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

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## ABSTRACT

La Aldea area is dedicated to intensive agriculture for export. Irrigation water comes mainly from three dams located upstream, but groundwater is intensively used in drought periods. There are more than 370 large diameter wells (depths ranging from 4 to 47 m), cutting alluvial materials (20 m thick) in the valley axis, with Miocene basalts located under the alluvial material and in the surrounding mountains. Several hydrogeochemical groundwater families can be distinguished, depending on the exploited materials and/or the existence of some modifying processes. Cl-Mg and Cl-Na-Mg waters are related to basalts, while Cl-Na high saline waters are associated with the hydrothermal alteration of volcanic materials (Tabladas family). These waters mix with the alluvial groundwater, producing Cl-Na-Ca or Cl-Mg waters that can evolve to Cl-SO4-Na and SO4-Cl-Na, with high nitrate contents (reaching 500 $mg.L^{-1}$) when irrigation returns are present. 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 hydrochemical fingerprint of the hydrothermal altered materials in the northern end of the La Aldea valley is distinguished by high concentrations of Sr and B and, in a lesser degree of Rb, Cs, Li, U, Mo and As. The anthropogenic influence on the trace element content is inexistent or too low to be detected.

**Key words:** Trace elements, hydrogeochemistry, irrigation returns, hydrothermal alteration, Gran Canaria

## 1. INTRODUCTION

The study area is located on the western edge of Gran Canaria (Canary Islands, Spain), in La Aldea de San Nicolás municipality (Fig. 1).

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.

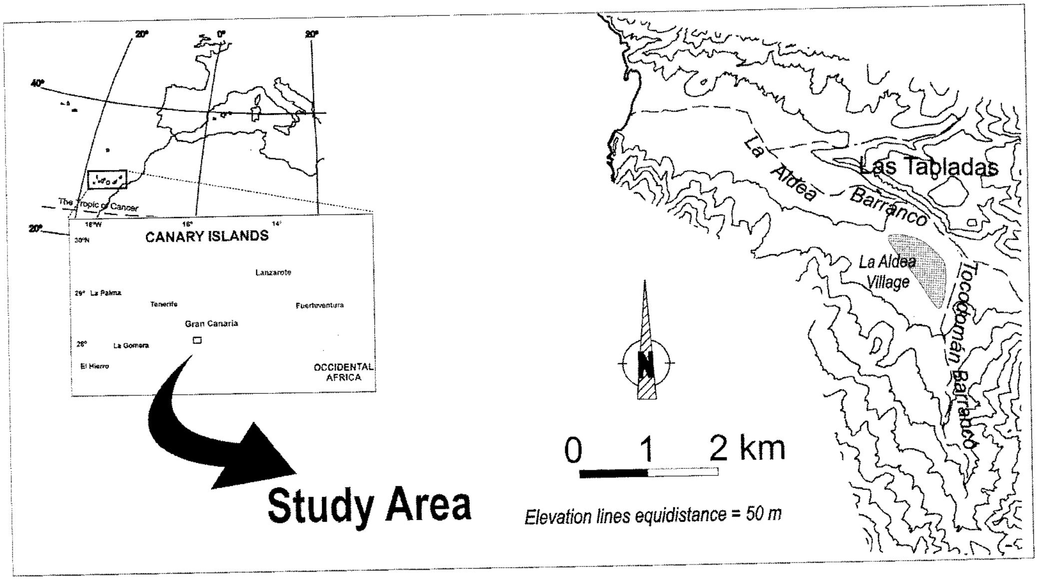


**Figure 1.** Location of the study area.

The hydrogeology of the area has been studied in depth since 1992, and has been the subject of several research projects. Well inventory begun in 1992 and was the basis for the first hydrogeologic characterization of La Aldea Aquifer carried out in the context of a European Project addressing pesticides (Muñoz *et al.*, 1996). This study confirmed the agricultural contamination of the area and pointed out the existence of a natural contribution of saline waters from the north of the valley to the La Aldea Aquifer. The saline contribution was studied under a new project, financed by the Water Authority of Gran Canaria (Consejo Insular de Aguas de Gran Canaria). These studies identified a natural hydrogeochemical fingerprint in the groundwater related to the rich Cl-Na hydrothermal multicolored materials locally known as *azulejos* (Cabrera Santana *et al.*, 2006). The hydrogeological and hydrogeochemical characterization was developed in a large project and the results were made known in several publications (Muñoz *et al.*, 2002; Bejarano *et al.*, 2002; Muñoz *et al.*, 2003) and a Doctoral Thesis (Muñoz, 2005).

The present study shows the results of the hydrogeochemical study of the trace elements of the La Aldea Aquifer.

## 2. AQUIFER SYSTEM DESCRIPTION

### 2.1. Hydrogeologic characterization

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 area'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 (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 (Fig. 1), 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 (Muñoz *et al.*, 1996).

### 2.2 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 20,000 $\mu S.cm^{-1}$. 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 the aridity. This effect has been observed in the rainwater collectors installed in the zone and (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 (Table 1). 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 waters mix with the alluvial groundwater, producing Cl-Na-Ca or Cl-Mg waters and can evolve to Cl-SO4-Na and SO4-Cl-Na with high nitrate contents when irrigation returns are present (Furel family and Center of Valley).

**Table 1.** Characteristics of the selected wells and representative groundwater families.

| 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 |

## 3. 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. Results are shown in table 2, expressed in $\mu g.L^{-1}$.

## 4. DISCUSION 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 (Fig. 3). 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 $mg \cdot L^{-1}$ of nitrates). In this case, irrigation returns are the cause of the natural hydrogeochemistry modification.

**Table 2.** Trace element data from selected wells in La Aldea Aquifer. Values are expressed in $\mu g.L^{-1}$. LD, limit of detection.

| 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 |

**Table 2.** (Continuation) Trace element data from selected wells in La Aldea Aquifer. Values are expressed in µg.L$^{-1}$. LD, limit of detection.

| Well Id | 244 | 389 | 245 | 623 | 4858 | 5107 | 4858A | 4858B | 2760 | 4669 | 779 | 1622 | 2714 | 4826 | 4834 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **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 |

The hydrochemical fingerprint of the *azulejos* -the hydrothermal altered materials at the northern edge of the valley- is distinguished by high concentrations of Sr and B (Table 2). 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.

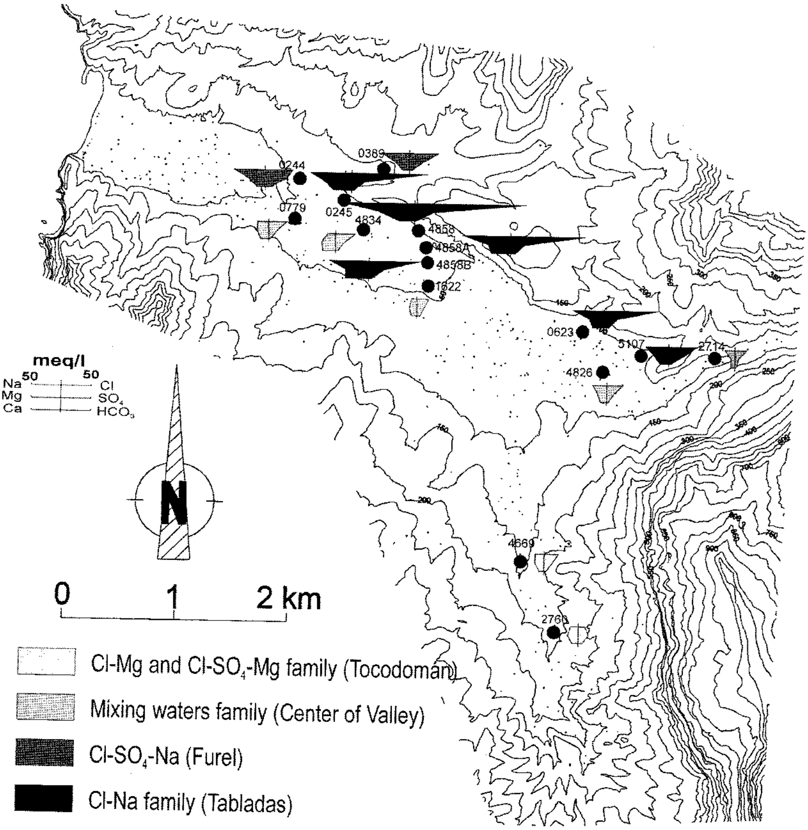


**Figure 2.** Stiff diagrams of groundwater from the wells sampled for trace elements. Four groundwater families have been differentiated, as indicated in the text.

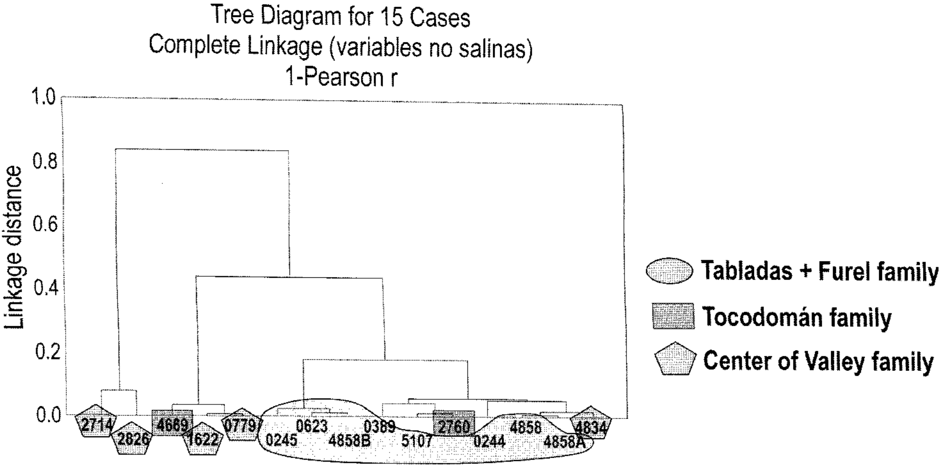


**Figure 3.** Cluster analysis of the trace element results for the non-saline affinity elements, indicating the hydrogeochemical families.

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