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STUDY OF THE QUALITY OF SOME ALGERIAN THERMAL WATERS

F. Bahri and A. Addou

Laboratoire STEVA, Faculté des sciences, Université de Mostaganem (Algérie)

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ABSTRACT

The study of thermal water quality is an essential parameter for the good health of people treated at a spa. Physico-chemical parameters (conductivity, pH, Cl^-, HCO_3^-, PO_4^{3-}, SO_4^{2-}, NO_3^-, NO_2^-, F^-, TH, Ca^{2+}, K^+, Mg^{2+}, Na^+ and DS) were measured on forty-one samples taken from fourteen different areas in Algeria. The temperature of the thermal waters samples at collection vary from 26°C to 86°C. pH values vary from 6.5 to 8.5, slightly neutral to moderately alkaline. 90.24% of the samples exhibit a relatively high salinity (DS = 550 – 5500mg.l^{-1}). The total hardness (TH) shows that these waters are moderately hard. Nitrite concentration analysis shows that the waters studied have very low content of this substance by W.H.O standards (0.1mgl^{-1}). The Schoeller-Berkaloff diagram revealed the importance of chloride-calcic waters, representing 46.4 % of the samples analysed. 19.5 % of the samples are bicarbonate-sodic and 14.6 % are chloride-sodic. Bicarbonate-calcic waters represent 9.7 % whereas other types: sulphate-calcic and chloride-bicarbonate are present in 4.9 % of the cases. The hydrogeochemical parameters (Mg^{2+} / Ca^{2+}, Na^+ / Ca^{2+}, Na^+ / Mg^{2+}, Na^+ / K^+, (Na^+ + K^+) / Cl^-, (Na^+ + K^+) / (Ca^{2+} + Mg^{2+}), Cl^- / SO_4^{2-}, Cl^- / HCO_3^-, (Cl^- + SO_4^{2-}) / HCO_3^-, CEV) were considered. The cationic exchange value (CEV) calculated for all the samples is positive for 58.5 %, negative for 31.7 % and close to zero for 9.8% of the samples analysed. The ratios Na^+ / Ca^{2+}, Na^+ / Mg^{2+} and (Na^+ + K^+) / (Ca^{2+} + Mg^{2+}) are high in 90.24 % of the samples. This shows the ions exchange process is important. The Mg^{2+} / Ca^{2+} ratio values show that 61,5% of the samples have had a sufficient contact true with the rock. The Cl^- / SO_4^{2-} ratio values are high in 85.36% of the thermal waters samples. This shows that the most of the Algerian thermal waters have developed for a long time in depth and reacting with the rock. The statistical analysis of the physico-chemical data gives positive correlation values enabling a good interpretation of the results and a suggestion for the form of ions present in waters as well as some information about the thermal waters origin. The therapeutic properties associated with thermal waters encourage people taking the waters at a spa to drink it. To that effect, the drink ability of the thermal waters was investigated. W.H.O standards were used to evaluate the thermal waters quality for drinking. According to total dissolved salt content (DS). Nineteen samples, (i.e. 46.34%) are fresh waters and twenty two (i.e. 53.66%) are brackish waters. With respect to hardness, the samples are classified as moderately hard (58.54% of the samples), very hard (36.58% of the samples) and soft (4.88% of the samples). Based on Cl^-, SO_4^{2-}, HCO_3^- concentrations, the samples were classified as follows : nineteen samples (i.e.46.34%) are lower in chlorine than W.H.O standards, (<15 meq.l^{-1}) and twenty two (i.e. 53.66%) are higher; twenty nine samples (i.e.70.73%) are lower than W.H.O in sulphates (<6 meq.l^{-1}) and twelve (i.e. 29.27%) are higher; twenty height (i.e. 68.29%) are lower than W.H.O in bicarbonates (<7 meq.l^{-1}) and thirteen (i.e. 31.71%) are higher. Sixteen samples (i.e. 39%) of the investigated waters are drinkable. They may be consumed without special precaution. On the other hand, twenty-five samples (i.e. 61%) are contra-indicated for consumption and should be pointed out to people taking waters at spas.

Key words: Thermal water, hydrogeochemistry and drinkability.

INTRODUCTION

Lahlou et al., (1998) studied 238 thermal springs throughout the Maghreb. They reported the geographic coordinates, temperature, pH, some major chemical components, and the surrounding lithology of each manifestation. Thermal waters in Algeria are situated in different and complex geological structure areas (Polvêche, 1960). Some of these are well-know and used mainly for therapeutic purposes, whereas others have not been investigated so far. Several geothermal surveys were carried out in this and surrounding areas (Dib, 1985; Rezig, 1991; Bouchareb-Haouchim, 1993; Kedaid and Mesbah, 1996). These earlier studies mainly deal with site descriptions, general geological and hydro geological properties of the area, particularly focused on geothermal possibilities. The origin of thermal waters is complex as several parameters have an effect on their composition and final properties: for example, volcanic regions, movement over hot areas, freeing of rock minerals, presence of carbon dioxide, contact time with rocks, nature of rocks (Lahlou et al., 1998; Félix, 1975; Hem, 1985; Rimi, 1990; Chicano and Bosch, 1996; Rimi et al., 1998). So are formed thermal waters with a given physico-chemical composition and type (Pomerol and Ricou, 1992). They reach the earth surface through numerous geological faults. This origin provides them with a regular flow rate in dependt from rainwater, a mineralization, a constant temperature and also rare gases with some relative radioactivity (Leenhardt-Salvan, 2001). Among the several classifications of thermal water, the chemical classification is the most used (sulphur, sulphate, chloride, bicarbonate and oligometallic waters (Handler, 1968). In common language, “thermal water” is any water, generally hot, with therapeutic properties acquired over long periods of time deep in Earth, through the geological layers of a given site. The use of thermal waters for therapeutic purposes is naturally determined by their chemical composition. The scientific studies of these waters as well as the increasing importance of balneology have promoted thermal waters to the rank of true health assistants. Due to the increased importance of thermal waters, in Algeria, this weak deals with the characterization, classification and the determination of drinkability of thermal waters existing in this country. The study of drinkability will let us to effectuate in further in vitro studies of phosphates precipitation.

MATERIALS AND METHODS

Sampling sites and sample collecting

Forty-one samples were collected in November 2001 and January 2002 from fourteen different areas in Algeria (table **I**; figure **I**). Water samples were filtered in situ through a 0.45 µm filter paper (Millipore). They were stored in polyethylene bottles which were cleaned in 10% nitric acid, washed several times with distilled water and finally rinsed with thermal water sample. All the samples were immediately brought to the laboratory and stored at 4°C before analysis.

Measurements and analysis

The various parameters were determined according to AFNOR standards (AFNOR, 1986, 1999). The physico-chemical parameters such as pH, temperature, electrical conductivity were measured in situ as soon as the samples were collected. Chloride ions (Mohr’s method), sulfate ions (nephelométric method), phosphate ions (colorimetric method), nitrate ions (salicylate method), nitrite ions (Zambelli method), hydrocarbonate ions (volumétric method) and fluoride ions (potentiométric method) were analyzed after filtration of the water samples by following procedures recommended by AFNOR (1986, 1999). The total hardness (TH) was determined by titration with EDTA. Dissolved solids (DS) was determined by evaporating progressively 1l of water sample at 100°C in Bain-marie. The residue was dried at 180°C for two hours (AFNOR, 1986, 1999).

Classification of the thermal waters

The main chemical constituent of the forty one water samples studied were determined by using the Schoeller-Berkaloff diagram.

Hydrogeochemistry of the thermal waters

In order to know the origin of the thermal waters studied we have chose and calculated the following ratios: Mg^{2+} / Ca^{2+}, Na^+ / Ca^{2+}, Na^+ / Mg^{2+}, Na^+ / K^+, (Na^+ + K^+) / Cl^-, (Na^++ K^+) / (Ca^{2+}+ Mg^{2+}), Cl^- / SO_4^{2-}, Cl^- / HCO_3^-, (Cl^-+SO_4^{2-}) / HCO_3^- (Rimi et al., 1998). The value of cationic exchange (CEV [Cl^- (Na^{2+}+ K^+) / Cl^-)]) was also calculated (Brown, 1998). The statistical analysis of the physico-chemical parameters was realized using the Matlab program data, version 6.5, Tool Books.

RESULTS AND DISCUSSIONS

Characterization of the thermal waters

Mean values of the various parameters are represented in Table -1.

The temperature of the thermal waters samples at collection vary from 26 to 86°C. The temperature of the spring depends on depth and upwelling speed (Ky and Steenkiste, 1995; Chicano et al., 2001; Gültekin and Ünsal, 2003; Cidu and Bahadj, 2000). The geothermal gradient notion shows that temperature raises by 1°C every 25-30 meters of depth (Ky and Steenkiste, 1995). This allows us to sais that Algerian thermal water varies from 180 to 2580 meters. pH values vary from 6.5 to 8.5, close to drinkable water pH values, slightly neutral to moderately alkaline (table **I**). 90.24% of the samples exhibit a relatively high salinity (DS = 550 – 5500mg.l^{-1}) except for the following waters: n°12 with 100mg.l^{-1}, n°24 with 400mg.l^{-1}, n°28 with 250mg.l^{-1} and n°33 with 450mg.l^{-1}. The electrical conductivity values, varying from 662 to 5760 µs.cm^{-1}, exceed the standard values (400 µs.cm^{-1}) except for the sample n°12. This increased salinity main be due to the lithological composition of the collection sites. However, these values are lower than chloride-sodic thermal waters which exceed 55000 µs.cm^{-1} (Chicano et al., 2001; Gültekin and Ünsal, 2003; Cidu and Bahadj, 2000). The total hardness (TH) shows that these waters are moderately hard. The major anions (Cl^-, HCO_3^-, SO_4^{2-}, and NO_3^-) as well as cations (Ca^{2+}, Na^+,Mg^{2+}, and K^+) in the waters are variable. This is due to the lithological composition of the collection sites bying over several different geological and complex structures (Polvêche, 1960). Nitrite concentration analysis shows that the waters studied have very low content of this substance by W.H.O standards (0.1mgl^{-1}). Nitrate content is also lower than W.H.O recommended limit (50mg.l^{-1}). These values are low in comparison with the thermal waters studied in Morocco (Cidu and Bahadj, 2000), in Spain (Chicano et al., 2001) and Turkey (Gültekin and Ünsal, 2003).

Thermal waters classification

The use of the Schoeller-Berkalof diagram (figure **II**) and the chemical classification of the mineral waters (Handler, 1968) enabled the classification of the thermal waters studied according to chemical type (table **I**).

The typography used revealed the importance of chloride-calcic waters, representing 46.4 % of the samples analysed. 19.5 % of the samples are bicarbonate-sodic and 14.6 % are chloride-sodic. Bicarbonate-calcic waters represent 9.8 % whereas other types: sulphate-calcic and chloride-bicarbonate are present in 4.9 % of the cases. According to the IAH (International Association of Hydro geologists) (1979), the thermal waters are of Na-Cl type (strong). The chemical classification of the Algerian thermal waters studied reveals that only 14.63% of the samples are Na-Cl (weak).

Hydrogeochemistry of the thermal waters

The origin of thermal waters may be known from the various ionic ratios calculated and reported in table **II**. The cationic exchange value (CEV) calculated for all the samples are positive for 58.5 %, negative for 31.7 % and close to zero for 9.8% of the samples analysed. Positive values of CEV indicate a greater exchange of Na^+ cation in the water for Ca^{2+} cation in the rock, and to a lesser extent for Mg^{2+} cation which is retained more strongly than Ca^{2+} cation (Hem, 1985). This phenomenon which causes the water hardening is more marked in 58.5% of the analysed samples (n° 1, 2, 3, 4, 5, 8, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 35, 36, 37, 39). Ca^{2+} and Mg^{2+} cations are the major cause of hardness in waters (Soltan, 1998; Leenhardt-Salvan, 2001). The CEV value close to zero means that the Na^+- Ca^{2+} exchange is weak. It is the case of 9.8% of the samples (n° 15, 32, 33, 34). The negative CEV value shows that the thermal waters tend to be sodic with sodium predominance in 31.7% of the samples (n° 6, 7, 9, 10, 11, 12, 13, 14, 16, 17, 38, 40, 41). The ratios Na^+ / Ca^{2+}, Na^+ / Mg^{2+} and $(Na^+ + K^+) / (Ca^{2+} + Mg^{2+})$ are high in 90.24 % of the samples exempt for samples: n° 35, 38, 40 and 41. This shows the ions exchange process is important. The Mg^{2+} / Ca^{2+} ratio values show that samples : n° 1, 2, 3, 6, 7, 8, 9, 10, 12, 13, 23, 24, 25, 26 and 27 have had a sufficient contact true with the rock. The Cl^- / SO_4^{2-} ratio values are high in 85.36% of the thermal waters samples exempt for samples: n° 13, 16, 17, 39, 40 and 41. This shows that the most of the Algerian thermal waters have developed for a long time in depht and reacting with the rock. The same conclusion may be drawn for the spatial development of the $(Cl^- + SO_4^{2-}) / HCO_3^-$ (Reed and Spycher, 1984) ratio in 80.49% of the cases except for samples: n° 6, 7, 8, 9, 10, 11, 12 and 13. These

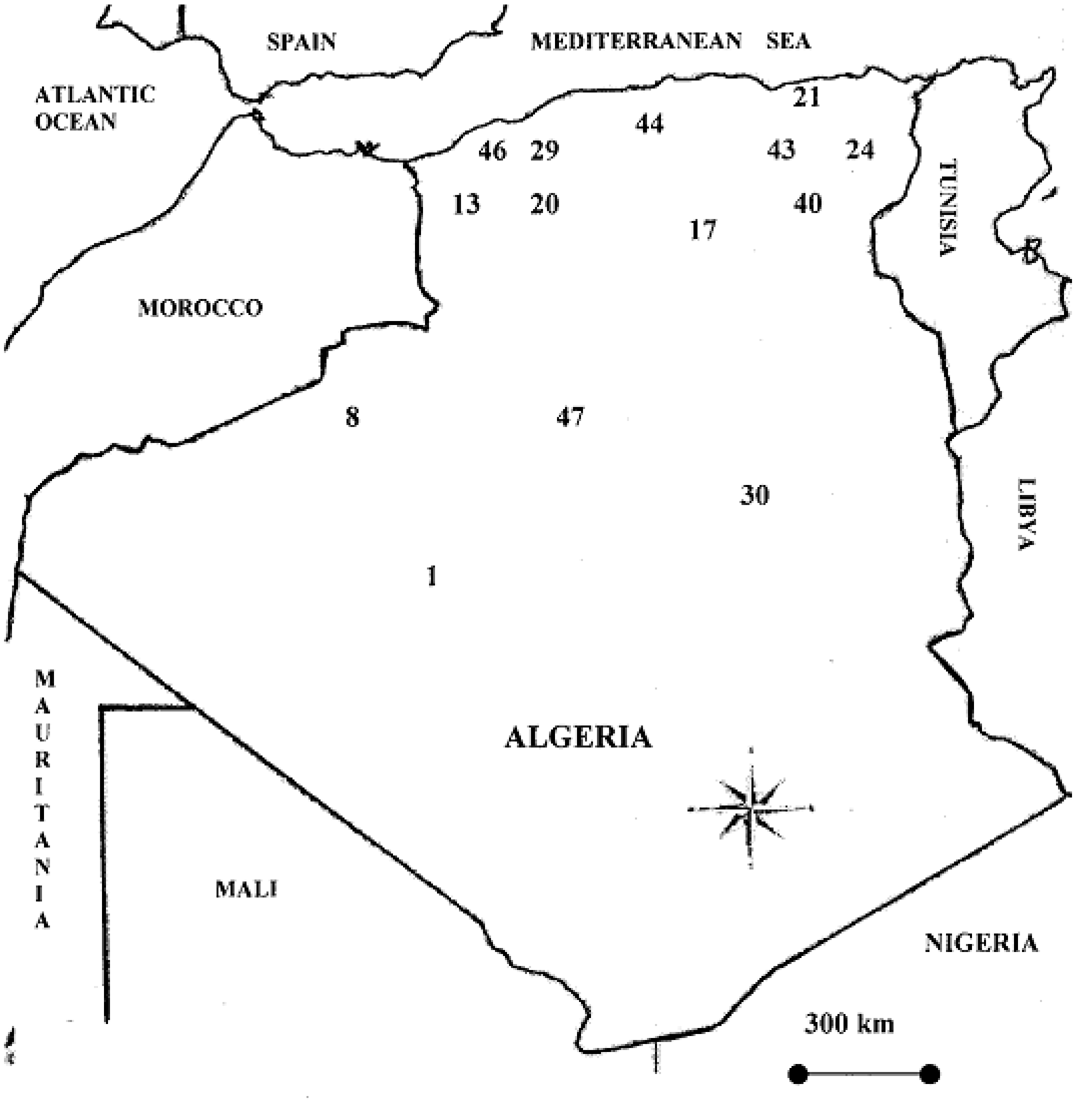

Fig. -1: Geographical local of the thermal waters studied in different wilaya of Algeria

results indicate that Algerian thermal waters arise from a mixture of sea water and cold growndwaters and waters resulting from interaction with rocks in the thermal aquifer layers.

The statistical analysis of the physico-chemical data of the samples (table**III**) shows positive correlation values (r: ranging from 0.44 to 0.66) between conductivity, dissolved solid (DS), chlorine and sodium. This is due to the fact that conductivity is related to dissolved salts content (DS) (Ciaccio, 1971) and that the prevailing constituents in dissolved salts are Cl^- and Na^+ ions.

The high correlation value (r = 0.72) between Cl^- and Ca^{2+} ions confins the prevalent chloride-calcic type in 50% of the samples (19, 20, 21, 23, 26, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41). Positive correlation values were observed between: Na^+– NO_3^-, Na^+– Cl^-, K^+– SO_4^{2-}, Zn - SO_4^{2-} et Ca^{2+} -Cl^-. This shows that these soluble salts are prevailing in most of the samples. Also,

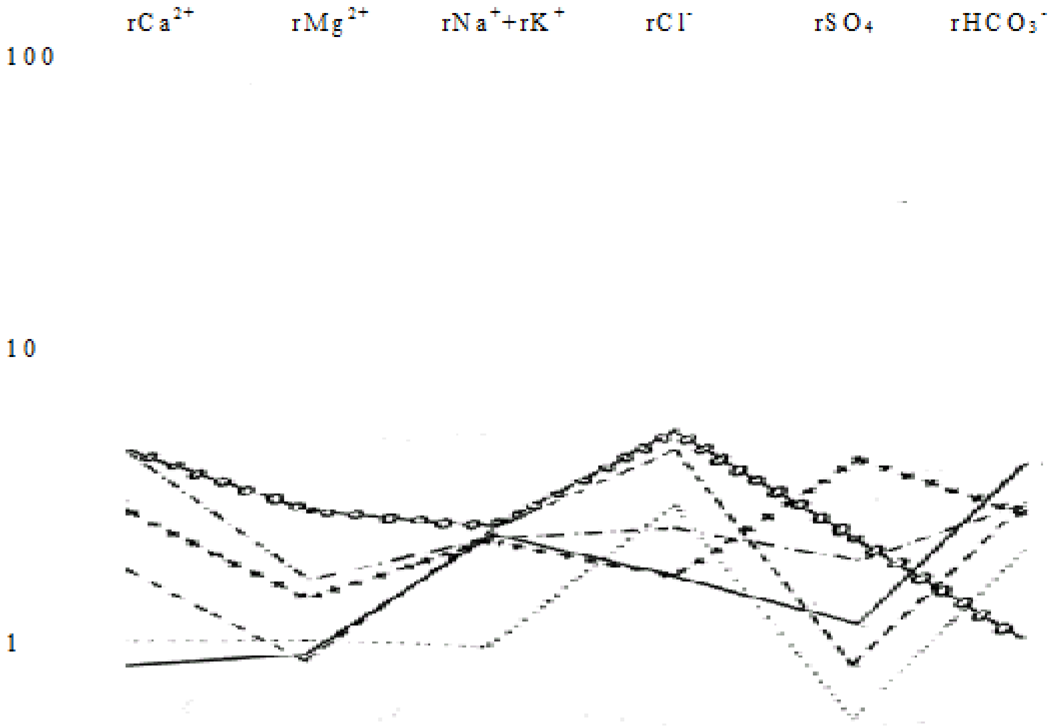

Fig. -2: Algerian thermal waters types according to SCHOLLER and BERKALOFF diagram Chloride-sodic (- - - - - -), chlorobicarbonate (. . . . . .), bicarbonate-calcic (-.-.-.-.-), Bicarbonate -sodic (______), sulfate-calcic (+ + + + +), chloride-calcic (—o-o-o-o-).

correlation values ranging from 0.45 to 0.9 were observed for Ca^{2+}- Mg^{2+}, Ca^{2+}– TH and Mg^{2+}–TH. This shows that Ca^{2+} and Mg^{2+} cations are the major cause of hardness in some samples (Soltan, 1998; Leenhardt-Salvan, 2001). Positive correlation coefficient values between Ca^{2+} - Cl^- (r = 0.12) and Ca^{2+} – PO_4^{3-} (r = 0.51) may be due to the presence of chloraptite mineral [Ca_5 $(PO_4)_3$ Cl] in the rocks which surrouding with these wells (Leenhardt-Salvan, 2001). The chloride ion presents a positive correlation (r ranging from 0.37 to 0.54) with Mg^{2+}, K^+ and Mn. This may be due to the presence of these metals as chloride in some samples. The positive correlation coefficients between conductivity - Na^+ (r = 0.44) and conductivity - Cl^- (r = 0.63), indicate the high mobility of these ions.

According to the IAH (International Association of Hydrogeologists) (1979), the thermal waters studied are of Na-Cl type (strong). The chemical classification of the Algerian thermal waters studied reveals that only 14.63% of the samples are Na^+-Cl^- (weak) (Fig. -**3**). The relations of the constituents in water samples from the study area are presented in figure **3**. The concentrations of these major ions were ploted against chloride, which is regarded as the chemical conservative for thermal waters of the Na^+–Cl^- type (1979). Weak positive correlation values were observed between Cl^--CE (Fig. -**3**.**a**), Cl^--Na^+ (figure **3**.**b**), Cl^-–Mg^{2+} (figure **3**.**c**), Cl^-–Ca^{2+} (Fig. -**3**.**d**), Cl^--SO_4^{2-} (Fig. - **3**.**e**). These results indicate that Algerian thermal waters arise from a mixture of sea water and cold growndwaters and waters resulting from interaction with rocks in the thermal aquifer layers.

Drinkability of thermal waters

The therapeutic properties associated with thermal waters encourage people taking the waters at a spa to drink it. To that effect, the drinkability of the thermal waters was investigated. The samples were classified according to total dissolved salt content (DS) (Davis and De Wiest, 1967). Nineteen samples, (i.e. 46.34%) are fresh waters and twenty

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Table -1: Chemical analyses of waters from the 41 hydrothermal springs, Algeria

N°	Site name	W.H.O standards / Sampling date	pH 6.5-8.5	T.°C	Cond 400	Cl^- 250	HCO_3^- 300	PO_4^{3-} 0.5	SO_4^{2-} 250	NO_2^- 0.1	NO_3^- 50	F^- 1	TH 50	DS 1000	Ca^{2+} 150	Na^+ 150	K^+ 12	Mg^{2+} 50	Water type
1	Boughrara	15.11.2001	7.61	42	699	340.8	378.2	0.68	59	0.026	3.98	0	12	550	150	151. 36	4.383	30.47	chloride-sodic
2	Chigueur	15.11.2001	7.15	32	4945	553.8	305	0.79	195	0.013	6.92	0	24.8	3200	343.12	2361. 3	14.908	140	chlorobicarbonate
3	Sidi El Abd Elli	29.12.2001	7.46	34	662	63.9	378.2	3.8	21	0.018	7.53	0.235	36	900	115.35	240.14	1.9162	38.48	chlorobicarbonate
4	Bouhdjar	17.11.2001	6.38	59	4857	603.5	597.8	1.54	94	0.013	4.77	0.07	38.1	3400	375	2483.2	44.186	124	chloride-sodic
5	Aïn El Hamda	17.11.2001	6.01	44	5760	582.2	915	0.52	68	0.013	3.49	0.183	43.1	4000	367	2399.9	65.747	134	chloride-sodic
6	Aïn El Djasre	12.11.2001	6.10	53	1854	170.4	915	0.62	144	0.016	6.24	0.19	24	5500	230	800. 4	21.492	126	bicarbonate-calcic
7	Aïn El Menbâ	12.11.2001	6.21	58	1662	173.95	915	0.03	172	0.020	6.79	0.08	24	650	240	820. 9	31.007	137	bicarbonate-sodic
8	Aïn El Chifa	12.11.2001	6.25	54	1701	166.85	915	0.62	178	0.016	7.02	0.185	24.5	800	230	693. 73	7.8156	111	bicarbonate-sodic
9	Aïn El Chellal	12.11.2001	6.11	47	1878	159.75	1098	0.52	127	0.011	6.72	0.173	24	750	220	652.19	28.475	133	bicarbonate-sodic
10	Aïn El Village	12.11.2001	6.67	62	1673	173.95	854	0.25	153	0.070	3.51	0	22.5	1050	232	751.73	33.158	138	bicarbonate-sodic
11	Aïn El Sekhour	12.11.2001	6.12	56	1600	156.2	976	1.11	110	0.018	6.98	0.163	23	850	163	702.98	12.876	120	bicarbonate-sodic
12	Aïn El Nekhla	12.11.2001	6.57	48	19	149.1	976	0.79	215	0.055	4.96	0.157	24	100	145	702.53	22.94	127	bicarbonate-sodic
13	La pépinière	12.11.2001	7.06	38	2095	156.2	854	0.29	347	0.018	19.09	0.162	29	1100	138.69	751.72	24.407	156	bicarbonate-sodic
14	HammamRabi.1	20.11.2001	6.93	42	2411	184.6	183	0.30	73	0.015	5.48	0.213	30	850	290	713. 3	14.986	142	bicarbonate-sodic
15	Sidi Aïssa.1	20.11.2001	7.30	46	3333	273.35	610	0.25	272	0.026	3.46	0.16	48.5	2750	304.86	1203. 1	18.999	155	sulphate-calcic
16	Rabi.2	20.11.2001	6.92	47	2438	170.4	549	0.03	729	0.015	5.23	0.149	32.5	1450	188.42	851.16	14.99	146	sulphate-calcic
17	Sidi Aïssa.2	20.11.2001	6.79	37	3324	227.2	488	0.19	788	0.013	3.05	0.2	48.5	2500	303.72	1048.3	23.197	172	chloride-sodic
18	Rhigha.1	25.01.2002	7.99	48	2844	411.8	268.4	1.38	420	0.018	3.54	0	131	3400	110	151.05	13.087	62.72	chloride-sodic
19	Rhigha.2	25.01.2002	7.58	45	2863	426	280.6	1.54	420	0.026	3.54	0	126	3400	118	151.55	13.888	57.86	chloride-calcic
20	El-Sharef.1	09.01.2002	6.80	25	2230	475.7	305	0.84	260	0.022	3.10	0.132	33	1000	261.34	149.24	23.972	57.95	bicarbonate-calcic
21	El-Sharef.2	09.01.2002	6.50	35	2541	539.6	292.8	0.57	280	0.030	2.66	0	39	1250	319.1	150.19	26.638	95	chloride-calcic
22	Timoudi	16.01.2002	6.5	30	1388	333.7	146.4	1.00	140	0.013	21.26	0	23	1000	222.41	130.73	26.738	48.75	chloride-calcic
23	Bouda	18.01.2002	6.8	26	3310	745.5	158.6	0.84	340	0.013	21.26	0.23	45	1250	349.97	148.56	56.28	110.8	chloride-calcic
24	Rouissette	13.012002	6.8	50	2425	525.4	170.8	1.11	330	0.013	3.10	0.235	53	400	418.53	150.54	46.79	123.0	bicarbonate-calcic
25	Zelfana.1	15.01.2002	7.43	42	1915	383.4	183	3.27	240	0.022	15.06	0.163	67	1650	159	151.77	16.643	61.48	bicarbonate-calcic
26	Zelfana.2	15.01.2002	7.60	41	2516	532.5	195.2	4.36	240	0.032	16.83	0	47	1450	298.61	149.13	17.927	92.55	chloride-calcic
27	Zelfana.3	15.01.2002	6.80	42	2504	546.7	146.4	0.46	330	0.016	15.95	0	45	1150	295.65	149.82	19.178	94.50	chloride-sodic
28	Zelfana.4	15.01.2002	6.80	40	1749	312.4	183	0.46	290	0.015	16.39	0	33	250	224.55	134.92	11.563	52.52	chloride-calcic
29	Beni Haroun	01.01.2002	7.16	48	5140	585.75	366	0.73	380	0.028	4.32	0.17	27.5	3350	271.79	2040.2	17.436	121	chloride-calcic
30	Monchar	01.01.2002	7.16	42	983	205.9	256.2	4.57	133	0.070	7.53	0.09	39	650	160	113.88	5.1191	37.13	chloride-calcic
31	Telghema	01.01.2002	7.50	42	873	191.7	256.2	5.44	142	0.022	7.23	0.135	38	800	147.69	108.93	4.77	35.997	chloride-calcic
32	Souna	01.01.2002	7.21	44	881	184.6	268.4	4.25	145	0.022	7.16	0.125	36	1000	168.26	110.53	4.8765	36.16	chloride-calcic
33	Es-Safsaf	01.01.2002	7.13	45	866	191.7	268.4	4.52	136	0.021	6.55	0.13	36	450	183.09	114.6	5.1963	37.55	chloride-calcic
34	Souna.2	01.01.2002	7.16	46	1004	205.9	256.2	4.79	128	0.022	6.43	0	35	600	174.53	122.23	5.5834	37.86	chloride-calcic
35	Azzaba	29.12.2001	7.07	36	2255	92.3	268.4	3.81	420	0.045	3.06	0.175	157	2700	50	455. 20	5.8114	106	chloride-calcic
36	Salihine	31.12.2001	7.38	54	2708	930.1	280.6	4.36	204	0.080	4.03	0.148	38	2000	247.19	149.4	24.748	63.28	chloride-calcic
37	Meskhoutine.1	29.12.2001	7.29	79	1973	355	329.4	5.44	260	0.022	3.08	0.163	61	1150	307.78	151.86	32.445	37.36	chloride-calcic
38	Ouled Ali.1	29.12.2001	7.08	48	1503	42.6	366	4.25	310	0.022	3.43	0.152	75	1450	39	35.685	6.0039	43.64	chloride-calcic
39	Meskhoutine.2	29.12.2001	7.07	86	806	347.9	353.8	5.14	240	0.022	3.31	0.19	64	1600	141.69	95.656	4.0778	30.60	chloride-calcic
40	Ouled Ali.2	29.12.2001	6.69	50	1347	49.7	378.2	5.14	260	0.021	3.02	0.09	68	800	33	39.489	8.4825	45.32	chloride-calcic
41	Ouled Ali.3	29.12.2001	6.78	48	852	71	378.2	4.52	270	0.022	3.31	0.075	55	950	36	41.729	8.7712	48.93	chloride-calcic

All concentrations are in mg l^{-1}; Cond., electrical conductivity (µS cm^{-1}) at 20°C;TH: total hardness in french degree; DS: dissolved solid in $mg.l^{-1}$.

Table **- 2**: Ionic ratios for 41 Algerian thermal waters studied (meq.l^{-1})

Ionic ratios Samples	C.E.V	Mg^{2+}/ Ca^{2+}	Na^+ / Ca^{2+}	Na^+ / Mg^{2+}	Na^+ / K^+	Na^++K^+/ Cl	Cl^-/ SO_4^{2-}	Cl^- / HCO_3^-	Cl+SO4^2/ HCO_3^-	(Na^++K^+) / (Ca^++Mg^2)
1	0.76	0.99	0.87	0.88	20.27	0.24	7.8	1.55	1.75	0.46
2	0.6	0.48	0.83	1.71	15.57	0.4	3.84	3.12	3.93	0.59
3	0.94	0.56	0.18	0.33	21	0.06	40.91	2.9	2.97	0.12
4	0.55	0.4	1.24	3.13	5.7	0.45	8.72	1.73	1.93	1.05
5	0.53	0.21	0.46	2.13	3.6	0.47	11.55	1.09	1.18	0.48
6	-0.48	1.14	3.42	3.01	11.95	1.48	1.6	0.32	0.52	1.74
7	-0.51	1.37	2.94	2.13	8.26	1.51	1.37	0.33	0.57	1.39
8	0.32	0.48	1.53	3.17	15.05	0.68	1.27	0.31	0.56	1.09
9	-0.63	2.18	5.13	2.36	9.07	1.63	1.7	0.25	0.39	1.79
10	-0.52	0.48	0.99	2.06	7.76	1.52	1.54	0.35	0.58	0.76
11	-0.09	0.43	1.41	3.29	13.55	1.09	1.92	0.28	0.42	1.06
12	-0.71	0.61	1.75	2.87	11.24	1.72	0.94	0.26	0.54	1.18
13	-0.64	0.67	0.95	1.41	10.48	1.64	0.6	0.31	0.83	0.62
14	-0.34	0.38	0.69	1.84	17.32	1.34	3.42	1.73	2.24	0.53
15	0.09	0.3	0.43	1.41	13.35	0.91	1.36	0.77	1.34	0.35
16	-0.46	0.41	0.7	1.72	17.39	1.45	0.32	0.53	2.22	0.53
17	-0.1	0.40	0.43	1.06	10.98	1.1	0.39	0.8	2.85	0.33
18	0.4	0.09	0.12	1.26	19.32	0.59	1.33	2.64	4.63	0.11
19	0.42	0.08	0.11	1.36	18.22	0.58	1.37	2.61	4.51	0.11
20	0.47	0.4	0.6	1.34	10.62	0.53	2.47	2.68	3.76	0.39
21	0.53	0.32	0.41	1.28	9.6	0.47	2.61	3.16	4.38	0.34
22	0.32	0.37	0.51	1.39	8.35	0.68	3.21	3.92	5.13	0.42
23	0.62	0.53	0.37	0.69	4.49	0.38	2.97	8.08	10.8	0.29
24	0.48	0.49	0.31	0.64	5.5	0.52	2.15	5.29	7.74	0.25
25	0.35	0.64	0.83	1.29	15.71	0.65	2.16	3.6	5.26	0.54
26	0.54	0.52	0.43	0.84	14.09	0.46	3	4.68	6.25	0.31
27	0.55	0.53	0.44	0.82	13.22	0.45	2.24	6.42	9.28	0.31
28	0.3	0.39	0.52	1.34	19.53	0.7	1.46	2.93	4.95	0.39
29	0.6	0.21	0.71	3.35	13.53	0.39	2.08	2.75	4.07	0.63
30	0.12	0.39	0.62	1.6	38.07	0.88	2.09	1.38	2.04	0.46
31	0.1	0.41	0.64	1.59	39.5	0.9	1.82	1.29	1.99	0.47
32	0.05	0.36	0.57	1.59	40	0.95	1.72	1.18	1.87	0.43
33	0.05	0.34	0.54	1.59	38.3	0.95	1.91	1.23	1.87	0.42
34	0.06	0.36	0.6	1.68	37.93	0.94	2.18	1.38	2.01	0.46
35	0.9	0.21	0.06	0.27	16	0.09	2.97	5.9	7.89	0.05
36	0.73	0.43	0.53	1.23	10.3	0.27	7.84	5.69	6.42	0.4
37	0.26	0.20	0.43	2.12	7.95	0.74	1.85	1.85	2.85	0.4
38	-0.42	0.13	0.06	0.43	10.33	1.42	0.19	0.2	1.27	0.05
39	0.56	0.36	0.59	1.63	41.6	0.43	1.96	1.69	2.55	0.44
40	-0.38	0.22	0.1	0.46	7.81	1.39	0.26	0.23	1.1	0.09
41	-0.02	0.19	0.08	0.44	8.23	1.02	0.36	0.32	1.23	0.07

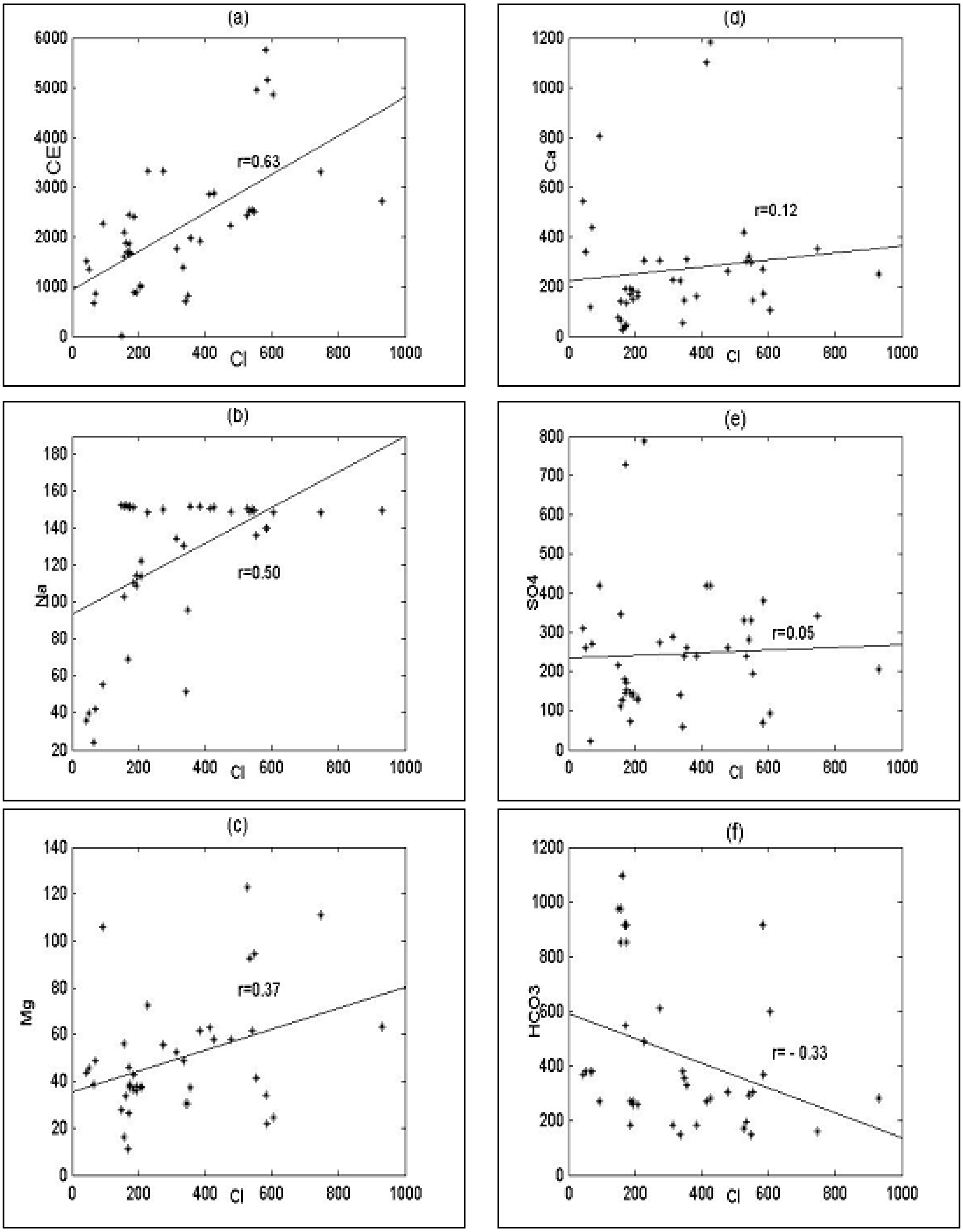

Fig. - 3: (a), (b), (c), (d), (e), (f) Relations between various ions versus chloride for thermal waters from 41 geothermal areas, Algerian (values in mg.kg^{-1})

Table - 3: Correlation coefficients of physico-chemical parameters for 41 Algerian thermal waters

	pH	Cond	Cl^-	HCO_3^-	TH	NO_3^-	$PO_4$3-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Fe^{2+}	Cr^{3+}	Cu^{2+}	Mn	Ni	Pb^{3+}	Zn	RS	Na^+
Cond.	-0.11																		
Cl^-	0.13	0.63																	
HCO_3^-	-0.64	0.02	-0.33																
TH	0.42	0.09	-0.02	-0.34															
NO_3^-	0.01	-0.05	0.16	-0.19	-0.22														
PO_4^{3-}	0.45	-0.42	-0.16	-0.43	0.31	-0.13													
SO_4^{2-}	0.17	0.24	0.05	-0.16	0.41	-0.05	-0.2												
Ca^{2+}	0.44	0.18	0.72	0.39	0.9	-0.19	0.51	0.45											
Mg^{2+}	0.25	0.16	0.37	-0.51	0.45	0.3	-0.03	0.45	0.48										
Fe^{2+}	-0.02	0.35	0.26	-0.04	0.22	-0.13	-0.1	0.01	0.27	-0.03									
Cr^{3+}	0.06	-0.02	0.19	-0.36	-0.01	0.7	-0.09	0.06	-0.02	0.30	-0.03								
Cu^{2+}	0.05	-0.02	0.15	-0.19	-0.11	-0.1	-0.05	-0.01	0.08	0.18	0.1	-0.03							
Mn	0.13	0.34	0.01	-0.02	0.71	-0.34	-0.03	0.24	0.68	0.30	0.18	-0.14	0.01						
Ni	-0.17	-0.09	-0.16	0.07	-0.25	-0.03	-0.12	-0.09	-0.21	-0.13	-0.14	0.10	0.11	-0.18					
Pb^{3+}	-0.29	-0.06	-0.16	0.17	-0.01	-0.04	-0.03	-0.11	-0.36	-0.14	-0.10	0.02	0.01	-0.03	-0.01				
Zn	0.01	-0.18	-0.14	-0.3	0.11	0.11	0.22	0.31	0.22	0.03	0.02	0.10	0.40	0.04	0.03	-0.01			
RS	-0.01	0.66	0.29	0.18	0.33	-0.28	-0.20	0.18	0.31	-0.04	0.31	-0.19	-0.17	0.47	-0.19	-0.06	-0.24		
Na^+	-0.11	0.44	0.51	0.11	-0.17	0.21	-0.49	0.21	-0.03	0.19	0.18	0.20	0.03	-0.10	-0.05	-0.07	-0.31	0.24	
K^+	-0.47	0.17	0.54	0.26	-0.16	0.13	-0.45	0.21	-0.05	0.28	-0.03	0.03	0.01	0.10	0.01	0.02	-0.16	0.23	0.54

Table -4: Various criteria used for evaluate the drinkables of 41 thermal waters samples

Criteria Samples	DS	Class	SO_4	Class	HCO_3	Class	TH	Class	Cl	Class	Genesis r	meteoric Class
1	3400	Brackish	1.95	Normal	9.8	Higher	7.62	Mod. hard	17	Higher	< 1	Deep
2	4000	Brackish	1.42	Normal	15	Higher	2.4	Soft	16.4	Higher	< 1	Deep
3	550	Fresh	1.23	Normal	6.2	Normal	2.4	Soft	9.6	Normal	< 1	Deep
4	3200	Brackish	4.06	Normal	5	Normal	4.96	Mod. hard	15.6	Higher	< 1	Deep
5	850	Fresh	1.52	Normal	3	Normal	6	Mod. hard	5.2	Normal	< 1	Deep
6	2750	Brackish	5.66	Higher	10	Higher	9.7	Very. hard	7.7	Normal	< 1	Deep
7	5500	Brackish	3	Normal	15	Higher	4.8	Mod. hard	4.8	Normal	< 1	Deep
8	650	Fresh	3.58	Normal	15	Higher	4.8	Mod. hard	4.9	Normal	< 1	Deep
9	800	Fresh	3.71	Normal	15	Higher	4.9	Mod. hard	4.7	Normal	< 1	Deep
10	750	Fresh	2.65	Normal	18	Higher	4.8	Mod. hard	4.5	Normal	< 1	Deep
11	1050	Brackish	3.19	Normal	14	Higher	4.5	Mod. hard	4.9	Normal	< 1	Deep
12	850	Fresh	2.29	Normal	16	Higher	4.6	Mod. hard	4.4	Normal	< 1	Deep
13	1000	Fresh	4.48	Normal	16	Higher	4.8	Mod. hard	4.2	Normal	< 1	Deep
14	1100	Brackish	7.23	Higher	14	Higher	5.8	Mod. hard	4.4	Normal	< 1	Deep
15	1450	Brackish	15.1	Higher	9	Higher	6.5	Mod. hard	4.8	Normal	< 1	Deep
16	2500	Brackish	16.4	Higher	8	Higher	9.7	Very. hard	6.4	Normal	< 1	Deep
17	3350	Brackish	7.92	Higher	6	Normal	5.5	Mod. hard	16.5	Higher	< 1	Deep
18	1650	Brackish	5	Normal	3	Normal	13.4	Very. hard	10.8	Normal	< 1	Deep
19	900	Fresh	0.44	Normal	6.2	Normal	7.2	Mod. hard	1.8	Normal	< 1	Deep
20	2700	Brackish	8.75	Higher	4.4	Normal	31.4	Very. hard	26	Higher	< 1	Deep
21	1150	Brackish	5.42	Normal	5.4	Normal	12.2	Very. hard	10	Normal	< 1	Deep
22	1450	Brackish	6.46	Higher	6	Normal	15	Very. hard	1.2	Normal	< 1	Deep
23	1600	Brackish	5	Normal	5.8	Normal	12.8	Very. hard	9.8	Normal	< 1	Deep
24	800	Fresh	5.42	Normal	6.2	Normal	13.6	Very. hard	1.4	Normal	< 1	Deep
25	950	Fresh	5.63	Normal	6.2	Normal	11	Very. hard	2	Normal	< 1	Deep
26	2000	Brackish	3.34	Normal	4.6	Normal	7.6	Mod. hard	26.2	Higher	< 1	Deep
27	650	Fresh	2.77	Normal	4.2	Normal	7.8	Mod. hard	5.8	Normal	< 1	Deep
28	800	Fresh	2.96	Normal	4.2	Normal	7.6	Mod. hard	5.4	Normal	< 1	Deep
29	1000	Fresh	3.02	Normal	4.4	Normal	7.2	Mod. hard	5.2	Normal	< 1	Deep
30	450	Fresh	2.83	Normal	4.4	Normal	7.2	Mod. hard	5.4	Normal	< 1	Deep
31	600	Fresh	2.66	Normal	4.2	Normal	7	Mod. hard	5.8	Normal	< 1	Deep
32	1450	Brackish	5	Normal	3.2	Normal	9.4	Very. hard	15	Normal	< 1	Deep
33	1150	Brackish	6.88	Higher	2.4	Normal	9	Very. hard	15.4	Higher	< 1	Deep
34	250	Fresh	6.04	Normal	3	Normal	6.6	Mod. hard	8.8	Normal	< 1	Deep
35	1000	Fresh	5.42	Normal	5	Normal	6.6	Mod. hard	13.4	Normal	< 1	Deep
36	1250	Brackish	5.83	Normal	4.8	Normal	7.8	Mod. hard	15.2	Higher	< 1	Deep
37	400	Fresh	6.87	Higher	2.8	Normal	10.6	Very. hard	14.8	Normal	< 1	Deep
38	1250	Brackish	7.08	Higher	2.6	Normal	9	Very. hard	21	Higher	< 1	Deep
39	100	Fresh	2.92	Normal	2.4	Normal	4.6	Mod. hard	9.4	Normal	< 1	Deep
40	3400	Brackish	8.75	Higher	4.4	Normal	26.2	Very. hard	11.6	Normal	< 1	Deep
41	3400	Brackish	8.75	Higher	4.6	Normal	25.2	Very. hard	12	Normal	< 1	Deep

$$r = \frac{\left(K^{+} + Na^{+}\right) - Cl^{-}}{SO_4^{2-}} \quad , \mathrm{DS}\ (\mathrm{mg.l^{-1}}),\ SO_4^{2-},\ \mathrm{HCO_3^-},\ \mathrm{TH},\ \mathrm{Cl^-}\ (\mathrm{meq.l^{-1}})$$

two (i.e. 53.66%) are brackish waters (table **IV**). With respect to hardness (Klimentov, 1983), the samples are classified as moderately hard (58.54% of the samples), very hard (36.58% of the samples) and soft (4.88% of the samples) (table IV). Based on Cl^-, SO_4^{2-}, HCO_3^- concentrations (O.M.S, 1993) (table **IV**), the samples were classified as follows: nineteen samples (i.e.46.34%) are lower in chlorine than W.H.O standards, (<15 meq.l^{-1}) and twenty two (i.e. 53.66%) are higher; twenty nine samples (i.e.70.73%) are lower than W.H.O in sulphates (<6 meq.l^{-1}) and twelve (i.e. 29.27%) are higher; twenty height (i.e. 68.29%) are lower than W.H.O in bicarbonates (<7 meq.l^{-1}) and thirteen (i.e. 31.71%) are higher. The DS (Davis and De Wiest, 1967), TH (Klimentov, 1983), Cl^-, SO_4^{2-}, HCO_3^- concentrations (O.M.S, 1993), the hydro geochemical parameters (Na^{2+} / Ca^{2+}, Na^+ / Mg^{2+}, Na^+ / K^+, (Na^{2+} + K^+) / Cl^-, (Na^{2+}+ K^+) / (Ca^{2+}+ Mg^{2+}), Cl^- / SO_4^{2-}, Cl^- / HCO_3^-, (Cl^- +SO_4^{2-}) / HCO_3^- et CEV) (Rimi et al., 1998, Chicano et al., 2001) results and the W.H.O normative classification (O.M.S, 1993) show that 39 % of the thermal waters are drinkable (samples N° 1, 3, 7, 8, 9, 11, 12, 14, 20, 22, 28, 30, 31, 32, 33, 34). The 61% of the remaining samples are not good for consumption. These are hard waters with a mineral content evidely exceeding W.H.O.

Conclusion

From the range of temperatures (26 to 86°C) of the forty-one samples investigated, it can be inferred that Algerian thermal waters depths range from 780 to 2580 m. The samples are slightly to moderately neutral. The relatively high salinity shows that sea water or marine sediments might have influenced the chemical composition of the thermal waters. The major anions (Cl^-, HCO_3^-, SO_4^{2-}, and NO_3^-) and the major cations (Ca^{2+}, Na^+, Mg^{2+}, and K^+) in the thermal waters are variable. This may be due to the variability of the litho logic composition in the sampling areas. Nitrate content in investigated waters is lower than W.H.O recommended limits (50mg.l^{-1}). The Scholler and Berkallof diagram enabled the classification of the forty-one thermal waters as follows: chloride- calcic (46.4%), bicarbonate-sodic (19.5%), chloride-sodic (14.6%), bicarbonate-calcic (9.8%), bicarbonate-sulphates-calcic (4.9%) and chlorobicarbonate (4.9%) waters. Hydro geochemical parameters indicate a possible contamination with sea water, but their chemical composition was diluted more strongly by ground waters. Interactions of this mixture with receiving rocks have contributed to see waters hardening. The statistical analysis of the physico-chemical data gives positive correlation values enabling a good interpretation of the results and a suggestion for the form of ions present in waters as well as some information about the thermal waters origin. Sixteen samples (i.e. 39%) of the investigated waters (samples 1, 3, 7, 8, 9, 11, 12, 14, 20, 22, 28, 30, 31, 32, 33, 34) are drinkable. They may be consumed without special precaution. On the other hand, twenty-five samples (i.e. 61%) are contra-indicated for consumption and should be pointed out to people taking waters at spas.

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