Geochemical assessment of the Acoculco geothermal area's waters and their potential impact on population

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1) Objective

A study of selected groundwaters sampled in Acoculco was conducted to evaluate their geochemistry and potential impact on the local population. The waters, sampled in 2016-18 within the Gemex project in collaboration with CICESE*, were analyzed for major and minor elements, also focusing on some trace metals of environmental concern. In order to assess the seasonality impact on the chemistry, samples from dry and wet seasons were examined. On behalf of the Gemex project, 49 waters (26 from the wet and 23 from the dry season) were collected by CICESE in the Acoculco geothermal area. Chemical analyses were performed by ICP-MS and ICP-OES.

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2) Descriptive statistics

General statistics data are reported in Tables 1 and 2 (for the wet and the dry seasons, respectively).

Data evidence a wide concentration range for some trace elements as a consequence of the lithological heterogeneity typical in the geothermal environment.
This applies mainly to S and As, while in the case of Mn can be related to the redox conditions' variability.

	EC	pH	T	Al	Ca	Fe	K	Mg	Mn	Na	As	Cd	Co	Cr	Cu	Ni	Pb	Sb	U	V	Zn
	µS/cm		°C	mg/L							µg/L										
Samples Number	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26
Min	11.1	3.40	12.9	.03	.69	.05	.17	.17	.01	.57	.10	.001	.09	.02	.03	.01	.01	.01	.01	.02	.10
Max	786	7.33	27.2	17.4	48.2	4.0	32.4	13.2	2.38	68.8	651	1.45	11.8	7.29	13.7	9.53	2.39	14.7	.22	9.05	224
Mean	207	5.21	18.1	5.70	18.4	3.62	5.81	4.47	.63	12.4	61.5	.11	2.88	.61	3.84	2.80	.33	3.41	.04	.96	66.0
Standard Deviation	216	1.22	3.48	6.52	16.9	7.86	6.89	4.10	.74	14.9	138	.29	3.51	1.40	4.19	2.89	.54	4.87	.04	2.03	71.1
Median	128	5.03	17.4	2.49	11.4	1.51	3.75	3.07	.25	8.54	9.92	.02	1.41	.27	2.03	1.97	.12	1.00	.03	.28	26.3
Coeff. of Variation	104	23.4	19.3	114	91.8	217	119	91.7	119	120	225	259	122	228	109	103	165	143	106	212	108

Table 1. General statistic for the water sampled in the wet season

	EC	pH	T	Al	Ca	Fe	K	Mg	Mn	Na	As	Cd	Co	Cr	Cu	Ni	Pb	Sb	U	V	Zn
	µS/cm		°C	mg/L							µg/L										
Samples Number	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23
Min	2.80	3.42	9.80	.002	1.98	.03	.42	.60	.003	2.34	.10	.001	.001	.001	.03	.01	.001	.01	.01	.001	.10
Max	1556	7.94	28.2	31.7	67.3	17.9	35.1	19.2	5.02	674	1933	7.34	3.7	4.27	27.2	25.0	.82	19.9	.34	4.52	638
Mean	519	5.24	2.6	3.11	31.6	3.17	1.8	8.16	.82	56.3	226	.85	4.74	.46	4.98	4.33	.23	2.01	.08	.76	78.6
Standard Deviation	398	1.44	5.52	7.05	19.3	4.52	1.3	5.28	1.07	137	499	1.81	8.58	.87	5.91	6.28	.23	4.18	.10	.98	144
Median	475	4.71	2.3	.17	29.0	2.02	8.03	7.00	.75	21.1	7.64	.09	.60	.23	3.56	2.38	.17	.96	.03	.42	3.9
Coeff. of Variation	76.8	27.5	26.8	226	61.2	143	94.8	64.7	130	243	221	212	181	188	119	145	100	208	128	130	184

Table 2. General statistic for the water sampled in the dry season

3) Groundwater quality assessment

Data show that some elements have quite high concentrations, being related to the emissions of geothermal fluids. These levels, in many cases, exceed the local and international limits for drinking water (Tables 3 and 4).

Al and Fe reached values up of 17.4 and 40.0 mg/L in the wet season and 31.7 and 17.9 mg/L in the dry season. Even if these elements may not be necessarily toxic, they can affect the quality of farming products.

More attention, instead, is necessary for As, whose hazard to human health is well known, since concentration up to 651 (wet season) and 1933 µg/L (dry season) were found. Such levels highlight the effect of the deep-rising hydrothermal fluids and the water-rock interaction.

pH evidences, on the whole, acidic values, with a mean of 5.21 in the wet season and 5.24 in the dry season, and minimum values that fell to about 3 (far from the guideline range of 6.5-8.5).

Parameter	Ref. Value	Parameter	Ref. Value
Al	0.20	Mn	0.15
As	0.01	Na	200
Cd	0.05	Pb	0.01
Cu	2.00	Zn	5
Fe	0.30	pH	6.5-8.5
Concentrations as mg/L			

Table 3. Drinking water guidelines in Mexico

Parameter	WHO	EPA	EU
Al	0.20	0.05-0.2	0.2
As	0.01	0.01	0.01
Cd	0.003	0.005	0.005
Cr tot	0.005	0.1	0.005
Cu	2.0	1.0	2.0
Fe	--	0.3	0.2
Mn	0.05	0.05	0.05
Na	200	--	200
Pb	0.01	0.015	0.01
Zn	3.0	5.0	--
pH	6.5-8.5	--	6.5-8.5
EC	2500	--	2500
Concentrations as mg/L; EC as µS/cm			

Table 4. International guidelines for drinking waters

4) Principal Component Analysis

The PCA (Principal Component Analysis) calculated on the wet season samples highlighted four groups (Figure 1, upper graph):

- **A**: includes the waters with the highest concentrations in Fe, Al, Ni and, Zn;
- **B**: represented only by a sample strongly enriched in Pb, V, Cr, U and, Cu;
- **C**: contains the samples with the highest concentrations in major elements (Ca, Mg, Na, K, Mn) and, As;
- **D**: includes the water with the lowest pH.

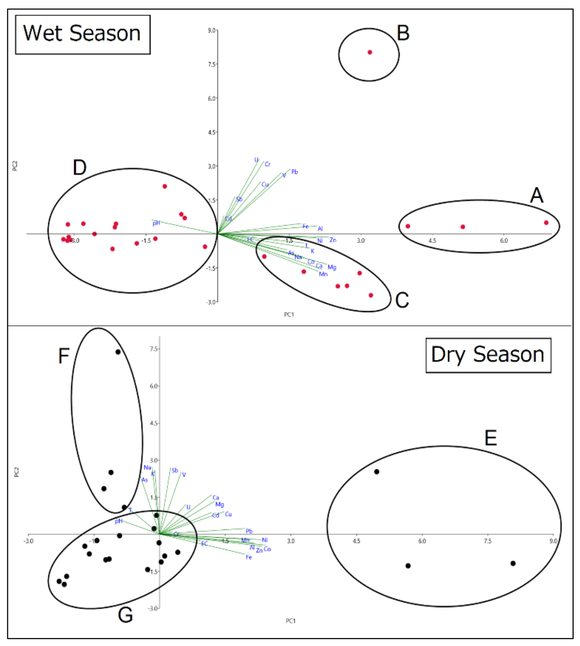

Figure 1. PCA results for dry and wet season waters

The PCA for dry season evidenced three groups (Figure 1, lower graph):

- **E**: waters with the highest Fe, Pb, Ni, Co and Zn levels;
- **F**: waters with the highest Na, K and, above all, As concentration (close to an active hydrothermal area,);
- **G**: waters with an intermediate concentration between the ones of the groups E and F.

5) Data correlations and Cluster Analysis

Correlations were calculated on the entire dataset. Among the major elements, Al and Fe exhibited the highest number of significant correlations as they are the main constituents of both minerals of primary and secondary formation. Among the minor elements, Zn showed the most significant correlations, especially with Ni (*r=0.93*), Co (*r=0.92*) and Mn (*r=0.86*). A remarkable correlation has also been found between Pb and Cr (*r=0.83*).
The dry season data showed less occurrence of significant correlations. Indeed, in the wet season, the rainwater excess promotes the solubilization and subsequent leaching of those elements with higher geochemical affinity from volcanic rocks minerals and hydrothermal deposits. In the dry season, instead, the ionic species display reduced mobility owing to the prevalence of absorption phenomena and the lack of hygroscopic water continuity between the free pores of the embedding rocks. This is further confirmed by the Cluster Analysis (Figure 2): the diagram of the wet season shows smaller distances between the variables and the clusters.

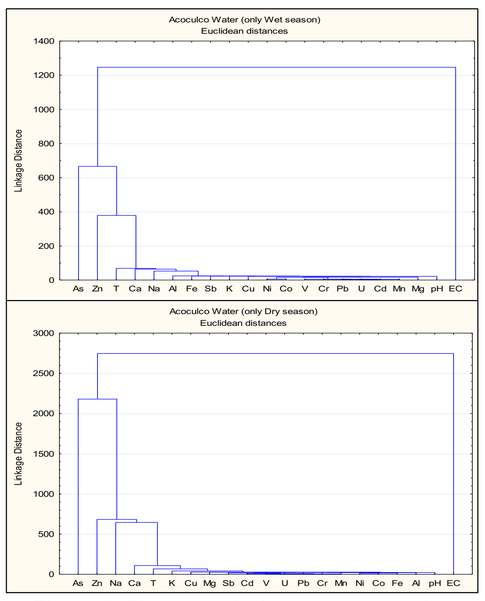

Figure 2. Cluster analysis on water samples (wet and dry seasons)

6) Conclusion

The geothermal activity and the rain seasonality seem to primarily affect the chemistry of the waters. In the dry season, the waters are characterized by enrichment in some elements while in the wet season the effect of dilution by rainfall prevails.
Since farming is a key activity in the area, particular attention must be paid in monitoring the quality of the water utilized for cultivation and animal feeding. The concentration levels of some elements and, in particular of As, are such as to pose serious problems for the animal's health themselves and for that of the consumers. A continuous quality control management of these products should be considered, in order to obtain the highest quality of the products and the end-user guarantee.

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