Revista SUG Nº18, 20 – 38 (publicado 11/2013)
Sociedad Uruguaya de Geología

GROUNDWATER ARSENIC CONTENT IN RAIGÓN AQUIFER SYSTEM (SAN JOSE, URUGUAY)

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ABSTRACT

As a Medical Geology research issue, an environmental arsenic risk assessment study in the most important sedimentary aquifer in southern Uruguay is presented. The Raigón Aquifer System is the most exploited in Uruguay. It has a surface extent of about 1,800 square kilometres and 10,000 inhabitants in San Jose Department, where it was studied. Agriculture and cattle breeding are the main economic activities and this aquifer is the basic support. The groundwater sampling was done on 37 water samples of PRENADER (Natural Resources Management and Irrigation Development Program) wells. Outcropping sediments of Raigón Formation and the overlying Libertad Formation were also sampled in the Kiyú region. The analyses were performed by inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS). The results showed 80% samples with arsenic levels exceeding the 10 µg/l of WHO as limit for waters, and 11% exceeds the 20 µg/l limit of uruguayan regulation. The median, maximum and minimum water arsenic concentrations determined have been 14.24, 24.19 and 1.44 µg/l, respectively. On the other hand, nine sediment samples of Raigón and Libertad Formations in Kiyú region were analysed and yielded median, maximum and minimum arsenic concentrations of 5.03, 9.82 and 1.18 ppm, respectively. This issue leads to the supposition that the population, as well as industrial and agricultural activities, are consuming water with arsenic concentrations over the national and international maximum recommended limit.

Key words: arsenic, groundwater, Raigón Aquifer System, San José, Uruguay

RESUMEN

Como una aproximación a la Geología Médica en Uruguay se presentan los resultados de un estudio sobre el estado del Sistema Acuífero Raigón en relación a la presencia de arsénico, en el entendido que es el acuífero más explotado en el país. En particular, el área cubierta por este trabajo es de unos 1800 km^2 en un territorio con una población de unos 10,000 habitantes en el departamento de San José. La colecta de aguas del acuífero se realizó en perforaciones de la base de datos de PRENADER (Proyecto de Manejo de Recursos Naturales y Desarrollo del Riego) obteniéndose 37 muestras, y sobre 9 muestras de sedimentos tanto de la Formación Raigón como la suprayacente Libertad en afloramientos de la región de Kiyú. Los análisis fueron realizados mediante ICP-MS. Un 80% de las muestras de aguas analizadas mostraron contenidos mayores a los límites de la OMS (10 µg/l) y un 11% de las muestras superaron el límite de la OSE (20 µg/l). El valor medio, máximo y mínimo determinado en el caso del agua subterránea fue de 14.24, 24.19 and 1.44 µg/l, respectivamente. Por otro lado, las nueve muestras de sedimentos analizados mostraron concentraciones media, máxima y mínima de arsénico de 5.03, 9.82 and 1.18 ppm, respectivamente, descartándose en principio un origen geogénico.

Palabras clave: arsénico, aguas subterráneas, Sistema Acuífero Raigón, San José, Uruguay

INTRODUCTION

Humans are exposed to toxic arsenic primarily from air, food, and water. Thousands and thousands of people are suffering from the toxic effects of arsenicals in many countries all over the world due to natural groundwater contamination, as well as industrial effluent and drainage problems. As the overviews given by Smedley (2006, 2009), Ravenscroft et al. (2009), Bundschuh et al (2009a, 2009b), Bundschuh and Litter (2010), and Jean et al. (2010) show in half of about 70 countries the problem was recently detected. In almost these countries the problem of water resources contamination by arsenic has a geogenic origin. In Latin America in 14 out of 20 countries As constitutes a potential health risk (Smedley 2009). The number of people potentially exposed to As in drinking water exceeding the provisional WHO (2001, 2004) limit for As (10 µg/l) is estimated around 14 million, 4 of them in Argentina (Bundschuh and Litter 2010). In Latin America, this new As provisional guideline value became law (in chronological order) in Honduras (1995), Costa Rica (1997), El Salvador (1997), Colombia (1998), Guatemala (1998), Nicaragua (1999), Panama (1999), Bolivia (2004), Brazil (2005), Argentina (2007), and Chile (2008). Only few countries have higher limits: Uruguay, Peru, and Venezuela still maintain the 50 µg/L limit; Mexico has a regulatory limit of 25 µg/l. Mexico (Rodriguez et al. 2004), Argentina, Chile and Perú (Fernández-Turiel et al. 2005). In contrast, the occurrence of the As problem has been reported from 10 countries only within the last 10-15 years (references). These countries comprise Bolivia, Brazil, Colombia, Cuba, Ecuador, El Salvador, Guatemala, Honduras, Nicaragua, and Uruguay. Wide regions of the Chaco-Pampean plain in central and northern Argentina, between the Andes and the Parana River, are the largest affected areas. Here the principal primary As is volcanic ash which is found in the sediments of this plain (e.g. Nicolli et al. 1985, 2009, 2010; Smedley et al. 2005, 2009; Bundschuh et al. 2004, 2008; Bhattacharya al. 2006). The occurrence of this volcanic ash in the alluvial sediments extends in the nearby plains of Bolivia, Paraguay and Uruguay.

The occurrence of As, in both groundwater of the Raigón Aquifer System (RAS) and sediments, in southern Uruguay is studied and an environmental arsenic risk assessment is performed. The RAS is the most important aquifer used for water supply in the country (DINAMIGE 2009). This study covers an area of about 1,800 square kilometres in which about 10,000 inhabitants are living (INE 2011).

In Uruguay, Quaternary ash deposits were considered as a possibility of primary source of high As levels in southern aquifers by some researchers (Montaño et al. 2006, Manganelli et al. 2007; Guerequiz et al. 2007). Chemical analyses of sediments in this study allow us to reconsider that hypothesis, at list for Raigón Aquifer. Unfortunately, data and systematic studies of arsenic in drinking water have not been taken into account to assess population's exposure and health impacts. Medical Geology is being developed in this country as an emerging discipline within the areas of geosciences and biosciences.

Preliminary research work performed by the authors of this paper showed As levels exceeding 10 µg/l in some water samples from the Raigón aquifer in Uruguay (figure 1). This issue leads to the presumption that the population as well as the industrial and agricultural activities could be consuming water with As concentrations exceeding the provisional WHO guideline over the International maximum recommended limits of 0.01 mg/l (WHO 2001) and may contribute to health risk (WHO 2001).

In Uruguay, governmental authorities manage the water resources (Art. 47, National Constitution). The waters Code (Law # 14.859) gives juridical sustain to the Uruguayan's water supply. With the purpose to prevent environmental contamination, water control is managed by 253/79 Decree and the subsequently modified 232/88, 698/89 and 195/91 Decrees. According to actual or potential use, four water categories are established (DINAMA 2006; Table 1). It was reconsidered the limit value by a governmental commission (GESTA AGUA 2008) and finally modified to 20 µg/l (UNIT 2008).

TABLE 1. Categories of water for different uses and respective maximum arsenic concentrations allowed in Uruguay (DINAMA 2006).

Class	Description
1	Conventional treatment water for public supply. Maximum As concentration: 0.005 mg/l.
2a	Water for vegetables consumed directly by people and irrigated by a moisten system. Maximum As concentration: 0.05 mg/l.
2b	Water for recreation. Maximum As concentration: 0.005 mg/l.
3	Water for hydric fauna and flora preservation, or vegetable irrigation that is not directly consumed by people or eventually irrigated by no moisten system. Maximum As concentration: 0.005 mg/l.
4	Water belonging to stream currents crossing urban or suburban areas, and water for irrigation of products not consumed by people. Maximum As concentration: 0.1 mg/l.

Since 1950´s the use of groundwater resources in Uruguay has been increased. The industrial and agriculture demand is still satisfied by mainly surface waters but almost all dairy farm activity is supported by water wells. Since 1996, governmental project PRENADER with external financial support (World Bank) executed more than three thousand wells in all the country. A complete water well database including geological description and hydrogeological data resulted. The PRENADER database has been consulted in order to select water wells for sampling in this study.

GEOGRAPHICAL AND GEOLOGICAL SETTING

The studied Raigón Aquifer System is located in San José department, southern Uruguay (Figure 1). The de la Plata and San José rivers with a few creeks (San Gregorio, Luis Pereira, Castellanos) compose the main surface drainage system in this area. The morphological relief is moderately undulated with low altimetry cotes (60 meters) towards the rivers and creeks. Near the coastline in Kiyu the geomorphology can be characterized as a coastal plain between 10 - 20 meters height. The climate is humid and template with a mean annual rainfall of 1100 mm and annual mean temperature of 22º C (Cfa type in Köppen classification, DINAME 2011). Agriculture and cattle rising are the main economic activities in that region.

The studied area belongs to the Santa Lucía sedimentary basin. This basin is the southwestern segment of an extensional and dextral wrenching corridor related to the early Atlantic break-up pull-apart system (SALAM Santa Lucia-Laguna Merín, Rossello et al 2000). It was filled by 2,500 meters by Mesozoic volcanoclastic sediments and about 200 meters of Cenozoic siliciclastic sediments. The complete Cenozoic sequence includes in the base continental sediments from the Late Oligocene (Fray Bentos Formation, 80 meters), and in the top coastal Holocene deposits (Villa Soriano Formation, 20 meters). Also, marine and coastal sediments of the Miocene Camacho Formation (35 meters); deltaic and fluvial sediments grouped into Raigón Formation (40 meters); the coastal Pleistocene Chuy Formation (15 meters); and the continental Pleistocene Libertad (30 meters) and Dolores (10 meters) Formations that complete the stratigraphic framework of this sequence (Spoturno et al 2004, see Table 2).

Raigón Formation shows stratified yellowish coarse ortho-conglomerates, polimictic gravel and calcareous cement. White yellowish coarse to fine sands, wackes and green lenticular mud are interbedded. Channel filled, sand barriers and even tabular flood-plain and delta-front deposits are the most common facies observed in this area. These deposits represent processes of fluvial and deltaic environments. They reach 40 to 50 meters of thickness. The outcrops of this unit are related to the main drainage systems, like San Gregorio, Mauricio, del Tigre, Valdez, Pavón, Sarandí, Tropa Vieja, and Flores creeks (see Figure 2).

RAIGÓN AQUIFER SYSTEM

The RAS (Postiglione et al 2009) -which is the most important in Uruguay according to DINAMIGE (2009) - belongs to the Coastal Province (Montaño et al. 2006) and spreads over about 1800 square kilometers in the southern San José Department (Figure 1). It is intensively exploited to cover the water demands of agriculture and dairy farm activities representing 30% of total annual groundwater used in Uruguay. It is enclosed in the Raigón and Chuy Formations, which are mainly composed by gravel, sand and muddy sediments (Goso *in* Bossi 1966; Spoturno et al 2004).

TABLE 2. Lithostratigraphic and hydrostratigraphical units in the studied area

LITHOSTRATIGRAPHIC UNIT	MAIN LITHOLOGIES AND SEDIMENTARY ENVIRONMENTS	AGE	HYDROLOGICAL UNIT
Villa Soriano Formation	Coarse to fine quarzitic sands; black and gray mud and clay with bivalve mollusks. Coastal barriers, lagoons, microestuaries.	Holocene	aquifer
Formación Dolores	Clay and silt, brownish wackes. Alluvial and coastal plains.	Late Pleistocene	aquitard
Chuy Formation	Coarse to fine quarzitic sands; yellowish gravels with fossil traces; green clay with mollusks. Coastal barrier - lagoons.	Medium Pleistocene	aquifer
Libertad Formation	Brownish clays, silts, mud and diamictites, with vertebrate fossils. Mud flows and aeolian sediments.	Early medium Pleistocene	aquitard
Raigón Formation	Yellowish and white gravels, coarse to fine sands, green clays. Fluvial and deltaic.	Pliocene	aquifer
Camacho Formation	Green clays and silts, fine white sands, with abundant mollusk bivalves and trace fossils. Coastal estuarine deposits.	Miocene	brackish aquifer
Fray Bentos Formation	Brownish and pink mud; pink diamictites. Cemented by carbonates. Alluvial plains.	Late Oligocene	aquitard

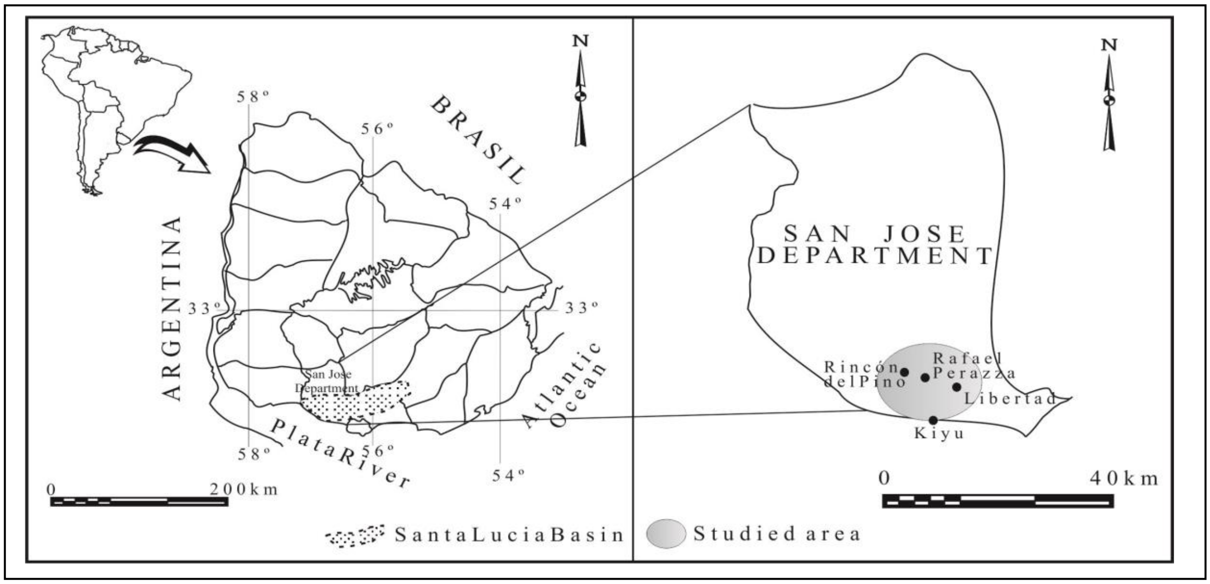

FIGURE 1A) Location map of Santa Lucia basin. 1B) The studied area and main localities

The RAS is structurally divided by the San José River into two portions: the north-eastern and southern subsystems. It is underlain and overlain by the Fray Bentos and Libertad Formations, respectively. These two units are mainly constituted by fine sediments, pink silts and brownish mud. During the last decades several studies were made to understand the hydrological framework regarding the physical, chemical and isotopic properties of Raigón aquifer (Besouat et al 2000 a and b; Postiglioen and Gorfain 2006; Gorfain et al 2006; Postiglione et al 2009). Hydrogeochemical and isotopic characterization was done on RAS using Oxygen 18, Deuterium and Tritium. The results of Tritium were used for dating the groundwater. Those contributions show that the waters of zones of low cover and outcrops with greater saline load are previous to the year 1953 (Plata et al 2003). Also indicate that the zones of the aquifer where the cover is thicker and where the salinity is low are the waters between 1980 and nowadays. Some authors referred that recharge in non-outcropping areas is mainly by Libertad Formation area (Postiglione et al 2005).

The RAS shows unconfined, semiconfined and confined behaviour due to the multilayer type characteristics (Heinzen et al 2003). Groundwater is predominantly of sodium-bicarbonate type groundwaters. The principal hydrogeological characteristics referenced in literature are resumed in Table 3.

Manganelli et al (2007) have found median As concentrations of 16.9 µg/l (range: 13.5 - 18.9 µg/l) in groundwater of Raigón Aquifer. In addition, these authors have shown that distal sediments of this aquifer in San José department have groundwater with higher As concentrations compared to groundwater from proximal facies (Canelones department). Otherwise in San José department Goso et al (2008) referred As concentrations of 14.5 µg/l (range: 24.2 – 1.4 µg/l).

TABLE 3. Hydrogeological parameters and properties of Raigón aquifer (Montaño et al 2006).

Trasmisivity (T)	300 – 600 m^2/day
Storativity (S)	10^{-2} – 10^{-4}
Yield (Q)	10 – 100 m^3/h
Specific capacity (q)	1 – 10 m^3/h/m
Annual recharge	370 ×10^6 m^3/year
Mean groundwater age	50 years
	50 m

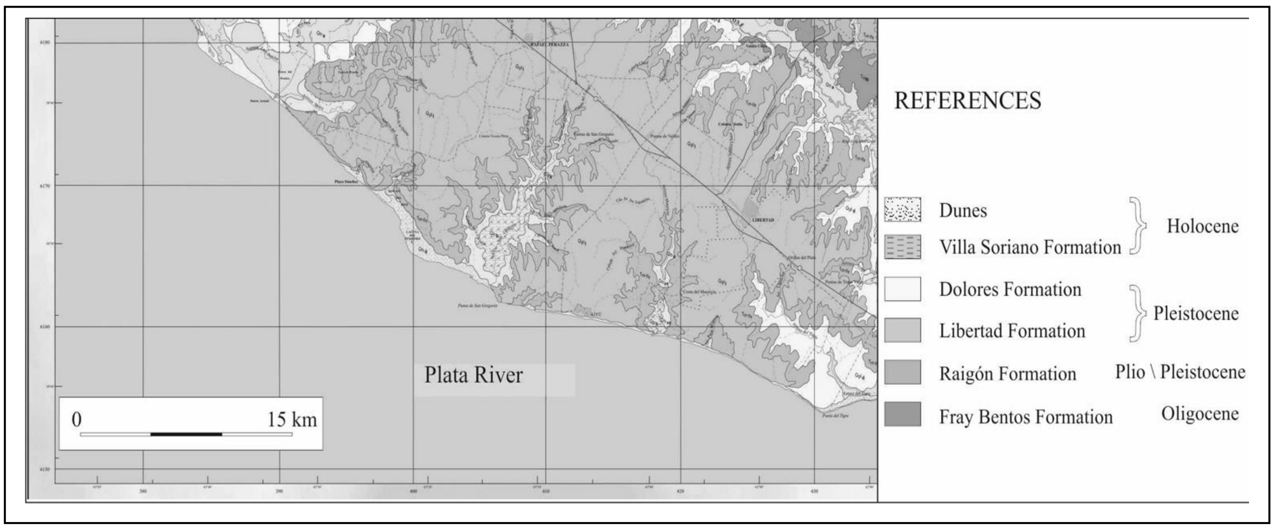

FIGURE 2. Geological map of the studied area (Spoturno et al. 2004).

MATERIALS AND METHODS

Groundwater samples were collected from RAS in southern San José department around Libertad city, Rafael Perazza, Rincón del Pino, Puntas de Valdéz and Kiyú localities. In total, thirty-seven water wells were selected for sampling. The wells of this aquifer were selected using the PRENADER Project database (Figure 3). Nine sediment samples were collected in stratigraphic sections of sea cliffs in Kiyú locality, because in that location are the best outcrops of Raigón (seven samples) and Libertad (two samples) Formations in the area.

The pH, specific electrical conductivity and temperature of groundwater were determined in the field. The chemical characterization (major and trace elements) of waters and sediments were carried out by both inductively coupled plasma-optical emission spectrometry (ICP-OES, VG Plasma Quad PQ2 + Termo Group-VG) and inductively coupled plasma-mass spectrometry (ICP-MS). The samples were acidified (1% HNO3, v/v) to analyze Na, K, Mg, Ca, $SO4^{2-}$, Cl^{-}, Si, Al, As, B, Ba, Br, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Rb,Sb, Sr, Th, U, V and Zn (Fernández-Turiel et al. 2000 a, b).

For hydrochemical characterization both Stiff and Piper diagrams were plotted using the free Qualigraf software in portuguese version.

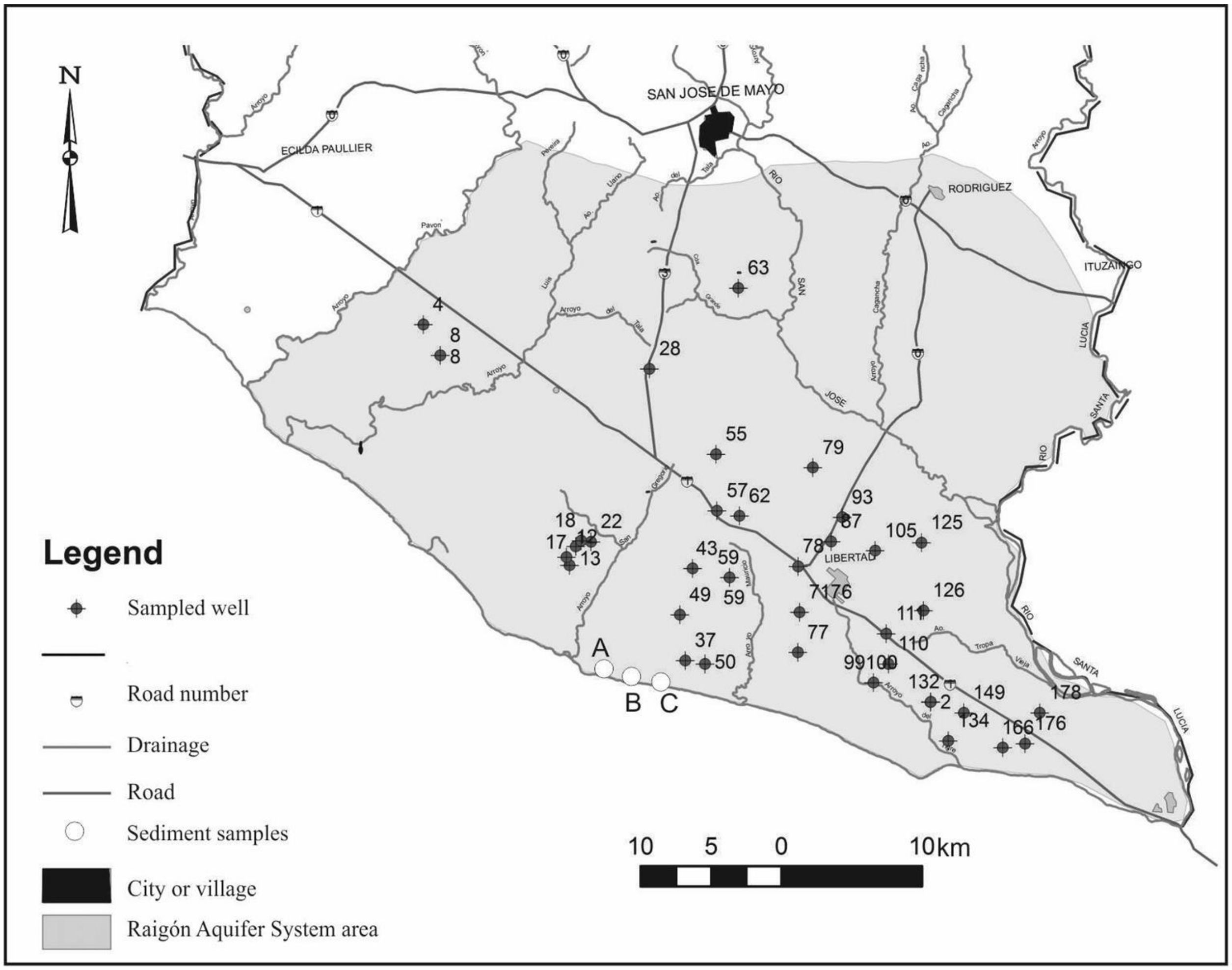

FIGURE 3. Location of RAS and groundwater/sediment sampling points (modified from Postiglione et al 2005)

RESULTS AND DISCUSSION

The compositional variability of the studied groundwaters of the RAS is shown in the Piper diagram (Figure 4). Most waters are of the sodium bicarbonate type.

A comparison between the obtained results and the thresholds of the Decree 253/79 (and the subsequent modifications of Decrees 232/88, 698/89 and 195/91; OSE 2006; DINAMA 2007) shows that some pH values fall outside the 6.5–8.5 range recommended for drinking water (Tables 4 and 5). One sample reached 6.35 pH value. The pH variability is attributed to lithological variations in the aquifers. Spring determinations of temperatures showed a mean value of 20.3 ºC for these waters.

In addition, the zinc concentrations in many samples (18) are higher than the threshold for drinking water (30 µg/l). The highest observed value of Zn content (3.406 mg/l) is interpreted as being related to the deterioration of well materials. In 27 cases, phosphorous concentrations largely exceed 25 µg/l, which is the maximum threshold recommended by the regulations for water uses of Classes 1, 2a, 2b and 3. The mean of this element value is 130.85 µg/l (Table 6).

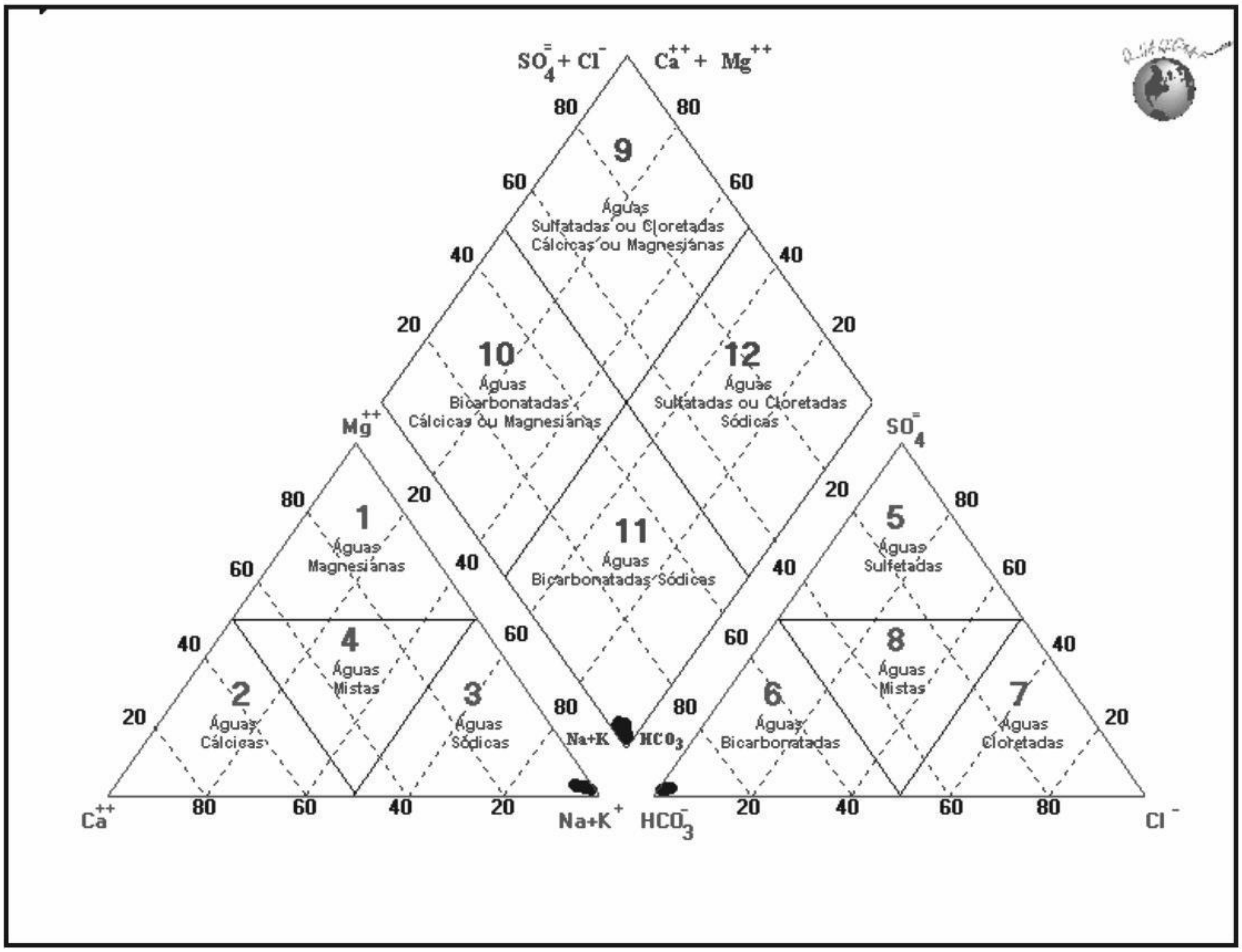

FIGURE 4. Piper diagram for groundwater samples

When the analytical results are plotted into the Stiff diagram most of them show the same trend, a sodium bicarbonate water type.

According to the scale in meq/l were separated Stiff diagrams into three groups to classify the water in scales of 10, 20 and 100 meq/l (Figure 6). It should be noted that the determination of the scales are automatically performed by the software performs in function of the concentrations.

Regarding to arsenic, only six samples (out of 37) have concentrations below 10 mg/l making them available according to the WHO limit values for drinking water (WHO 2004). Four of the samples exceeded 20 µg/l of As which is the maximum acceptable limit value to the Uruguayan state drinking water supplier (OSE 2006). If we consider the limit values from nearby countries, such as Argentina and Chile, most (31) of the groundwater samples would not be acceptable for human consumption (Figure 7).

All rocks contain some arsenic, typically between 1 and 5 ppm. Higher concentrations are found in some igneous and sedimentary rocks. There are several arsenic-bearing minerals, including arsenopyrite (AsFeS), realgar (AsS) and orpiment (As_2S_3). Soils, which are formed by breakdown of rocks and weathering to clays, usually contain between 0.1 and 40 ppm of As, having on average 5-6 ppm. In this case, a few Cenozoic sediments analyzed, from both Raigón and the overlying Libertad Formations, show normal As concentrations. Also, the southern Santa Lucia Basin basement rocks are mainly granitic and gneissic suites (Spoturno et al., 2004) allowing us to not consider a geogenic origin in this case. In Table 7 As concentration in sediments of both Libertad and Raigón Formations are shown. One analysed sample of Libertad Formation is a resedimented wacke with volcanic ash components (SJ 01/A). On the other hand cumulative applications of arsenical pesticides and herbicides were used for decades by farmers in this region. Also, it was very common in uruguayan´s vineyards the use of sodium arsenite as a fungicide (named Arsenite Tofana in Uruguay www.mgap.gub.uy/dgssaa/.../Resabril09_220509.xls).

Some authors estimated the age of recharge water in at least sixty years (1953) based on hydrogeochemical models using Tritium isotopes (Gorfain et al 2006; Postiglione & Gorfain 2006, Postiglione et al 2009).

TABLE 4. Coordinates and physical parameters of each well and water sampled

ID sample	x	y	z	pH	T (ºC)	Conductivity mS	TDS (ppt)
4	395421	6186654	33	7,48	20	0	0
8	396624	6184474		7,32	23,5	0,85	0,44
12	405567	6170147	11	7,07	21,1	0,67	0,34
13	405801	6169564	20	7,02	20,4	0,7	0,36
17	406240	6170894	15	7,2	21,4	1,03	0,53
18	406614	6171308	33	7,19	20,6	0,93	0,47
22	407325	6171229	11	7,08	20,1	0,77	0,4
28	411485	6183517	39	7,33	21,9	0,64	0,34
37	414028	6162800	35	7,34	21	0,85	0,44
43	414556	6169326	*	7,16	21,7	1,29	0,66
50	415425	6162558	30	7,38	21,3	0,78	0,4
55	416217	6177454	34	6,64	21,5	0,52	0,27
57	416283	6173441	45	7,17	20,7	1,88	0,96
62	417879	6173062	34	7,27	21,7	1,01	0,52
63	417798	6189258	35	6,99	21,4	0,63	0,32
71/76	422159	6166229	14	7,36	21,2	0,87	0,45
77	422030	6163365	23	7,44	21,5	0,82	0,42
78	422055	6169478	33	7,2	20,5	0,97	0,49
79	423109	6176495	21	6,87	20,4	0,06	0,3
93	425189	6172970	30	6,82	21,5	0,58	0,3
99/100	427415	6161224	17	7,32	22	0,73	0,37
105	427542	6170600	26	7,14	26,7	0,56	0,29
110	428475	6162556	28	7,14	20	0,76	0,39
111	428324	6164706	19	7,22	21,1	2,21	1,14
125	430830	6171164	6	7,03	20,8	0,57	0,3
126	430969	6166354	19	6,93	21,7	0,94	0,48
132	431487	6159850	11	7,11	17,6	0,1	0,05
134	432739	6157095	16	7,41	18	0,43	0,22
149	433834	6159079	23	7,07	17,5	0	0
166	436611	6156603	4	6,53	18,4	0	0
176	438197	6156896	5	6,35	17,9	0	0
178	439249	6159083	7	6,52	17,2	0	0

TABLE 5. Minimum, maximum, and mean physical parameters of groundwater samples

	Max.	Min.	Mean
pH	7,48	6,35	7,15
Conductivity (mS)	7,68	0,00	0,634
Temperature (º C)	26,7	17,1	20,3
TDS (ppt)	1,14	0,00	0,36

TABLE 6. Minimum, maximum and mean ion concentrations in Raigón Aquifer System

ion	unit	min	max	mean	ion	unit	min	max	mean
Ca	mg/L	12.81	122.11	45.87	*Ag*	µg/L	0.00	0.00	0.00
Mg	mg/L	4.43	30.64	14.09	*Cd*	µg/L	0.01	0.24	0.05
Na	mg/L	66.50	277.86	114.06	*Sn*	µg/L	0.02	0.52	0.05
K	mg/L	2.28	12.55	5.58	*Sb*	µg/L	0.53	6.73	2.03
Si	mg/L	5.11	35.98	28.80	*Te*	µg/L	0.01	0.05	0.03
Cl	mg/L	12.15	334.58	63.86	*Cs*	µg/L	0.01	0.01	0.01
SO_4	mg/L	6.80	151.40	26.23	*Ba*	µg/L	41.33	249.67	121.31
HCO_3	mg/L	205.74	578.70	378.61	*La*	µg/L	0.01	0.16	0.04
Li	µg/L	3.97	31.80	15.36	*Ce*	µg/L	0.01	0.39	0.09
Be	µg/L	0.01	0.07	0.03	*Pr*	µg/L	0.01	0.04	0.03
B	µg/L	74.81	315.52	161.09	*Nd*	µg/L	0.01	0.18	0.06
Al	µg/L	3.41	55.25	8.20	*Sm*	µg/L	0.02	0.04	0.03
P	µg/L	2.69	846.54	130.85	*Eu*	µg/L	0.01	0.03	0.02
Ti	µg/L	0.08	4.16	0.73	*Gd*	µg/L	0.01	0.04	0.02
V	µg/L	9.77	55.42	36.14	*Tb*	µg/L	0.00	0.00	0.00
Cr	µg/L	0.09	1.46	0.58	*Dy*	µg/L	0.02	0.03	0.02
Fe	µg/L	0.12	462.79	24.03	*Ho*	µg/L	0.00	0.00	0.00
Mn	µg/L	0.14	21.79	1.97	*Er*	µg/L	0.01	0.02	0.01
Co	µg/L	0.03	0.28	0.09	*Tm*	µg/L	0.00	0.00	0.00
Ni	µg/L	0.59	3.60	1.29	*Yb*	µg/L	0.00	0.00	0.00
Cu	µg/L	0.44	20.11	3.17	*Lu*	µg/L	0.00	0.00	0.00
Zn	µg/L	7.61	3406.98	152.35	*Hf*	µg/L	0.01	0.65	0.08
Ga	µg/L	0.01	0.03	0.01	*Ta*	µg/L	0.00	0.00	0.00
Ge	µg/L	0.01	0.25	0.10	*W*	µg/L	0.01	0.17	0.04
As	µg/L	1.44	24.19	14.01	*Pt*	µg/L	0.01	0.01	0.01
Se	µg/L	0.15	4.70	1.73	*Au*	µg/L	0.01	0.32	0.05
Br	µg/L	144.06	1157.43	392.52	*Hg*	µg/L	0.01	0.05	0.03
Rb	µg/L	0.95	4.36	1.66	*Tl*	µg/L	0.01	0.01	0.01
Sr	µg/L	119.40	992.42	408.57	*Pb*	µg/L	0.10	2.60	0.36
Y	µg/L	0.01	0.16	0.04	*Bi*	µg/L	0.00	0.00	0.00
Zr	µg/L	0.01	0.40	0.07	*Th*	µg/L	0.01	0.04	0.03
Nb	µg/L	0.01	0.02	0.01	*U*	µg/L	0.03	12.37	3.43
Mo	µg/L	0.37	4.09	1.19					

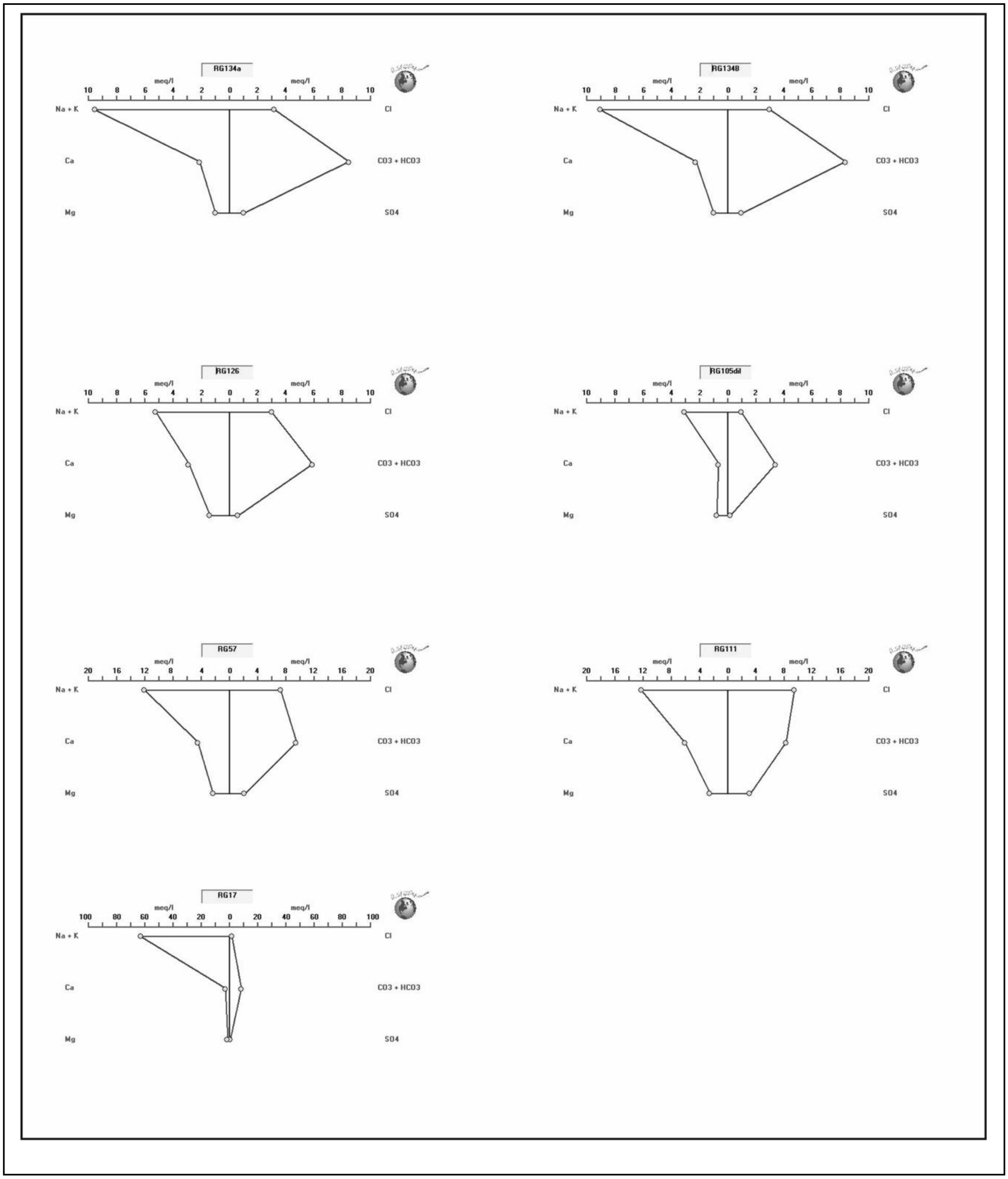

FIGURE 5. Different scale meq/L Stiff diagram for representative groundwater samples of the RAS.

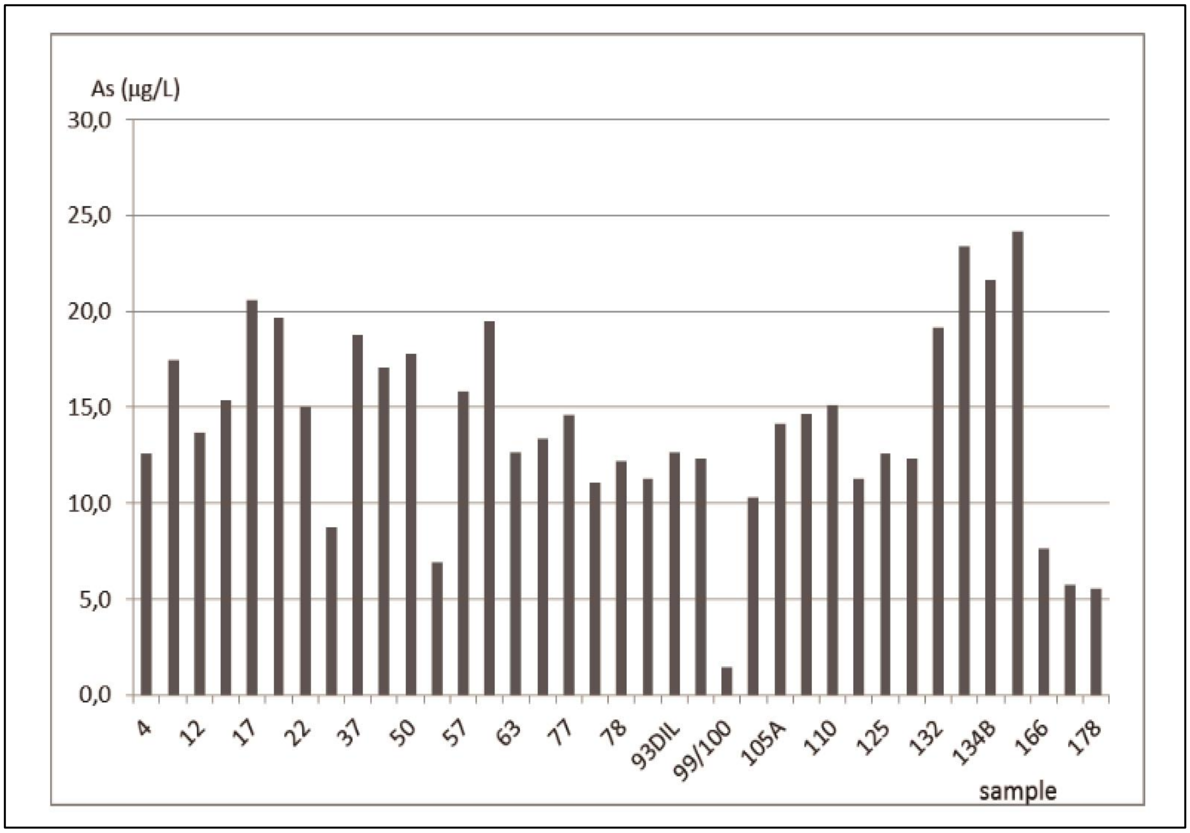

FIGURE 6. As concentration of each groundwater sample

TABLE 7. As content of sediment samples of the Raigón and Libertad Formations

Sample	Unit	As (ppm)
SJ.01	Libertad Fm.	2.67
SJ.01/A	Libertad Fm.	7.13
SJ.01/B1	Raigón Fm.	8.80
SJ.01/B2	Raigón Fm.	9.82
SJ.01/C	Raigón Fm.	4.75
SJ.02/A	Raigón Fm.	1.40
SJ.02/A 9	Raigón Fm.	6.28
SJ.02/B	Raigón Fm.	1.18
SJ.02/C	Raigón Fm.	3.25

The compositional variability of the studied groundwater in the San José Department was shown in the Chadha (1999) [(Ca2+ + Mg2+) – (Na+ +K +)] vs. [(HCO3 -) – (Cl – + SO 4 2–)] diagram (Figure 7) by Manganelli et al (2007). The waters of Raigón aquifer system were classified as sodium bicarbonate and sodium chloride types.

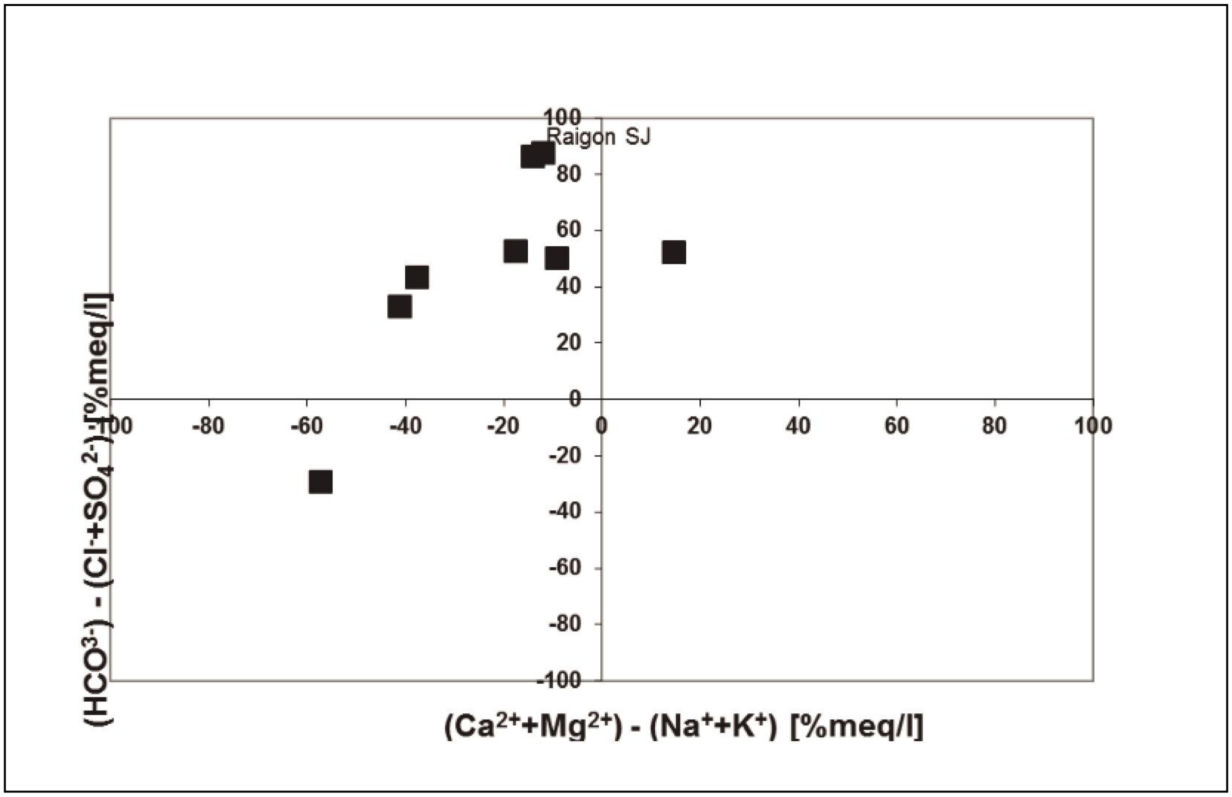

FIGURE 7. Chadha diagram for Raigón aquifer system in San Jose Department (Manganelli et al 2007).

FIGURE 8. A) View of an irrigation well in production. B) Detail view of pump installation in a farm´s well near Kiyú locality. See the chemical packing residues all around the well.

CONCLUSIONS

In southern San José Department live about ten thousand people. The data on groundwater quality from the RAS revealed the presence of significant concentrations of arsenic. In addition, a high content of phosphorus and zinc in many samples from this aquifer system is observed. From the standpoint of Uruguayan law Decree 253/79, as amended by Decrees 232/88, 698/89 and 195/91 including DINAMA (2006) and OSE (2006), the limit is exceed in 11% of samples analyzed. If WHO (2001, 2004) regulations for drinking water are taken into account, this situation becomes problematic because 80% of water samples are contaminated. The average and maximum concentration of arsenic observed are 14.1 µg/l and 24.19 µg/l, respectively (Figure 6).

A few sediment analyses in both Raigón and Libertad Formations allow us to postulate a tentative anthropogenic origin for these anomalous As concentrations. Probably, the most significant anthropogenic source of arsenic in this region is from cumulative applications of arsenical pesticides and herbicides used for decades byfarmers. It was observed *in situ* (Figure 8 a and b) that the incorrect fertilizers waste management and its intensive use could be the main cause of anthropogenic pollution. More chemical analyses in soils, sediments and rocks must be done to prove this hypothesis. In this case, this situation would be a consequence of bad practices in agriculture from many years ago.

The present results contribute to the background data for the assessment of toxic metals in one of the most important aquifer systems in Uruguay, and to evaluate the exposure health risks of the human and animal population. Also to support future management of these groundwater resources aiming to prevent long-time exposure and development of associated diseases (Mañay 2010). In Uruguay, systematic evaluation of geological materials and their relationships with environmental toxicological aspects is a matter of concern that have to be taken into account in an official way.

The characterization of the water supply and its main uses for human and animal populations is important to evaluate toxic element concentrations and their health impacts. There is also a need on the systematic studies of exposed population at risks (human and animal) facing a typical interactive problem between geology and health; that is, with a Medical Geology approach. Further research is also required to establish relationships between natural geological factors and the development of prevalent diseases.

Acknowledgments

The referred project took part of a cooperation between the University of the Republic (Uruguay) and CSIC from Spain (Ref. 2005UY0001).

We thank to DINACYT -Uruguay for the project support through the Technological Development Program PDT # 45/14 which included the doctoral thesis work of MSc. Rosario Guerequiz. This young geolologist, got a very severe disease and died in 2010, leaving her research data unpublished so this is as a "posthumous tribute" where her thesis research advancements and preliminary conclusions have been shown.

CYTED Iberoarsen Network and the International Medical Geology Association contributed with scientific and technical support to improve the knowledge on environmental arsenic and health impacts, with a multidisciplinary approach in Uruguay.

We also appreciate the support of the Scientific and Technical Services, University of Barcelona, as well as M. Aulin, Flavia Ruggieri and Margarita Sienra.

This work was performed under the Research Consolidated Groups SGR-2005-795 PEGEFA (Petrology and Geochemistry Basic and Applied) and SGR-2005-00589 (Mineral Resources), funded by AGAUR-DURSI, Generalitat de Catalunya. Thanks to Dr. J. Bundschuh and Dr. E.Peel for the suggestions to the first manuscript.

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