Groundwater Contamination with Arsenic and Other Trace Elements in an Area of the Pampa, Province of Córdoba, Argentina

HUGO B. NICOLLI,* JOSE M. SURIANO,
MIGUEL A. GOMEZ PERAL, LUIS H. FERPOZZI,* and
OMAR A. BALEANI*
Departamento de Geoquímica y de Aplicaciones
Geológicas de la Teleobservación
Comisión Nacional de Investigaciones Espaciales
Av. Mitre 3100
1663-San Miguel, Buenos Aires, Argentina

ABSTRACT / A geochemical study of groundwater of the pampa in the province of Córdoba, Argentina, was performed; the area covered approximately 10,000 km².

Physical-chemical parameters, dissolved solids, and seven trace elements were determined in 60 selected water samples. Systematic and accurate measurements of arsenic, flourine, and vanadium were performed for the first time. Three trace element contaminants not reported earlier were found: an important one, selenium, and two others of less known effects, uranium and molybdenum.

Eighty-four percent of the water analyzed showed arsenic contents over 0.05 mg/L, maximum contaminant level established by the U.S. Environmental Protection Agency (1982). The frequency distribution of trace elements was analyzed, and its fit to the lognormal distribution was proved by means of the Pearson and Kolmogorov–Smirnov test; the geo- graphic distribution of the seven trace elements was mapped and its correlation with the anion-cation composition of the water was studied.

The maximum arsenic, fluorine, vanadium, and uranium contents were found in the western part of the area under study, in waters containing dominant alkali metals in the cation composition. Maximum selenium and antimony contents were found in the eastern part of the area, while molybdenum distribution does not show any relationship with the other two groups. In addition, the geographic distribution of the trace elements seems to be related to the subsurface structure, which has been inferred using interactive digital analysis of Landsat imagery. The movements of the subsoil have disturbed surface and subsurface drainage influencing the water salinity and trace element contents.

In order to investigate the origin of the contamination, 54 loess samples were collected in wells at depths ranging from the surface down to the water table. This loess, which has a high proportion of volcanic components, mainly rhyolitic glass, exhibits a chemical composition corresponding to that of a dacite.

The loess and the volcanic glass show anomalous contents of all contaminant trace elements, mainly arsenic and selenium. For this reason loess is considered the most important contamination source in the groundwater under study.

Introduction

The development of extended zones of the Argentine pampa region presenting good agricultural and cattle-raising conditions is restricted by the quality of the available water resources. The main problems are high salinity in underground and even surface water and the presence of certain trace elements in amounts that turn out to be toxic for inhabitants and cattle; these problems acquire a particular importance because the area under study is densely populated and offers a great agricultural and livestock development.

Early in this century an endemic disease due to contamination of drinking water with arsenic became known. This disease was called HACRE (*h*idroarsenicismo *c*rónico *r*egional *e*ndémico, Chronic Endemic Regional Hydroarsenicism) and is connected to the development of a particular type of skin cancer (Astolfi and others 1981). The occurrence of the disease is so common that it is known as "Bell Ville disease," due to the name of one of the most important cities in the region. High fluorine and vanadium contents in that same drinking water had also been reported in previous papers. Up to 1985, the origin of the problem had not been systematically investigated; there were neither accurate measurements nor distribution maps of the contaminants.

The first step in a research program was a systematic sampling of groundwater following the U.S. Geo-

---

*Also affiliated with: Consejo Nacional de Investigaciones Científicas y Técnicas, Buenos Aires, Argentina.
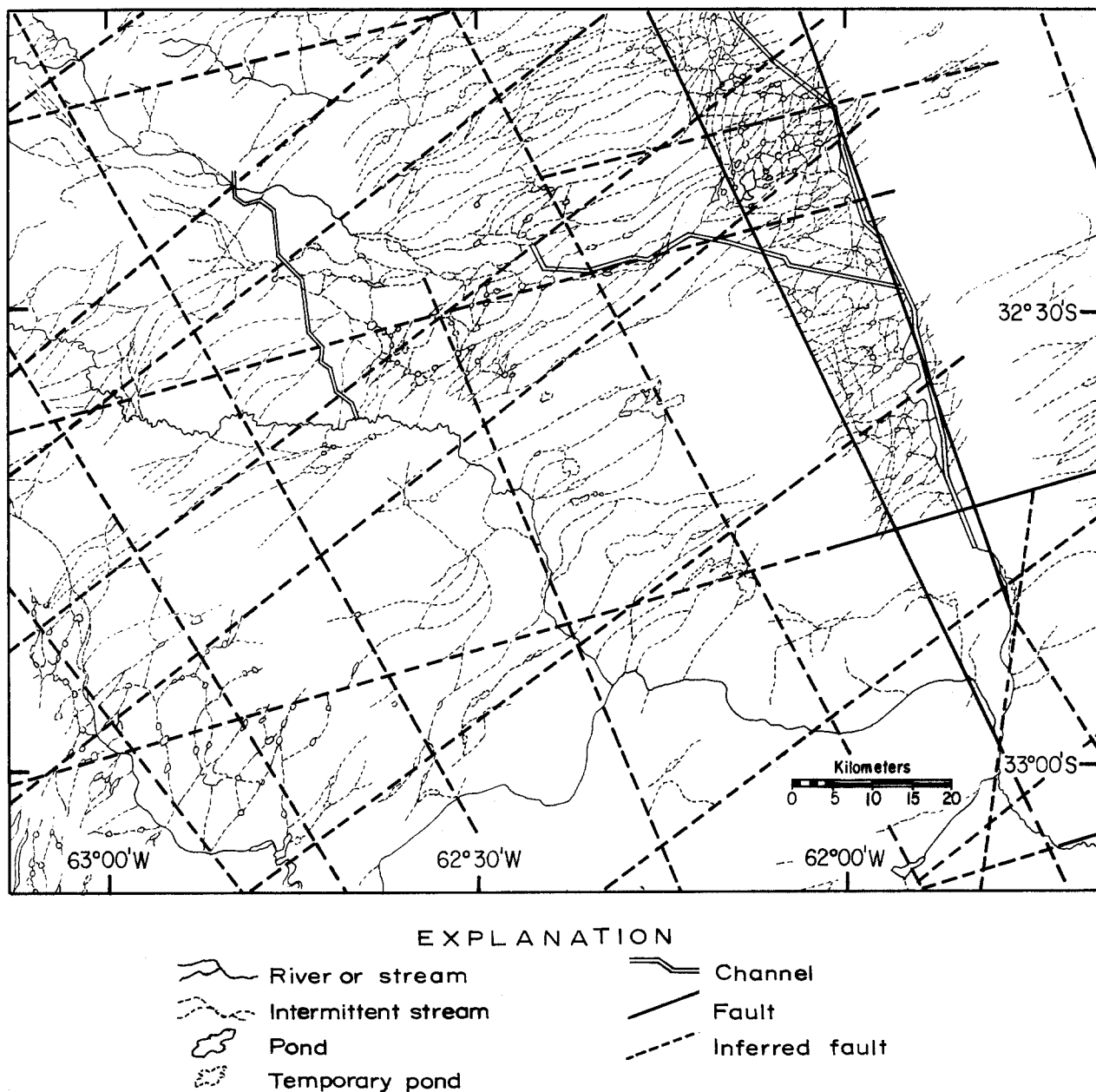
Figure 1. Map of drainage and structural lineaments of the area under study made from Landsat II image 244-083 July 24, 1981, modified by interactive digital analysis and computer processing techniques.

logical Survey procedure (Brown and others 1970; Wood 1976).

This was followed by the determination of trace elements using neutron activation. The results were subjected to statistical analysis for the study of trace element distribution and correlation, and their relationship to the anion and cation facies of groundwater. The corresponding distribution maps were then drawn. At the same time the geology of the area was studied by interpretation of computerized Landsat imagery and the results were compared.

On the other hand, the sedimentologic and geochemical study of the loess in the area was started. Mössbauer spectrometry was applied to the study of volcanic glass and clays, which are important components of loess in Argentina. Trace element contents in loess and in volcanic glass separated from loess were determined by neutron activation.
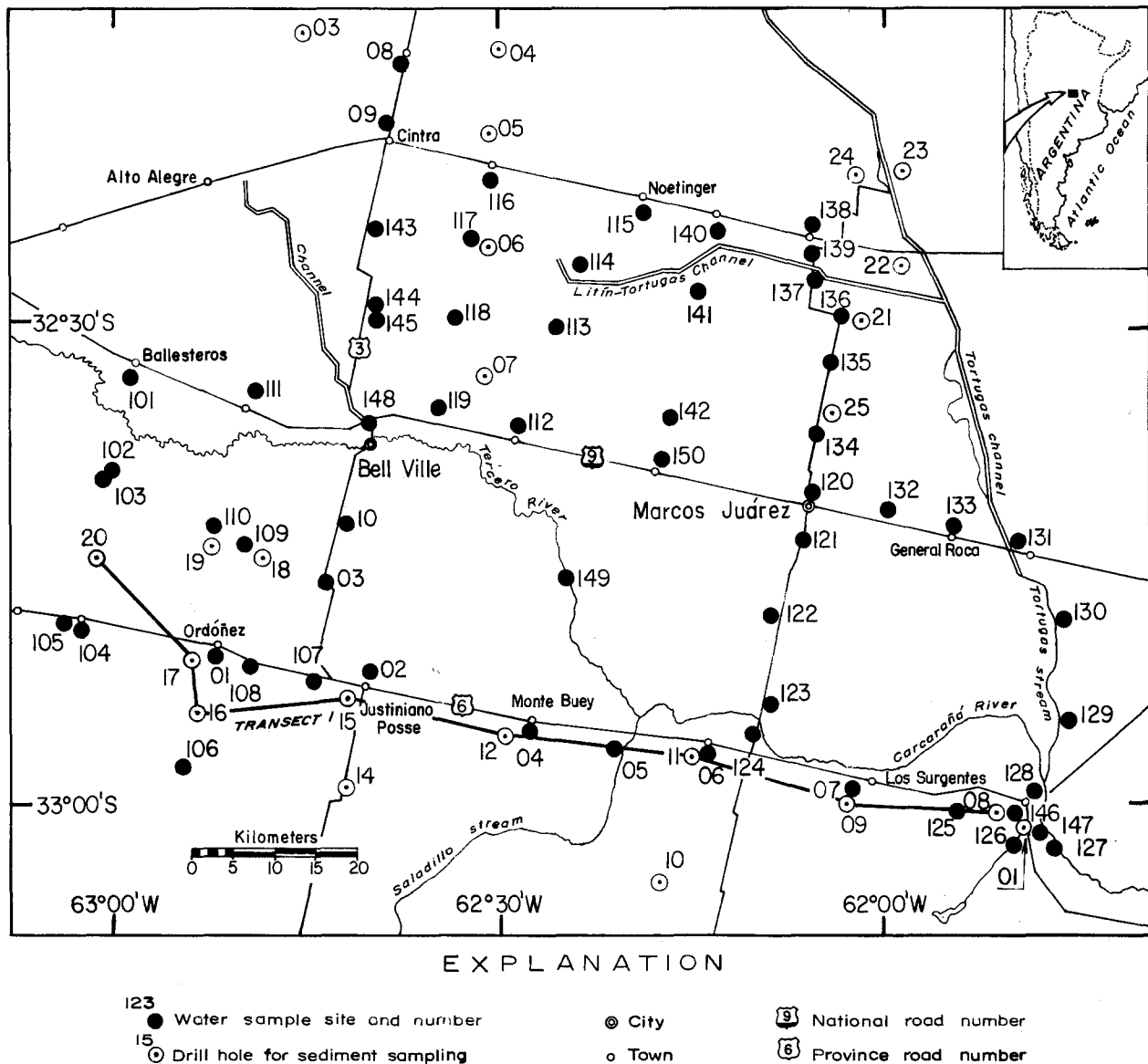
Figure 2. Location of ground water and loess sampling in an area of the pampa, province of Córdoba, Argentina.

The first results of the research, those concerned with ground water chemistry, are discussed at length in a paper published by the National Academy of Sciences in Córdoba, Argentina (Nicolli and others 1985).

General Geology

This study comprises an area of approximately 10,000 km², located between long. 61°45'W and 63°W, and lat. 32°20'S and 33°S. The area, found within the geologic province known as the Chaco Pampeana

plain, is a relatively depressed flat region ("Pampa hundida," Castellanos 1959), comprised between two regional faults. Its altitudes above sea level range from 90 to 150 m and its overall slope (eastwards) is 0.06 percent. On the east and west it is bound by other parts of the same plain that are at a somewhat higher level.

The climate corresponds to a subhumid-to-semiarid zone, with annual average rainfall of 800 mm; two-thirds of the irregular rains concentrate in summer. The annual mean temperature is 16.5°C. Prevailing soils are Brunizem, Chestnut, and Reddish Chestnut (Vázquez 1979) developed on loess-type sediments. In

Table 1. Chemical analyses of groundwater.[a]

Parameters and constituents	Minimum	Maximum	Average	Most frequent values		Samples percentage
				From	To	
Temperature (°C)	15.4	21.5	18.1	17.0	19.0	59
pH (field)	7.0	8.3	7.8	7.5	7.9	52
pH (laboratory)	7.70	8.76	8.13	7.80	8.20	54
Specific conductance (field) (micromhos per cm at 25°C)	659	13,400	4,044	1,000	3,162	50
Specific conductance (laboratory) (micromhos per cm at 25°C)	845	12,989	4,148	1,930	5,180	50
Residue (105°C) (grams per liter)	0.556	10.780	3.530	1.468	6.813	64
Residue (180°C) (grams per liter)	0.524	10.672	3.436	1.468	6.813	60
Lithium (Li^+)	0.02	0.25	0.09	0.05	0.15	68
Sodium (Na^+)	67.0	3,320	1,034	398.0	1,585	54
Potassium (K^+)	7.41	102.5	35.88	19.3	51.8	50
Magnesium (Mg^{2+})	0.11	253.7	39.41	4.64	46.4	62
Calcium (Ca^{2+})	3.94	343.3	50.51	10.0	56.2	56
Bicarbonate (HCO_3^-)	200.0	1,512	624.9	464.0	774.0	52
Sulfate (SO_4^{2-})	71.1	4,250	1,083	178.0	1,780	70
Chloride (Cl^-)	46.8	3,362	675.9	178.0	1,780	62
Hardness (as $CaCO_3$)	17.3	1,902	290.8	46.4	464.0	64
CO_2	1.3	24.0	8.6	4.64	14.7	56

[a]Cations, anions, $CaCO_3$, and CO_2 contents in mg/L.

zones with deficient drainage, saline-alkalic soils are found.

The drainage network seen in the map (Fig. 1) developed over a paleotopography modified mainly by climate changes and tectonic reactivation that took place during the Pleistocene. At present the drainage is deficient because of the low regional W-E slope, since the faults prevailing in the subsurface have an almost N-S orientation and generate structures that are normal to the runoff direction.

The main surface watercourse is the Tercero River which flows between 4–10 m high loess bluffs. Although it has few tributaries there is an important intake of phreatic water. Its freshwater becomes moderately saline when traversing the area under study (total dissolved solids increase from 0.5 to 5.0 g/L). This is also the case of phreatic water in the area.

Since this plain developed over a thick sedimentary cover, it is difficult to study the tectonic features on the surface. However, the interpretation of Landsat imagery obtained by interactive digital processing and the study of the drainage systems made it possible to infer the subsurface structure also represented in the map (Fig. 1).

The observation of these images disclosed the presence of structural lineaments corresponding to a fault system. The dominant set (N-NW strike) determines the existence of elongated blocks which define the regional morphologic aspect. The major relative movements (uplifting, sinking, tilting) have taken place

among those blocks and their effects are evidenced in the drainage network and in the different agronomic properties of the soil. Other fracture sets are found: one with an E-NE strike influencing the southern continuity of the blocks and two others with NE strikes, less developed and conjugated with the former fractures.

The Precambrian or lower Paleozoic crystalline basement has been found at depths of 2,000 and 3,000 m. The basin is filled with Paleozoic, Mesozoic (only Cretaceous), and Cenozoic (Tertiary and Quarternary) sediments.

The Quaternary age is mainly represented by loess-like sediments mostly made up of abundant pyroclastic material. These sediments have been classified as loess (Frenguelli 1925; Teruggi 1957) although their composition is not the same as that of loess from Europe, Asia, and North America. The contaminated aquifer under study is found in them.

Water Sampling and Analytical Methods

Sixty groundwater samples were collected from the wells shown in Figure 2. In 70 percent of the wells, the phreatic water was found between 3 and 8 m, with extreme depths of 2 and 15 m. The sampling was performed according to the U.S. Geological Survey standards (Brown and others 1970; Wood 1976) modified by Nicolli and Gamba (1979) and Nicolli (1982), and the analyses were made according to U.S. Geological survey procedures (Skougstad and others 1979).
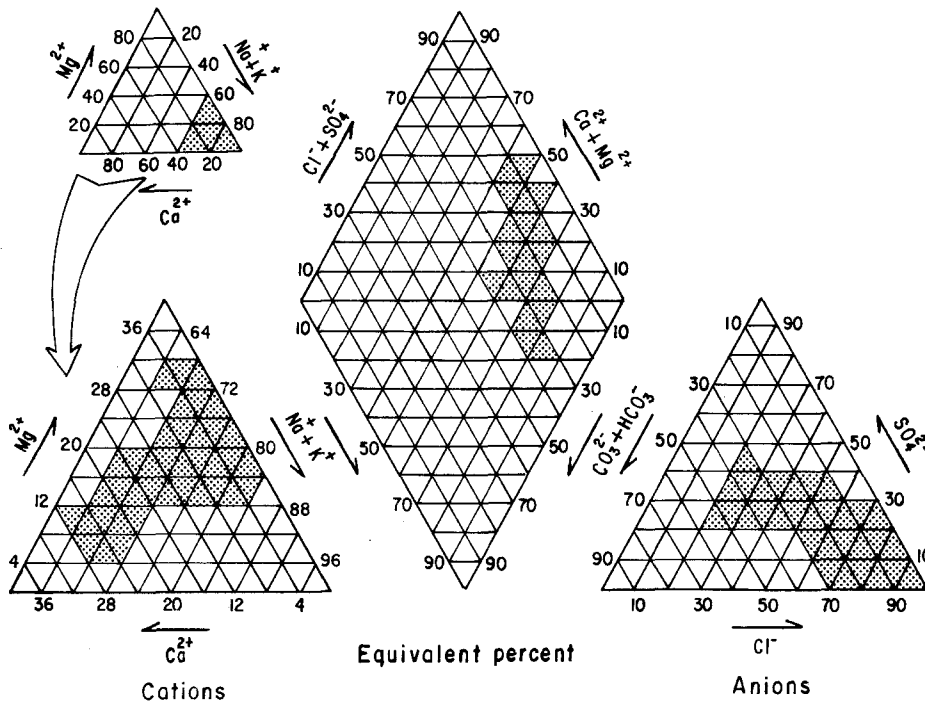
Figure 3. Classification diagram for anion and cation facies in terms of major ion-percentages in groundwaters.

Temperature, pH, specific conductance, dissolved oxygen, and turbidity were determined instrumentally in situ. The pH and specific conductance measurements were carried out again at the laboratory and the dry residue was determined at 105°C and 180°C. The following components were determined: Li^+, Na^+, and K^+ by emission flame photometry; Mg^{2+} and Ca^{2+} by EDTA complexometry; HCO_3^- and CO_3^{2-} by potentiometric titration; SO_4^{2-} by turbidimetry without the use of additives and Cl^- by measuring its activity with an ion-selective electrode; CO_2 contents were found by calculation.

As, Se, Mo, Sb, and U were determined by neutron activation applying a special procedure developed for this specific purpose (Bertini and Cohen 1984). V was determined by spectrophotometry and F by measurements of ionic activity with an ion-selective electrode.

Geochemistry of Water

The results of the groundwater analyses are summarized in Table 1. Minimum, maximum, and average cation-anion values and physical-chemical parameters are presented. The three right-hand columns show the range of the most frequent values (for a lognormal distribution) and the total population percentage.

All waters are alkaline, 44 percent being moderately saline and 38 percent slightly saline. Fifty-two percent of the samples are very hard waters.

Statistical Analysis

A good fit of the frequency distribution of anions, cations, and physical-chemical parameters to the lognormal distribution was found applying the Chi-square test. The distribution functions of the seven trace elements analyzed also show a good fit to the lognormal distribution.

Furthermore, through the Kolmogorov–Smirnov test it was found that: (1) the frequency distributions of pH (field) and specific conductance (laboratory) show the best fit to Erlang distribution; (2) the frequency distributions of dry residue (105° and 180°C), Li^+, Na^+, and HCO_3^- show the best fit to gamma distribution; (3) the frequency distribution of Cl^- shows the best fit to beta distribution, and (4) the distribution functions of the remaining constituents and parameters, and the trace elements, show the best fit to the lognormal distribution (Nicolli and others 1985).

Ion Composition of Ground Water and Distribution of Trace Elements

Figure 3 is a classification diagram for anion and cation facies in terms of major-ion percentages. When considering the cation composition, it is seen that alkali-metal type waters prevail and, considering the anion composition, mostly no-dominant type, some bicarbonate or sulfate-type and a few cloride-type waters are found.

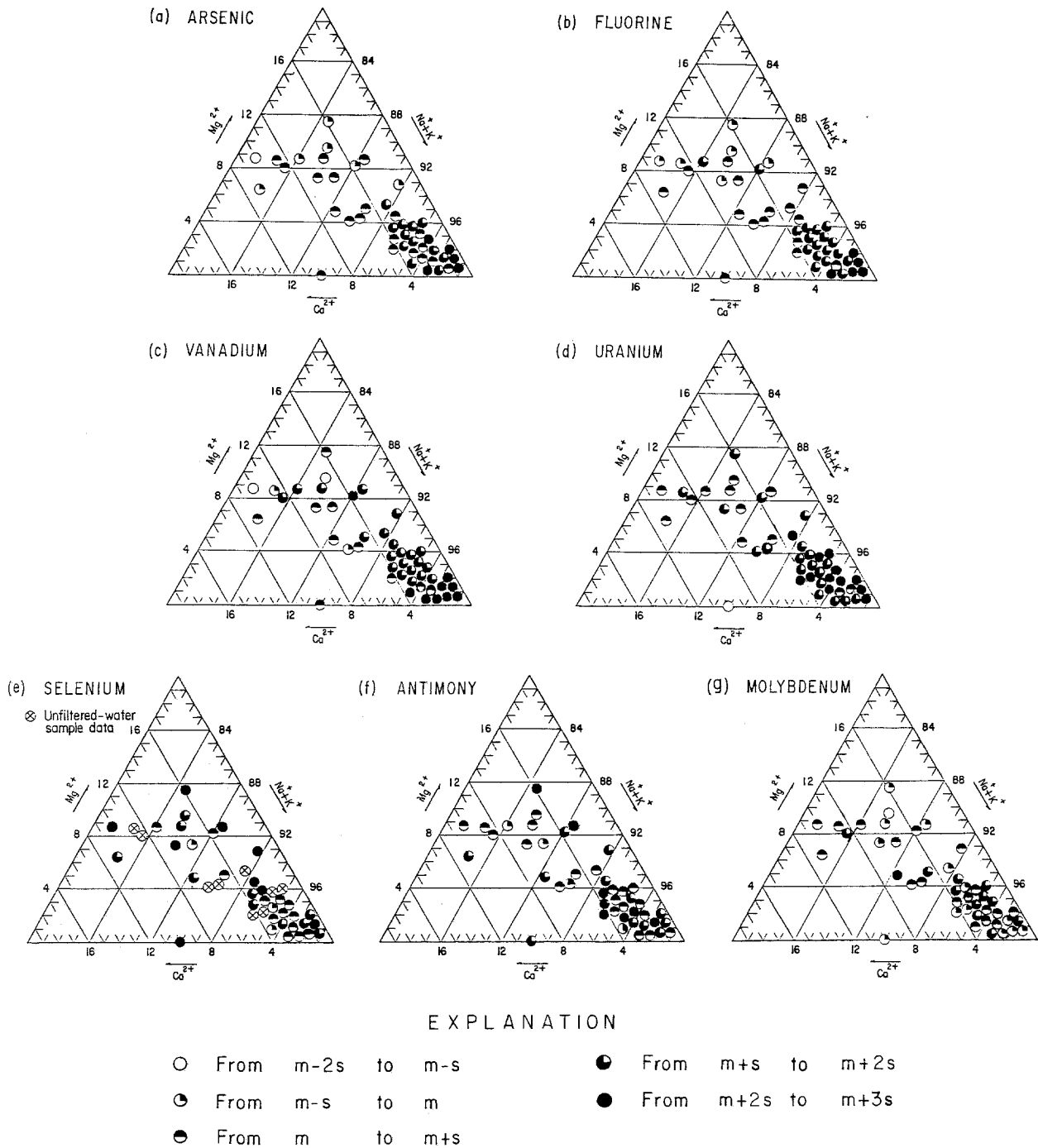Figure 4 is a cation classification diagram where the

Figure 4. Relationship between cation composition and trace-element contents in groundwater samples. The symbols representing the variation in trace element content have been drawn assuming a lognormal distribution with intervals shown in Table 2.

circle shadings represent the distribution of the seven trace elements studied. Trace element contents have been plotted on each triangle, grouping them in six intervals comprised between $m - 3s$ and $m + 3s$; these intervals are defined as functions of the median

and standard deviation, assuming a lognormal distribution of trace elements. The corresponding values are shown in Table 2.

The higher contents of arsenic, fluorine, vanadium, and uranium correspond, in general, to alkali-

Table 2.   Lognormal distribution of trace elements in groundwaters. Limits of intervals determined from median and standard deviation.[a]

Intervals	As	F	V	U	Se	Sb	Mo
m − 3 s	6.0	110	7.90	1.45	0.09	0.09	2.20
m − 2 s	21.0	225	24.5	3.62	0.25	0.27	9.80
m − s	73.0	580	71.0	9.20	0.72	0.79	43.5
m	255	1,325	212	23.0	2.05	2.27	195
m + s	920	3,100	640	58.0	5.90	6.50	905
m + 2 s	3,320	7,200	1,880	147.0	17	19.0	4,150
m + 3 s	11,500	16,500	5,550	365.0	49	54.0	18,000

[a]Contents in μg/L.

metal type waters. Selenium and antimony, in contrast to the former group, do not show a clear relationship between their content variation and the major cations.

In their relationship to anions, the trace elements of the first group (As, F, V, and U) tend to increase their content in no-dominant to chloride-type waters. Selenium and antimony show an inverse relationship in regard to the first group. Molybdenum does not present any relationship to the other two groups.

Figure 5 is a set of maps showing the distribution of trace elements in groundwater from the area under study. These maps were also drawn using the data corresponding to the intervals listed in Table 2.

In the geographic distribution of trace elements there also appear the two aforementioned groups. Arsenic, fluorine, vanadium, and uranium (Fig. 5a–d) show maximum contents in the western part of the area, close to the town of Ordóñez. The second group, composed of selenium and antimony (Fig. 5e and f), on the other hand, show maximum contents in the eastern part of the area. Both groups have an inverse relationship between each other. No relationship between the distribution of molybdenum (Fig. 5g) and that of the other two groups has been found.

Sedimentology

Fifty-four samples were collected from nine wells drilled on transect 1 which traverses the study area (Fig. 2). The maximum depth reached was 5.3 m, one sample being collected every 0.5 m below the C soil horizon and above the water table.

A textural analysis was performed separating the fractions by sieving and pipetting, at one-phi grade intervals, and the statistical parameters (Folk and Ward 1957) were computed (Table 3). This analysis showed that the dominant sediment is a clayey silt (average composition 60.5 percent silt, 27.0 percent clay, 12.5 percent sand) with average mean size of grains M_ϕ = 7.0 (0.0078 mm), very poorly sorted (σ_1 = 2.91), very

positive-skewed (average S_{K_1} = 0.47) and platykurtic (average K_G = 0.85).

Polarizing microscopy was used for the mineralogical study of sand and coarse-silt fractions, and X-ray diffraction for those of fine silt and clay. Among light minerals greaters than 10-μm size, the main components are feldspars and volcanic glass. Feldspar contents commonly vary from 45 to 70 percent (average: 60 percent) and volcanic glass contents vary from 25 to 50 percent (average: 35 percent). Decreasing amounts of quartz, muscovite, calcite, and lithic fragments were found. Opal and chalcedony, in lesser proportions, present an irregular distribution.

In the fraction corresponding to the 0.5–0.05 mm interval, an estimate of heavy-mineral contents was made by a count of 1,000 grains per sample. The results ranged from 4.8 to 12.1 volume percent with an average of 8.4. The most abundant heavy minerals are pyroxenes and amphiboles (hypersthenes, enstatite, hornblende, and lamprobolite). Biotites and epidotes are less abundant, and garnet, tourmaline, apatite, zircon, chlorite, and rutile are scarce.

The X-ray diffraction analysis disclosed the presence of low-crystallinity minerals, illite prevailing over smectites. Dominant interstratified illite-montmorillonite has been determined, as well as scarce pure montmorillonite, kaolinite, and interstratified chlorite-montmorillonite.

In the 0.5–0.05 mm fraction, volcanic glass was concentrated using an isodynamic separator and bromoform-acetone mixtures. A final washing was performed using a sodium-hexametaphosphate solution as a dispersant agent in an ultrasonic vibrator; an entirely clean glass was thus obtained (greater than 99 percent degree of purity). This material was studied using polarizing microscopy and Mössbauer spectrometry. Classical procedures were used for the determination of major constituents in selected volcanic glass samples (Table 4) and neutron activation was applied for the determination of trace elements (Table 5).
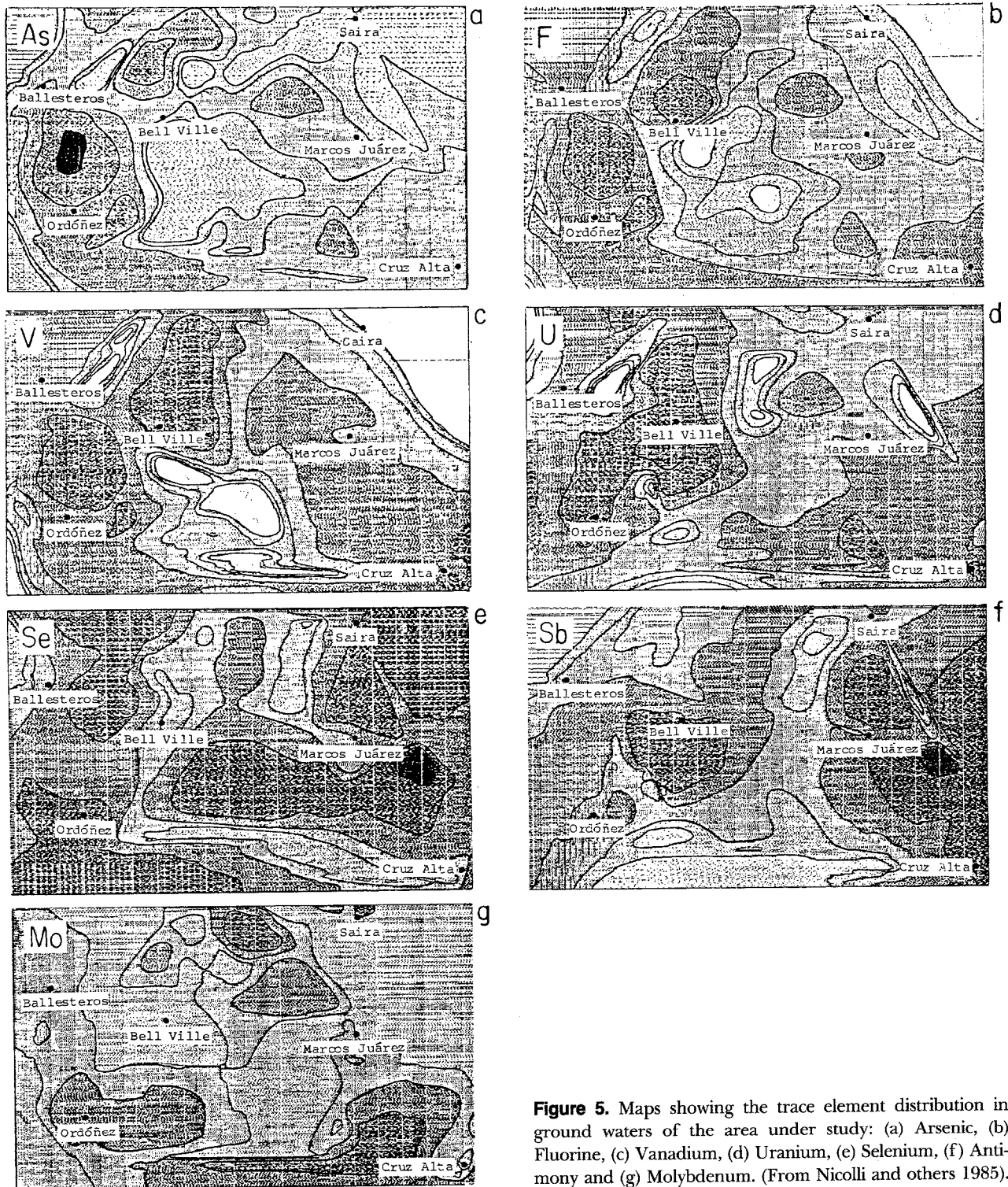
Figure 5. Maps showing the trace element distribution in ground waters of the area under study: (a) Arsenic, (b) Fluorine, (c) Vanadium, (d) Uranium, (e) Selenium, (f) Antimony and (g) Molybdenum. (From Nicolli and others 1985).

Table 3. Textural parameters of selected samples of loess.

Well no.	Sample no.	Depth (m)	Sand (%)	Silt (%)	Clay (%)	Md	M_ϕ	σ_1	S_{k_1}	K_G	Heavy minerals in volume percent
20	07	3.50	19.7	64.4	15.9	5.2	6.0	2.43	0.54	1.28	10.1
16	05	3.35	19.7	63.4	16.9	5.0	6.1	2.72	0.63	1.19	9.8
17	04	1.65	18.1	57.7	24.2	5.1	6.5	2.99	0.65	0.78	12.1
18	08	3.60	11.1	65.9	23.0	5.8	6.8	2.83	0.50	0.88	8.0
15	08	3.85	10.9	67.8	21.3	6.2	6.8	2.68	0.35	0.73	9.8
12	04	2.35	15.0	62.2	22.8	5.6	6.7	2.85	0.53	0.95	6.1
11	09	4.10	5.3	60.0	34.7	7.0	7.7	2.94	0.33	0.73	6.5
09	07	3.30	3.8	61.1	35.1	7.3	7.9	2.95	0.26	0.69	4.8
08	08	3.85	4.0	61.9	34.1	6.8	7.7	2.92	0.38	0.69	5.7
Average (54 samples)			12.5	60.5	27.0	6.0	7.0	2.91	0.47	0.85	8.4

[a]Md = median, M_ϕ = mean size (graphic), σ_1 = standard deviation, S_{k_1} = skewness, and K_G = kurtosis.

Table 4. Chemical composition of glass separated from selected samples of loess.[a]

	V-20-07	V-16-05	V-17-04	V-18-04	V-18-08	V-15-08	V-12-04	V-11-09	V-09-07	V-08-08	Average
SiO_2	72.6	72.3	73.4	73.8	73.1	71.6	73.3	72.3	71.8	71.9	72.6
Al_2O_3	13.1	13.5	13.3	12.7	13.0	14.0	13.3	13.4	14.5	14.2	13.5
Fe_2O_3	0.78	1.00	0.67	0.76	0.97	0.85	0.65	0.97	0.88	0.76	0.83
FeO	0.72	0.61	0.65	0.57	0.69	0.68	0.54	0.55	0.59	0.58	0.62
MnO	0.05	0.06	0.06	0.06	0.06	0.06	0.07	0.07	0.07	0.05	0.06
MgO	0.58	0.52	0.63	1.00	0.81	0.82	0.37	0.86	1.01	0.56	0.72
CaO	1.51	1.24	1.01	1.00	1.02	0.98	1.10	1.06	1.27	1.64	1.18
Na_2O	4.08	3.98	4.18	3.96	4.06	4.40	3.92	3.85	3.85	3.78	4.01
K_2O	4.13	4.36	4.47	4.42	4.14	4.13	4.56	4.11	4.28	3.68	4.23
TiO_2	0.55	0.54	0.53	0.47	0.48	0.54	0.54	0.38	0.34	0.76	0.51
P_2O_5	0.05	0.05	0.04	0.14	0.06	0.05	0.11	0.05	0.05	0.03	0.06
L.O.I.[b]	2.04	2.02	1.21	1.31	1.86	2.06	1.65	2.51	1.70	2.24	1.86

[a]Contents in weight percent.

[b]L.O.I. = Lost on ignition at 925°C for 45 min.

Table 5. Trace element contents determined by neutron activation in glass separated from selected samples of loess.[a]

Trace element	Minimum	Maximum	Geometric mean
As	6.83	10.4	8.71
Se	1.11	2.56	1.79
U	2.78	5.69	4.20
Sb	0.204	0.559	0.314
Mo	<3	4.45	3.65

[a]Contents in ppm.

Mössbauer spectrometry was also used in the analysis of the clay minerals separated from volcanic glass by means of sodium-hexametaphosphate washing. Table 6 shows the Mössbauer parameters at room temperature corresponding to one sample of clean glass (sample V-17-04) and one of clay mineral separated by washing (sample A-17-04). The Mössbauer parameters of sample A-17-04

showed the presence of montmorillonite (Heller-Kallai and Rozenson 1981). The spectrum was resolved into two Fe^{3+} doublets and a weak sextuplete due to the presence of iron oxides. The line widths (Γ) are slightly broadened probably because of a low degree of amorphousness.

The Mössbauer parameters of sample V-17-04 indicated the dominant presence of Fe^{2+} ions, which represent 92 percent of the total iron content in the sample; the remaining 8 percent corresponds to the Fe^{3+} ions (Kurkjian and Sigety 1968; Mysen and others 1984). The low Fe^{3+} content and the high width values do not allow the separation of $Fe^{3+}{}_{oct.}$ from $Fe^{3+}{}_{tetra.}$ contributions. The corresponding line width values are characteristic of the amorphous state.

Geochemistry of Loess

Chemical analyses were performed on selected samples of loess from the collection referred to in the

Table 6. Mössbauer parameters at room temperature.

Sample	Fe^{2+}			Fe^{3+}		
	I.S.[a]	Q.S.	Γ	I.S.	Q.S.	Γ
A-17-04				0.25 (1)	0.78 (7)	0.42 (3)
				0.23 (1)	0.38 (5)	0.39 (7)
V-17-04	1.04 (2)	2.11 (3)	0.60 (1)	0.21 (7)	1.1 (1)	0.60 (2)

[a]I.S. = isomer shift relative to Rh; Q.S. = quadrupole splitting; Γ = peak width.

Table 7. Chemical composition of selected samples of loess.[a]

Constituent	Minimum	Maximum	Average
SiO$_2$	59.4	64.1	61.3
Al$_2$O$_3$	14.6	16.2	15.4
Fe$_2$O$_3$	3.48	4.55	3.94
FeO	0.51	0.93	0.80
MnO	0.01	0.11	0.07
MgO	1.55	2.33	1.87
CaO	3.43	5.51	4.45
Na$_2$O	2.91	5.71	4.62
K$_2$O	2.23	2.43	2.33
TiO$_2$	0.64	0.77	0.70
P$_2$O$_5$	0.15	0.18	0.17
Lost on ignition (925°C)	3.28	5.63	4.45

[a]Contents in weight percent.

sedimentology section (Ferpozzi 1985). The minimum, maximum, and average contents of major constituents, shown in Table 7, presented remarkable differences in regard to the loess from Missouri (Ebens and Connor 1980), Iowa and Kansas (Taylor and others 1983), Achenheim, France (Buraczyńsky 1980), Kaiserstuhl, Germany, New Zealand, and Nangking, China (Taylor and others 1983).

The fact that the components of volcanic origin are abundant in this sediment decided the comparison of the results obtained with the chemical composition of volcanic rocks. The diagrams of Church (1975) (Fig. 6a) and of Cox and others (1979), cited by Fisher and Schmincke (1984) (Fig. 6b), were found useful for this purpose. The average composition of these sediments corresponds to that of a dacite, a rock of common occurrence in the southern Andes.

Table 8 shows the minimum and maximum contents and the geometric mean of five trace elements determined by neutron activation: arsenic, selenium, uranium, antimony, and molybdenum.

Arsenic contents vary between 5.51 and 37.3 ppm (geometric mean: 16.7 ppm). These contents are 9 times higher than the values given by Taylor (1964) for the upper crust. Other references are the loess analyses from Missouri (Ebens and Connor 1980)

which gave a geometric mean of 8 ppm (with a 95 percent expected range between 5 and 15 ppm).

Selenium determination gave contents between 1.10 and 2.30 ppm (geometric mean: 1.53 ppm). Taylor (1964) established a value of 0.05 ppm for the upper crust, and Ebens and Connor (1980) determined a geometric mean of 0.18 ppm in the loess from Missouri (with a 95 percent expected range between 0.005 and 0.7 ppm).

Uranium contents in the sediment under study show a minimum of 1.25 ppm and a maximum of 8.0 ppm (geometric mean: 2.99 ppm). The uranium content given by Taylor (1964) for the upper crust is 2.7 ppm, and Taylor and others (1983) give values from 1.82 to 3.04 ppm for the mentioned loess from the USA, Germany, China, and New Zealand.

Antimony contents vary between 0.251 and 0.88 ppm (geometric mean: 0.545 ppm). The upper crust content is 0.2 ppm (Taylor 1964).

The molybdenum contents found range from 2.2 to 5.2 ppm. The upper crust Mo content is 1.5 ppm (Taylor 1964). For Missouri loess (Ebens and Connor 1980) all data are below the limit of analytical determination (3 ppm).

In the loess of this area all analyzed trace element contents are remarkably anomalous. They thus constitute a potential source of contamination of groundwaters, particularly arsenic and selenium.

In addition, since volcanic glass is an important metastable component of this type of loess, it was specially studied using Mössbauer spectrometry after it was separated from the sediment. Its chemical composition was determined in 10 samples applying classical chemical procedures (Table 4) and five of its trace elements were analyzed by neutron activation (Table 5).

The composition of the volcanic glass is typically rhyolitic (Fig. 6a and b). SiO$_2$ content varies between 71.6 and 73.8 percent (average: 72.6 percent); Na$_2$O content, between 3.78 and 4.40 percent (average: 4.01 percent) and K$_2$O content, between 3.68 and 4.56 percent (average: 4.23 percent).

Arsenic content in volcanic glass varies between 6.83 and 10.4 ppm (geometric mean: 8.71 ppm); selenium content, between 1.11 and 2.56 ppm (geo-
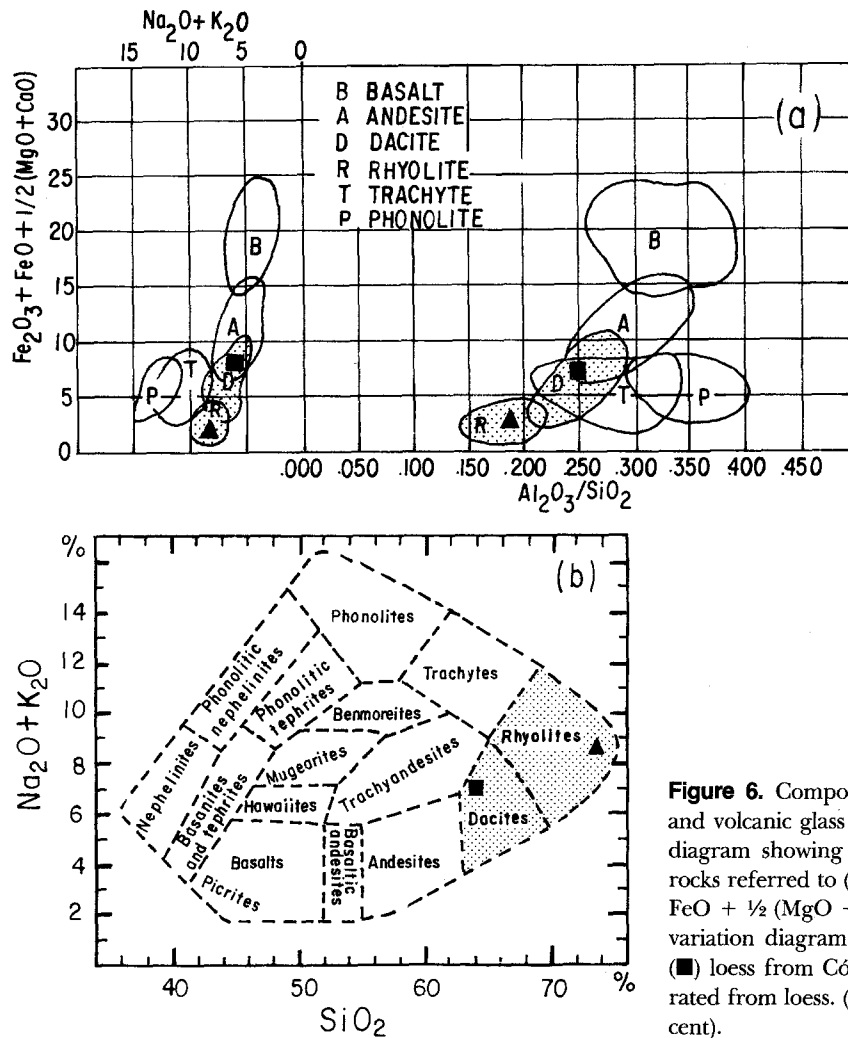
Figure 6. Composition of loess from Córdoba, Argentina, and volcanic glass separated from it, plotted on (a) a triaxial diagram showing variation field of most common volcanic rocks referred to (Al_2O_3/SiO_2), $(Na_2O + K_2O)$ and $[Fe_2O_3 + FeO + \frac{1}{2}(MgO + CaO)]$ parameters, and (b) an alkali-silica variation diagram showing major groups of volcanic rocks: (■) loess from Córdoba, Argentina; (▲) volcanic glass separated from loess. (Concentration of the oxides in weight percent).

Table 8. Trace element contents determined by neutron activation in selected samples of loess.[a]

Trace element	Minimum	Maximum	Geometric mean
As	5.51	37.3	16.7
Se	1.10	2.30	1.53
U	1.25	8.0	2.99
Sb	0.251	0.88	0.545
Mo	2.2	5.2	3.4

[a]Contents in ppm.

metric mean: 1.79 ppm); uranium content, between 2.78 and 5.69 ppm (geometric mean: 4.20 ppm); antimony content, between 0.204 and 0.559 ppm (geometric mean: 0.314 ppm) and molybdenum content, between <3 and 4.45 ppm (geometric mean: 3.65 ppm). As a reference, it may be mentioned that Onishi and Sandell (1955) report an average arsenic content of 5.9 ± 0.9 ppm in glasses from silicic volcanic rocks. Sarna-Wojcicki and others (1979; 1984) report ura-

nium contents between 2.34 and 13.78 ppm in glass from various Pliocene and Pleistocene volcanic formations in the USA.

Discussion

It is evident that water contamination phenomena in the research area respond to natural causes. This evidence results from verifying the geographic distribution of the trace elements analyzed, their correlations, and the relationships between the variations of trace element contents and the water anion-cation facies. Furthermore, both trace element groupings (As, F, V, and U on one hand, and Se and Sb, on the other) are characteristic of natural distribution laws.

Water contamination with arsenic in the area under study has been known since the beginning of this century. The continued ingestion of this type of water causes several pathological conditions generally known as HACRE.

Table 9. Trace element analyses of groundwater.[a]

Trace element	Minimum content	Maximum content	Geometric mean	Most frequent values		
				From	To	Sample percentage
As	18.7	3,810	164	100.0	316.2	46
F	256	6,290	1,187	681.3	3,162	62
V	9.0	1,715	281	100.0	316.2	49
U	1.9	166	29.5	15.85	100.0	70
Se	0.356	24.2	2.93	1.58	3.98	47
Sb	0.31	29.2	2.38	1.00	3.162	46
Mo	5.9	6,280	77.7	46.42	464.2	54

[a]Trace element contents in μg/L.

The most common manifestation of this disease is cancer of epithelia. High selenium content in drinking water is also attributed carcinogenic effects. However, the combined effects of both trace elements have not been definitely established yet; some authorities even suggest that the combination of both should mitigate their individual effects (IARC Working Group on the Evaluation of the Carcinogenic Risk of Chemicals to Man 1975). For the above reasons, the discovery of selenium contamination combined with arsenic contamination in the groundwater of the area under study is of the greatest importance (Nicolli and others 1985).

In Table 9 it may be seen that arsenic contents in the water samples studied are found in the range 18.7–3,810 μg/L (average: 418 μg/L). Eighty-two percent of the samples analyzed exceed the maximum contaminant level of 50 μg/L, established by the U.S. Environmental Protection Agency (1982).

It should be taken into account that selenium contents presented in Table 9 correspond to filtrated water samples, and that selenium is strongly concentrated in the suspended sediment. Several analyses in samples settled (not filtered) according to the standards of the U.S. Public Health Service (1962) showed selenium contents between 119 and 498 μg/L, namely, between 20 and 50 times the maximum contaminant level, 10 μg/L, accepted by the U.S. EPA (1982).

As regards fluorine, in 42 percent of the samples it exceeds EPA's maximum contaminant level (1,400 μg/L), the maximum determined value being 6,290 μg/L. The pathological effects of high fluorine content in drinking water are better known than those of other trace elements (V, Mo, and U). Furthermore, the combined effects of the high contents of all these trace elements in the groundwaters of the area have not been studied up to the present, since the pathological manifestations of HACRE have been entirely attributed to high arsenic contents.

In this area, the waters have been subjected to geochemical analysis and the distribution of trace elements has been determined; therefore, the magnitude and distribution of the contamination are now known. At present, the study area has been extended to 30,000 km² and research is oriented to a more accurate determination of the sources of the contaminants and the processes giving place to their concentration in water. For that reason, further sedimentologic and geochemical studies of loess are being performed.

As a result of the mineralogic study of that type of loess, it has been possible to demonstrate the presence of several components with a certain chemical reactivity in that environment (pH of ground waters: 7.0–8.3; pH of sediments: 8.5–9.5), such as volcanic glass, feldspars (with kaolinization and sericitization processes), illite, smectites, calcium carbonate concretions, etc. From those components, volcanic glass has been selected and separated for a more detailed study, given its high proportion in the sediment.

Neutron activation analyses of selected loess samples and volcanic glass have demonstrated anomalous contents of the contaminant trace elements. On the other hand the pH measurements in groundwaters and in sediments reveal favorable conditions for the dissolution of volcanic glass (Longhnan 1969). Mössbauer spectrometry shows that the clay mineral closely associated with volcanic glass is montmorillonite. In addition, it was possible to recognize an iron oxide phase with a low degree of amorphousness. The volcanic glass analyzed shows 82 percent of the iron content in the form of Fe^{2+} and line-width values that are characteristic of the amorphous state. The volcanic glass can thus be considered the most important source of trace elements contaminating the groundwaters in the area.

Conclusions

From the results of the present research on the contamination of ground water with trace elements in the

pampa, province of Córdoba, Argentina, a number of conclusions can be drawn:

1. A strong natural contamination of groundwater with arsenic and selenium has been proved in the area under study. The arsenic content of 46 percent of the samples analyzed ranged between 100 and 316.2 µg/L with a maximum value of 3,810 µg/L. The selenium content of 47 percent of the samples analyzed ranged between 1.58 and 3.98 µg/L, with a maximum content of 24.2 µg/L. The selenium content in unfiltered groundwater samples varies between 119 and 498 µg/L.

2. High trace-element contents in groundwater have also been found: fluorine (62 percent of the samples analyzed, between 618.3 and 3,162 µg/L with a maximum of 6,290 µg/L), vanadium (49 percent of the samples analyzed, between 100 and 316.2 µg/L with a maximum of 1,715 µg/L), molybdenum (54 percent of the samples analyzed, between 46.42 and 464.2 µg/L with a maximum of 6,280 µg/L and uranium (70 percent of the samples analyzed, between 15.85 and 100 µg/L with a maximum of 166 µg/L).

3. Groundwaters are alkaline; 14 percent of the samples are nonsaline; 38 percent, slightly saline; 44 percent, moderately saline; and 4 percent, very saline. The hardness range is as follows: 20 percent of the samples are soft, 14 percent are moderately hard, 12 percent are hard, and 54 percent are very hard. (Water classificiation according to U.S. Geological Survey standards).

4. The highest arsenic, fluorine, vanadium, and uranium contents (As >920 µg/L; F >3,100 µg/L; V >640 µg/L; U >58 µg/L) are found in waters with the highest sodium and potassium contents [(Na$^+$ + K$^+$) equivalents percent >92; (Mg^{2+} + Ca^{2+}) equivalents percent <8].

5. The geographic distribution of trace elements in groundwaters shows two groupings: the first group comprises arsenic, fluorine, vanadium, and uranium, and the other, selenium and antimony.

6. The chemical composition of the loess under study, which has a high proportion of volcanic components, corresponds to that of a dacite.

7. The loess and one of its main components, volcanic glass, show anomalous contents of all contaminant trace elements, particularly arsenic (geometric means: 16.7 ppm from loess and 8.71 ppm from volcanic glass) and selenium (geometric means: 1.53 ppm from loess and 1.79 ppm from volcanic glass). For that reason, they are considered the most important groundwater contamination source in this area.

Acknowledgments

References Cited

Astolfi, E. A. N., A. Maccagno, J. C. García Fernández, R. Vaccaro, and R. Stimola, 1981, Relation between arsenic in drinking water and skin cancer: Biolog. Trace Element Res., v. 3, p. 133–143.

Bertini, L. M., and I. M. Cohen, 1984, Determination of arsenic, antimony and selenium in water by neutron activation and coprecipitation with bismuth sulphide: Fifth Internat. Conf. on Nuclear Methods in Environment and Energy Research, Mayaguez, Puerto Rico; Proceedings CONF-840408 (PE 84017348), p. 340–347.

Brown, E., M. W. Skougstad, and M. J. Fishman, 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geol. Survey, Techniques of Water-Resources Investigations, book 5, chapter A 1, 160 p.

Buraczyński, J., 1979, Caractéristiques lithologiques des loess d'Achenheim (près de Strasbourg, France): Acad. Sci. Hungaricae Acta Geol., v. 22, p. 229–253.

Castellanos, A., 1959, Posibles desplazamientos, en el pasado, de las redes potamográficas en la llanura cordobesa: Boletín de Estudios Geográficos, no. 19, Inst. Geografía, Univ. Nac. de Córdoba, p. 29–63.

Church, B. N., 1975, Quantitative classification and chemical comparison of common volcanic rocks: Geol. Soc. America Bull., v. 86, p. 257–263.

Ebens, R. J., and J. J. Connor, 1980, Geochemistry of loess and carbonate residuum: U.S. Geol. Survey Prof. Paper 954-G, 32 p.

Ferpozzi, L. H., 1985, Geoquímica del arsénico y de otros elementos asociados en sedimentos limo-loessicos del sudeste de la provincia de Córdoba. III—Geoquímica de los sedimentos: Tech. Int. Rep., CONICET, 55 p.

Fisher, R. V., and H. U. Schmincke, 1984, Pyroclastic rocks: New York, Springer-Verlag, 528 p.

Folk, R. L., and W. C. Ward, 1957, Brazos River bar: a study in the significance of grain size parameters: Jour. Sed. Petrology, v. 27, p. 3–26.

Frenguelli, J., 1925, Loess y limos pampeanos: Anales Soc. Arg. Estudios Geográficos Gaea, v. 1, p. 1–88.

Heller-Kallai, L., and I. Rozenson, 1981, The use of Mössbauer spectroscopy of iron in clay mineralogy: Phys. Chem. Minerals, v. 7, p. 223–238.

IARC Working Group on the Evaluation of the Carcinogenic Risk of Chemicals to Man, 1975: IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man, v. 9, p. 245–260.

Kurkjian, C. R., and E. A. Sigety, 1968, Coordination of Fe^{3+} in glass: Phys. Chem. Glasses, v. 9, p. 73–83.

Loughnan, F. C., 1969, Chemical weathering of the silicate minerals: New York, Elsevier, 154 p.

Mysen, B. O., D. Virgo, and F. A. Seifert, 1984, Redox equilibria of iron in alkaline earth silicate melts: relationship between melt structure, oxigen fugacity, temperature and properties of iron-bearing silicate liquids: Am. Mineral., v. 69, p. 834–847.

Nicolli, H. B., 1982, Técnica de muestreo de aguas para el análisis de oligoelementos por activación: Tech. Int. Rep. C.N.I.E., G.E. 82/01, 8 p.

Nicolli, H. B., and M. A. Gamba, 1979, Guía para el muestreo geoquímico de aguas y salmueras: Pub. C.N.I.E., G.E. 79/01, 23 p.

Nicolli, H. B., T. E. O'Connor, J. M. Suriano, M. M. L. Koukharsky, M. A. Gómez Peral, L. M. Bertini, I. M. Cohen, L. I. Corradi, O. A. Baleani, and E. G. Abril, 1985, Geoquímica del arsénico y de otros oligoelementos en aguas subterráneas de la llanura sudoriental de la provincia de Córdoba: Miscelánea no. 71, Acad. Nac. Ciencias, Córdoba, 112 p.

Onishi, H., and E. B. Sandell, 1955, Geochemistry of arsenic: Geochim. Cosmochim. Acta, v. 7, p. 1–33.

Sarna-Wojcicki, A. M., H. R. Bowman, and P. C. Russell, 1979, Chemical correlation of some late Cenozoic tuffs of northern and central California by neutron-activation analysis of glass and comparison with X-ray fluorescence analysis: U.S. Geol. Survey Prof. Paper 1147, 15 p.

Sarna-Wojcicki, A. M., H. R. Bowman, C. E. Meyer, P. C. Russell, M. J. Woodward, G. McCoy, J. J. Rowe, Jr., P. A. Baedecker, F. Asaro, and H. Michael, 1984, Chemical analysis, correlations, and ages of upper Pliocene and Pleistocene ash layers of east-central and southern California: U.S. Geol. Survey Prof. Paper 1293, 40 p.

Taylor, S. R., 1964, Abundances of chemical elements in the continental crust: a new table: Geochim. Cosmochim. Acta, v. 28, p. 1273–1285.

Taylor, S. R., S. M. McLennan, and M. T. McCulloch, 1983, Geochemistry of loess, continental crustal composition and crustal model ages: Geochim. Cosmochim. Acta, v. 47, p. 1897–1905.

Teruggi, M. E., 1957, The nature and origin of Argentine loess: Jour. Sed. Petrology, v. 27, p. 322–332.

U.S. Environmental Protection Agency, 1982, Maximum contaminant levels (subpart B of part 141, National interim primary drinking-water regulations): U.S. Code of Federal Regulations, Title 40, Part 100 to 149, revised as of July 1, 1982, p. 315–318.

U.S. Geological Survey, 1979, Methods for determination of inorganic substances in water and fluvial sediments. In M. W. Skougstad, M. J. Fishman, L. C. Friedman, D. E. Erdmann, and S. S. Duncan, Eds, Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chapter A 1, 626 p.

U.S. Public Health Service, 1962, Drinking water standards, 1962: U.S. Public Health Service Pub. 956, 61 p.

Vázquez, J. B., 1979, Suelos. In: J. B. Vázquez, R. A. Miatello, and M. E. Roqué (Directors), Geografía de la Provincia de Córdoba, Córdoba, Fundación Banco Prov. de Córdoba, p. 435–458.

Wood, W. W., 1976, Guidelines for collection and field analysis of groundwater samples for selected unstable constituents: U.S. Geol. Survey Techniques of Water-Resources Investigations, book 1, chapter D 2, 24 p.