ENVIRONMENTAL IMPACT BY SPILL OF GEOTHERMAL FLUIDS AT THE GEOTHERMAL FIELD OF LOS AZUFRES, MICHOACÁN, MEXICO

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Abstract. Monitoring of surface water and shallow aquifers inside and outside of the Los Azufres geothermal field during the period November 1994 to May 1996 led to the detection of some contamination of surface water and shallow aquifers due to exploitation of the deep brines. Leaking of evaporation ponds and pipelines, occasionally overflowing of reinjection wells and pond rims as well as outflowing of brines during rehabilitation or drilling operations, are potential contamination sources within the cycle of geothermal production. Temporarily and/or permanently increased trace elements concentrations, especially Fe, Mn, F, B, and As in surface waters within the geothermal field as well as up to 10 km outside, were observed. Maximum values of 125 and 8 mg L^{-1} were observed for B and As, respectively. The discharge of hypersaline geothermal brines also causes salinization of surrounding soils. It occasionally happens that cattle drink from the brines. The use of the river for irrigation and drinking water supply in the surrounding regions may cause accumulation of toxic elements in the human food chain or may endanger the public health. The establishment of a closed geothermal production cycle can be achieved by simple remediation techniques, such as sealing of the pond walls, removal of overflow channels, direct reinjection without any reposal time in evaporation ponds, as well as an improved security and control system.

Keywords: brine spill, environmental impact, Geothermal field, Los Azufres, Mexico, surface contamination, trace elements

1. Introduction

In comparison with conventional types of energy sources, the use of geothermal water is considered to be relatively free of environmental impact. In theory, the extraction of hot geothermal fluids from a deep reservoir to the surface, the generation of electricity using the vapor phase and the subsequent underground reinjection of the liquid phase should represent a closed hydrological cycle without any contact with the biosphere or atmosphere. Nevertheless, during the last few years, a variety of environmental impacts were registered world-wide related to the production of geothermal energy. Some examples from several geothermal fields are:

- *Subsidence.* The extraction of large quantities of geothermal fluids from the underground can cause the dewatering of the deep aquifer and the compaction of the grain structure of the subsoil, leading to subsidence of the terrain. In the Travale-Radicondoli geothermal field in North Italy, a maximal subsidence

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rate of 2.5 cm y^{-1} was detected from 1973 to 1983 (Di Filippo *et al.*, 1995). A maximum rate of 45 cm y^{-1} and total subsidence of 13 m were observed in the geothermal field of Wairakei, New Zealand, representing the highest measured subsidence values worldwide (Allis, 1990).

– *Disappearance of natural thermal manifestations.* Fluid extraction from the upper part of the geothermal reservoir may cause the lowering of the piezometric water level of communicating, shallow aquifers and consequently drying out of natural thermal springs (Hunt and Glover, 1996).

– *Radioactive emission.* In the Nufarul District in Romania, geothermal water is applied for direct heating of private households. The natural radioactivity of the geothermal water, such as increased Radon-222 and Radium-226 values, represents a potential health risk for humans (Cosma *et al.*, 1995).

– *Noise emission.* During the perforation and well cleaning stages, maximal noise values of 120 dBA were registered (Brown, 1995). During the normal production of geothermal water noise is still a severe environmental problem, which may be solved by means of special mufflers.

– *Destruction of cultural sites and nature reserve areas.* Due to the magmatic origin of geothermal reservoirs, many geothermal production sites are located within remote volcanic nature reserve zones. Also, the impact on cultural and religious sites, such as the Mt. Apo National Park in Southern Philippines gives rise to protests from the native people (Ote and de Jesus, 1995).

– *Endangered animal and plant species.* Migrating birds use evaporation ponds of the Cerro Prieto geothermal field in North Mexico as a resting-place in winter. In 1994, a 40% decrease of the bird population could be related to the toxic effect of high B- and As-values of the pond brines (Gutiérrez *et al.*, 1995).

– *Damages by reinjection.* In the U.S. 20% of 70 geothermal fields investigated show impacts, such as cooling down of the reservoir fluids by time, contamination of aquifers, ground heaving and induced seismic activity caused by geothermal reinjection (Sanyal *et al.*, 1995).

– *Emission of H_2S and CO_2.* In most geothermal fields, the CO_2 and H_2S gas of the vapor phase is emitted directly to the atmosphere. The oxidation of H_2S to SO_2 and its subsequent reaction to sulphate ions within the atmospheric produces aerosols representing a major component of acid rain (Charlson *et al.*, 1978), although the rate of atmospheric oxidation is unknown (Brown and Webster, 1993). In Iceland, the geothermal production causes an annual emission of 50 000 to 80 000 t of CO_2 and 8000 t of H_2S into the atmosphere (Kristmannsdóttir and Ármannson, 1995):

– *Contamination of surface runoffs.* In the geothermal field of Lahendong and Dieng, Indonesia, geothermal brines are discharged into the adjacent rivers (Radja and Sulasdi, 1995). The amount of 13 t/h are discharged in the latter case.

This paper presents results from an environmental assessment study conducted on the subterranean and surface hydrological system of the geothermal field of Los Azufres, Mexico. The long-term field study was carried out from November 1994 to June 1996. The study includes information about the main contamination sources within the geothermal field, the type of contaminants most abundant, the lateral and quantitative distribution of contaminants within and outside of the geothermal field, as well as an evaluation of the risk potential for the environment and some practical remediation proposals. Environmental impact by atmospheric emission of H_2S and CO_2, by noise emission, subsidence, or the disappearance of endangered species is not considered as part of this study. The risk potential of metal enriched precipitates from the bottom of the evaporation ponds will be discussed elsewhere.

2. Los Azufres: Location and Production Cycle

The region of Los Azufres is one of several Pleistocene silicic volcanic centres with active geothermal systems in the Mexican Volcanic Belt (Aguilar *et al.*, 1987). The geothermal field, which is located 220 km NW of Mexico City and 80 km E of the Michoacán state capital Morelia has been used for exploitation since 1982 (Figure 1). As part of the geothermal production, 11 wells are used for reinjection, 13 for study purposes and 24 production wells, connected with 10 power units, generate an installed total capacity of 98 MW (Suárez *et al.*, 1995). It represents the second most important geothermal field in Mexico. Directly after their rise from a reservoir depth between 600 and 3500 m, the geothermal fluids are separated at the surface (Figure 2): The vapor phase with a total of 988 t/h is used for electric power generation (Hernández-Lagunas, 1997a,b), whereas 626 t/h of geothermal brines are temporarily stored in more than 15 temporary and permanent evaporation ponds before being reinjected through a system of pipelines having a total length of 52 km back into the reservoir. As a consequence, the fluids are cooled down from an initial outflow temperature of $> 90°$C to a reinjection temperature of approximately 40°C. However during the cooling process in open ponds, there is evaporation and a water loss of about 10% occurs. The object of the preliminary deposition within the ponds is mainly to cool down the brines. As a secondary effect of evaporation and cooling processes, an accumulation of sediments can be observed at the bottom of the ponds which is due to mineral precipitation.

3. Environmental Frame

Since 1988, the declaration of a national law for the protection of the ecological balance and the environment (Diario Oficial de la Federación, 1988) assigns an initial evaluation of the ecological consequences as a requirement for each national

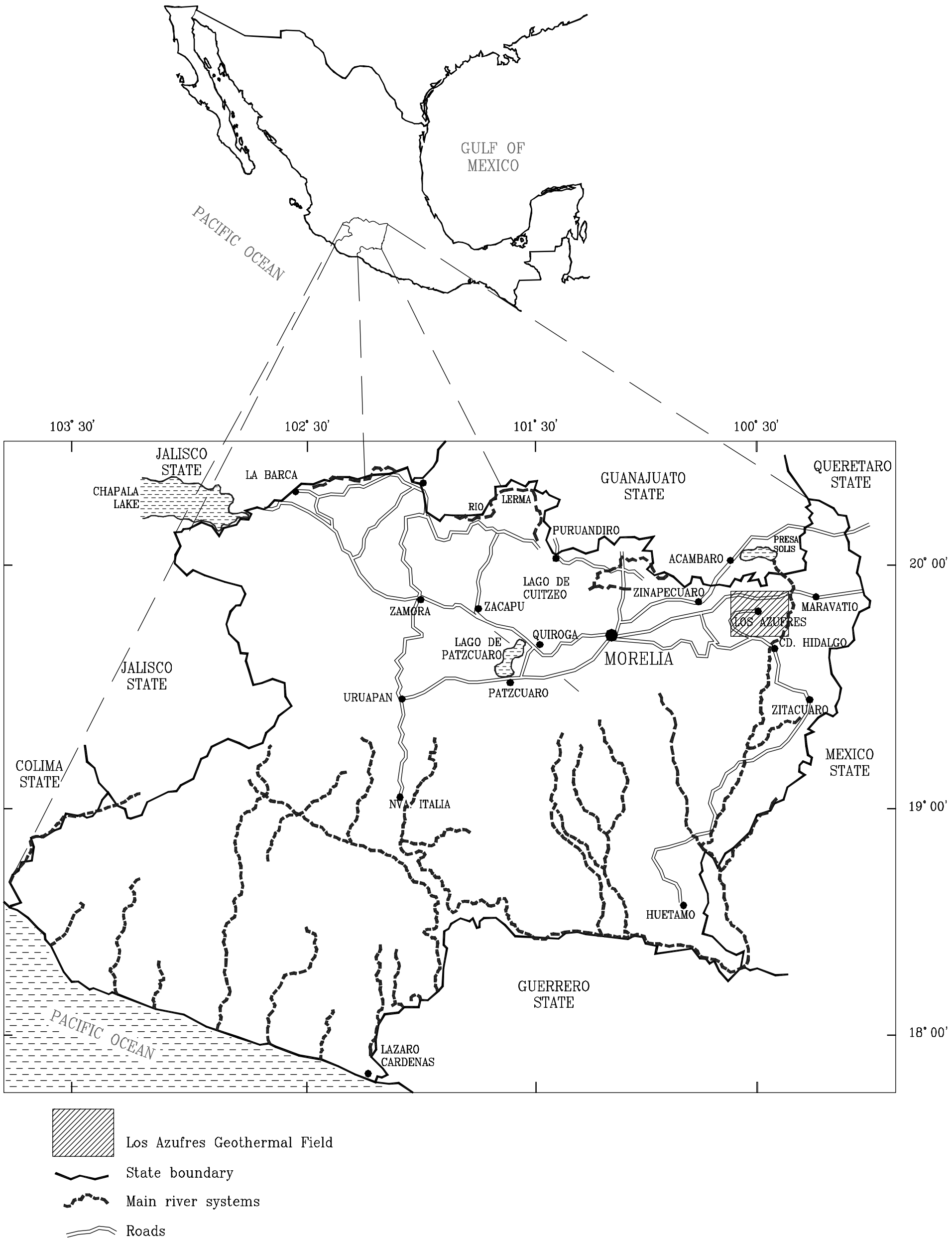

Figure 1. Topographical location of the Los Azufres geothermal field in the central part of Mexico and in the eastern part of the State of Michoacán.

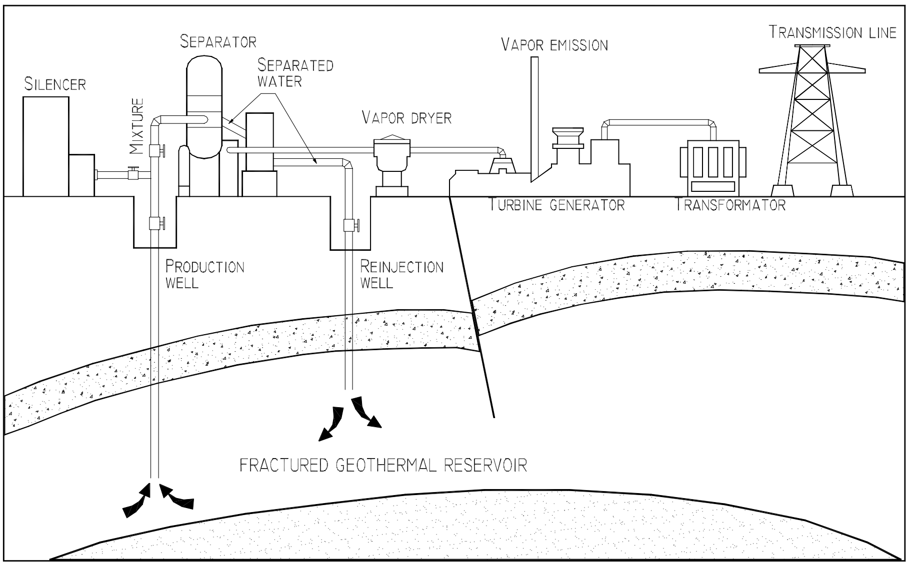

Figure 2. Scheme of the geothermal production cycle at the Los Azufres field.

development program. Additionally, the legal frame for the ecological selection and development of exploitable geothermal deposits was defined in 1989 (Diario Oficial de la Federación, 1989). However, formerly developed geothermal fields in Mexico, such as Cerro Prieto, Los Humeros and Los Azufres, are operated without any environmental assessment studies. Recently, some environmental impact studies were conducted in the initial phase of recent geothermal projects, such as Las Tres Vírgenes in the State of Baja California Sur (Ortega *et al.*, 1993; Argüelles *et al.*, 1994) and Acoculo in the State of Puebla (Torres *et al.*, 1999).

The geothermal field of Los Azufres is characterised by the mountain ranges of San Andrés, which are covered by a dense needle tree population at an elevation between 2500 and 3000 m.a.s.l. They form part of a national nature reserve since 1979 (*Zona de Protección Forestal*, SARH). The use of these zones is restricted by special environmental law (Becerra, 1994). On the other hand, environmental damage to the needle tree population by the construction of access roads and well platforms, forced the governmental operator of the geothermal field, the *Comisión Federal de Electricidad* (CFE), to initiate a reforestation program. Until 1993, 552 000 trees were planted (Quijano, 1993). In general, environmental studies on the impact of the Los Azufres geothermal production system on surface runoffs and subterranean flows were never conducted in the past.

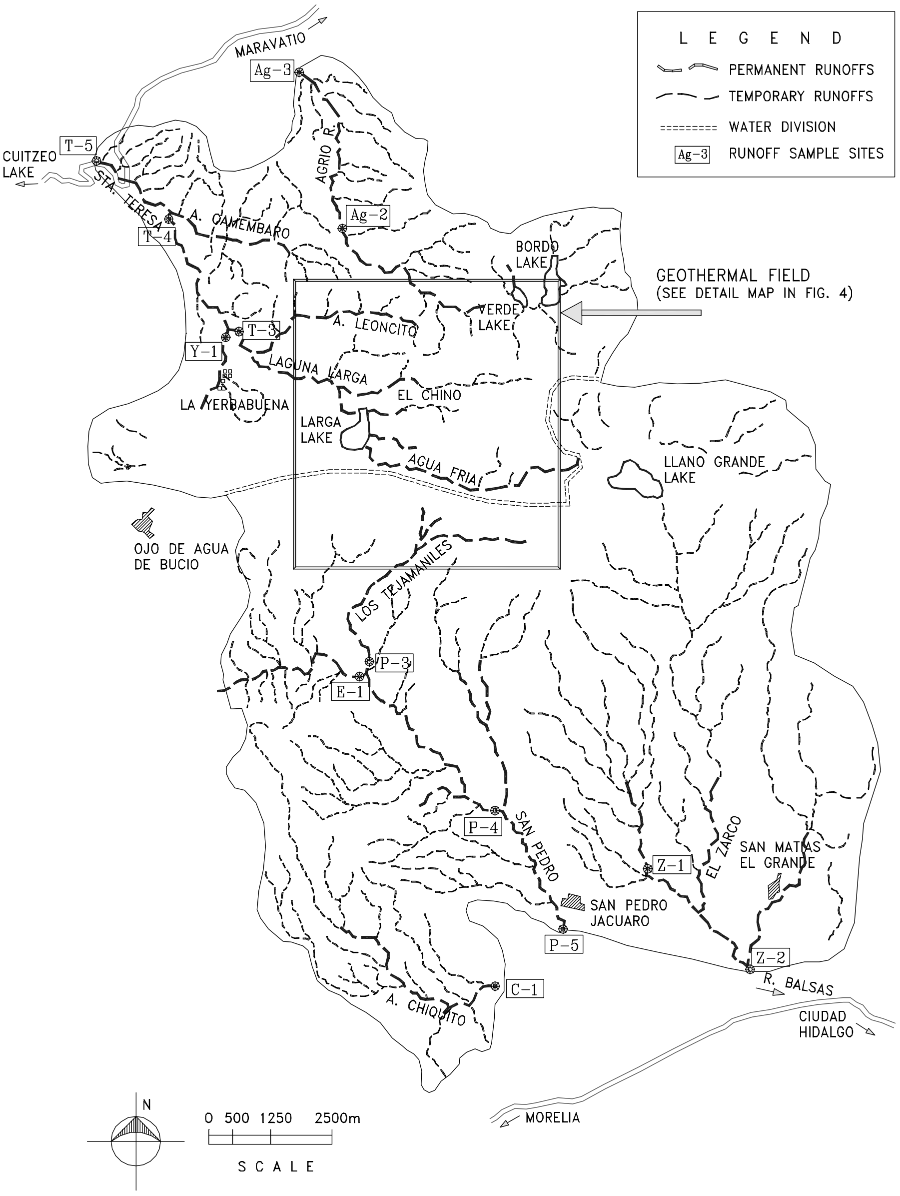

Figure 3. Location of the sampled sites outside of the geothermal field.

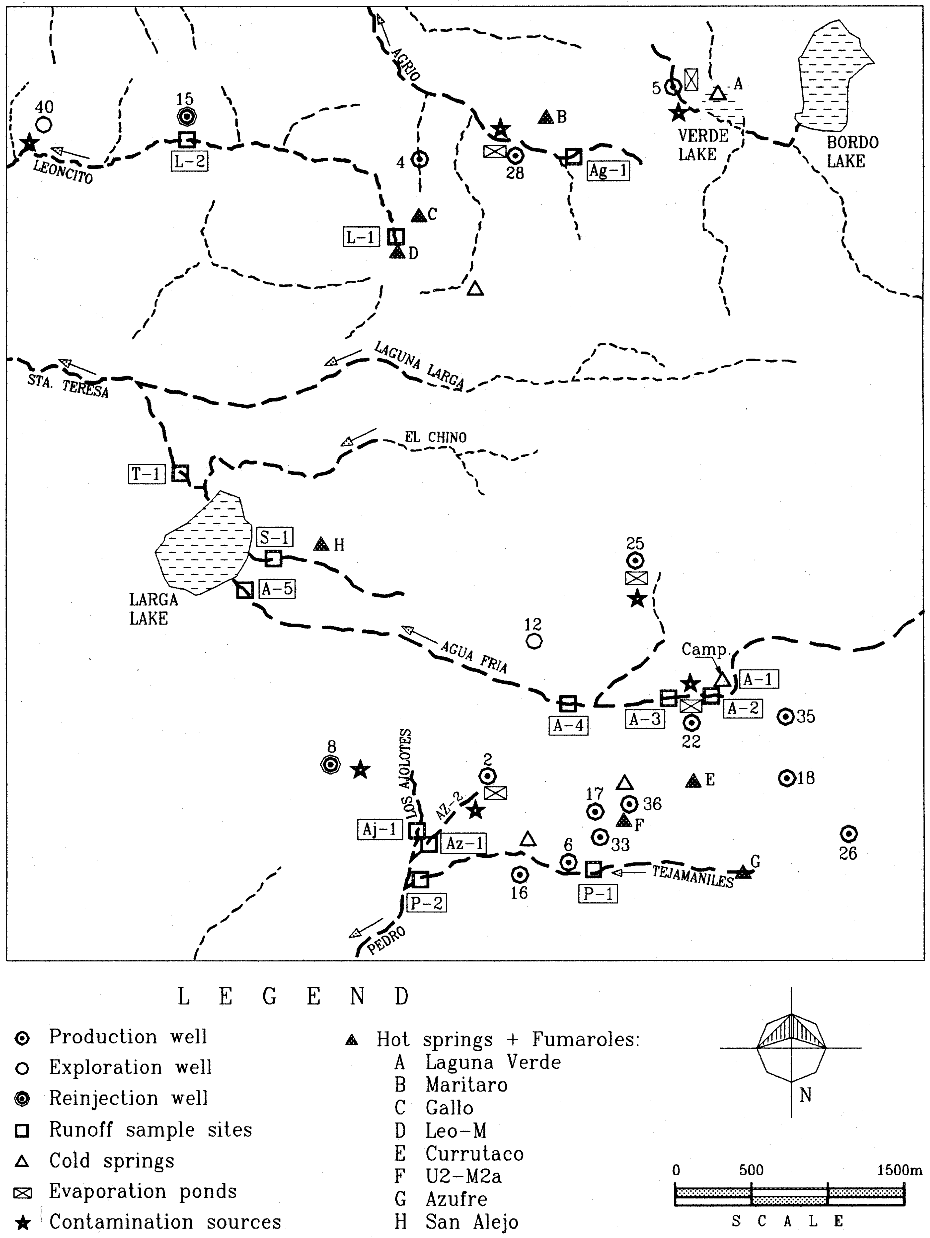

Figure 4. Location of the discussed production, exploration, and reinjection wells and their adjacent evaporation ponds. Also shown is the location of some cold and hot springs as well as the sampled sites inside of the geothermal field. The asterisk illustrates potential contamination sources by the contact of geothermal brine with the surface.

4. Methods

From November 1994 to June 1996, a total of 115 water samples were taken from cold and thermal springs, runoffs, lakes, and from inflowing and outflowing geothermal brines of the evaporation ponds as well as brines from leaking sites. The location of the sample sites inside and adjacent to the geothermal field are shown in Figure 4, those located outside are shown in Figure 3. The samples were filtered (0.45 μm filter size), acidified with HNO_3 Suprapur, and analyzed for their major and trace element concentration by the ICP-MS method at the *Institute for General and Environmental Ecology* in Tharandt/Saxony, Germany. The sequencial multi-elemental analysis was realized by the addition of multi-element standards and special spikes for concentrated samples. Some rare elements, such as Au, Zr, Y, Nb, and Ru, were excluded from the quantitative analysis as an initial semi-quantitative procedure showed concentrations in the lower ppt range. Fe, As, and the anions were measured by the AAS and ion chromatograph technique, respectively, at the *Faculty of Geological Sciences* at the Technical University of Freiberg/Saxony, Germany.

5. Results

5.1. CHEMICAL COMPOSITION AND RISK POTENTIAL OF GEOTHERMAL BRINE

The major and trace element composition of the geothermal brines from the production wells Az-2, Az-5, Az-22 and Az-28 is illustrated in Table I, the drainage water in Table II, and 59 samples from springs and rivers are shown in Tables IIIa to IIIe. Besides increased salt concentration of the NaCl-type brine (Birkle, 1998), the fluids from the Los Azufres reservoir are considerable enriched in B, Si, As, F, Rb, Cs, Sr, Mo, Se and W (in decreasing order). With values up to 24 000 μg L^{-1} and 560 000 μg L^{-1}, the elements As and B exceed hundred- to thousand fold the international drinking water standards.

Characteristic tracer elements of the deep fluids can be defined by calculating the ratio between the elemental composition of the geothermal brines and meteoric surface water. The average composition of the geothermal brines (Table I) and the chemical composition of the cold ‘Camp’ spring (so named by the authors), located adjacent to the operator plant (Figure 4), were used as representative initial components. The very low mineralisation and a tritium concentration of 4.7 T.U. ± 0.6, measured in November 1994, indicate the meteoric character and recent origin of the ‘Camp’ spring (Birkle, 1998). Values less than one indicate the depletion of the specific element, whereas values more than one imply its enrichment as part of the deep fluids. Elements, such as Cd and Fe are encountered more frequently in cold springs, whereas HCO_3^- and Hg are distributed homogeneous in both environments. With an abundance factor between 5 and 58, the elements Si, Zn, Cr, Ni,

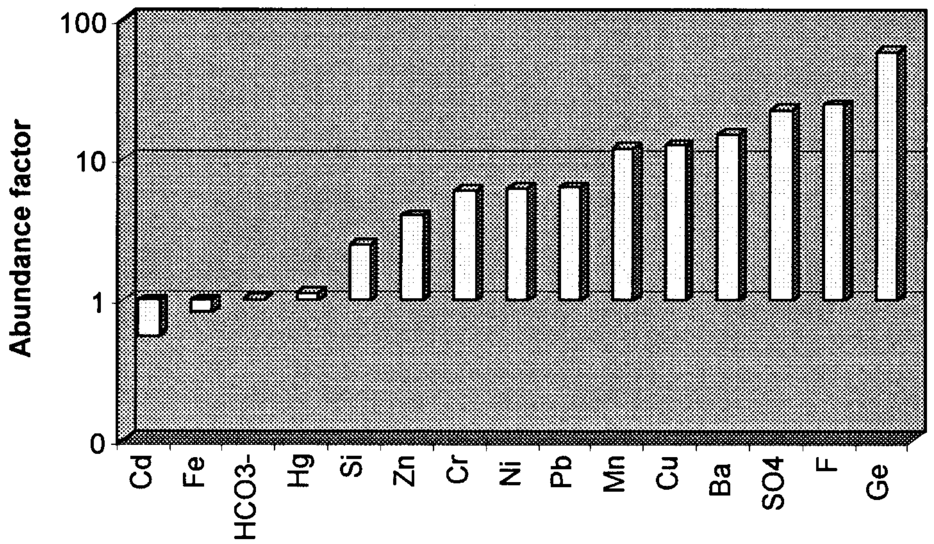

Figure 5. Comparison of the abundance of Cd, Fe, HCO_3^-, Hg, Si, Zn, Cr, Ni, Pb, Mn, Cu, Ba, SO_4, F, and Ge in geothermal brine with meteoric water from the study area.

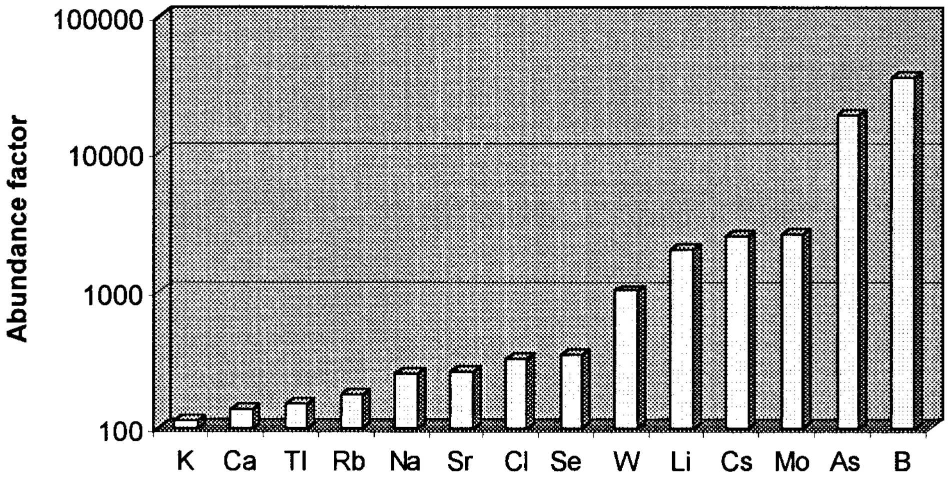

Figure 6. Comparison of the abundance of K, Ca, Tl, Rb, Na, Sr, Cl, Se, W, Li, Cs, Mo, As, and B in geothermal brine with meteoric water from the study area.

Pb, Mn, Cu, Ba, SO_4, F, and Ge are more abundant in geothermal brines as in cold springs (in increasing order) (Figure 5). The dominance of K, Ca, Tl, Rb, Na, Sr, Cl, Se, W, Li, Cs, Mo, As, and B in geothermal fluids is reflected by an abundance factor between 100 (K) and 35 500 (B) (Figure 6). Especially W, Li, Cs, Mo, As, and B are very suitable as geothermal tracer (in increasing order).

TABLE I

Minimal, maximal and average major and trace element concentrations of the geothermal waters at the well systems Az-2, Az-5, Az-22 and Az-28 (in μg L^{-1})

Element	Minima	Maxima	Average	Element	Minima	Maxima	Average
pH	5.8	7.2	–	Zn	22.2	146	49.9
Cond. μS cm^{-1}	5200	11 980	7140	Ga	2.4	5.0	2.8
Na	553 000	3 208 000	2 247 000	Ge	22.2	45.8	35.0
K	96 400	627 000	455 000	As	5100	24 000	19 000
Li	8000	36 500	19 700	Se	168	633	351
Ca	1400	150 000	7000	Rb	1614	4845	3568
Mg	<50	<2000	–	Sr	141	6866	1327
Cl	2 658 000	6 130 000	3 668 000	Mo	154	1036	514
SO_4	10 300	374 000	88 700	Ag	0.2	3.3	1.1
NO_3	<10 000	14 000	–	Cd	0.40	2.1	1.4
HCO_3^-	4900	81 700	34 420	Cs	2551	4630	3244
B	180 000	560 000	355 000	Ba	9.4	378	57.9
Si	139 000	210 000	173 400	W	11.8	202	100.8
F	9000	17 000	12 200	Hg	0.8	9.9	4.1
Cr	5.1	18.0	11.8	Tl	7.2	40.2	30.3
Mn	14.8	45.2	26.1	Pb	2.5	8.3	4.6
Co	0.7	1.4	1.0	U	<0.5	<0.5	<0.5
Ni	10.8	19.8	14.0	Fe	23	810	81.3
Cu	5.9	39.7	16.1				

5.2. DISTINCTION OF NATURAL AND ANTHROPOGENIC CONTAMINATION

A large number of natural hydrothermal features such as hot springs and fumaroles exist in the mountain area of Los Azufres. Their trace element concentrations cause a natural distribution of contaminants in the environment. How can this natural contamination be distinguished from the man made impact by means of geothermal fluids?

Rare elements are concentrated in a very typical manner within the hot springs and the deep fluids: Figure 7 compares the composition of natural hot springs, such as Currutaco, Marítaro, San Alejo and Gallo (Location in Figure 4), with geothermal brine from production wells. It can be shown, that deep geothermal fluids are enriched in As, Rb, Cs, Sr, Mo, Se, W, Ba, Ge, Tl, Ni, and Cr, whereas natural surface outcrops are depleted in those elements. Cu, Zn, Hg, Pb, Cd, U and Ag are distributed in a similar manner in both geothermal waters and hot springs. Thus,

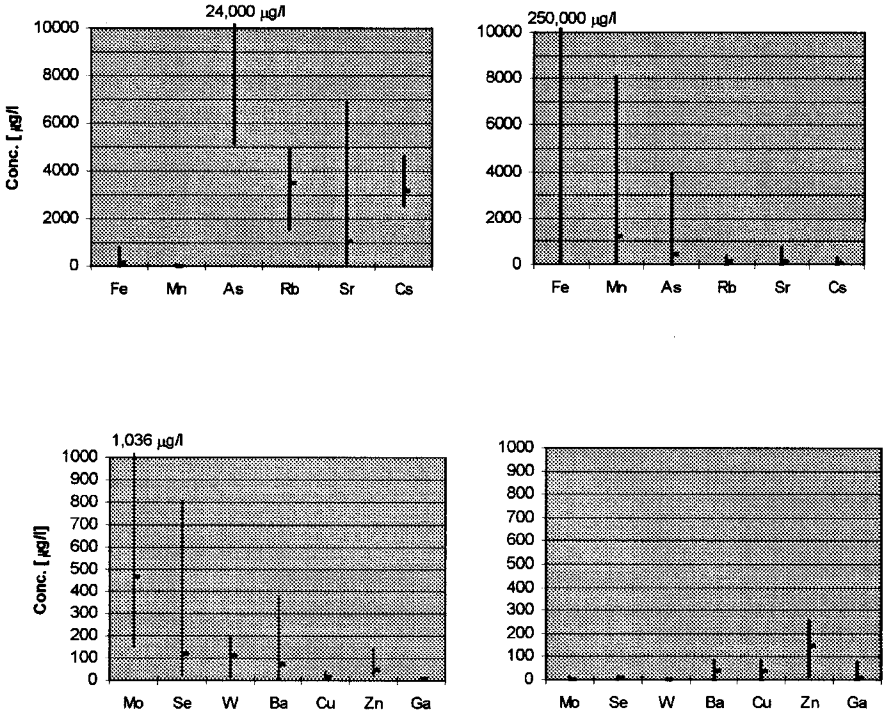

Figure 7. Comparison of the composition of the geothermal water from the Los Azufres reservoir (left column) with hot springs and fumaroles from the surface area of the geothermal field (right column).

they are not very useful for the detection of contamination sources in geothermal fields.

Considering the characteristics of both, cold and hot springs, the minor elements As, Rb, Cs, Mo, Se, W, Ge and Tl are very useful as tracers for the detection of hydrological surface systems, that are contaminated by geothermal brines. Also, the major elements Cl, Na, Li and partially K and B are applicable as geothermal tracers, due to their abundance in geothermal fluids and their depletion in surface manifestations, whereas Ca, Mg, F, Si, HCO_3^- are distributed more homogeneous in both environments. On the other hand, elements like Fe, Mn and Ga dominate in surface water.

5.3. CONTAMINATION SOURCES DETECTED

5.3.1. *Leaking Evaporation Ponds*

Based on site observations and chemical analysis, the man-made evaporation ponds represent the major contamination source for the spreading of contaminants from the geothermal production cycle into discharging, proximal and distal surface run-off systems. The ponds, which are used for the storage of geothermal water, are

Photo 1. Fractures and permeable material of the pond wall (right side of the photo) of the leaking Az-22 pond (production towers and evaporation pond of the Az-22 unit in the background) cause the spill of oxidized geothermal brine into the adjacent stream (river course from the upper left part of the photo towards the lower, central part).

surrounded by man-made walls. The material is derived from the close surroundings, built with fresh or altered andesitic or rhyolitic rock fragments, and inter bedded by change with loam or clay soils as fine material. Special techniques such as the consolidation of the wall layers or the application of geo textiles were not applied during construction. Vertical fractures, humid spots, discharging oxidised brines and salt crust at the external part of the pond walls are obvious indicators for active seepage processes. These field observations are confirmed for the evaporation ponds adjacent to the individual production wells Az-2, Az-5, Az-22 (Photo 1), Az-25, and Az-28.

5.3.2. *Overflowing Evaporation Ponds*

Temporary increases in withdraw rates of the production wells and a too low calculated storage volume of the ponds cause periodically increased water levels in the basins. To prevent damage of the pond walls by increased water levels, special overflow channels have been constructed at the rim of some evaporation ponds e.g. Az-28 or Az-25. In practice, this technique causes direct spill of geothermal brine to the environment during increased water levels. In the case of the well Az-2, geothermal brine discharged over the rim of the evaporation pond during July and August 1995 for an unknown time period. Damage from this, such as landslides

Photo 2. Geothermal brine discharged over the rim of the evaporation pond of the Az-2 well unit during July and August 1995. Damages from this, such as landslides and fractures on the rim and the exterior part of the wall, were provisionally sealed with sand bags.

and fractures on the rim and the exterior part of the wall, were provisionally sealed with sand bags (Photo 2).

5.3.3. *Overflowing Reinjection Wells*

Fluctuations in the amount of fluid arriving from the production wells may cause the overflow of reinjection wells, as observed in December 1995 for the reinjection well Az-8. The composition of the formerly natural lagoon, which is used for the storage of accidental spill brine, is shown in Table II (Az-8*).

5.3.4. *Leaking Pipelines*

During construction and deviation work, some pipelines of the geothermal network system remained unsealed for several hours or days. As a consequence, geothermal brine was spilled to the forest soil, as it was observed in May 18, 1996, at a distance of 200 m from the production well Az-2.

5.3.5. *Perforation and Repair Work*

During new perforation projects of geothermal wells or during their subsequent rehabilitation, the outflow of geothermal brine at the surface was observed in some individual cases in Los Azufres. Probably due to maintenance work at the well Az-40 and /or due to the new perforation of the Az-61 well, the spill of geothermal brine caused increased trace metal concentration in the adjacent river Leoncito.

The measured concentrations close to both wells are the highest values, measured in any runoff system as part of this study. Although no pipeline was encountered between the wells and the river, the peak of trace metal concentrations and its slow downstream dilution indicates the spill of geothermal brine.

5.3.6. *Safety Measures*

Each individual production unit with its production well and evaporation pond is surrounded by a fence. However the gates are permanently open and thus give free access to the units. Grazing farm animals, such as cattle, horses and sheep from the highlands enter the production units and sometimes drink geothermal water from the ponds. A potential health risk can arise from the high trace elements content of the brines, which may be accumulated in the animal bodies and subsequently enter into the human food chain. In May 1996 e.g. around 20 animals were encountered simultaneously in the close vicinity of each well at Az-5, Az-17, Az-18, and Az-36.

5.4. DISTRIBUTION OF CONTAMINANTS

5.4.1. *Source Contamination (Evaporation Pond Spills)*

As a consequence of leaking and overflowing evaporation ponds, the following case studies of spill events were observed and documented during field observations.

At the exterior part of the sealing walls of several evaporation ponds, such as at the production units Az-2, Az-5 or Az-22, the outflow of highly mineralised, Fe-oxidised drainage water in the form of small springs along fractures were detected. This observation and the chemical analysis of this drainage water indicates the migration of geothermal water through the pond walls and the unsaturated zone at the bottom of the ponds due to the high permeability and fracturing of the filling material. Table II shows a summary of the chemical composition of the discharging drainage water from the individual evaporation ponds, adjacent to the wells Az-2, Az-5, Az-22, and Az-28 during different sample events. Each of the collecting ponds receives brine water from more distal wells, as well as from its adjacent well.

The outflow from the pond system Az-2 shows permanently increased concentration during three sample periods, such as in Na (up to 3.5 g L^{-1}), Cl (up to 7.9 g L^{-1}), B (up to 405 000 μg L^{-1}), Fe (up to 220 000 μg L^{-1}), Mn (up to 12 210 μg L^{-1}), Sr (up to 7653 μg L^{-1}), Rb (up to 5289 μg L^{-1}) and As (up to 2000 μg L^{-1}). The concentrations for Cl (up to 3.4 g L^{-1}), B (up to 630 000 μg L^{-1}), Li (up to 39 800 μg L^{-1}), As (up to 30 000 μg L^{-1}), and Cs (up to 3118 μg L^{-1}) of the outcropping spring at the bottom of the pond wall at the production unit Az-22 are very increased in comparison with the natural background concentrations of surface water (Table II). On the other hand, lower concentrations of the drainage water, as observed at the unit Az-5, can be explained by the dilution of geothermal brine with meteoric water and/or sorption processes in the unsaturated soil zone (Birkle, 1998).

TABLE II

Major and trace element concentration of drainage water from different evaporation basins, outflowing at the base of the ponds (concentrations in μg L^{-1}) (* s. chapter 5.4.1., ˆ in chapter 5.4.3.)

Locality: Well unit	Az-2	Az-2	Az-2	Az-5	Az-8*	Az-8*	Az-22	Az-22	Az-25ˆ	Az-28
Sampling period	11/94	01/96	05/96	11/94	06/95	01/96	01/96	05/96	01/96	11/94
Temp. [°C]	28.7	22.0	22.0	20.8	23.5	7.0	48.0	26.0	19.0	18.5
pH	5.7	5.8	6.1	4.9	7.2	7.9	7.0	7.3	4.8	5.8
Cond. [μS cm^{-1}]	3690	5590	12 480	2120	2530	4550	5270	6150	2710	270
Na	1 071 000	1 659 000	3 566 000	331 000	714 000	300 000	1 628 000	2 801 000	679 000	13 000
K	216 000	333 000	781 000	44 800	192 000	99 000	437 000	545 000	169 000	4600
Li	6800	12 200	18 900	6900	9800	3900	19 500	39 800	2600	<50
Ca	77 500	90 500	300 000	80 200	50 100	12 300	7500	30 000	32 700	9600
Mg	9140	10 100	10 000	29 260	2810	880	<2000	<2000	9140	1420
Cl	1 870 000	2 632 000	7 967 000	1 052 000	1 615 000	1 797 000	2 739 000	3 467 000	1 413 000	8000
SO_4	18 000	31 400	32 200	<2000	13 600	389 000	103 000	30 900	<10 000	39 200
NO_3	<10 000	69 900	<10 000	n.m.	<10 000	<10 000	<10 000	n.m.	<10 000	n.m.
HCO_3^-	105 000	43 500	21 600	1400	29 500	79 200	52 000	116 000	1200	40 700
B	143 000	254 000	405 000	108 000	110 000	180 000	271 000	630 000	87 000	3000
Si	58 500	69 900	165 000	22 300	38 100	68 100	135 000	121 000	21 400	41 000
F	8000	n.m.	13 200	<10 000	3100	9000	10 000	<10 000	<10 000	<10 000
Cr	5.10	17.6	14.8	7.20	6.20	17.2	21.3	32.6	10.2	0.95
Mn	12 210	11 034	4077	510	231	63.2	38.8	466	10 485	320

TABLE II

Continued

Locality: Well unit	Az-2	Az-2	Az-2	Az-5	Az-8*	Az-8*	Az-22	Az-22	Az-25ˆ	Az-28
Sampling period	11/94	01/96	05/96	11/94	06/95	01/96	01/96	05/96	01/96	11/94
Co	23.6	25.2	6.20	12.4	1.70	<5.0	<5.0	5.33	23.6	7.09
Ni	26.3	15.2	22.6	9.10	13.0	16.3	16.3	22.2	23.9	3.83
Cu	106	9.45	21.6	27.0	46.7	11.8	8.42	18.3	5.00	63.4
Zn	134	43.8	191	87.0	211	<30.0	34.4	238	644	129
Ga	8.20	4.53	25.40	6.60	3.60	<5.0	<5.0	13.5	9.75	2.04
Ge	16.6	20.7	11.5	<6.0	8.70	23.4	31.0	30.6	1.47	0.70
As	830	1500	2000	7.00	5500	16 000	21 000	30 000	5.00	15.0
Rb	1121	1691	5289	69.3	1058	2263	1648	3052	516	12.5
Sr	1270	1872	7653	1395	647	1614	154	258	690	129
Mo	10.3	6.70	109	<5.0	46.0	99.8	204	126	1.95	1.05
Ag	0.60	<5.0	4.20	<5.0	0.40	<5.0	<5.0	14.3	0.53	<0.5
Cs	347	648	3485	5.80	785	1880	2813	3118	20.2	1.03
Ba	1212	1634	2921	1084	374	440	<20.0	398	6538	389
W	n.d.	<2.0	0.10	<2.0	6.10	36.7	87.5	23.0	<0.2	<0.2
Hg	1.50	<9.0	0.40	<9.0	<9.0	<9.0	<9.0	<9.0	<9.0	4.94
Tl	3.10	<5.0	29.1	<5.0	5.70	10.42	12.4	16.9	3.69	<0.5
Pb	139	4.06	8.7	12.0	20.1	7.11	<4.0	26.3	2.60	10.6
Cd	1.60	0.40	5.3	<5.0	1.60	0.70	0.56	0.70	0.99	1.00
U	2.90	3.01	1.2	<5.0	<5.0	0.51	<0.5	2.97	<0.5	<0.5
Se	222	173	484	66.6	198	267	331	245	41.60	5.10
Fe	142 000	220 000	3000	1020	750	800	440	12 900	270	390

5.4.2. *Contamination of River Water*

As a consequence of its topographical position along a mountain ridge, all springs and brooks of the geothermal field area discharge towards external regions in a radial pattern. The northern part of the geothermal field discharges to the Lago Cuitzeo basin, whereas the southern part discharges towards the Balsas basin. Figures 3 and 4 show the lateral distribution of the surface runoffs, the water division at the centre of the geothermal field, and the sample sites. The rivers were sampled at different sites along their course during various seasons to obtain a representative image of the temporal and lateral distribution of geothermal contaminants in the surface water. The most important rivers of the study zone and the chemical composition of 59 samples from 29 stations are shown in Table IIIa to IIIe.

(a) River Sta. Teresa

June 1995: The mentioned river starts its course at the natural lagoon *Laguna Larga* and leaves the geothermal field in NW-direction. Along a distance of 8.3 km, water samples were taken from one site inside (T-1) and 4 sites outside the geothermal field (T-2, T-3, T-4, T-5) during three field periods (June 1995, January 1996, May 1996). Figure 8 shows the lateral distribution of trace elements from upstream (T-1) towards downstream sites (T-5) from the sampling period in June 1995. The sites T-1 and T-2 are characterised by natural, low concentrations of meteoric water. Between T-2 and T-3, the inflow of the contaminated Leoncito river increases abruptly the trace element composition of the Sta. Teresa river. Especially Cl (3.9 g L^{-1}), Na (1.0 g L^{-1}), B (125 000 μg L^{-1}), Li (24 300 μg L^{-1}), F (16 300 μg L^{-1}), As (8200 μg L^{-1}), Cs (1094 μg L^{-1}), and Mn (1252 μg L^{-1}) concentrations of the Leoncito river (sample L-3) show the highest values during the study period. The contamination of the river Leoncito is probably due to rehabilitation and perforation work at the wells Az-40 and Az-61 (s. Chapter 5.3.5.). Its origin at upstream is characterised by the natural background values (L-1).

900 m downstream of the inflow of the Leoncito river, the Sta. Teresa river (sample T-3) is still enriched in Cl (651 000 μg L^{-1}), Na (269 000 μg L^{-1}), B (67 000 μg L^{-1}), F (13 400 μg L^{-1}), Li (4500 μg L^{-1}) (not shown in Figure 8), As (3200 μg L^{-1}), Fe (1050 μg L^{-1}), Mn (850 μg L^{-1}), Cs (521μg L^{-1}), Ba (222 μg L^{-1}), Zn (187 μg L^{-1}), Se (68 μg L^{-1}), Pb (22.1 μg L^{-1}), and Tl (6.8 μg L^{-1}), but the lower concentrations indicate dilution effects.

Dilution, sorption and precipitation processes cause decreasing concentrations in the downstream part of the course. After a distance of 3.2 km, between the sites T-3 and T-4, most trace metal concentrations are still 80% (Cr) to 2800% (As) higher than the background values of the non contaminated upper course of the river. The As concentration decreases from 3200 to 300 μg L^{-1}, but still do not reach the natural background concentrations of < 10 μg L^{-1}.

Similar, the concentration of major elements, such as Cl and B, is reduced from 651 000 to 125 000 μg L^{-1} and from 67 000 to 7000 μg L^{-1}, respectively (Table IIIa). On the other hand Mn, Ni, Co, Cu, Sr, Ba, Se, and Fe meet their

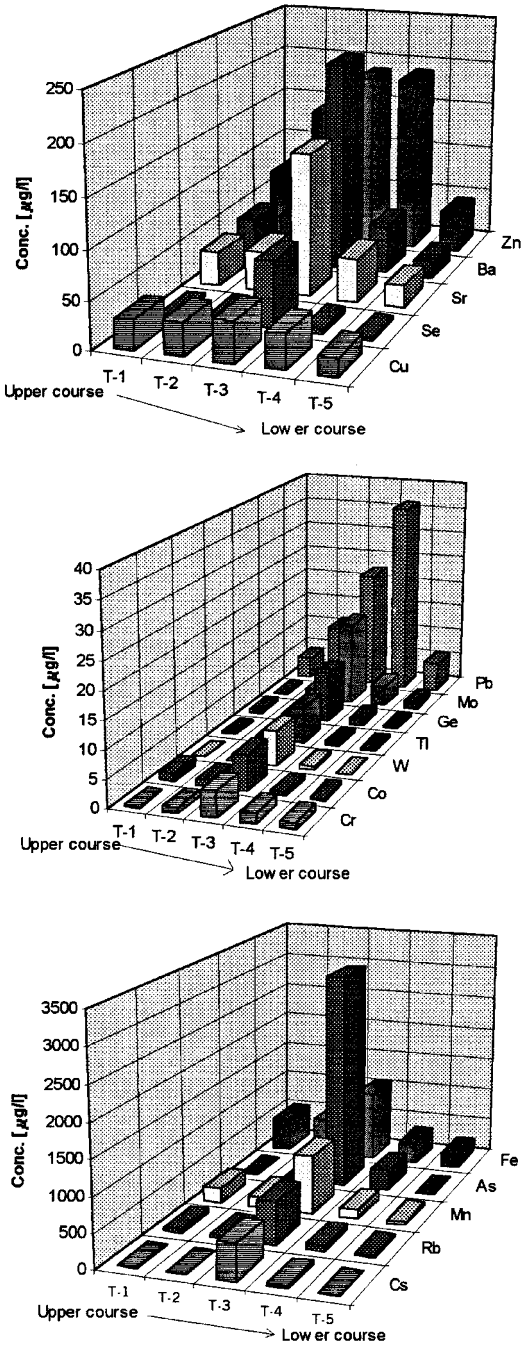

Figure 8. Lateral distribution of trace elements from the Sta. Teresa river in June 1995. The monitored sites are distributed from its source within the geothermal field towards sites in the external parts of the geothermal field.

TABLE IIIa

Major and trace element concentrations from springs and surface runoffs in and outside of the geothermal field (conc. in μg L^{-1}, n.m. = not measured)

SAMPLE	T-1	T-2	T-3	T-3	T-3	T-4	T-5	T-5	T-5	L-1	L-2	L-2	L-2
PERIOD	Jun-95	Jun-95	Jun-95	Jan-96	May-96	Jun-95	Jun-95	Jan-96	May-96	Jan-96	Jun-95	Jan-96	May-96
Temp. [°C]	19.8	16.8	23.9	11.0	17.0	23.7	20.4	6.0	20.0	64.0	19.2	12.5	12.0
pH	4.7	5.9	4.0	6.6	4.9	6.8	6.9	7.3	7.4	2.2	2.6	2.8	3.1
Cond. [μS cm^{-1}]	100	100	1350	90	110	220	50	51	64	560	680	660	700
Na	14 000	9000	269 000	7000	47 700	54 000	95 000	8000	28 200	4000	12 000	9000	19 500
K	14 600	11 200	115 000	9800	10 400	16 800	6300	6000	6600	4300	9100	8300	2600
Li	<500	100	4500	<50	470	700	<50	100	40	<50	<50	<50	80
Ca	4400	4100	19 500	4100	n.m.	4700	2700	3100	<500	3400	7300	4200	4000
Mg	920	990	2600	1170	n.m.	1310	920	1060	<500	1470	2650	1970	1900
Cl	28 000	11 800	651 000	16 100	37 100	125 000	14 100	6200	21 800	8400	32 000	36 900	26 800
SO$_4$	42 200	35 500	58 100	37 700	31 700	14 000	11 500	15 300	18 900	268 000	344 000	344 000	51 600
NO$_3$	2700	2300	19 300	2000	4300	3400	3700	2900	2700	1700	<2500	n.m.	3300
HCO$_3^-$	2100	7000	n.m.	1000	41 500	14 500	20 500	18 800	19 000	<100	<100	<100	<100
B	<100	<100	67 000	<100	<100	7000	<100	<100	<100	600	<100	2700	<100
Si	57 000	34 400	52 100	65 700	62 800	55 100	270 000	62 700	68 200	129 000	89 100	131 000	133 000
F	<100	<100	13 400	1000	<1000	<1000	<1000	<1000	<1000	<1000	25 300	n.m.	<1000
Cr	<0.5	0.97	4.60	0.54	<0.5	1.78	1.10	<0.5	1.01	0.72	1.66	1.30	1.61
Mn	213	164	850	65.6	156	134	44.4	13.5	16.5	122	223	229	209
Co	1.42	0.89	6.40	0.51	0.66	0.70	<0.5	<0.5	<0.5	2.26	4.98	3.95	3.64

TABLE IIIa

Continued

SAMPLE	T-1	T-2	T-3	T-3	T-3	T-4	T-5	T-5	T-5	L-1	L-2	L-2	L-2
PERIOD	Jun-95	Jun-95	Jun-95	Jan-96	May-96	Jun-95	Jun-95	Jan-96	May-96	Jan-96	Jun-95	Jan-96	May-96
Ni	4.20	7.73	<7.0	1.44	0.86	3.21	3.60	0.96	0.82	3.27	6.36	4.62	4.10
Cu	30.3	33.9	41.6	3.27	1.60	35.9	19.16	1.60	2.51	6.64	44.7	7.31	6.52
Zn	71.0	145	187	19.5	17.8	188	43.31	12.9	15.7	49.9	148	60.2	60.8
Ga	<0.5	0.89	<5.0	<0.5	<0.5	0.64	0.55	<0.5	<0.5	<0.5	0.99	0.70	0.88
Ge	0.68	0.52	9.40	<0.6	0.55	1.10	<0.6	<0.6	<0.6	1.66	2.85	2.41	2.22
As	8.00	10.0	3200	8.00	2.00	300	5.00	7.00	4.00	7.00	16.0	10.0	14.0
Rb	60.5	45.6	620	43.0	54.7	90.9	28.1	26.8	37.1	31.5	42.3	38.2	40.6
Sr	35.7	41.1	150	44.8	35.4	45.5	23.1	24.4	25.7	2.26	30.6	27.9	24.0
Mo	<0.5	1.59	15.4	<0.5	<0.5	3.82	1.29	<0.5	<0.5	<0.5	0.76	<0.5	<0.5
Ag	<0.5	<0.5	<5.0	5.88	<0.5	0.68	1.06	2.48	<0.5	<0.5	<0.5	<0.5	<0.5
Cs	6.22	5.87	521	5.27	9.99	50.4	2.11	2.69	3.52	3.30	5.43	4.26	5.59
Ba	42.2	52.9	222	37.1	51.1	50.2	18.2	10.9	13.1	<2.0	51.1	51.1	41.5
W	<0.2	<0.2	6.40	<0.2	<0.2	0.69	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Hg	1.73	<0.9	<9.0	<0.9	<0.9	1.06	0.88	<0.9	<0.9	<0.9	5.14	<0.9	<0.9
Tl	<0.5	<0.5	6.80	<0.5	<0.5	0.80	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Pb	3.87	10.9	22.1	0.71	0.39	36.1	5.55	0.71	2.80	0.55	13.4	1.11	1.39
Cd	<0.5	<0.5	<5.0	<0.5	<0.5	0.67	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
U	<0.5	<0.5	<5.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.68	0.43	0.60
Se	<3.0	4.43	68.2	<3.0	<3.0	6.47	3.41	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Fe	500	550	1050	270	38.0	310	210	120	170	8800	16 000	18 200	20 900

TABLE IIIb

Major and trace element concentrations from springs and surface runoffs in and outside of the geothermal field (conc. in μg L^{-1}, n.m. = not measured)

SAMPLE PERIOD	L-3 Jun-95	A-1 Nov-94	A-1 May-96	A-2 Jun-95	A-2 May-96	A-3 Jun-95	A-3 May-96	A-4 Nov-94	A-4 Jun-95	A-4 May-96	A-5 Jun-95	A-5 May-96	P-1 Nov-94
Temp. [°C]	16.2	22.4	23.0	22.6	22.0	23.4	23.0	20.8	24.9	22.5	24.4	18.5	22.0
pH	3.6	5.9	5.8	5.5	6.7	5.6	6.5	5.7	6.7	7.2	6.7	7.3	6.6
Cond. [μS cm^{-1}]	2760	40	37	40	30	120	72	320	510	95	280	100	410
Na	995 000	5 000	9 000	5000	7300	29 000	15 900	98 000	149 000	29 500	71 000	47 700	128 000
K	266 000	5400	4000	4800	3300	12 100	6200	28 500	40 100	8800	20 400	9700	18 700
Li	14 000	<50	10	<50	<10	300	60	1200	1690	90	900	300	160
Ca	24 300	90	<50	1900	n.m.	2600	50	2500	4500	<50	4500	<500	10 700
Mg	4410	150	<50	310	n.m.	370	<500	310	560	<50	490	<500	3220
Cl	3 897 000	<5000	11 200	<5000	10 800	77 000	25 800	155 000	194 000	38 900	120 000	42 500	40 000
SO_4	209 000	3000	3900	4100	<2000	4500	3900	4000	13 700	4700	22 500	4400	190 000
NO_3	105 000	2000	1700	2900	3800	<2500	3400	<1000	2600	2500	<2500	3900	<1000
HCO_3^-	<100	28 200	33 900	30 900	33 900	37 100	38 400	26 400	44 500	32 400	33 500	31 900	102 000
B	125 000	11 000	<100	<100	<100	n.m.	<100	15 000	20 000	4100	6000	5300	24 000
Si	59 300	n.m.	69 500	28 600	44 600	48 600	53 300	46 000	224 000	52 400	24 100	40 400	68 500
F	16 300	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	2000
Cr	8.35	0.85	1.94	0.81	1.34	1.62	1.59	<5.0	6.60	0.82	2.60	<0.5	5.60
Mn	1252	2.55	2.16	63.9	143	108	204	37.1	151	134	43.4	4.01	2922
Co	13.6	<0.5	<0.5	<0.5	0.71	<0.5	0.54	<5.0	<5.0	<0.5	1.12	<0.5	<5.0

TABLE IIIb

Continued

SAMPLE	L-3	A-1	A-1	A-2	A-2	A-3	A-3	A-4	A-4	A-4	A-5	A-5	P-1
PERIOD	Jun-95	Nov-94	May-96	Jun-95	May-96	Jun-95	May-96	Nov-94	Jun-95	May-96	Jun-95	May-96	Nov-94
Ni	18.7	13.5	2.25	3.95	1.45	2.81	1.33	<7.0	<7.0	1.29	5.58	<0.7	25.5
Cu	39.3	54.1	1.27	19.7	5.89	18.2	5.00	22.9	49.6	4.72	27.6	2.34	44.5
Zn	227	149	12.5	29.4	34.1	46.9	16.7	162	111	27.6	116	15.3	65.5
Ga	1.42	0.52	<0.5	0.51	1.40	0.55	0.56	<5.0	<5.0	<0.5	<0.5	<0.5	<5.0
Ge	11.9	0.72	0.60	0.71	0.71	1.09	0.79	6.20	7.10	0.85	1.88	<0.6	6.90
As	8200	4.00	1.00	6.00	4.00	190	18.0	1100	1700	40.0	630	60.0	70.0
Rb	1292	21.1	20.2	20.2	20.7	55.6	30.0	165	241	39.0	146	40.8	65.0
Sr	226	5.51	5.02	15.5	13.8	23.6	16.2	27.7	50.5	18.7	43.8	18.3	134
Mo	41.1	1.90	<0.5	1.53	<0.5	6.65	<0.5	11.4	20.3	<0.5	6.06	0.60	5.20
Ag	1.48	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<5.0	<5.0	<0.5	<0.5	<0.5	5.70
Cs	1094	1.42	1.29	1.80	1.27	33.2	5.08	142	219	8.86	110	14.3	29.5
Ba	177	20.8	3.80	8.84	35.6	18.7	27.6	303	31.4	24.3	43.1	16.8	171
W	26.3	<0.2	<0.2	0.21	<0.2	0.87	<0.2	3.90	5.10	<0.2	1.43	<0.2	<2.0
Hg	<0.9	3.67	<0.9	1.35	<0.9	2.27	<0.9	<9.0	<9.0	<0.9	3.52	<0.9	14.7
Tl	13.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<5.0	<5.0	<0.5	0.76	<0.5	<5.0
Pb	7.13	7.68	0.73	3.66	4.00	3.86	1.76	8.00	17.7	2.20	12.4	0.69	21.7
Cd	1.4	2.53	<0.5	<0.5	<0.5	<0.5	<0.5	<5.0	<5.0	<0.5	0.61	<0.5	<5.0
U	<0.5	<0.5	<0.5	<0.5	1.12	<0.5	<0.5	<5.0	<5.0	<0.5	<0.5	<0.5	<5.0
Se	36.6	5.07	<3.0	4.36	<3.0	4.89	<3.0	<30.0	<30.0	<3.0	<3.0	<3.0	<30
Fe	2900	26.0	100	680	2040	780	1670	280	2060	1020	1780	460	4200

TABLE IIIc

Major and trace element concentrations from springs and surface runoffs in and outside of the geothermal field

SAMPLE	P-1	P-2	P-2	P-2	P-3	P-3	P-4	P-4	P-5	P-5	P-5	Az-1	Az-1
PERIOD	May-96	Jun-95	Aug-95	May-96	Jun-95	May-96	Jun-95	May-96	Jun-95	Jan-96	May-96	Jun-95	Aug-95
Temp. [°C]	28.0	25.8	n.m.	21.0	19.5	13.0	21.6	13.0	16.8	15.0	18.0	19.7	n.m.
pH	6.4	7.0	7.1	7.9	6.6	7.3	7.7	8.2	7.4	8.1	8.0	5.8	6.6
Cond. [μS cm^{-1}]	450	480	530	540	260	280	167	165	182	170	160	760	350
Na	121 000	145 000	156 000	153 000	74 000	96 400	29 000	48 800	29 000	26 000	27 800	215 000	94 000
K	16 400	32 400	31 800	32 600	19 300	17 600	11 200	9800	10 400	10 800	7200	47 000	21 600
Li	670	320	610	310	300	730	100	90	100	60	40	620	370
Ca	7700	5200	9400	<500	7000	2000	11 900	4700	12 500	14 800	2700	27 600	9300
Mg	2100	1290	1830	<500	2790	1100	10 930	2100	12 400	13 410	1600	10 930	2470
Cl	56 500	159 000	204 000	133 000	71 800	42 300	<5000	16 400	<5000	7200	14 900	384 000	130 000
SO_4	123 000	155 000	n.m.	40 200	72 000	34 900	22 000	21 300	21 700	21 000	19 100	72 000	n.m.
NO_3	2600	3200	n.m.	5800	3400	2200	<1000	2800	3000	2000	3300	1700	n.m.
$HCO_3{}^-$	285 000	52 400	n.m.	176 000	39 100	148 000	147 000	172 000	152 000	170 000	161 000	8500	n.m.
B	<100	19 000	n.m.	49 900	5000	6300	<100	<100	<100	<100	680	22 000	n.m.
Si	96 600	55 800	n.m.	65 400	49 200	102 000	62 900	78 700	50 500	75 400	81 300	42 200	n.m.
F	2200	2400	n.m.	3400	1300	1600	<1000	<1000	<1000	<1000	<1000	<1000	n.m.
Cr	1.07	<5.0	1.86	0.53	1.05	0.54	0.79	1.26	0.76	2.12	0.98	<5.0	0.95
Mn	1109	264	695	67.5	40.7	21.8	38.9	22.0	46.5	19.0	30.7	1055	284
Co	<0.5	<5.0	0.87	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<5.0	0.68

TABLE IIIc

Continued

SAMPLE	P-1	P-2	P-2	P-2	P-3	P-3	P-4	P-4	P-5	P-5	P-5	Az-1	Az-1
PERIOD	May-96	Jun-95	Aug-95	May-96	Jun-95	May-96	Jun-95	May-96	Jun-95	Jan-96	May-96	Jun-95	Aug-95
Ni	1.41	31.8	1.76	1.09	5.43	1.17	3.77	1.99	3.88	1.88	1.21	<7.0	2.91
Cu	3.63	23.4	4.32	4.03	31.2	4.65	28.5	5.18	53.2	3.85	2.91	32.1	3.07
Zn	11.3	220	22.0	14.2	127	18.0	127	18.0	86.5	15.1	12.2	256	17.2
Ga	<0.5	<5.0	0.61	<0.5	0.67	<0.5	0.60	<0.5	0.54	<0.5	<0.5	4.70	<0.5
Ge	1.61	6.50	1.75	2.98	1.68	0.68	0.90	<0.6	0.64	<0.6	<0.6	<6.0	1.99
As	70.0	50.0	70.0	51.7	42.0	35.0	25.0	15.0	20.0	16.0	14.0	45.8	23.0
Rb	71.5	109	115	106	76.4	65.0	34.2	23.7	28.3	27.5	22.9	189	86.4
Sr	103	78.5	144	54.5	76.0	85.0	114	87.8	115	107	109	246	156
Mo	5.71	16.1	5.90	16.5	9.43	8.88	3.38	1.81	3.11	1.31	1.34	<5.0	3.61
Ag	<0.5	<5.0	17.3	<0.5	<0.5	<0.5	<0.5	<0.5	1.38	<0.5	<0.5	<5.0	0.95
Cs	17.0	44.7	49.4	21.7	29.3	17.3	7.78	3.43	4.99	3.65	2.79	44.5	15.7
Ba	124	200	158.5	55.6	42.2	38.1	47.4	25.0	30.8	26.8	24.0	381	131
W	<0.2	<2.0	<0.2	<0.2	0.27	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<2.0	<0.2
Hg	<0.9	<9.0	<0.9	<0.9	1.47	<0.9	1.44	<0.9	1.30	<0.9	<0.9	<9.0	<0.9
Tl	<0.5	<5.0	0.80	<0.5	0.53	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<5.0	<0.5
Pb	1.10	8.80	1.38	1.05	7.40	1.13	7.96	1.15	7.99	0.80	0.86	13.1	1.29
Cd	<0.5	<5.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<5.0	<0.5
U	<0.5	<5.0	<0.5	0.62	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<5.0	<0.5
Se	<3.0	<30.0	5.93	<3.0	4.75	<3.0	5.03	<3.0	3.90	<3.0	<3.0	20.8	4.23
Fe	1470	570	790	280	280	150	200	310	190	180	240	790	160

TABLE IIId

Major and trace element concentrations from springs and surface runoffs in and outside of the geothermal field (conc. in μg L^{-1}, n.m. = not measured)

SAMPLE	Az-1	Aj-1	Aj-1	S-1	S-1	E-1	E-1	Ag-1	Ag-1	Ag-2	Ag-3	Y-1	Y-1
PERIOD	May-96	Aug-95	May-96	Jun-95	May-96	Jun-95	May-96	Jun-95	May-96	Jun-95	Jan-96	Jun-95	Jan-96
Temp. [°C]	13.0	n.m.	23.0	30.8	40.0	17.7	16.0	21.3	17.0	21.4	6.0	17.9	14.0
pH	6.7	6.7	7.4	2.6	3.1	6.6	7.2	2.8	4.6	7.5	7.7	6.6	7.6
Cond. [μS cm^{-1}]	580	100	210	160	180	210	110	1020	300	300	240	60	43
Na	249 000	21 000	83 400	7000	37 900	29 000	28 200	76 000	82 200	62 000	17 000	8000	5000
K	37 600	7000	15 100	15 800	10 400	10 800	4400	18 500	15 800	17 300	6100	5000	6300
Li	330	100	540	<50	210	<50	<10	<50	1070	140	100	<50	<50
Ca	5700	6000	1600	2300	<500	21 800	2800	50 800	5300	20 100	8100	2800	3500
Mg	1100	3930	<500	310	<500	16 860	900	20 020	700	7350	1920	1010	1080
Cl	265 000	38 500	17 100	<5000	27 700	3800	11 400	28 500	98 200	65 700	42 000	<5000	<5000
SO_4	24 300	n.m.	34 600	77 900	36 300	16 000	8400	660 000	38 400	120 000	20 000	8800	7000
NO_3	6000	n.m.	3000	<1000	<1000	3100	2400	9800	<1000	6700	5200	3700	2400
HCO_3^-	52 700	21 700	106 000	<100	<100	101 000	134 000	<100	5100	69 700	49 400	22 800	21 400
B	28 600	n.m.	3600	n.m.	2500	<100	<100	15 000	18 500	39 000	3200	<100	<100
Si	62 900	n.m.	139 000	26 200	110 000	27 400	70 800	87 600	38 500	87 600	64 000	62 800	66 700
F	<1000	n.m.	1800	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	1000
Cr	2.23	0.77	0.70	0.69	<0.5	1.12	0.86	5.00	1.51	0.73	1.88	0.67	<0.5
Mn	1056	142	15.6	75.3	33.5	112	46.0	1454	300	138	32.2	20.6	10.1
Co	1.94	<0.5	<0.5	<0.5	<0.5	0.54	<0.5	11.6	8.58	1.21	<0.5	<0.5	<0.5

TABLE IIId

Continued

SAMPLE	Az-1	Aj-1	Aj-1	S-1	S-1	E-1	E-1	Ag-1	Ag-1	Ag-2	Ag-3	Y-1	Y-1
PERIOD	May-96	Aug-95	May-96	Jun-95	May-96	Jun-95	May-96	Jun-95	May-96	Jun-95	Jan-96	Jun-95	Jan-96
Ni	1.72	4.35	0.81	6.54	<0.7	9.01	1.27	<7.0	6.60	4.54	2.36	3.58	0.80
Cu	3.15	4.07	2.46	51.0	2.33	54.4	6.37	57.8	8.01	36.5	4.31	22.9	1.31
Zn	21.9	15.4	13.7	198	16.0	133	19.5	126	49.6	91.5	15.3	160	11.5
Ga	0.80	<0.5	<0.5	<0.5	<0.5	0.69	<0.5	<5.0	<0.5	0.62	<0.5	0.48	<0.5
Ge	1.97	0.70	3.12	0.90	0.90	2.35	0.56	6.80	0.88	1.23	<0.6	<0.6	<0.6
As	180	9.00	40.0	23.0	14.0	24.0	8.00	38.0	11.0	28.0	28.0	5.00	3.00
Rb	148	27.8	68.4	61.0	58.8	29.1	13.3	77.5	82.4	49.3	42.7	27.0	26.0
Sr	174	52.6	16.5	7.95	3.53	196	87.3	409	172	251	237	21.1	18.9
Mo	0.71	<0.5	6.96	0.91	<0.5	2.26	<0.5	<5.0	1.18	2.97	1.46	1.96	<0.5
Ag	<0.5	24.3	<0.5	0.89	<0.5	<0.5	<0.5	<5.0	<0.5	0.45	<0.5	<0.5	3.74
Cs	25.6	6.04	5.17	5.22	5.23	1.54	0.37	27.7	42.2	9.27	6.80	1.74	1.06
Ba	363	40.3	11.6	17.5	3.85	50.1	16.5	52.2	105	72.7	101	6.96	4.32
W	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<2.0	<0.2	<0.2	<0.2	0.19	<0.2
Hg	<0.9	1.56	<0.9	3.56	<0.9	1.76	<0.9	<9.0	<0.9	0.81	<0.9	0.81	<0.9
Tl	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<5.0	0.50	<0.5	<0.5	<0.5	<0.5
Pb	1.54	1.05	0.73	7.72	0.63	7.72	3.47	9.70	2.08	7.32	1.23	6.13	1.40
Cd	<0.5	<0.5	<0.5	0.71	<0.5	<0.5	<0.5	<5.0	<0.5	<0.5	<0.5	<0.5	<0.5
U	<0.5	<0.5	0.57	<0.5	<0.5	<0.5	<0.5	<5.0	<0.5	<0.5	<0.5	<0.5	<0.5
Se	4.12	<3.0	<3.0	<3.0	<3.0	3.63	<3.0	<30.0	<3.0	5.04	<3.0	4.33	<3.0
Fe	20 100	1120	130	1190	580	1330	420	20,900	500	1170	750	110	110

TABLE IIIe

Major and trace element concentrations from springs and surface runoffs in and outside of the geothermal field

SAMPLE	Y-1	C-1	C-1	Z-1	Z-2	Z-2	Z-2
PERIOD	May-96	Jun-95	May-96	Jun-95	Jun-95	Jan-96	May-96
Temp. [°C]	16.0	22.3	17.0	23.5	25.1	16.5	15.0
pH	7.3	6.8	7.3	7.0	7.0	7.7	7.6
Cond. [μS cm^{-1}]	50	66	67	125	120	110	75
Na	17 400	11 000	9000	18 000	17 000	14 000	9000
K	3300	5600	3700	11 900	8500	8500	3700
Li	150	<50	<10	<50	<50	<50	10
Ca	3300	5500	700	9700	11 800	11 800	3100
Mg	1100	2820	<500	8030	8720	9280	900
Cl	13 700	<5000	10 300	15 900	<5000	<5000	9500
SO_4	8100	10 100	10 900	22 400	14 800	23 600	6500
NO_3	3600	<1000	2900	3800	3400	3600	2900
HCO_3^-	27 700	60 200	63 400	<100	102 000	87 100	84 600
B	<100	<100	<100	<100	<100	<100	320
Si	62 800	30 000	59 000	43 000	169 000	58 600	40 200
F	<1000	<1000	<1000	<1000	<1000	1000	<1000
Cr	<0.5	1.04	1.38	0.89	0.74	3.0	0.50
Mn	<2.0	53.9	45.4	130	169	90.5	72.6
Co	<0.5	<0.5	<0.5	0.77	0.49	<0.5	<0.5
Ni	<0.7	5.21	1.51	5.88	2.75	1.49	0.98
Cu	0.52	55.8	2.71	39.1	17.7	7.30	2.20
Zn	<3.0	195	17.6	162	58.1	80.9	13.2
Ga	<0.5	0.52	<0.5	0.68	0.55	<0.5	<0.5
Ge	<0.6	<0.6	<0.6	<0.6	0.57	<0.6	<0.6
As	3.00	3.00	4.00	4.00	3.00	2.00	1.50
Rb	23.8	8.69	6.76	21.9	16.8	15.4	9.82
Sr	17.9	57.1	54.2	108	120	114	79.4
Mo	<0.5	4.42	<0.5	31.3	1.45	0.81	<0.5
Ag	<0.5	0.53	<0.5	0.95	<0.5	0.80	<0.5
Cs	1.09	0.21	0.56	0.25	0.21	<0.26	<0.26
Ba	2.48	23.9	14.3	67.1	39.9	36.0	24.4
W	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Hg	<0.9	0.83	<0.9	<0.9	0.83	<0.9	<0.9
Tl	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Pb	<0.4	9.68	1.11	7.41	2.40	2.59	1.27
Cd	<0.5	0.47	<0.5	<0.5	<0.5	<0.5	<0.5
U	<0.5	<0.5	<0.5	0.46	0.46	0.50	<0.5
Se	<3.0	4.99	<3.0	5.15	3.82	<3.0	<3.0
Fe	39.0	380	440	500	1050	840	650

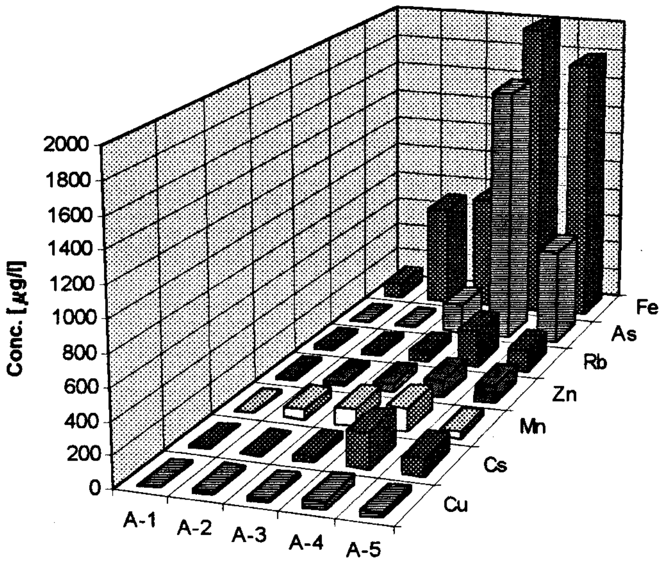

Figure 9. Lateral Cu, Cs, Mn, Zn, Rb, As, and Fe distribution during the downstream of the river Agua Fría, located inside of the geothermal field (June 1995).

natural background values due to their lower solubility characteristics. On the last 2 km, between T-4 and T-5, concentrations similar to T-1 and L-1 are found.

January and May 1996: The extremely high trace element concentrations found in June 1995, related to the inflow of mineralised water from the Leoncito river into the Sta. Teresa river, were not detected. Especially, a decline in the concentration of the typical geothermal tracer elements Cl, Na, B, F, Fe, As, Rb, Sr, Cs, Ge, Zn, and Co was observed. B and As were found to be less than 100 μg L^{-1} and 10 μg L^{-1}, respectively at station T-3. This irregular distribution of the river composition indicates the temporary character of the brine spills at the Sta. Teresa river.

(b) River Agua Fría

This river has its origin E of the operator plant of the geothermal field (Figure 4), subsequently passing close to several production wells and evaporation ponds (Az-35, Az-22, Az-12), and discharging westwards into the natural lagoon Laguna Larga. Its recharge is derived from several small springs within the Quaternary alluvial fillings of the Agua Fría valley.

June 1995: Figure 9 shows the lateral distribution of the trace element concentrations, starting from the upper course springs (sample A-1). Samples of river water were taken before (site A-2) and after (site A-3) the adjacent evaporation pond from the production well Az-22, close to the well Az-12 (site A-4) and the Laguna Larga (A-5). All samples were taken within the geothermal field area. Passing the Az-22 evaporation pond, the low background concentrations of the upstream sites (A-1, A-2) become slightly increased at site A-3, especially in As (190 μg L^{-1}), Ba (18.7 μg L^{-1}), and Rb (55.6 μg L^{-1}). This is also valid for some major elements, such as Cl (77 000 μg L^{-1}), Na (29 000 μg L^{-1}), and K (12 100 μg L^{-1}) (Table IIIb). This is assumed to be due to the discharge of small amounts of geothermal water from the pond walls into the adjacent river. Further downstream the sample at A-4 is characterised by even higher trace element concentrations as the geothermal contamination from a tributary causes further increase in trace element concentrations. The tributary is affected by recharging springs and shallow aquifers that are contaminated by infiltrated geothermal brine from the evaporation pond of the well Az-25. The impact on the shallow aquifer is discussed in chapter 5.4.3. Over a distance of 1800 m, between A-4 and A-5, the trace elements show the following pattern:

- Mn, Ga, and Se concentrations meet the background concentrations.
- B, Cr, Cu, Ge, and Mo are still slightly increased.
- Fe, As, F, Rb, Zn, Cs, Sr, and Pb still show increased levels.
- Ba, Cd, and Co show even higher concentrations which must be explained by interaction processes with the river bed.

May 1996: Similar to the case of the Sta. Teresa river the same sites (A-2 to A-5) show lower concentrations for this sample period as in June 1995. This is probably due to lower spill rates of geothermal brines and/or less dilution by rainfall in June 1995. The second option is supported by lower discharge rates of the runoff systems in June 1995 in comparison with May 1996 (Birkle, 1998). On the other hand, the values for As, Zn, Rb, Cs, Ge, Sr, Mo, and Pb are still above the normal background concentrations of the upper stream springs.

(c) River Tejamaniles/ San Pedro

May 1996: The hot spring Azufres in the SE part of the geothermal field represents the origin of the Tejamaniles river. After passing the wells Az-6, 33, 17 and 16 and recharging by the river Los Ajolotes and ‘Az-2’ (so named by the authors), the San Pedro river flows out of the geothermal field in a southern direction. 1100 m downstream of the Azufres spring, elevated levels were measured for Na (121 000 μg L^{-1}), Si (96 600 μg L^{-1}), Cl (56 500 μg L^{-1}), F (2200 μg L^{-1}) (not shown in Figure 10), Fe (1470 μg L^{-1}), and Mn (1109 μg L^{-1}), whereas the values for Ba (124 μg L^{-1}), Sr (103 μg L^{-1}), Rb (72 μg L^{-1}), As (70 μg L^{-1}), and Mo (5.7 μg L^{-1}) (sample P-1 in Figure 10 and Table IIIc) were slightly higher than the natural background concentrations of meteoric water. This increase is related to the natural source of mineralised water by the Azufres spring. Towards the SW-part of the geothermal field, the river becomes more diluted, which is shown in the composition of sample P-2. Due to the subsequent inflow of the stream Az-2 (sample Az-1), the mineralization of the Tejamaniles river increases. On the other side, the long flow distance of 3.4 km between the stations P-2 and P-3 reduces the

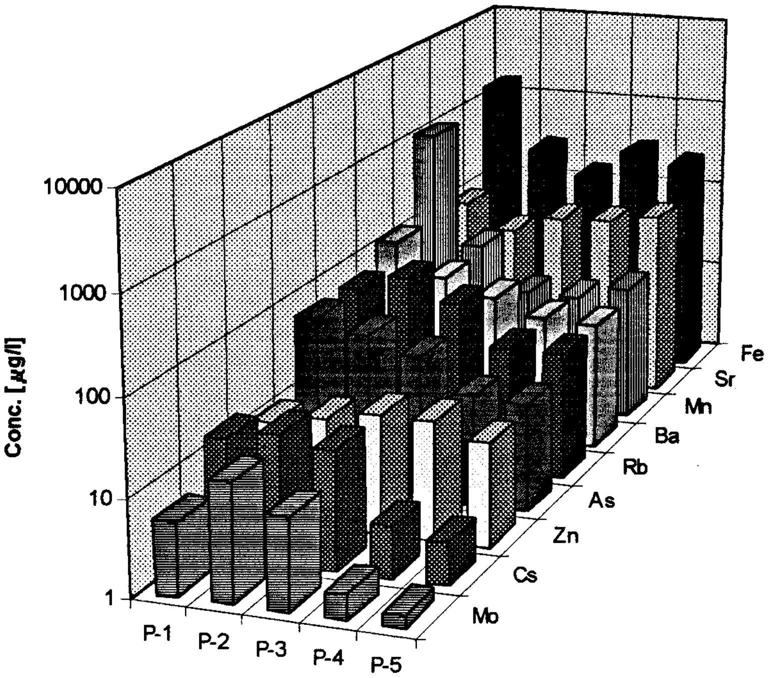

Figure 10. Lateral distribution of the trace elements Mo, Cs, Zn, As, Rb, Ba, Mn, Sr, and Fe during the course of the Tejamaniles/San Pedro river. The station P-1 is still located close to the source of the river, whereas the downstream stations are located outside of the geothermal field area.

trace metal concentration towards upper stream levels. The As values decline from 52 to 35 μg L^{-1}, Mn from 68 to 22 μg L^{-1}, and Rb from 106 to 65 μg L^{-1}, while B values are at 6300 μg L^{-1}. The tributary river Az-2 receives some geothermal brine, assumed to be spilled from the leaking evaporation pond, located adjacent to production well Az-2. Due to the additional input of shallow aquifers from the Tejamaniles Valley into the Az-2 runoff, the concentrations are diluted (sample Az-1 in Table IIId). However concentrations of 265 000 μg L^{-1}, 249 000 μg L^{-1}, 28 600 μg L^{-1}, 20 100 μg L^{-1}, 1056 μg L^{-1}, 363 μg L^{-1}, and 180 μg L^{-1} for Cl, Na, B, Fe, Mn, Ba, and As, were monitored 100 m before its inflow into the Tejamaniles river (sample Az-1).

Outside the geothermal field the sampling sites P-4 and P-5, 9.9 and 13.4 km from their common origin are characterised by a slow decrease in their trace element composition. This can be attributed to various processes, such as dilution by recharging meteoric water as well as mineral sorption by alluvial clays and trace metal precipitation.

June 1995: Figure 11 compares the lateral distribution of the Mn, As, and Cs concentrations of the Tejamaniles river stations in June 1995 and May 1996. In

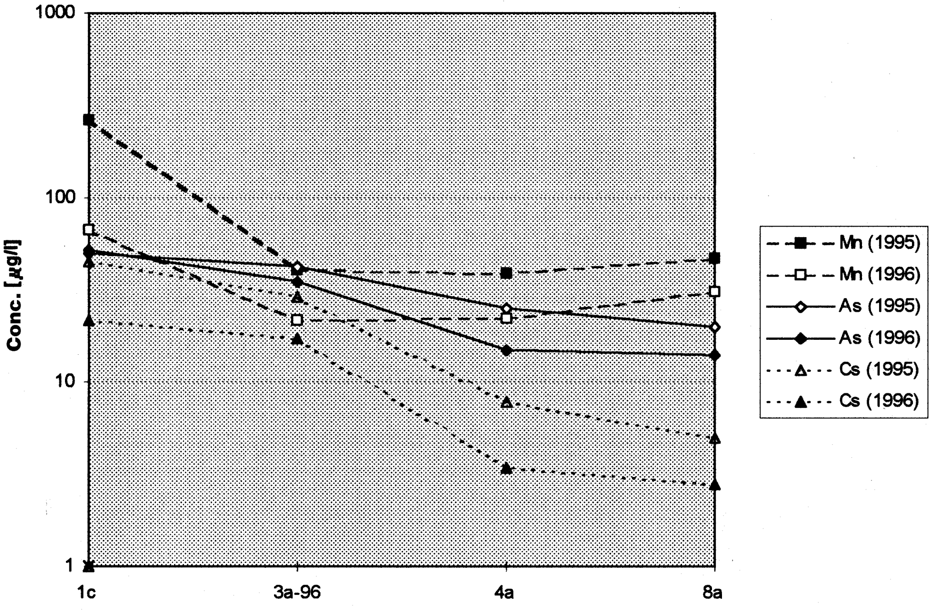

Figure 11. Comparison of the lateral distribution of the Mn, As, and Cs concentrations of the Tejamaniles river stations in June 1995 and May 1996.

both sampling periods, a decrease could be observed in the downstream direction. As in other river systems, the June 95 period is characterised by increased concentrations due to dryer climatic conditions with less dilution by rainfall and less flow discharge.

5.4.3. *Contamination of Groundwater Systems*

Andesitic flows and rhyolitic domes form the volcanic stratigraphy of the Los Azufres area. The common fracturing of the volcanic rocks cause the deep infiltration of meteoric water and the lack of shallow piezometric water levels in the mountain ranges of Los Azufres (Birkle *et al.*, 1997). An exception are those valleys where Quaternary alluvium has built a shallow, porous aquifer with restricted extension.

Taking into account the specific geological conditions, it was difficult to prove the environmental impact of geothermal spills on the shallow aquifer system. In the case of the well Az-25, the unsealed evaporation basin probably caused the vertical infiltration of geothermal brine into the shallow valley aquifer. Approximately 300 m below the well, the mineralised water discharges at the surface as a small spring. The saline spring water composition from November 1994, comprising a mixture of meteoric water with geothermal fluids, is shown in Table II (Az-25). As a consequence of the high salt content of the geothermal component, evaporation processes and a low discharge rate of the spring, the surrounding dark-grey to black soil is covered by a white salt crust with an areal extension of ca. 1000 m^2. Besides the increased concentrations of the major elements Na (679 000 μg L^{-1}) and Cl (1 413 000 μg L^{-1}), the trace elements B (87 000 μg L^{-1}), Mn (10 485 μg L^{-1}), Ba (6538 μg L^{-1}), Sr (690 μg L^{-1}), Zn (644 μg L^{-1}) and Rb (516 μg L^{-1}) were found with abnormally high concentrations.

5.5. RISK ASSESSMENT

The following environmental risk evaluation is based on the long-term monitoring and analysis of the river systems within and outside of the geothermal field and its comparison with national and international water standards. The Mexican norm NOM-001-ECOL-1996 from the Environmental Ministry (Secretaría de Medio Ambiente, 1996), establishes the maximum permitted values for metals and non metals in waste water rivers for a) agricultural irrigation and b) for public urban use. The international World Health Organization (WHO, 1993) and the Environmental Protection Agency (EPA, 1982; 1990) established MCL (Maximum Contamination Levels) for drinking water. The maximum concentrations of both standards are shown in Table IV.

Table V shows all rivers within and outside of the geothermal field and their trace metal concentrations that exceed the EPA and WHO drinking water standards. Enclosed is also the evaluation of some smaller streams, which are discussed in detail in Birkle (1998).

Inside of the geothermal field, all river systems exceed the EPA and WHO drinking water standards, especially for the elements Fe, Mn, As, B, Hg, Pb, F and Se. The principal surface water systems of the Los Azufres zone, Sta. Teresa and Tejamaniles/San Pedro, represent a considerable risk for human health and the environment.

The maximal B-values of 67 000 μg L^{-1} of Sta. Teresa, measured still inside of the geothermal field exceed 220-fold the WHO-drinking water norm of 300 μg L^{-1}. Other maximum concentrations worth mentioning are: As with 3200 μg L^{-1} (WHO: 10 μg L^{-1}), F with 13 400 μg L^{-1} (WHO: 1500 μg L^{-1}), Fe with 1050 μg L^{-1} (WHO: 50 μg L^{-1}), Mn with 850 μg L^{-1} (WHO 50 μg L^{-1}) and Se with 68.2 μg L^{-1} (WHO: 10 μg L^{-1}).

The high trace elements were found several km towards urbanised areas: The samples from site T-4, located 5 km outside of the geothermal field still exceed the WHO-standards. B, As, and Fe reach values of 7000 μg L^{-1}, 300 μg L^{-1}, and 310 μg L^{-1}, respectively. About 8 km outside of the geothermal field (station T-5), the impact of geothermal brine by the Leoncito stream could not be detected anymore. A potential health risk arises for the village Yerbabuena with several hundred inhabitants due to the lack of a drinking water system and the use of the Sta. Teresa and Leoncito rivers for private consumption and agricultural purposes. 500 m NE of the urbanisation, the As and B concentrations of the Leoncito stream were found to be 8200 μg L^{-1} and 125 000 μg L^{-1} in June 1995.

TABLE IV

Maximal permitted trace element concentration for drinking water (WHO and EPA norms) and for river waste water, used for irrigation, urban purposes and aquatic life protection (Mexican Laws). (symbol – means not existing)

Norms: Elements	WHO	USA: EPA (MCLG)	Mexico: NOM-001-ECOL-1996 (a) Irrigation	Mexico: NOM-001-ECOL-1996 (b) urban use
As	10	50	200	100
B	300	1000	–	–
Cd	3	5	200	100
Cr	50	100	1000	500
Cu	2000	1300	4000	4000
F	1500	4000	–	–
Fe	50	–	–	–
Hg	1	2	10	5
Pb	10	0	500	200
Mn	50	–	–	–
Mo	70	–	–	–
Ni	20	100	2000	2000
Se	10	10	–	–
Tl	–	0.5	–	–
Zn	5000	–	10 000	10 000

Inside the geothermal field, the elements B, F, Fe, Mn, As, Ba, Mo, and partly Ag of the Tejamaniles/San Pedro river water exceeded permanently the WHO and EPA MCL's. The samples from outside, which represent the lower course of the river, show lower concentrations than samples from the upper course. The MCL exceeding values of up to 240 μg L^{-1} for Fe, and 20 μg L^{-1} for As were still detected after a flow distance of 13 km (station P-5). A latent environmental risk can arise due to the presence of some adjacent villages in the far field of the geothermal field, such as San Pedro Jacuaro, which use the river water for irrigation and cattle farming.

Permanently increased concentrations in B, As, Fe, Mn of the Agua Fría river, caused by the inflow of geothermal brine from the Az-22 and Az-25 production units, can affect a small community, located adjacent to the operator camp of the geothermal field and the well Az-12. The values of B (4140 – 20 000 μg L^{-1}), As (40 – 1700 μg L^{-1}), Fe (89 – 2060 μg L^{-1}) and Mn (37 – 151 μg L^{-1}) violating permanently the WHO MCL's.

Concerning the Mexican norm for wastewater discharge, the As-concentration especially is exceeded in several cases: The Agua Fría river (samples A-3, A-4,

TABLE V

List of trace elements in river water within and outside of the geothermal field, which exceed the international drinking water standards (EPA, WHO). Some rivers are located either inside or outside of the geothermal field (symbol –). Permanent exceeding elements are referred to at least 2 sampling periods. Thus, for rivers with just one sampling period (for example Leoncito), the permanent values can not be given

River	Inside of the geothermal field:		Outside of the geothermal field:	
	Temporary exceed	Permanent exceed	Temporary exceed	Permanent exceed
Sta. Teresa	B, Pb, Hg	Fe, Mn	B, F, As, Mn, Ba, Hg, Pb, Se	Fe
Yerbabuena	–	–	Mn, Fe, F	?
Leoncito	F, B, Pb, Hg	Fe, Mn, As	B, F, As, Fe, Mn, Tl, Se	?
Chino	As, Hg	Fe, Mn	–	–
San Alejo	B, Hg, Mn	Fe, As	–	–
Agua Fría	Pb, Hg	B, Fe, As, Mn	–	–
Agrio	Pb	B, Fe, Mn, As	B, Fe, As	?
Tejamaniles/ San Pedro	Pb, Hg	B, F, Fe, Mn, As	B, F, Hg	Fe, Mn, As
Az-2	Pb, Se	B, Fe, Mn, As	–	–
Los Ajolotes	Mn, As, Ag, Hg	B, Fe, F	–	–
Erendira	–	–	As, Hg, Mn	Fe
El Chiquito	–	–	Pb	Fe, Mn
El Zarco	–	–		Fe, Mn

A-5) exceeds permanently the maximum permitted As-concentration of 100 and 200 μg L^{-1} for irrigation and urban use, respectively. Inside (samples T-2, T-3) and outside (T-4, T-5) of the geothermal field, the Sta. Teresa river shows temporary, especially in June 1995, norm exceeding concentrations for As. Probably due to the intermittent character of the geothermal spills, the streams Az-2 and Leoncito exceed temporarily the maximum MCL As-values of up to 180 and 8200 μg L^{-1}, respectively.

Due to water/rock interaction processes, catalysed partly by hot springs and fumaroles, all rivers of the study area are characterised by slightly increased background concentrations of some trace elements, especially in Fe and Mn, but also in Pb and Hg. Small streams, such as San Alejo (samples S-1), and Erendira (E-1), seem not affected by spills of geothermal brines, but are related to natural mineralised hot springs. The increased B, Fe, Mn, and As concentrations of the Agrio river (Ag-1, Ag-2, Ag-3) are due to the recharge of the Marítaro fumarole in its upper course. Dissolution from hydrothermal altered bed rock explains the permanent increased Fe and Mn concentrations of the Yerbabuena (Y-1), El Chiquito (C-1) and El Zarco streams (Z-1, Z-2) (Table IIIe).

5.6. TOTAL TRACE ELEMENTS DISCHARGE BY RIVER SYSTEMS

In June 1995, flow measurements of all surface streams discharging from the geothermal field towards outer regions, as well as an analysis of their chemical composition were conducted. Based on this information, the total daily amount of transported trace element for each individual river was derived. Table VI shows the total mass for each element in kg per day.

Due to the negligible background concentration of the natural hydrological system, it can be assumed that almost 100% of the calculated mass of metals and non metals is derived from spills of geothermal brine into the river systems. This environmental impact is caused by artificial exploitation of geothermal fluids from a deep reservoir and spill to the surface environment.

Assuming a constant discharge rate and similar trace element concentration for the entire year, a total mass of 152 tons of Si, 65 tons of B, and 2.6 tons of As will be discharged annually from the geothermal production area towards outer parts.

5.7. ENVIRONMENTAL DAMAGE

The extraction of geothermal brine from a deep reservoir to the surface and its distribution into the hydrological system has caused the following environmental damage:

- *Contamination of surface waters and aquifers.* All rivers inside of the geothermal field, such as the Sta. Teresa, Agua Fría and Tejamaniles river, are permanently affected by increased concentrations of major and trace elements especially of Cl, Na, F, Mn, Fe, B, As. The concentrations of these geothermal tracer elements are greater than the international EPA and WHO drinking water standard. Furthermore, the rivers Sta. Teresa, Agua Fría, Leoncito and Az-2 exceed the Mexican norm of wastewater in rivers. Very critical are the temporary and in some cases the permanent contamination of rivers, discharging the geothermal load towards urban areas outside of the geothermal field.
- *Health risk.* As an indirect consequence of the geothermal spills, the use of the contaminated river water for consumption and irrigation could arise a long term health risk for the urban population as well as for the cattle.
- *Salinisation of soils.* The evaporation of the saline geothermal brines, for example around discharging springs, causes the formation of salt crusts and the barrenness of the affected soils.
- *Ecological effects.* As a consequence of the formation of some unfertile soil zones and high salt and metal contents in the river and aquifer systems, damage is expected for the flora of the forest protection area of Los Azufres. Biological damage however was not analysed quantitatively as part of this study.

TABLE VI

Load of trace elements in surface water in kg day^{-1}, discharging towards outside of the geothermal field. (- Concentration below detection limit)

River/ element	Tejamaniles	Az-2	Agrio	Leoncito	Agua Fría	Alejo	Chino	Sum
Cr	–	–	0.001	0.01	0.01	<0.001	<0.001	0.02
Mn	0.14	1.49	0.12	0.79	0.13	0.22	0.16	3.04
Co	–	–	0.001	0.01	<0.001	–	<0.001	0.01
Ni	0.02	–	0.004	0.01	0.02	0.02	0.01	0.08
Cu	0.01	0.05	0.03	0.02	0.08	0.15	0.05	0.40
Zn	0.11	0.36	0.08	0.14	0.35	0.58	0.24	1.87
Ga	–	0.01	0.001	0.001	–	–	–	0.01
Ge	0.003	–	0.001	0.01	0.01	0.003	0.001	0.02
As	0.03	0.06	0.02	5.17	1.90	0.07	0.02	7.27
Rb	0.06	0.27	0.04	0.81	0.44	0.18	0.08	1.87
Sr	0.04	0.35	0.21	0.14	0.13	0.02	0.02	0.92
Mo	0.01	–	0.003	0.03	0.02	0.003	0.02	0.08
Ag	–	–	0.0004	0.001	–	0.003	–	0.004
Cs	0.02	0.06	0.01	0.69	0.33	0.02	0.01	1.14
Ba	0.10	0.54	0.06	0.11	0.13	0.05	0.03	1.03
W	–	–	–	0.02	0.004	–	–	0.02
Hg	–	–	0.001	–	0.01	0.01	0.003	0.03
Tl	–	–	–	0.01	0.002	–	–	0.01
Pb	0.005	0.02	0.01	0.004	0.04	0.02	0.01	0.10
Cd	–	–	–	0.001	0.002	0.002	–	0.005
U	–	–	–	–	–	–	0.001	0.001
Se	–	0.03	0.004	0.02	–	–	–	0.06
Fe	0.30	1.11	0.99	1.83	5.37	3.49	1.05	14.1
Si	28.9	59.4	74.2	37.4	72.7	76.7	68.4	417.8
Li	0.17	0.87	0.12	8.83	2.71	0.62	–	13.3
F	1.24	1.27	–	10.3	0.30	0.59	0.23	13.9
B	9.85	31.0	33.0	78.8	18.1	7.41	–	178.2

5.8. REMEDIATION PROPOSALS

The main purpose of any remediation technique for the geothermal field should assure the establishment of a closed production cycle. The contact of the geothermal brines with the atmosphere and the biosphere must be avoided. Technical and operational solutions, similar to remediation measures of municipal landfills, are proposed:

Evaporation ponds:

- Excavation of the permeable and fractured pond wall material and the bottom strata.
- Sealing of the pond walls and bottom by impermeable clay layers and/or geo textiles.
- Removal of the artificial overflow channels at the rim of the evaporation ponds.
- Expanding of the storage volume of the evaporation ponds, or better direct reinjection without evaporation ponds.

Production and operational control:

- Complete injection of the geothermal brines from the surface by reinjection wells.
- Direct injection of the geothermal brines without any temporary residence time in evaporation ponds.
- Avoidance of temporary spills of geothermal brines during perforation and repair work.
- Improved control systems to assure the restricted access to the production units.

6. Discussion

The monitoring of the river systems proved a lateral distribution of the geothermal contaminants up to 10 km outside of the geothermal field. Although the mountain ranges of Los Azufres are characterised by a very low population density, the contamination of the hydrological system with geothermal brine should be prevented. Due to the high mineralisation with trace elements, such as B, As, Cs, and Sr the brines imply a toxic potential for the biosphere. Their composition is of natural origin, but exclusively the man made influence in the form of geothermal energy production, causes the contact of the deep reservoir fluids with the surface environment.

Hydrothermal surface features in Los Azufres, such as hot springs and fumaroles, appear to represent a similar type of high mineralised geothermal fluids as the deep reservoir type. Nieva *et al.* (1983, 1987) propose the heating of shallow aquifers by the vertical rise of geothermal vapor, which would indicate the existence of communication pathways between the surface and the reservoir. Indeed, the discharge of natural mineralised hot springs can cause some impact on rivers, such as the Erendira stream. On the other hand, strong variations in their chemical composition exclude the possibility of a common origin for hydrothermal sources and the geothermal fluids. The detection of increased concentrations of the tracer elements Cl, Na, B, As, Cs, Rb, and Sr in the Los Azufres rivers proves the inflow of geothermal brine into the surface water.

Especially critical for the environment are some local spill accidents, such as the case of the Leoncito spill from June 1995, which caused a peak increase of the trace element concentrations in the lower course of the runoff system.

This paper presents the results of an environmental assessment study for a limited time period of 20 months, and included a total of 5 field periods and 115 water samples. To obtain a long-term statement about the environmental conditions of the geothermal field of Los Azufres, a continuing periodical sampling and monitoring, as well as flow measurements of the principal runoff systems is proposed.

7. Conclusions

In countries with favourable hydrogeological and volcanological conditions with high geothermal depth gradient, which is the case for the Transmexican Volcanic Belt, the use of non conventional types of energy sources, such as geothermal energy, represent a very economic and environmental-friendly alternative in comparison with conventional types of energy sources. On the other hand, the presented study indicates possible environmental impacts due to the technical and administrative operation in the special case of the Los Azufres geothermal field. Although a variety of environmental impacts in and outside of the geothermal field were detected, the proposed remediation techniques, such as the sealing of the evaporation ponds, are technically feasible at relatively low costs.

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