Volcanogenic mercury pollution in the ground water system of La Palma, Canary Islands, Spain

Contaminación de mercurio de origen volcanico-hidrotermal en el acuífero de la Palma. Islas Canarias, España

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ABSTRACT

Mercury measurements in ground waters from La Palma, Canary Islands, revealed high Hg levels (up to 1500, µg/L) in some portions of the volcanic aquifer. This Hg pollution does not seem to be related to anthropogenic activities; therefore, a volcanogenic origin might be a potential Hg source.

RESUMEN

Deterrninaciones de mercurio en las aguas subterráneas de La Palma, Canary Islands, han reflejado niveles altos de mercurio (hasta unos 1500, µg/L) en algunas porciones de este acuifero volcánico. Esta contaminación de Hg no parece estar relacionada con actividades antropogénicas, y por consiguienrte puede estar relacionada con un origen volcánico.

Key words: *Mercury, Pollution, Ground Water, La Palma, Canary Islands*

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Introduction

Mercury pollution has made headlines since the disaster in Minamata Bay (Japan) in the 1950s where many people died following the long-term consumption of fish polluted with methylmercury release by the local industry (D'Itri and D'Itri, 1977). Mercury contamination related to anthropogenic activities is not uncommon and has been describe in many different regions. Natural mercury pollution as a result of volcanic-geothermal activity has been also described from New Zeland, Hawaii, Papua New Guinea, Canary Islands, Iceland, Japan, and USA (Eshleman *et al.*, 1971; Coderre and Steinthorsson, 1977; Weissberg *et al.*, 1978; Phelps and Buseck, 1980; Varekamp and Buseck, 1981; Williams, 1985; Pérez and Williams, 1990; Hernández *et al.*, 1994). Changes in Hg concentrations in soils in geothermal areas have been used to detect changes in fluid flow resulting from seismic activity or magmatic intrusion suggesting the dynamics of volatile Hg in these systems (Varekamp and Buseck, 1984a). After reviewing all these cases, it is evident that natural as well as anthropogenic sources of mercury may pollute the environment.

Sampling and analytical procedures

We collected waters from springs, well and galleries at La Palma, Canary Islands (Fig.1). Water samples for Hg

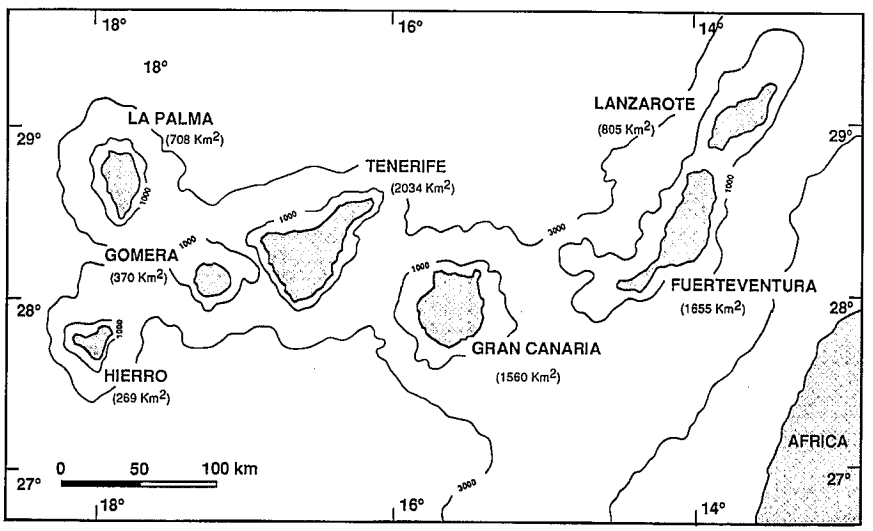

Fig. 1.- La Palma, the Northwesternmost Island in the Canarian archipielago.

Fig. 1.- La Palma, la isla más Noroccidental del archipielago Canario.

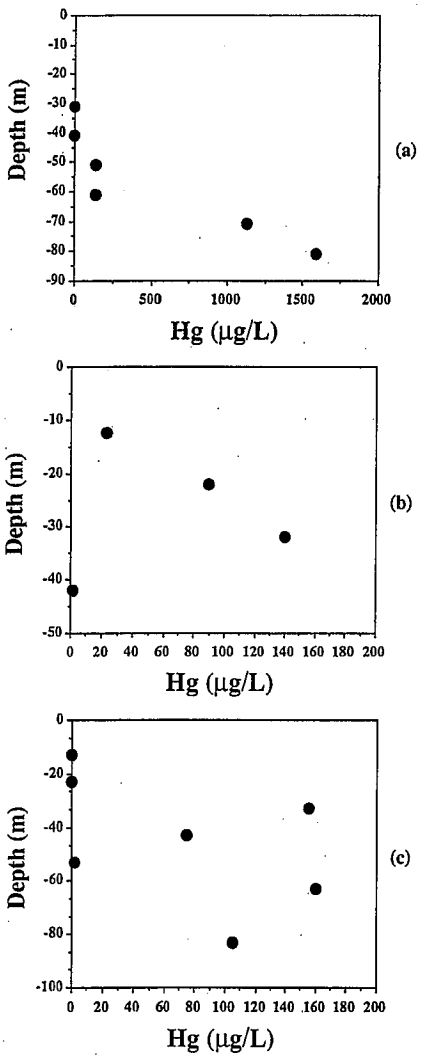

Fig. 2.- Vertical distribution of Hg concentrations in (a) El Rayo, (b) Fajana, and (c) Cooperativa la Fuerza wells. All of them located along Barranco de Las Angustias, La Palma Island.

Fig. 2.- Distribución vertical de los niveles de concetración de Hg en los pozos (a) El Rayo, (b) Fajana, y (c) Cooperativa La Fuerza. Todos ellos localizados a lo largo del Barranco de Las Angustias.

Sple.	Name	pH	Cond. (µS/cm)	Hg (µg/L)	IBE (%)	Sple.	Name	pH	Cond. (µS/cm)	Hg (µg/L)	IBE (%)
LP01	S. Fajana	8.20	1160	< 0.2	- 6.9	LP38	El Rayo	7.93	910	1586.2	+8.2
LP02	S. Ferrera	7.24	450	< 0.2	- 5.4	LP39	Casitas	7.66	1020	445.2	+2.1
LP03	S. Llano	7.11	400	< 0.2	- 4.9	LP40	Zona Alta	7.83	1680	50.8	+1.5
LP04	Cerco	7.67	160	< 0.2	- 1.1	LP46	C. La Fuerza	7.80	980	159.9	- 1.8
LP05	Cerco	8.00	150	< 0.2	- 2.7	LP49	Altaguna	8.44	190	0.7	+6.7
LP06	Cuevitas	8.61	90	< 0.2	- 5.2	LP50	Verduras	9.02	40	17.1	- 3.9
LP07	Cuevitas	8.74	100	< 0.2	- 7.0	LP51	Spring Tab.	7.72	560	178.4	+0.1
LP08	Pajaritos	8.23	90	< 0.2	- 6.8	LP52	Spring Tab.	7.15	610	85.1	- 0.7
LP09	Pajaritos	8.08	110	< 0.2	- 1.9	LP53	Risco Liso	8.60	120	40.6	- 8.8
LP10	Girineldos	8.35	110	< 0.2	- 5.5	LP54	Risco Liso	7.89	530	83.1	- 3.2
LP11	Girineldos	8.39	100	< 0.2	- 7.3	LP55	Risco Liso	7.84	340	20.8	+0.5
LP12	H. Vergas	6.30	240	< 0.2	- 7.7	LP56	B. del Agua	9.18	90	77.5	+8.3
LP13	El Rio	7.23	130	< 0.2	- 2.0	LP57	B. del Agua	8.81	80	144.4	+5.9
LP14	Loros Bajos	8.57	80	< 0.2	- 8.9	LP58	Sp. Pinos	8.07	450	< 0.2	- 9.2
LP15	Loros Altos	8.70	120	< 0.2	+2.1	LP59	Dos Aguas	5.73	3500	122.7	+3.6
LP16	R. Arboles	8.62	140	< 0.2	- 7.8	LP60	Ribacera	6.41	2470	159.9	+8.7
LP17	R. Arboles	8.57	70	< 0.2	+0.7	LP61	La Fuerza	7.53	1820	11.9	- 4.5
LP18	Tocaderos	7.49	270	< 0.2	- 3.7	LP62	San Miguel	7.79	1470	16.5	- 2.9
LP19	La Faya	7.05	140	< 0.2	- 5.6	LP63	El Salto	6.96	1320	74.9	+2.6
LP20	Meleno	8.37	90	< 0.2	- 7.6	LP64	Juan Graje	7.48	2290	243.0	+3.5
LP21	Meleno	8.20	80	< 0.2	- 8.4	LP65	El Duque	7.83	1070	135.9	- 3.2
LP22	California	7.40	92	< 0.2	- 0.4	LP68	La Fajana	7.81	680	140.1	- 8.3
LP23	California	7.47	85	< 0.2	- 6.8	LP28	Palacios	6.70	1830	1.7	+8.1
LP24	Herradura	7.89	1870	1.7	- 4.8	LP29	Morriña	8.00	1210	12.9	+7.9
LP25	Candelaria I	7.46	1570	< 0.2	- 1.2	LP30	S. Antonio	7.19	1480	11.9	- 1.1
LP26	Candelaria II	7.83	1480	< 0.2	+4.4	LP31	San Isidro	7.46	1470	0.3	+2.2
LP27	Peña Horeb	6.76	2020	1.7	+7.6	LP32	Prosperidad	7.90	1220	7.9	- 1.9

IBE: Ion Balance Error

Tabla 1.- Concentración de Hg en las aguas subterraneas de la Palma, Islas Canarias, España.

Table 1.- Observer mercury concentrations in the ground water system of La Palma, Canary Island, Spain.

measurements were filtered (0.45 µlm) and acidified with distilled HNO^3 lN in situ. Samples were storedin 60 cc. glass containers for Hg measurements by AAS-Hydride Generation. Additional water samples were also filtered, acidified, and storage in 500 cc. HDPE bottles for all trace elements analysis including Hg by ICP-MS at Louisiana State University.

Results and discussion

Seventy two water samples have been analyzed, sixty four from ground water and eight from springs. All samples were collected during an intensive ground water field survey carried out during the summer of 1993 at La Palma Island. Water samples were mainly collected in Taburiente caldera, northeastern, and midwestern sections of La Palma taking in consideration geological and hydrological characteristics of the aquifer. Mercury concentrations are shown in Table 1. Some samples were selected to perform Hg analysis by using different analytical methods: AAS-Hydride Generation and ICP-MS. Analysis of these results showed that observed Hg concentration differences were less than 10%. In the case of ground water samples with 500 µg/L of Hg analytical differences were less than 5% while in samples with 50 µg/L of Hg were less than 10%.

Spring and ground water samples from the northeastern section of La Palma do show Hg levels below detection limit (< 0.2 µg/L) with the exception of the ground water samples collected at the Herradura well (1.7 µg/L). Spring and ground water samples collected at Taburiente caldera showed higher Hg concentrations than those observed in the northeastern section and had a range from 0.7 to 178.0 µg/L.

Three different areas will be discussed for the midwestern section of La Palma: Las Angustias and Tenisca Barrancos as well the coastal aquifer zone. Ground water samples from Las Angustias showed the highest observed Hg concentration in the ground water system of La Palma, 1586.2 µg/L, and the range of Hg levels is from < 0.2 to 1586.2 µg/L. Spatial variations of Hg concentrations along Barranco de Las Angustias are very significant from site to site. Three geochemical vertical profiles of Hg were performed in three wells from which ground water is not being exploited from human or agricultural consumption, Cooperativa La Fuerza, El Rayo, and Fajana. Hg concentrations along this vertical profiles showed normally an increase trend of Hg in with depth, but it was not case for samples collected at La Fajana well. Ground water samples from Barranco Tenisca showed a range of Hg levels from 11.9 to 74.9 µg/L, and spatial variation analysis indicate a decreasing trend of Hg concentrations from El Salto to La Fuerza well. This observation was not detected in the case of ground water samples collected along Barranco de Las Angustias. Ground water samples from the coastal aquifer of midwestern La Palma had a range of Hg concentrations from 1.7 to 11.9 µg/L.

Significant number of ground water exploitation sites showed Hg levels much higher than 1µg/L which is the permissible limit of Hg concentration in drinking water for human consumption according to who standards. These anomalously high Hg values represent an important threat to environmental and health issues in the community of La Palma Island. Most of the ground waters which showed high Hg levels are not used for human consumption, but it still an important problem related to water quality of the volcanic aquifer of La Palma.

According to the spatial distribution of Hg levels in the volcanic aquifer of La Palma, these high Hg concentrations seem not be related to anthropogenic activities. It has been previously formulated that agricultural activities in the Canary

Islands have played a major role in the pollution of coastal aquifers in the Canarian archipelago (Davis and Jiménez, 1975; Custodio *et al.*, 1984; Farrujia de la Rosa *et al.*, 1994). Most of the agriculture activity in the Canary Islands is mainly concentrated in the coastal areas due to better climatic conditions, but high Hg concentrations have been found even far away from these zones. Hg pollution due to agriculture activities is mainly related to the use of mercurial pesticides which were commonly used in the past, but these products have also relatively high levels of As, which showed very low concentrations in the ground water system of La Palma. In addition, no industrial activity, which can pollute the ground water system with Hg, exist in La Palma Island; therefore, this Hg pollution has to be related to natural process.

Two are the potential natural mechanisms that we believe can add Hg into the ground water system of La Palma. Both mechanisms are different but also related to each other since they have the same origin, volcanogenic. A potential explanation could be that water-rock interaction might release absorbed Hg from fine particles linked to weathering products of volcaniclastic rocks from La Palma Island where a significant degree of hydrothermal metamorphism is characterized by a relatively complete low pressure-high temperature facies encompassing the zeolite-prehnite-pumpellyte and greenschist facies (Schiffman and Staudigel, 1994). Presumably, mercury rising in geothermal fluids has been and is being retained by reducing conditions in the subsurface and well oxygenated ground waters might scavenging this absorbed Hg. White *et al* (1970) found that waters from geothermal areas vary greatly in their mercury contents, and the sediments and fine-grained muds associated with these waters are often greatly enriched in mercury. This enrichment is most likely due to a partial retention of mercury vapor or mercury present in the water (White el at. 1970). Hydrothermal alteration products related to La Palma's seamount complex formation could be one of the best traps to absorb Hg in the subsurface. Therefore, Hg determinations in these type of alteration products as well as in fresh and weathered basaltic rocks from La Palma is needed to investigate this hypothesis. An abnormal mercury concentration was found in samples from a geothermal drill hole at Krafla, northern Iceland. At a depth of 98 m rocks contained visible amounts of pyrite, while samples from 78 and 104 m did not. This horizon of pyrite-rich rocks contained more than three times the mercury content of the rocks above and below it (Coderre and Steinthorsson, 1977). These mineralogical variations might play also a significant role in the spatial variations of Hg in the ground water system of La Palma.

Another potential source is the actual release and posterior rising of Hg from the volcanic-geothermal system into shallower positions in the ground water system de La Palma. The abudance of Hg°(vap) in geothermal emissions suggest that Hg°(vap) is present in the liquid phase of geothermal systems. When a vapor phase develops from a geothermal fluid, Hg partitions strongly into the vapor as Hg°(vap). Vapor transport at shallow level then results in the formation of Hg halos around shallow aquifers as well as in the flux of Hg to the atmosphere. (Varekamp and Buseck, 1984b). Robertson *et al.* (1977, 1978) report data from a vareity of thermal systems in the USA, noting that 80% or more of the Hg in the gases occurred as Hg°(vap). Hg is enriched in volcanic gases and tends to leave the magma during an early stage of degassing (Varekamp and Buseck, 1981); therefore a possible magmatic contribution of Hg to hydrothermal solutions cannot be excluded. High $^3He/^4He$ ratios in gases related to the rich-Co_2 discharge at Dos Aguas and dissolved in ground water samples from Barranco Las Angustias suggest a significant mantelic signature which is the highest observed helium-3 emission in the Canarian archipelago (Pérez *et al.*, 1994). This observation support this mechanism of actual released Hg from the volcanic-hydrothermal system to shallow positions in the ground water system.

Conclusions

High Hg concentrations have been found in the ground water system of la Palma, Canary Islands. This Hg pollution cannot be related to anthropogenic activities because of the lack of evidences for potential sources of Hg originated by human activities in La Palma Island. These anomalously high Hg levels must be related to natural process which seem to be linked with La Palma's volcanic activity

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