7
Ionic concentrations in the Mhamid Oasis groundwater exceeding the maximum allowable limits set by WHO and EU for drinking purposes

Parameter	Unit	Drinking water limits		Samples with limit exceeded [%]	
		WHO	EU	WHO	EU
<i>EC</i>	[$\mu\text{S}/\text{cm}$]	2500	2500	100	100
Na^+	[mg/dm^3]	200		100	
Ca^{2+}	[mg/dm^3]	200		100	
Mg^{2+}	[mg/dm^3]	150		100	
SO_4^{2-}	[mg/dm^3]	250	250	100	100
Cl^-	[mg/dm^3]	250	250	100	100
Fe	[mg/dm^3]		0.2		100
As	[$\mu\text{g}/\text{dm}^3$]	10	10	100	100
Mn	[mg/dm^3]		0.05		23
Ni	[$\mu\text{g}/\text{dm}^3$]	70	20	0	36
NH_4^+	[mg/dm^3]		0.5		64

Conclusions

The aim of the present study was to identify processes determining the variations in chemistry of groundwater alluvial waters used for agriculture within oasis in hot arid zone. The study was conducted in relatively small Mhamid oasis, in southern Morocco. The applied statistical, hydrochemical, and geochemical modelling methods allowed identification of the main processes determining the chemical composition of alluvial waters in the Mhamid Oasis, namely: dissolving of evaporates, particularly halite, precipitation of carbonate minerals, particularly calcite and dolomite, and ion exchange involving replacement of Ca^{2+} by Na^+ . Despite the small surface of study area, alluvial waters from the eastern and western part of the oasis appeared to strongly differ in concentrations of investigated parameters. Within the Oasis, *EC* values and concentrations of main components in the alluvial waters displayed generally a several-fold (3.5-6.5x) increase, with a maximum rise recorded for cobalt (20x) and chromium (35x). This resulted from the east to west water flow in the alluvia and regulation of flow in the Draa river. Several times higher concentration of ions responsible for salinisation of water and consequently of soils in the western part of the oasis have significance for the agricultural activity of inhabitants of these areas. There has been observed a steady decrease in water recharge of alluvial deposits in the western part of the oasis, which leads to a further increase in water salinity and may cause dramatic shortage of water for agriculture purposes in this part of the oasis.

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References

- [1] Pórcel R, de León-Gómez H. Groundwater origin and its hydrogeochemistry through GIS maps in Linares Region, Mexico. *J Water Resource Protect.* 2013;5:1-12. DOI: 10.4236/jwarp.2013.58A001.

- [2] Boukhari K, Fakir Y, Stigter TY, Hajhouji Y, Boulet G. Origin of recharge and salinity and their role on management issues of a large alluvial aquifer system in the semi-arid Haouz plain, Morocco. *Environ Earth Sci.* 2015;73:6195-6212. DOI: 10.1007/s12665-014-3844-y.
- [3] Lgourna Z, Warner N, Bouchaou L, Boutaleb S, Tagma T, Hssaisoune M, et al. Nitrate contamination of alluvial groundwater in the Ziz basin, southeastern Morocco. *Mor J Chem.* 2014;2:447-451. <https://revues.imist.ma/?journal=morjchem&page=article&op=view&path%5B%5D=2417>.
- [4] Jilali A, Abbas M, Amar M, Zarhloule Y. Groundwater contamination by wastewater in Figuig Oasis (Eastern High Atlas, Morocco). *Nature Environ Pollut Technol.* 2015;14:275-282. [http://www.neptjournal.com/upload-images/NL-52-10-\(8\)D-228.pdf](http://www.neptjournal.com/upload-images/NL-52-10-(8)D-228.pdf).
- [5] Rochdane S, Reddy DV, El Mandour A. Hydrochemical and isotopic characterisation of Eastern Haouz plain groundwater, Morocco. *Environ Earth Sci.* 2015;73:3487-3500. DOI: 10.1007/s12665-014-3633-7.
- [6] Fekkoul A, Zarhloule Y, Boughriba M, Barkaoui A, Jilali A, Chafi A, et al. Groundwater contamination by nitrates, salinity and pesticides: case of the unconfined aquifer of Triffa Plain (Eastern Morocco). *AQUA mundi.* 2011;04034:123-130. <http://jsrad.org/wp-content/2015/Issue%201,%202015/12%202015-2-1-59-61.pdf>.
- [7] Farhat B, Mammou AB, Kouzana L, Chenini I, Podda F, De Giudici G. Groundwater chemistry of the Mornag Aquifer System in NE Tunisia. *Resource Geol.* 2010;60:377-388. DOI: 10.1111/j.1751-3928.2010.00142.x.
- [8] Saibi H, Mesbah M, Moulla AS, Guendouz AH, Ehara S. Principal component, chemical, bacteriological, and isotopic analyses of Oued-Souf groundwaters (revised). *Environ Earth Sci.* 2016;75:272. DOI: 10.1007/s12665-015-4878-5.
- [9] Dłużewski M, Kozłowski R, Szczucińska A. Potential use of alluvial groundwater for irrigation in arid zones - Mhamid Oasis (S Morocco). *Ecol Chem Eng S.* 2017;24(1):129-140. DOI: 10.1515/eces-2017-0010.
- [10] Belkhirri L, Mouni L, Boudoukha A. Geochemical evolution of groundwater in an alluvial aquifer: Case of El Eulma aquifer, East Algeria. *J Afr Earth Sci.* 2012;66-67:46-55. DOI: 10.1016/j.jafrearsci.2012.03.001.
- [11] Sowers J, Vengosh A, Weinthal E. Climate change, water resources, and the politics of adaptation in the Middle East and North Africa. *Clim Change.* 2011;104:599-627. DOI: 10.1007/s10584-010-9835-4.
- [12] Huebener H, Kerschgens M. Downscaling of current and future rainfall climatologies for southern Morocco, Part II: Climate change signals. *Int J Climatol.* 2007;27:1065-1073. DOI: 10.1002/joc.1457.
- [13] Chaponniere A, Smakhtin V. A review of climate change scenarios and preliminary rainfall trend analysis in the Oum er Rbia basin, Morocco. International Water Management Institute, Working Paper 110, Drought Series. 2006;8:23. http://www.iwmi.cgiar.org/Publications/Working_Papers/working/WOR110.pdf.
- [14] Karmaoui A, Messouli M, Yacoubi Khebiza M, Ifaadassan I. Environmental vulnerability to climate change and anthropogenic impacts in dryland (Pilot Study: Middle Draa Valley, South Morocco). *Earth Sci Climatic Change.* 2014;S11:002. DOI: 10.4172/2157-7617.S11-002. DOI: 10.4172/2157-7617.S11-002.
- [15] Busche H. Hydrology of the Draa Basin. In: Schulz O, Judex M, editors. *Impetus Atlas Morocco: Research Results 2000-2007*, 3rd ed. Department of Geography, University of Bonn, Germany. 2008:43-44. <http://www.impetus.uni-koeln.de/en/impetus-atlas/impetus-atlasmorocco.html>.
- [16] Warner N, Lgourna Z, Bouchaou L, Boutaleb S, Tagma T, Hsaisoune M, et al. Integration of geochemical and isotopic tracers for elucidating water sources and salinization of shallow aquifers in the sub-Saharan Drâa Basin, Morocco. *Appl Geochem.* 2013;34:140-151. DOI: 10.1016/j.apgeochem.2013.03.005.
- [17] Schulz O, Busche H, Benbouziane ADRPE. Inflows and outflows of the Mansour Eddahbi reservoir. Data. Morocco. 2004. Decadal Precipitation Variances and Reservoir Inflow in the Semi-Arid Upper Drâa Basin (South-Eastern Morocco). In: Zereini F, Hötzl H, editors. *Climatic Changes and Water Resources in the Middle East and North Africa.* Berlin Heidelberg: Springer-Verlag; 2008. ISBN: 9783540850465.
- [18] Carrillo-Rivera JJ, Ouyse S, Hernández-García GJ. Integrative approach for studying water sources and their vulnerability to climate change in semi-arid regions (Drâa Basin, Morocco). *Int J Water Resources Arid Environ.* 2013;2:26-36. [http://www.pspw.org/attachments/article/339/IJWRAE_2\(1\)26-36.pdf](http://www.pspw.org/attachments/article/339/IJWRAE_2(1)26-36.pdf).
- [19] Dłużewski M, Krzemień K. Physical Geography of the Coude du Draa Region. In: Skiba S, Krzemień K, editors. *Contemporary Evolution of the Natural Environment of the Region between Antiatlas and Sahara (Morocco).* Prace Geograficzne IGI GP UJ. 2008;118:23-36. <http://www.geo.uj.edu.pl/publikacje.000121?&menu=3&nr=pg11803&brf=summary>.
- [20] Timm NH. *Applied Multivariate Analysis.* New York: Springer-Verlag; 2002. DOI: 10.1007/b98963.
- [21] Härdle WK, Simar L. *Applied Multivariate Statistical Analysis.* Berlin Heidelberg: Springer-Verlag; 2003. ISBN: 9783662058022.
- [22] Piper AM. A graphic procedure in geochemical interpretation of water analyses. *Am Geophys Union Trans.* 1944;25:914-923. DOI: 10.1029/TR025i006p00914.
- [23] Hem JD. Study and interpretation of chemical characteristic of natural water. U.S. Geological Survey Water-Supply Paper. 1985;2254:263. <https://pubs.usgs.gov/wsp/wsp2254/pdf/wsp2254a.pdf>.

- [24] Parkhurst DL, Appelo CAJ. User's guide to PHREEQC (ver. 2) A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US Geological Survey, the Water Resources Investment, Rept. 1999;99:4259. <ftp://brrftp.cr.usgs.gov/pub/dlpark/geochem/pc/phreeqc/manual.pdf>.
- [25] Ciaccio LL. Water and Water Pollution. 1st ed. New York: Marcel Dekker Incorporated; 1971. ISBN: 9780824711184.
- [26] Ma JZ, Wang XS, Edmunds WM. The characteristics of ground-water resources and their changes under the impacts of human activity in the arid Northwest China - a case study of the Shiyang River Basin. *J Arid Environ.* 2005;61:277-295. DOI: 10.1016/j.jaridenv.2004.07.014.
- [27] Vanderzalm JL, Jeuken BM, Wischusen JDH, Pavelic P, Le Gal La Salle C, Knappton A, et al. Recharge sources and hydrogeochemical evolution of groundwater in alluvial basins in arid central Australia. *J Hydrol.* 2011;397:71-82. DOI: 10.1016/j.jhydrol.2010.11.035.
- [28] Brins N, Boudoukha A. Statistical and hydrochemical groundwater's classification of the plain El-Outaya. Biskra-Algeria. *Courrier de Savoir.* 2011;11:41-46. <http://revues.univ-biskra.dz/index.php/cds/article/view/463>.
- [29] Brahim AY, Benkaddour A, Agoussine M, Ait Lemkadem A, Yacoubi LA, Bouchaou L. Origin and salinity of groundwater from interpretation of analysis data in the mining area of Oumjrane, Southeastern Morocco. *Environ Earth Sci.* 2015;74:4787-4802. DOI: 10.1007/s12665-015-4467-7.
- [30] Bouchaou L, Michelot JL, Vengosh A, Hsissou Y, Qurtobi M, Gaye CB, et al. Application of multiple isotopic and geochemical tracers for investigation of recharge, salinization, and residence time of water in the Souss-Massa aquifer, southwest of Morocco. *J Hydrol.* 2008;352:267-287. DOI: 10.1016/j.jhydrol.2008.01.022.
- [31] Matter JM, Waber HN, Loew S, Matter A. Recharge areas and geochemical evolution of groundwater in an alluvial aquifer system in the Sultanate of Oman. *Hydrogeol J.* 2005;14:203-224. DOI: 10.1007/s10040-004-0425-2.
- [32] Dłużewski M, Gierszewski P, Michno A, Sobczak K, Biejat K. The influence of the morphological processes on agriculture development in mountains Valley in semiarid areas. *Int J Environ Water.* 2012;3:30-47. <http://ijew.edwr.org/component/k2/item/35-the-influence-of-the-morphological-processes-on-agriculture-development-in-mountain-valleys-in-semiarid-areas.html>.
- [33] Andrade A, Stigter TY. Hydrogeochemical controls on shallow alluvial groundwater under agricultural land: case study in central Portugal. *Environ Earth Sci.* 2011;63:809-825. DOI: 10.1007/s12665-010-0752-7.
- [34] Ettayfi N, Bouchaou L, Michelot JL, Tagma T, Warner N, Boutaleb S, et al. Geochemical and isotopic (oxygen, hydrogen, carbon, strontium) constrains for the origin, salinity, and residence time of groundwater from a carbonate aquifer in the Western Anti-Atlas Mountains, Morocco. *J Hydrol.* 2012;438-439:97-111. DOI: 10.1016/j.jhydrol.2012.03.003.
- [35] Laftouhi N, Vanclooster M, Jalal M, Witam O, Aboufirassi M, Bahir M, et al. Groundwater nitrate pollution in the Essaouira Basin (Morocco). *Comptes Rendus Geosci.* 2003;335:307-317. DOI: 10.1016/S1631-0713(03)00025-7.
- [36] Jilali A, Zarhloue Y, Georgiadis M. Vulnerability mapping and risk of groundwater of the oasis of Figuig, Morocco: application of DRASTIC and AVI methods. *Arab J Geosci.* 2015;8(3):1611-1621. DOI: 10.1007/s12517-014-1320-3.
- [37] Golchin I, Moghaddam MA. Hydro-geochemical characteristics and groundwater quality assessment in Iranshahr plain aquifer, Iran. *Environ Earth Sci.* 2016;75:317. DOI: 10.1007/s12665-015-5077-0.
- [38] Jalali M. Groundwater geochemistry in the Alisadr, Hamadan, Western Iran. *Environ Monit Assess.* 2009;166:359-369. DOI: 10.1007/s10661-009-1007-5.
- [39] Thakur T, Rishi M.S, Naik PK, Sharma P. Elucidating hydrochemical properties of groundwater for drinking and agriculture in parts of Punjab, India. *Environ Earth Sci.* 2016;75:467. DOI: 10.1007/s12665-016-5306-1.
- [40] Christian WJ, Hopenhayn C, Centeno JA, Todorov T. Distribution of urinary selenium and arsenic among pregnant women exposed to arsenic in drinking water. *Environ Res.* 2006;100:115-122. DOI: 10.1016/j.envres.2005.03.009.
- [41] Thundiyil JG, Yuan J, Smith AH, Steinmaus C. Seasonal variation of arsenic concentration in wells in Nevada. *Environ Res.* 2007;104:367-373. DOI: 10.1016/j.envres.2007.02.007.
- [42] Tagma T, Hsissou Y, Bouchaou L, Bouragba L, Boutaleb S. Groundwater nitrate pollution in Souss-Massa basin (south-west Morocco). *Afr J Environ Sci Technol.* 2009;3:301-309. DOI: 10.5897/AJEST09.076.