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WAPO²

TRACE ELEMENTS IN GROUNDWATER OF LA ALDEA AQUIFER (GRAN CANARIA, CANARY ISLANDS)

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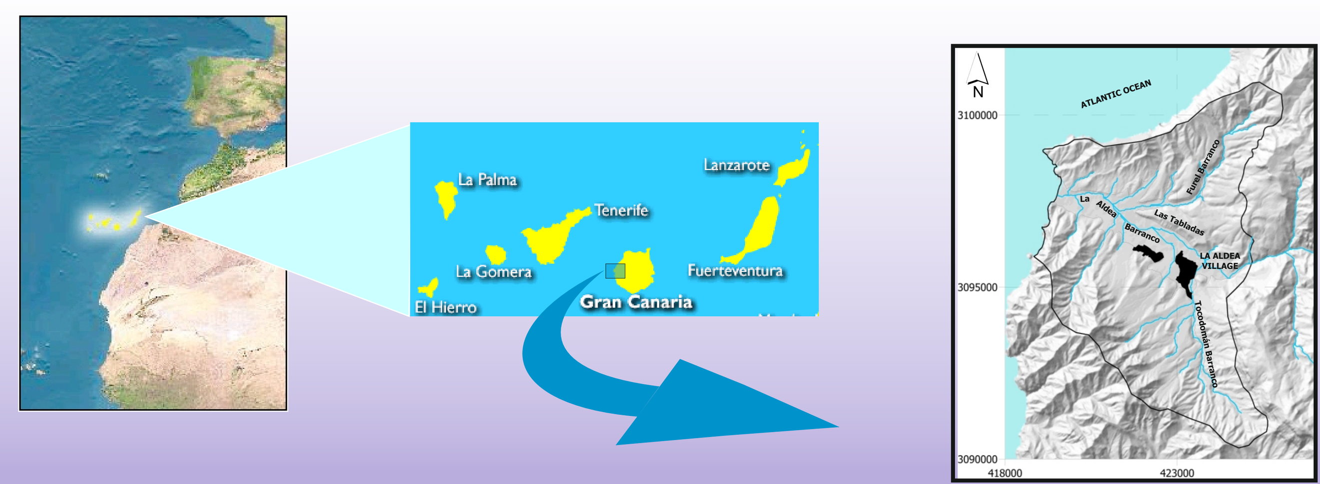
INTRODUCTION

La Aldea village is located at the end of La Aldea Valley, with slopes between 1% and 10%. This valley constitutes a deep ravine ("Barranco") surrounded by high mountains that has been excavated in volcanic materials. The heights vary from sea level to 1,415 m. Relief is hard due to the intense erosive activity developed in the island. The valley is wide in the coastal zone, where important agricultural activity has been developed since the 80's. Most of the coastal part of the valley is dedicated to intensive agriculture for export, with a cultivated surface of 645 Ha and an agriculture water consumption of 6.5 hm^3/year. Mostly tomatoes but also cucumber and tropical fruits are cultivated in greenhouses. Irrigation water supply mainly comes from three dams situated upstream. Groundwater is commonly mixed with dam waters, and is intensively exploited during droughts.

The hydrogeology of the area has been studied since 1992, and has been the subject of several research projects, including hydrogeologic and hydrogeochemistry studies. The present study shows the results of the hydrogeochemical study of the trace elements of the La Aldea Aquifer.



STUDY AREA

AQUIFER SYSTEM DESCRIPTION

The insular aquifer has been conceptualized as a stratified, heterogeneous unique body of groundwater. The recharge is produced mainly at the top of the island, with groundwater circulation taking place towards the coast and with discharges in the middle highs of the island. In the past, the island's important water supply resources came from these springs. Today they are dry and the supply is based on the exploitation of groundwater by wells. Groundwater flow is canalized preferably by the more permeable materials, proximal to the surface (SPA-15, 1974; Custodio et al., 1989, Custodio and Cabrera, 2003).

La Aldea valley lies in Miocene Basalts (14.5-14.1 Ma), consisting of a succession of basaltic and basanitic lava flows and fall pyroclasts. In the upper part of the valley, volcanic tuffs, ignimbrites and lava flows of Traquitic-rhyolitic Fm (14.1-13 Ma) crop out, in tectonic contact with the Miocene Basalts. Las Tabladas area is a complex structure located at the NE of the study area; it is made up of sedimentary materials from Las Palmas Detritic Fm. (Mio-Pliocene age) and volcanic materials of Pliocene age (Roque Nublo group) and Plio-Quaternary age. The valley bed is formed by 15-20 m thick alluvial conglomerates that overlie the Miocene Basalts.

There are more than 370 wells in the zone. All the wells located in the inner part of the aquifer perforate the alluvial conglomerates, and some of them reach the Miocene Basalts below, exploiting the groundwater from both materials. In Tocodomán valley, the wells only perforate Miocene Basalts. Groundwater flows from East to West, carrying the water laterally from the volcanic materials to the alluvial sediments. In the central part, the Miocene Basalts act like an aquitard and the alluvial conglomerates are the main aquifer.

HYDROGEOCHEMISTRY

Good quality groundwater flows through the alluvial materials, but it is progressively salinized on its way to the sea. During droughts and when groundwater coming upstream decreases, dilution of saline groundwater is reduced and groundwater salinity increases, sometimes making it useless for irrigation (Cabrera et al., 2000).

Muñoz (2005) establishes four origins for the salinity of groundwater:

1) Lithologic contribution due to the influence of the hydrothermal altered volcanic rocks (Azulejos). These waters are located in Las Tabladas boundary and can reach an electrical conductivity of 20 $mS.cm^{-1}$. High residence times in Miocene Basalts may also increase the salinity.

2) Irrigation returns, indicated by high contents of nitrates (up to 500 $mg.L^{-1}$) and sulphates.

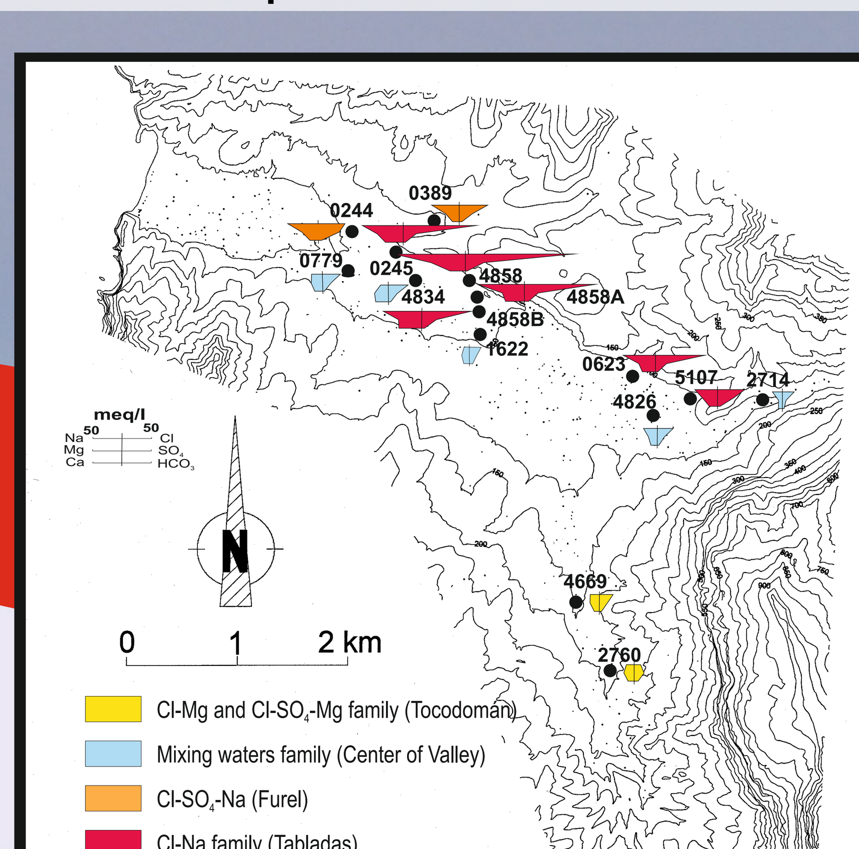
3) Climatic effect: increase of salinity of recharge due to aridity. This effect has been observed in the rainwater collectors installed in the zone.

4) Sea water intrusion in some wells located in the coastal part of the aquifer.

These processes produce different hydrochemical families, depending on the host rocks of the aquifer and the different mixing degrees between them. Cl-Mg and Cl-Na-Mg waters are related to basalts (Tocodomán family), while Cl-Na high saline waters are associated with hydrothermal altered volcanic rocks (Tabladas family). These water mix with the alluvial groundwater, producing Cl-Na-Ca or Cl-Mg waters and can evolve to Cl-SO_4-Na and SO_4-Cl-Na with high nitrate contens when irrigation returns are present (Furel family and Center of Valley).

Family	Characters	Representing Wells
Tocodomán Family	Cl-Mg to Na-Mg	4669; 2760
Tabladas Family	Cl-Na, very high salinity	4858; 4858A; 245; 623; 5107
Furel Family	Cl-Na with SO_4 high salinity	244, 389
Center of Valley	Mixing water, high NO_3	2714; 4826; 1622; 4838; 779

Stiff diagrams of groundwater from the wells sampled for trace elements



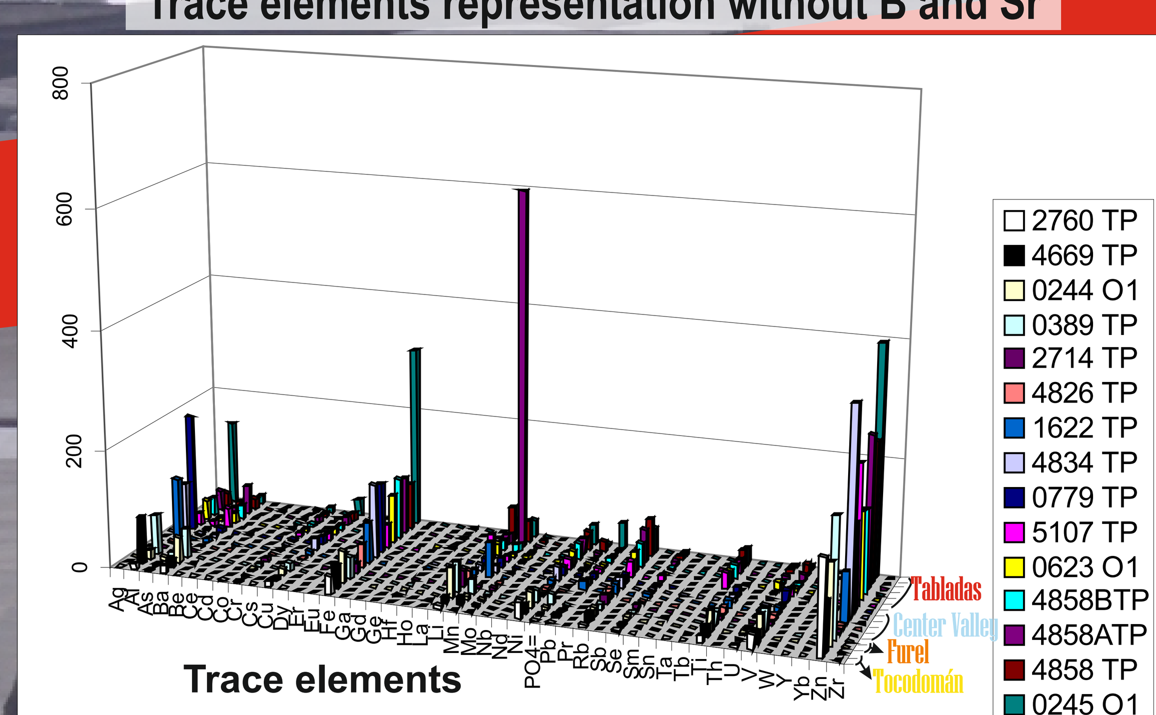
METHODS AND RESULTS

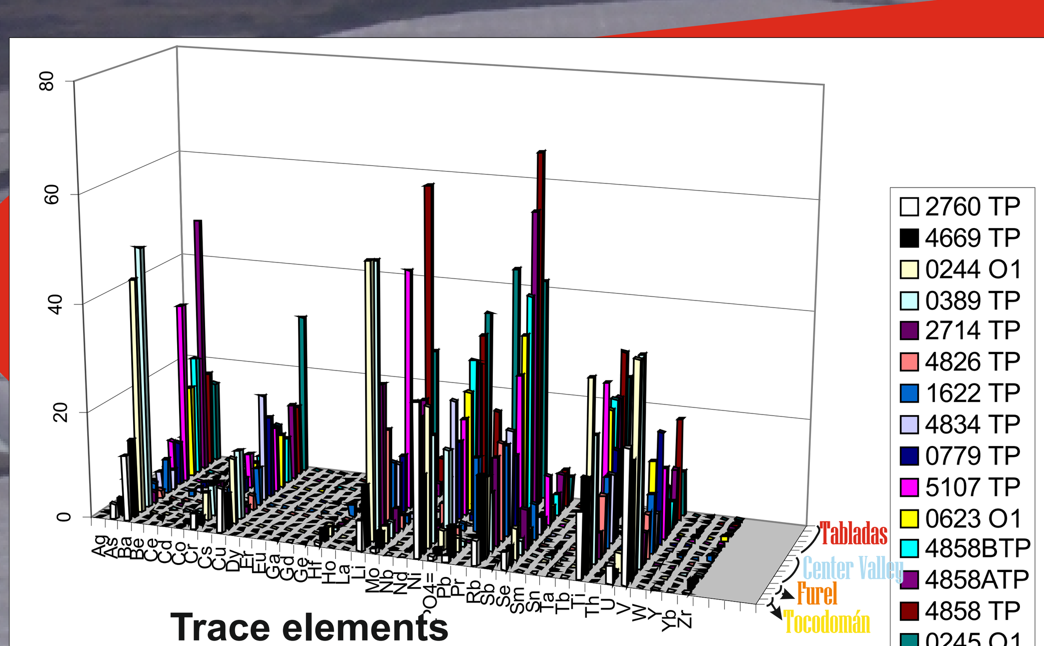
Trace elements were analyzed in the groundwater from 15 wells. These wells were selected as representative of the four hydrogeochemical families (Table 1). Figure 2 shows the Stiff diagrams for the groundwater of the wells where trace elements have been analyzed.

The sampling was made in May 2000. The methods of analysis used included inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Analysis included Ag, Al, As, B, Ba, Be, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La, Li, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Se, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tm, U, V, W, Y, Yb, Zn, Zr.

Well Id	244	389	245	623	4858	5107	4858A	4858B	2760	4669	779	1622	2714	4826	4834
Li	51.0	50.3	26.3	19.6	58.2	44.9	18.3	15.8	5.7	11.3	10.7	11.3	27.4	18.3	10.1
Be	0.08	0.03	0.03	0.07	0.03	0.03	0.1	0.1	0.06	0.03	0.13	0.08	0.1	0.07	0.01
B	1935	1383	987	1282	2134	535	1201	1286	533	357	545	175	309	508	173
Al	15.3	66.9	142.4	33.4	23.3	20.4	34.9	31.4	9.0	80.8	199.0	104.5	1.6	4.1	88.6
Ti	34.2	23.2	25.1	22.0	30.5	27.8	22.7	23.2	12.2	17.3	16.5	13.2	4.7	10.7	12.8
V	38.3	38.3	8.2	6.2	19.0	13.1	10.4	5.2	24.4	21.1	20.6	11.0	6.0	8.3	6.7
Cr	5.12	5.59	8.32	4.17	6.25	6.65	9.44	4.51	3.03	1.51	2.88	2.67	5.38	1.77	1.54
Co	0.71	0.55	1.27	0.74	0.97	0.55	1.20	1.08	0.32	0.50	0.54	0.67	0.12	0.24	0.62
Ni	26.1	20.0	34.5	22.4	30.9	18.0	26.3	27.7	28.4	14.4	14.6	9.6	2.4	5.7	23.1
Cu	12.2	13.0	30.3	10.1	13.2	12.3	14.5	8.8	8.4	6.4	15.1	7.0	1.4	2.7	20.1
Zn	135	200	394	148	240	235	257	141	161	84	147	83	3	5	348
Ga	0.01	0.02	0.03	0.02	0.02	0.01	0.12	0.03	0.01	0.02	0.02	0.01	< LD	0.01	0.02
Ge	0.01	< LD	< LD	< LD	< LD	< LD	< LD	< LD	0.04	0.06	0.04	0.05	0.06	0.05	0.02
As	5.93	5.76	6.91	5.94	9.88	7.46	8.22	6.59	2.90	3.02	3.09	1.71	2.05	2.97	2.97
Se	5.79	2.64	4.78	2.65	6.91	9.20	6.96	3.95	3.34	3.21	2.21	6.58	7.47	2.91	3.32
Rb	14.4	10.7	41.6	34.2	65.8	27.4	55.6	40.7	4.8	15.5	13.4	16.8	16.2	18.2	18.8
Sr	3454	2575	9725	7145	12068	4521	14137	13762	1822	2302	2834	2454	1127	2979	4386
Y	0.05	0.11	0.28	0.16	0.18	0.07	0.10	0.23	0.03	0.17	0.22	0.40	0.01	0.05	0.15
Zr	0.83	0.31	0.38	0.85	0.40	0.32	0.46	0.27	0.25	1.33	0.23	1.15	0.11	0.10	0.32
Nb	0.04	0.01	0.02	0.05	0.02	0.03	0.08	0.02	0.01	0.06	0.01	0.04	0.03	0.01	0.02
Mo	3.27	3.07	1.86	4.05	6.39	4.19	2.42	1.68	0.81	2.94	1.31	1.58	4.60	2.39	0.92
Ag	0.07	0.02	0.22	0.32	0.21	0.03	0.11	0.26	0.02	0.06	0.09	< LD	< LD	0.03	0.15
Cd	0.08	0.10	0.18	0.07	0.23	0.17	0.05	0.10	0.04	0.06	0.04	0.04	0.03	0.03	0.14
Sn	0.27	0.53	< LD	< LD	< LD	< LD	< LD	0.47	0.10	< LD	0.10	< LD	0.16	0.28	0.08
Sb	0.14	0.10	0.31	0.19	0.08	0.74	0.17	0.07	0.05	0.15	0.05	0.12	0.04	0.02	0.06
Cs	0.05	0.03	0.14	0.17	0.70	0.10	0.10	0.12	0.03	0.06	0.03	0.04	0.20	0.10	0.03
Ba	43.7	48.9	15.3	17.5	17.9	34.2	48.6	22.4	12.2	14.4	8.2	6.6	2.0	1.5	3.8
La	0.03	0.11	0.29	0.11	0.08	0.06	0.05	0.16	0.02	0.23	0.46	0.45	0.01	0.03	0.35
Ce	0.05	0.19	0.66	0.26	0.18	0.11	0.07	0.26	0.03	0.48	1.16	1.11	< LD	0.03	0.81
Pr	0.01	0.02	0.07	0.03	0.02	0.01	0.01	0.03	< LD	0.06	0.11	0.12	< LD	< LD	0.09
Nd	0.03	0.08	0.27	0.11	0.09	0.05	0.04	0.13	0.02	0.22	0.45	0.47	0.01	0.01	0.34
Sm	< LD	0.01	0.06	0.02	0.01	< LD	< LD	0.02	0.01	0.04	0.10	0.10	< LD	0.01	0.07
Eu	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	< LD	0.01	0.02	0.03	< LD	< LD	0.01
Gd	0.01	0.02	0.06	0.02	0.02	0.01	0.01	0.03	< LD	0.04	0.08	0.10	< LD	< LD	0.06
Tb	< LD	0.01	0.01	0.01	< LD	< LD	< LD	< LD	< LD	0.01	0.01	0.02	< LD	< LD	0.01
Dy	0.01	0.02	0.04	0.02	0.02	0.01	0.01	0.03	0.01	0.03	0.06	0.07	< LD	0.01	0.04
Ho	0.01	0.01	0.01	0.01	0.01	< LD	< LD	0.01	< LD	0.01	0.01	0.01	< LD	< LD	0.01
Er	0.01	0.01	0.02	0.01	0.01	0.01	< LD	0.02	< LD	0.01	0.03	0.03	< LD	< LD	0.02
Tm	< LD	0.01	0.01	0.01	< LD	< LD	< LD	< LD	< LD	< LD	< LD	0.01	< LD	< LD	< LD
Yb	0.01	0.02	0.02	0.01	0.01	< LD	0.01	0.01	0.01	0.02	0.02	0.03	< LD	< LD	0.01
Lu	< LD	< LD	0.01	< LD	< LD	< LD	< LD	< LD	< LD	< LD	< LD	0.01	< LD	< LD	< LD
Hf	1.97	0.67	0.53	1.78	0.79	0.78	0.75	0.48	0.57	2.13	0.31	2.14	0.26	0.29	0.31
Ta	0.04	0.04	0.02	0.04	0.02	0.03	0.03	0.01	0.01	0.02	0.01	0.02	0.02	0.01	0.01
W	0.08	0.04	0.01	0.06	0.10	0.06	0.08	0.01	0.02	0.06	0.02	0.02	0.16	0.01	0.02
Pb	2.71	1.23	43.25	5.56	3.44	7.81	3.23	9.01	1.30	5.64	8.54	13.89	0.01	0.21	7.95
Th	0.20	0.05	0.09	0.21	0.10	0.13	0.17	0.07	0.05	0.28	0.05	0.22	0.11	0.02	0.05
U	3.74	2.37	4.97	13.31	5.81	3.31	4.18	3.18	3.32	1.41	1.58	1.40	0.28	2.57	1.09

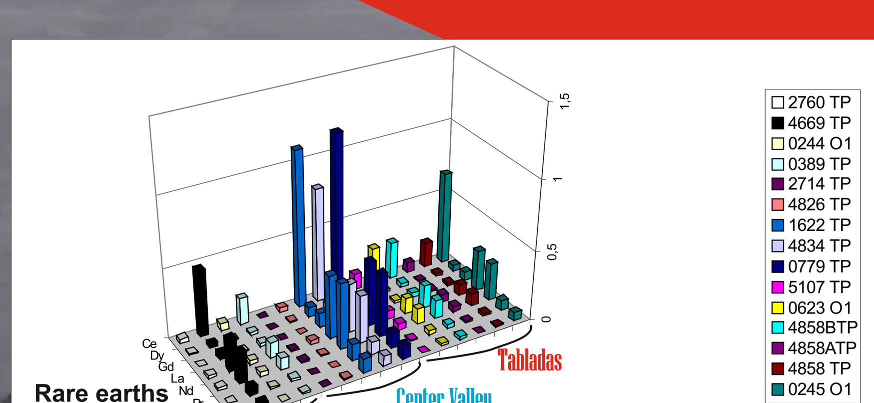
Trace elements representation without B and Sr



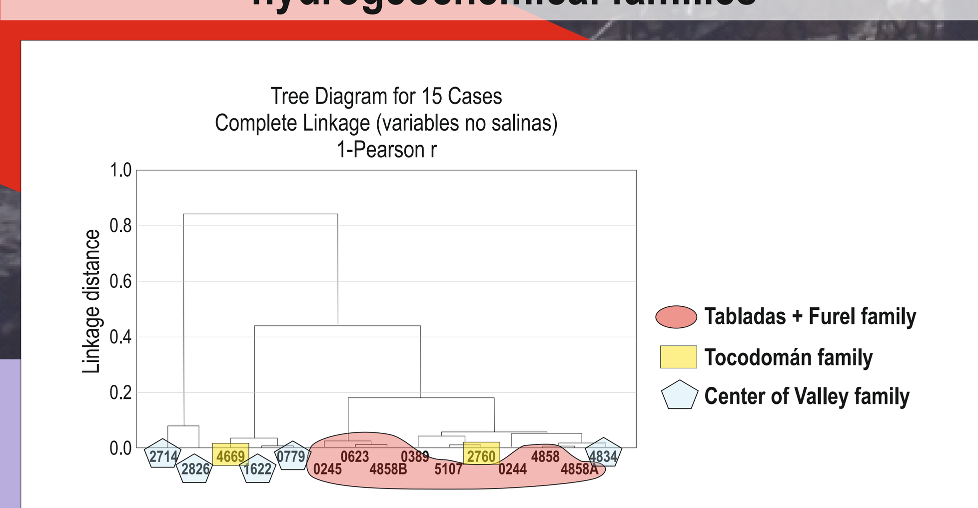


Trace elements representation without B, Sr, Al, Cu, Fe, Mn and Zn

Cluster analysis of the trace element results for the non-saline affinity elements, indicating the hydrogeochemical families



Rare Earths Elements representation



DISCUSSION AND CONCLUSIONS

The saline affinity trace elements allow us to distinguish the wells of the Tabladas and Furel families, those related to hydrothermal altered volcanic materials in the north of the La Aldea Valley. Exceptions include well no. 2760, located in the upper part of Tocodoman valley drilled in Miocene Basalts, which show clear effects of anthropogenic influences (440 $mg.L^{-1}$ of nitrates). In this case, irrigation returns must be the cause of the natural hydrogeochemistry modification.

The hydrochemical fingerprint of the *azulejos* (hydrothermal altered materials at the northern edge of the valley) is distinguished by high concentrations of Sr and B. At a different order of magnitude, concentrations of Rb, Cs, Li, U, Mo and As are also higher in the wells influenced by such materials. The hydrogeochemical fingerprints of the wells of Tocodomán and Valley Center families are quite similar, showing a greater or lesser influence of the *azulejos* fingerprint, depending of their location.

Taking into consideration the quality guidelines of the European Directive concerning the quality of water intended for human consumption (Directive 98/83/EC), some concentrations of B, Ni and Pb exceed the specified thresholds.

As a final conclusion, it can be pointed out that the hydrochemical fingerprint of the trace elements studied reflects the natural influences of the volcanic materials of the region as well as its alteration due to hydrothermal processes. The anthropogenic influence is inexistent or too low to be detected.

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