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CHEMICAL AND ISOTOPIC MONITORING OF RAINFALL AROUND THE LOS AZUFRES AND LOS HUMEROS GEOTHERMAL SYSTEMS: PRELIMINARY RESULTS

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ABSTRACT

A comparative chemical and isotopic study of rainwater at Los Azufres in 1995 and Los Humeros in 1996 is presented. Los Humeros is situated about 200 km east of Mexico City, whereas Los Azufres is 200 km west. The concentration of NO_3^- in samples from all sites in Los Humeros is very low. Alkalinity is positive for all sites at Los Humeros, whereas a few samples have negative values at Vivero, Los Azufres. Thus rain is not acidic at Los Humeros. A mixing model for Cl^-/SO_4^{2-} versus $\delta^{34}S$ suggests that there is 10-25% sulfate from sea spray in rainwater at Los Humeros, whereas there is less then 10% seaspray sulfate at Los Azufres.

These data suggest that the clouds formed in the Gulf of Mexico bring rain to the Central part of Mexico. Los Humeros is located east of any big industrial sites, therefore the rainwater has less anthropogenic SO_4^{2-} and NO_3^-. Rainwater at Los Azufres has contaminants from industrial sites to the east. It can be concluded that there is no discernable influence of geothermal emissions on rainwater acidity.

1. INTRODUCTION

Modern industrialization is directly related to global energy consumption, and energy generation is accompanied by environmental pollution. The consequences have been reflected in modification of local and global climate. The detrimental effects include greenhouse warming, sulfuric and nitric acid rains, loss of stratospheric ozone ultraviolet shield, increased airborne particulates, adverse health effects, decreased agricultural productivity, increased material corrosion, and destruction of and irreversible changes to natural ecological systems (Graedel and Crutzen, 1989; Schneider, 1989).

Goddard and Goddard (1990) presented comparative studies of air emission of contaminant gases, CO_2, SO_2 and NO_x which are produced from electrical generation using coal, oil, natural gas, geothermal with and without non-condensable gas injection. Bertel and van de Vate (1995) also show the relative effects of CO_2 emitted by different types of energy resources. These results indicate that the renewable geothermal resources are comparatively small burden on the environment.

But geothermal systems emit H_2S. The final destiny of the H_2S and the reaction mechanisms of transformation in the atmosphere are not yet clear. Theoretically, there is a possibility of oxidation of the H_2S to sulfuric acid in local precipitation. Muna and Bwire-Ojiambo (1986) conducted a study to determine pH and concentration of acidic components in the rainwater around the Olkaria geothermal field, Kenya. They found no appreciable effect of geothermal emissions on rainwater quality around the field.

The Comisión Federal de Electricidad (CFE) started a rainwater quality monitoring study in Los Azufres in 1993 (CFE, 1994). The Los Azufres geothermal field is about 200 km west of Mexico City. The geothermal system has an installed capacity of 88 MWe; seven back pressure units each of 5 MWe, two binary cycle units each of 1.5 MWe and one unit of 50 MWe with cooling tower to condense vapor. The emission of CO_2 and H_2S is 340 kg/hr/MWe and 3 kg/hr/MWe, respectively (Verma et al., 1998), based on concentrations in the vapor phase. But actually CO_2 and H_2S are highly soluble in the liquid phase. Therefore, the relative gas emissions from the 50 MWe unit with vapor condensation should be quite less (Verma et al., 1999).

The Los Humeros geothermal system is situated about 200 km east of Mexico City and has present installed capacity of 35 MWe, seven back pressure units each of 5 MWe. The preliminary results of rainwater monitoring at the Los Humeros geothermal system are reported by Estrada et al. (1997). The rainwater is alkaline which is probably due to uptake of dust particles. In this article we present a comparative evaluation of the rainwater chemical and isotopic composition in both the fields in order to understand the rainwater formation mechanism and the origin of acidic components.

2. DEFINITION AND QUANTIFICATION OF RAINWATER ACIDITY

Almost all studies on rainwater acidity have considered pH as a fundamental parameter. This approach was based on the very early definition of acidity as an excess of hydrogen ions with respect to the neutral point of water. Indeed, the hydrogen ion concentration is expressed in terms of pH (=-log $[H^+]$). Water at 25^oC with pH less than 7 are considered as acidic. However the concentration of hydrogen ion at pH=7 is 10^{-7} M. Thus in absolute sense the neutral (or pure) water has acidity of 10^{-7} M. Similarly, pure water at 100^oC has concentration of hydrogen ion as approximately 10^{-6} M.

Acidity in rainwater is thought to be due mostly to sulfuric and nitric acids which are formed with the oxidation of industrial or natural emissions of SO_2 ($+H_2S$) and NO_x. The dissolution of CO_2 also decreases the pH of rainwater, but it does not account for rainwater acidity. It has been accepted that the rain in clean atmosphere may have pH equal to 5.6 due dissolution of atmospheric CO_2 (Elson, 1972). The dissolution of CO_2 depends on the amount of local atmospheric CO_2 and temperature. Mukherjee and Nand (1981) suggested that the natural pH of precipitation would be higher than 5.6 in the tropical countries, prevailing higher temperatures, due to the lower dissolution rate of CO_2 than that of countries near to pole.

Additionally, pH is not an indication of the amount of acidity in rainwater. During titration the weak acids and bases, which are present in solution in undissociated form, also aggregate to acidity (stumm and Morgan, 1981). For example, a sample of rainwater with pH=3 has much less acidic effect than a highly concentrated geothermal brine of same pH. Thus the determination of rainwater pH is necessary, but it is not sufficient for the characterization and quantification of rainwater acidity. The acid base neutralizing capacity is a fundamental parameter.

In the case of carbonic systems the acid neutralizing capacity is termed alkalinity, while the base neutralizing capacity termed acidity (Stumm and Morgan, 1981). The terms alkalinity and acidity refer to how much strong acid or strong base a system is capable of neutralizing, respectively. Both of these terms are defined for certain pertinent equivalence points (EPs) for the system. Acidity is negative of alkalinity for the same reference EP point. There exist three equivalence points called the $H_2CO_3^*$EP, HCO_3^-EP and CO_3^{2-}EP. Therefore alkalinity could be defined with respect to either EP. However, in case of rainwater monitoring the alkalinity (or acidity) with respect to the $H_2CO_3^*$EP is a fundamental parameter and it is defined as

$$\mathbf{alk} = [HCO_3^-] + 2[CO_2^{2-}] + [OH^-] - [H^+]$$

The addition (or removal) of CO_2 does not change **alk**, whereas the pH of the solution decreases (or increases). Because the rainwater has very low amount of dissolved carbonic species, the alkalinity in rainwater was measured in this study with the Gran titration method (Stumm and Morgan, 1981 and Verma, 1995, 1998).

3. RESULTS AND DISCUSSIONS

Figure 1 shows the location of sampling points for rainwater at the Los Azufres and Los Humeros geothermal fields. Eight sampling sites were selected in Los Azufres to understand the space and time distribution of rainwater acidity, whereas seven sites were chosen in Los Humeros and it surroundings. We tried to select the sites to be at least 100 m from the geothermal emitting bodies such as fumaroles, production wells, etc. to avoid the direct influence of geothermal components on the rainwater samples.

Daily sampling of rainwater at Los Azufres was started in the last week of May, 1995 and continued up to the end of September, 1995. About 350 samples were analyzed from eight sites. In case of Los Humeros the sampling was conducted from July to October, 1996. The sampling could not be done on daily basis to due the difficulty in reaching sampling sites and limitations in funding. Some of the important results are presented in the following sections.

3.1 Temporal and spatial behavior of chemical species in rainwater

The concentrations of SO_4^{2-}, NO_3^- and Cl^- are less than 5 ppm in all the sites of Los Azufres except for Morelia in June (Verma et al. 1998, 1999). They suggested that the sites Morelia and Guadalajara could not have been influenced by the Los Azufres geothermal system. It has been predicted with a comparative evaluation of $\delta^{34}S$ values of rainwater sulfate that there exist two sources of atmospheric sulfur in the region and they are not related to the emissions of Los Azufres geothermal system (Verma et al., 1998, 1999). Therefore we will not include the data from the Morelia and Guadalajara sites for this study. Additionally, we are not concern here the variation of chemical species for a single storm as the bulk samples were collected for a period of rainfall. A decrease in sulfate and nitrate with time was observed in all the sites. However there is no appreciable decrease in Cl^-. The similar patterns were noted in case of Los Humeros, but the concentration of NO_3^- was very low in all the samples (Estrada et al., 1997).

In the first rainfall the atmosphere has a higher concentration of contaminants and dust particles. Thus there exists more possibility of elution of these components in the first period of rain. As the rain continues, the atmosphere has lower concentrations of these contaminants. The concentration of Cl^- does not show a similar trend as that for sulfate and nitrate, but remains constant. This means that the principal component for Cl^- is not dust particles or local emission. It can be concluded that the Cl^- has a sea-spray origin, whereas the dominant source of sulfate and nitrate could be from the industrial emissions in the region.

A good correlation between the electrical conductivity and total dissolved anions was observed (Estrada et al., 1997, Verma et al., 1998). The electrical conductivity depends on the amount of total dissolved ions (i.e. sum of cations and anions) in the solution. The total ionic charge on the anions should be equal to the charge on cations; the electrical conductivity should have good correlation with the total dissolved cations or anions. Thus the good correlation between the electrical conductivity and the sum of the concentration of SO_4^{2-}, NO_3^- and Cl^- indicates that these are the only major anions in the rainwater samples.

The values of pH do not show any tendency during the period of precipitation for each site. There is also no good correlation between pH and the dissolved anions, SO_4^{2-}, NO_3^- or Cl^-. The pH values have been considered fundamental parameter in rainwater characterization. Koch et al. (1986) conducted an interlaboratory comparison test for pH in rainwater. They found the range of value spans more than 0.3 pH unit among different laboratory measurements. During the present study reliable measurements of pH with a pH-meter were found to be difficult.

The values of alkalinity are very low and are positive for all sites except some samples from Vivero. The negative values of alkalinity indicate acidic rain. Fertilizers and seeds are stored near Vivero. Therefore, the ambient air may contain some of these acidic particles. Additionally, there are sites for experiments to understand the effect of H_2S on the growth of plants in the nursery. All these factors could contribute to the rainwater acidity at Vivero. There are no negative values of alkalinity in other sites in the region, which clearly indicates that there is no acidic rain in the region.

Figure 2 shows the relation between Cl^- and SO_4^{2-} for the averaged rainwater samples at Los Azufres and Los Humeros, together with the seawater Cl^-/SO_4^{2-} ratio line. This line was established by Herut et al. (1995). If rainwater contains Cl^- and SO_4^{2-} only from seaspray, the data point should fall on the line.

It can be seen that the rainwater points lie far above the seawater line. The points corresponding to Los Humeros (expect for El Texcal) are closer to the line than that for Los Azufres. In other words the rain at Los Azufres has more sulfate of origin other than the sea-spray.

The positive values of alkalinity also suggest that anions, such as sulfate, are not in acidic form in the rainwater. If sulfuric acid was present, the concentration of hydrogen ion should be balanced by the concentration sulfate. Thus both the sulfuric acid and nitric acids have been neutralized in the atmosphere or the sulfate and nitrate originated as salt particles. However, such low concentrations of neutralized sulfate and nitrate in the rainwater are not harmful to the environment.

3.1 Temporal and spatial behavior of $\delta^{34}S$ of dissolved sulfate in rainwater

Figure 3 shows the range of $\delta^{34}S$ values for major contributors to atmospheric sulfur (after Nielsen, 1974). Jenson and Nakai (1961) suggested three principal sources of sulfate in rainwater*: SO_2 produced by industry, H_2S originated from anaerobic bacteria and non-hygroscopic particles of SO_4^{2} from sea-spray*. The $\delta^{34}S$ value for seaspray sulfate is very uniform around 20 $^{o}/_{oo}$ (Thode et al., 1961, Sasakai, 1972, Nielsen, 1978 and Raab and Spiro, 1991). The $\delta^{34}S$ values for different natural and/or anthropogenic sources overlap, so it is hard to get concrete information about the contribution of different sources.

Mizutani and Rafter (1969) formulated a mixing model among the chemical composition of Cl^- and SO_4^{2-} and $\delta^{34}S$ of dissolved sulfate in rainwater for identification of sulfur sources and estimation of their relative contribution. They found that sulfate in seaspray was the main source of sulfate in rainwater at Gracefield, New Zealand. Cortecci and Longinelli (1970) applied the same method to demonstrate that the source of sulfate in rainwater in Pisa, Italy was atmospheric oxidation of SO_2 from industrial activity. Herut et al (1995) indicated that the sulfate in rainwater in Israel produced by mixing of two components, sea-spray and anthropogenic sources.

Figure 4 shows the Mizutani and Rafter's mixing model diagram. All the data from this study fall very close to a non-seaspray source. The data from Los Azufres could have less than 10% sulfur from sea-spray, whereas there is 10-25% sulfur from sea-spray in the rain at Los Humeros. Herut et al (1995) suggested that the anthropogenic and natural sulfur sources could produce rainwater sulfur isotopic values in the range –40 to 40 $^{o}/_{oo}$. In actuality, the isotopic values of rainwater sulfate around the world lie in the range –3 to 20 $^{o}/_{oo}$ and plot along a mixing line (Figure 4). It looks like that there are two end members; sea-spray and some other end member with isotopic composition around –0.3$^{o}/_{oo}$. It is surprising to observe such a good correlation for all the rainwater samples around the world. Apart from it, the applicability of sulfur isotopes in rainwater monitoring requires an improved understanding of all the mechanisms of formation and fractionation processes of rainwater sulfate (Holt et al, 1981, 1982).

4. CONCLUSIONS

The comparative study of rainwater at Los Azufres and Los Humeros provides some important clues on the origin of Cl^-, SO_4^{2-} and NO_3^-. The source of Cl^- in the rainwater is probably seaspray, whereas sulfate and nitrate are associated with more local sources. The concentration of nitrate in rainwater at Los Humeros is zero. Similarly all the values of alkalinity are positive in rainwater at Los Humeros. The amount of anthropogenic sulfur is relatively low at Los Humeros. All these evidences suggest that the rain at Los Humeros has fewer industrial contaminants than at Los Azufres.

A chemical and isotopic mixing model suggests that sulfur in rainwater at Los Azufres has less than 10% seaspray component, whereas rain al Los Humeros has 10-25%. The $\delta^{34}S$ values for the different non-seaspray sources of atmospheric sulfur overlap, which makes it difficult to determine the origin of the non-seaspray sulfur in rainwater at the geothermal fields. The $\delta^{34}S$ values of dissolved sulfate are a very useful parameter in identification of sulfur sources in the atmosphere, but it requires a detailed study to measure $\delta^{34}S$ in all the possible sources of sulfur emission in the region and in rainwater for long period of time.

It can be concluded that clouds forming in the Gulf of Mexico supply precipitation to the central part of Mexico. This is based on the evidences: (1) the west side of mountains in the central part of Mexico has relatively low amount of precipitation and (2) the location of the geothermal fields. Los Humeros is in the east of industrial sites and has no acidic rain; whereas Los Azufres is in the west of the industrial sites and has some acidic rain. There is need for a database of rainwater chemistry for a long period of time.

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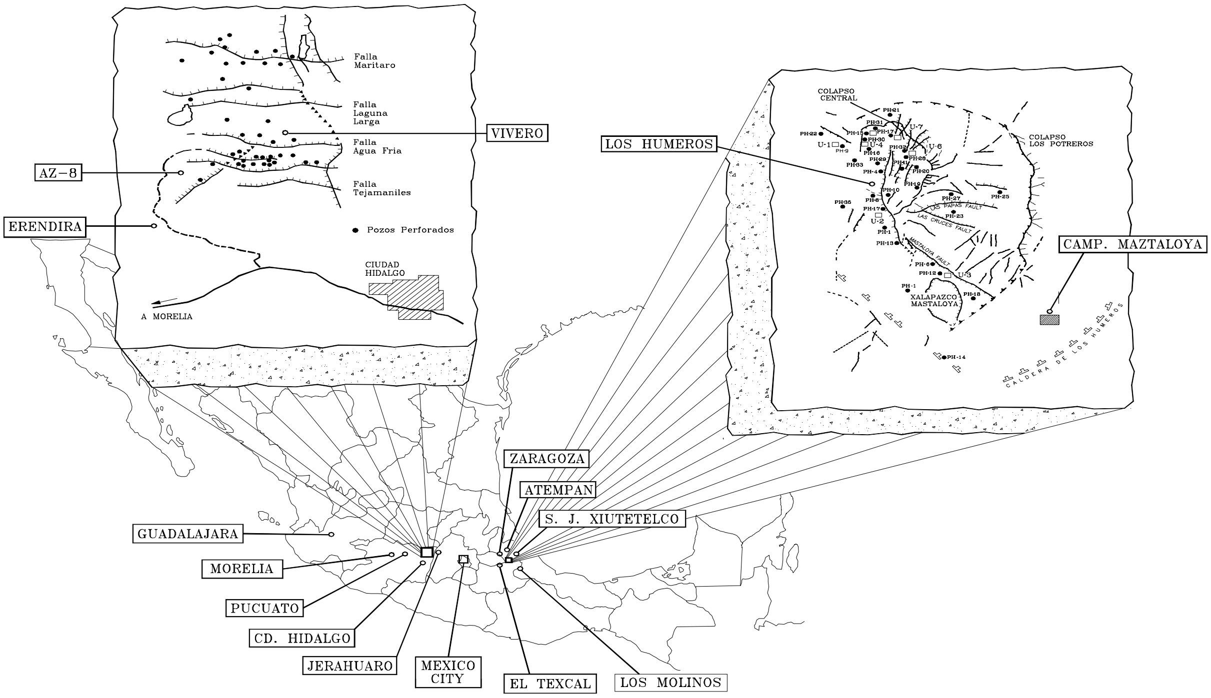

Figure 1: Location map of the rainwater sampling at the Los Azufres and Los Humeros geothermal systems

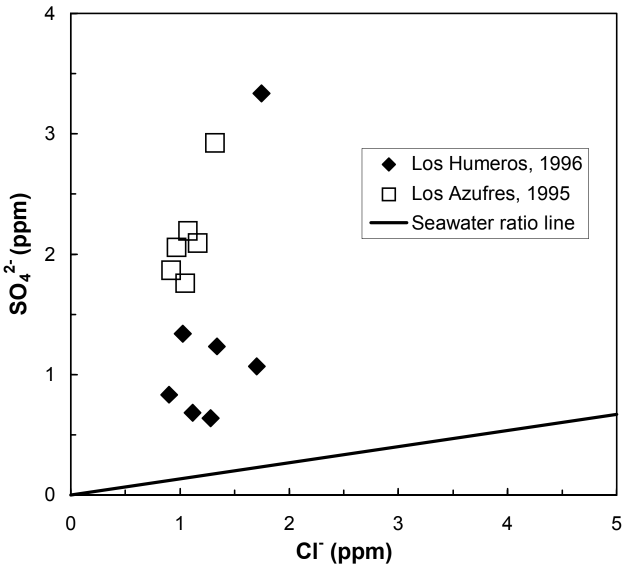

Figure 2: Plot of chloride and sulfate for the rainwater samples at Los Azufres and Los Humeros.

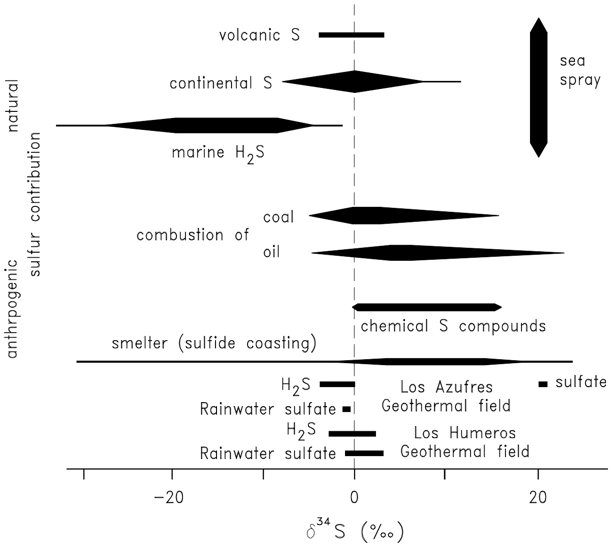

Figure 3: Distribution of $\delta^{34}S$ values in the major contributors to atmospheric sulfur. The $\delta^{34}S$ values for rainwater at Los Azufres and Los Humeros, and geothermal wells are also shown.

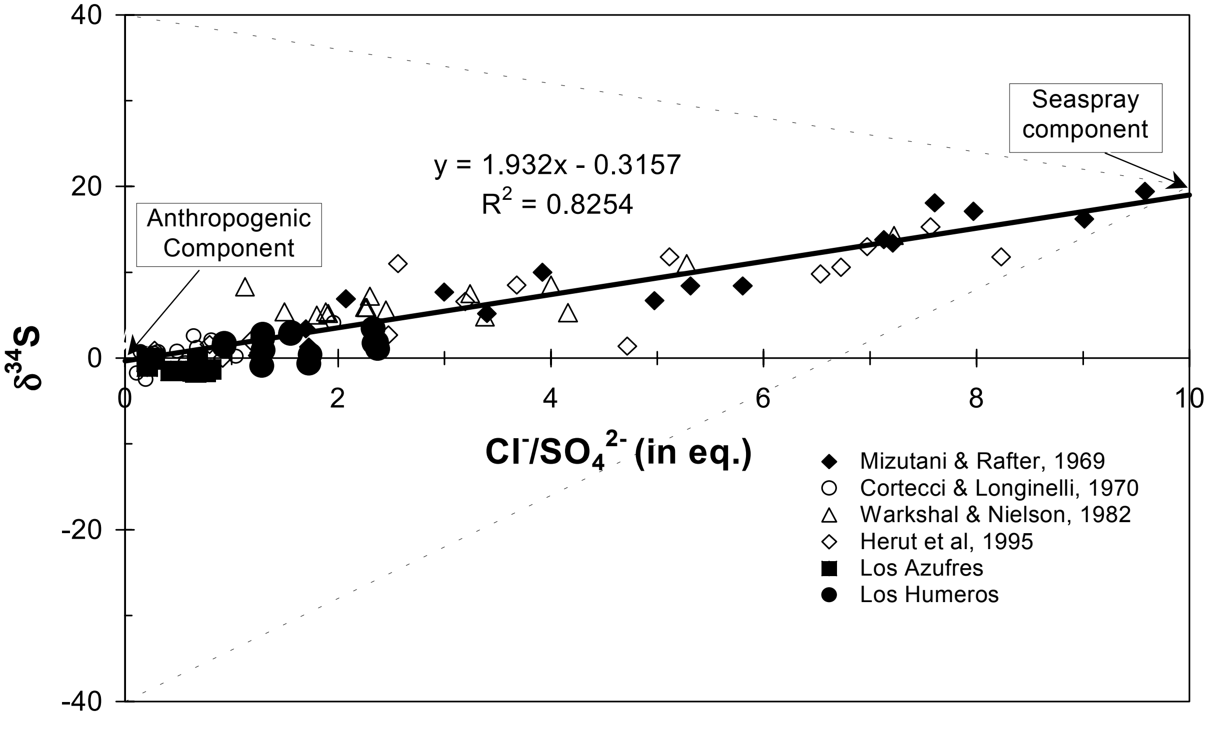

Figure 4: Chemical and isotopic mixing model diagram for rainwater (after Mizutani and Rafter, 1969; Herut et al., 1995 and Verma et al., 1999). All the points fall along a mixing line between two end-members, seaspray and an anthropogenic component with isotopic composition (-0.3 $^{o}/_{oo}$).