

Hydrochemical assessment of Hydrological Environmental Services in the recharge area in the Southwest of Mexico City

María E. Zabala^{1,2} · Sandra E. Martínez³ · María Perevochtchikova⁴ · G. Eduardo Sandoval-Romero⁵ · Nidya Aponte⁶

Received: 30 September 2016 / Accepted: 18 January 2017
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Abstract The aquifer recharge area that supplies water to Mexico City is being protected with the implementation of land use restrictions and with the use of payment schemes for maintaining environmental services (PES). In order to assess the effects of PES in the conservation soil area, the chemical and isotopic compositions of water from springs were characterized and the water baseline chemistry was established to provide a useful standard to monitor the water resources and to support the decision-making under current water management policies. A total of 32 water samples taken in four field surveys, during the dry and rainy season, and background chemical data from different information sources, were studied. The water salinity increases from southwest to northeast towards the urbanized area. The chemical composition of water is due to the occurrence of natural chemical interactions between water and rocks in aquifers and to the presence of effluents generated by human activities. In the forest area, water chemistry has not changed significantly over the past three decades and there are no major discernible trends in the

compiled water chemistry data, suggesting that PES has contributed in part to maintain the initial condition in the aquifer recharge area. The natural reference levels proposed have allowed the current chemical conditions in the system to be understood and can be implemented to monitor water resources in the area of conservation soil in the Sierra de Las Cruces with an acceptable degree of reliability.

Keywords Hydrological Environmental Services · Groundwater recharge · Groundwater chemical baseline · Conservation soil · Mexico City

Introduction

Environmental services related to water are formed by a set of conditions, processes and functions of the natural and artificial environment (MEA 2005; Brauman et al. 2007). The flows in the hydrological cycle vary temporally and

✉ María E. Zabala
mzabala@faa.unicen.edu.ar

Sandra E. Martínez
smartinez@acumar.gov.ar

María Perevochtchikova
mperevochtchikova@colmex.mx

G. Eduardo Sandoval-Romero
eduardo.sandoval@ccadet.unam.mx

Nidya Aponte
naponteh@gmail.com

¹ Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Av. Rivadavia 1917, C1033AAJ Ciudad Autónoma de Buenos Aires, Argentina

² Instituto de Hidrología de Llanuras “Dr. Eduardo Usunoff”, Av. República Italia 780, 7300 Azul, Buenos Aires, Argentina

³ Autoridad de Cuenca Matanza Riachuelo (ACUMAR), Esmeralda 255 PB, C1033AAJ Ciudad Autónoma de Buenos Aires, Argentina

⁴ Centro de Estudios Demográficos, Urbanos y Ambientales, El Colegio de México AC, Camino al Ajusco NW 20, Pedregal de Sta. Teresa, 10740 Ciudad de México, México

⁵ Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Ciudad de México, México

⁶ Posgrado en Geografía, Universidad Nacional Autónoma de México, Circuito de Posgrado, Ciudad de México, México

spatially mainly influenced by the meteorology, topography, substrate type and land uses. The land use changes can alter the distribution and yield of water, for example, if the runoff increases, the infiltration to the soil decreases in such a way that groundwater component may lose water, and the chemical water quality may change. There is a considerable body of research available on simulating hydrological provision environmental services (water yield) for various land uses, climates and human activities (Vigerstol and Aukema 2011; Fan and Shibata 2014; Deng et al. 2015), and some on pollutant retention service by alternative land uses (Bai et al. 2013). However, the knowledge of hydrochemical characteristics is important to determine the quality and the spatial and temporal variability of water that is provided to maintain environmental services (Bahar and Reza 2010; Ganyaglo et al. 2011).

The chemical quality of groundwater is influenced by natural and anthropogenic factors, such as: recharge water chemistry and the rate of recharge; aquifer mineralogy and the relative reactivity of minerals; groundwater residence times; groundwater exploitation patterns; or the existence of agricultural, industrial and/or urban activities in a watershed that can affect groundwater quality (Appelo and Postma 2005; Zabala et al. 2016). In the absence of pollution, groundwater chemistry mainly reflects the conditions and processes of the natural environment. Where these conditions occur, the groundwater quality is said to be natural, also called chemical baseline conditions (Edmunds and Shand 2008).

In this context, we focus on determining the quality attribute of the hydrological environmental service and the processes that drive them as a useful tool in the assessment and conservation of the water provision environmental service.

In Mexico, the Federal Payment for Environmental Services (PES) program started in 2003 by considering hydrological services, which sought to improve the population's well-being and to guarantee groundwater recharge in the high parts of watersheds with forest coverage (CONAFOR 2016). Although it has become one of the most important federal programs in the world, deficiencies in evaluating and monitoring the environmental services and the effects of PES program have been identified as the main constraints in the application of these mechanisms (Muñoz-Piña et al. 2008; Almeida Leñero et al. 2014).

In Mexico City, the PES program is applied in the mountain ranges surrounding the city, declared conservation soil under the Urban Development Act due to its importance in the recharge of the main sources supplying water to the city. In the year 2000, 59% of the territory of Mexico City (88,442 ha) was declared conservation soil, in

order to constrain the land use change, which in the period 1980–2000 had reached 165% mainly due to the urban sprawl and deforestation (Schteingart and Salazar 2003). Since 2003, this Act has been supplemented with the program of Payment for Hydrological Environmental Services (PHES). At present, this program protects about 19% of the total area of conservation soil (Perevochtchikova and Vázquez 2012). In this area, some studies of characterization of groundwater chemical composition were carried out (Cortez et al. 1989; Morales-Luis et al. 2000; Jujnovsky et al. 2010; Peñuela-Arévalo and Carrillo-Rivera 2013; Perevochtchikova et al. 2015).

This work aims to characterize the natural chemical and isotopic composition of water from springs located in the south of the Sierra de Las Cruces and to establish the groundwater baseline chemistry. The specific objectives are: to assess the possible spatial and temporal chemical change related to hydrological seasonality; to establish ranges of variation for major and some minor components; to deduce the potential processes controlling the natural chemical composition of water; and to propose concentration values for the upper limit of the natural background ranges as references for monitoring and control actions.

This study is part of the activities conducted in the framework of the Projects 155039 CB-CONACYT and 246947 PN-CONACYT in the Conservation Soil of the Mexico City, which is being developed by researchers of El Colegio de México and other institutions. The projects aim to socio-environmental analysis of the effects of the PES in order to improve the performance of this instrument of environmental policy.

Study area

General features

The study area is located in the south of the Sierra de Las Cruces, in the southwest of Mexico City. The studied springs outcrop in the Tlalpan and Magdalena Contreras delegations (Fig. 1a) mostly in territory under conservation soil with a population of over 900,000 inhabitants.

The relief is abrupt, with maximum altitudes of about 3900 masl sloping towards the plain, whose base level is 2240 masl.

The climate is semi-cold, sub-humid C_b(w₂)(w). According to the data of meteorological stations located in Tlalpan Delegation: El Guarda (2990 masl), El Calvario (2726 masl) and Desviación Alta to Pedregal (2296 masl), the average annual rainfalls for the periods 1961–2014,

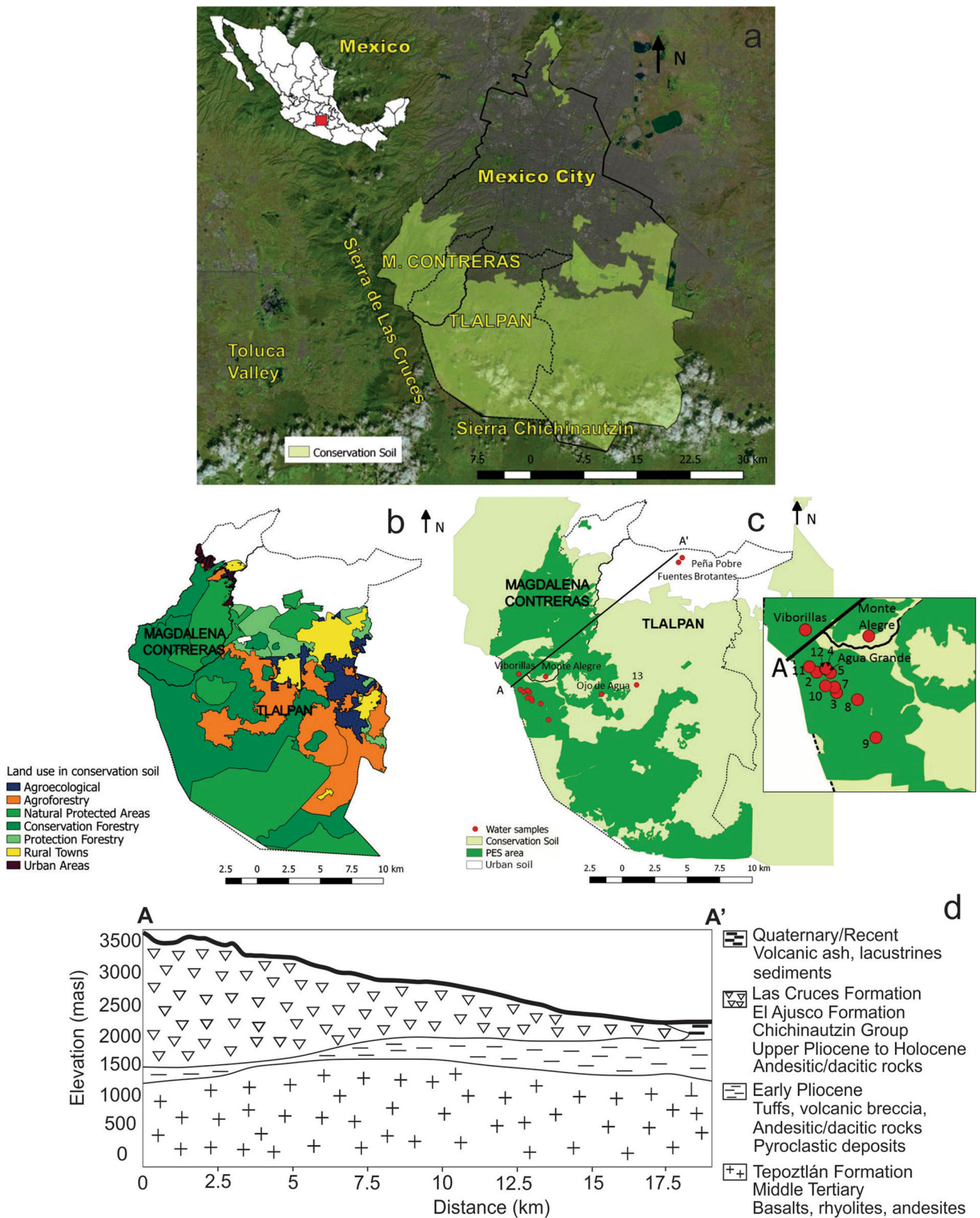


Fig. 1 **a** Location of the study area; **b** land uses in the conservation soil; **c** location of water samples studies, and PES areas; **d** illustrative geological cross section (modified from Edmunds et al. 2002)

1952–2014 and 1970–2014 are 1300, 1100 and 900 mm, respectively (Perevochtchikova et al. 2015). Rainfall decreases from southwest to northeast. The rainy season is between June and September, while the dry season is between December and April. The mean annual temperature of the air ranges from 8.3 to 10.3 °C (Saavedra Díaz 2013).

The rural area, or conservation soil, is covered by forest associated with herbaceous and arbustive vegetation (Fig. 1b). In some areas, there are seasonal agriculture and *pastizales* as in San Miguel and Santo Tomás Ajusco communities, rural settlements which have participated in the PHES program (Perevochtchikova and Rojo Negrete 2015). Despite the restrictions of use in the conservation soil, small urban areas have been developed in its border (Fig. 1b). Beyond the limit of the conservation soil, the urban soil is being developed according to Urban Development Act (Fig. 1c). In these areas, a large number of the settlements have septic tanks due to the difficulty and high costs of building infrastructure on the volcanic rock substrate and the old quarries and sand mines located in the area are often used as waste disposal sites (Aguilar and Santos 2011).

Geology and mineralogy

The Sierra de Las Cruces mountain range extends in a northwesterly–southeasterly direction in the central portion of the Trans-Mexican Volcanic Belt and forms the western boundary of the Mexico Basin (García-Palomo et al. 2008). This mountain range has a length of 110 km and a maximum altitude of about 3900 masl.

In the southern part of the Sierra de Las Cruces, the basement is composed of Cretaceous deposits (marine limestone, sandstone and shale) and of Middle Tertiary volcanic rocks (mainly the Tepoztlán Formation). The Middle Tertiary volcanic rocks are comprised of clastic materials, basalts, rhyolites and andesites (Arce et al. 2015). To the east of the Sierra de Las Cruces, there is a small area with tuffs, volcanic breccias and lavas of andesitic and dacitic composition (Early Pliocene) that are interdigitated with clastic and pyroclastic deposits (Pliocene).

Covering these units, three Quaternary geologic formations have been identified (the Las Cruces and El Ajusco formations, and the Chichinautzin Group) which represent different eruptive periods that took place from the upper Pliocene to Holocene (Delgado-Granados and Martín del Pozo 1993). These units are composed of volcanic rocks of dacitic and andesitic composition (García-Palomo et al. 2008; Arce et al. 2015) and are strongly fractured.

Overlapping the Chichinautzin Group, there are alluvial and colluvial deposits (Delgado-Granados and Martín del Pozo 1993). Towards the plain, eruptive events deposited a layer of ash which is interbedded with alluvial and fluvial

deposits that formed after the closure of the Mexico Basin. This deposit (Late Quaternary to Recent) is formed by volcanic ash, lacustrine clay, sand, silt and gravel.

Hydrogeology

Both the Cretaceous deposits and the Middle Tertiary volcanic sequences behave as an aquifer. The hydraulic properties of the Early Pliocene lacustrine and pyroclastic sequences are not known, but it is estimated that they behave as an aquitard. The Late Pliocene to Quaternary volcanic sequence behaves as an aquifer. Quaternary recent deposits behave as an aquifer and include the main aquitard that covers the plain centre (Edmunds et al. 2002).

The called Mexico City Metropolitan Zone (*Zona Metropolitana de la Ciudad de México*, ZMCM) aquifer, formed in both fractured rocks and granular deposits, is exploited intensively in the plain to supply 70% of the total water to the city (Martínez et al. 2015). This aquifer can behave as semi-confined, confined or unconfined aquifer, depending on the area being considered. In the studied area, it behaves as an unconfined aquifer.

The groundwater movement is controlled by the hydraulic gradients, lithology and geological structures (Edmunds et al. 2002). Under natural conditions, the recharge occurs in the Sierra de Las Cruces and Sierra Chichinautzin, at rates estimated between 30 and 50% of precipitation (Ortega and Farvolden 1989; Birkle et al. 1998; Ujnovsky et al. 2012). Part of the water infiltrated discharges in springs in the hillside and in the edge of the plain, and part of the water recharges the ZMCM aquifer (Carrera-Hernández and Gaskin 2008).

The occurrence of the springs is due to the lithological and structural characteristics of the volcanic sequences: the presence of permeable and less permeable materials, strongly fractured rocks with dominant directions north-west–southeast and northeast–southwest (Morales-Luis et al. 2000). In some cases such as Agua Grande spring, it outcrops in the union of fractures, while in Fuentes Brotantes spring, it outcrops in the contact between volcanic breccia and pyroclastic deposits with clay and silt (DGCOH 2000).

The discharge of springs varies seasonally and is correlated with the rainfall in the region (DGCOH 1992, 2000; SACMEX 2009, 2012; Perevochtchikova et al. 2015). In the study area, there are perennial and intermittent springs. The perennial springs are collected totally or partially for water supply to the Tlalpan (Monte Alegre, Agua Grande, Viborillas, Fuentes Brotantes and Peña Pobre springs) and Magdalena Contreras delegations (Ojo de Agua spring). Some intermittent springs can be collected into depressions and transported for uses in the rural communities.

Materials and methods

A total of 32 water samples were taken in four field surveys: April 2013, August 2013, April 2015 and September 2015. April samplings represent the dry season, while August and September samplings correspond to the rainy season. All samples taken in sampling 2013 (Agua Grande-AG, 2, 3, 4, 5, Ojo de Agua-OA, 7, 8, 9, 10, 11, 12 and 13) come from springs and are located in the high topographic sector in a forest area (Fig. 1c). Samples taken in 2015, OA, AG, Fuentes Brotantes (FB) and Peña Pobre (PP) samples come from springs, while Monte Alegre (MA) and Viborillas (VI) samples from streams. Even though the latter ones come from springs too, for reasons of accessibility they were collected a few metres downstream of the point where they outcrop. OA, AG, MA and VI samples are located in the high topographic sector, in a forest area, while FB and PP samples are located in the urban area.

Water samples were taken after electrical conductivity (EC), pH and water temperatures were stabilized. These parameters were measured by a multi parameter probe (Hanna), while alkalinity contents were measured in field using a water quality test kit (La Motte). The flow was measured with an automatic flow meter (Global Water).

Water samples were refrigerated and sent to the laboratory for analysis immediately after the sampling was completed. Cations and anions were analysed by ICP_OES and by HPLC respectively, at the laboratory Geoquímica Ambiental (Universidad Nacional Autónoma de México). All samples coming from 2013 and 2015 have an ionic balance error lower than 11%, except for the samples OA, AG, MA and VI corresponding to September 2015, which have an ionic balance error between 13 and 18%.

Isotopic analyses ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) correspond to samples taken in April and September 2015 and were analysed at the laboratory Hidrología Isotópica (*Universidad Nacional de Mar del Plata*) by laser spectroscopy; the analytical error was $\delta^{18}\text{O}$: $\pm 0.3\%$ and $\delta^2\text{H}$: $\pm 2.0\%$.

The study methodology involved: establishing ranges of variation for major and some minor components; assessing the spatial and temporal chemical-isotopic changes related to hydrological seasonality; deducing the potential processes controlling the chemical composition of groundwater; and evaluating the temporal changes in major components and EC values in relationship to periods on which the PHES has been implemented.

For this analysis only chemical data from AG, VI and MA samples could be collected from different information sources (DGCOH 1979, 1980, 1992; SACMEX 2012). Flow values corresponding to these sites and time periods were not available. All chemical analyses background used have ionic balance errors smaller than 11%. Proposing values for the upper

limit of natural background ranges for springs follow the guidelines proposed by the European Union (BRIDGE 2009). In this work, upper limits of natural background were calculated for major and some minor chemical components and physical variables using the 90th percentile.

A more detailed description of the methodology applied can be found in Zabala et al. (2016). For a clearer writing and reading of the text, the signs of the ions have been obviated in this work.

Results

Chemical water characteristics

All sites sampled in 2013 and some of the sites sampled in 2015 are located in the forest area (Fig. 1c). In this area in both surveys, the groundwater EC values vary between 40 and 100 $\mu\text{S}/\text{cm}$ with the exception of AG sample from April 2013 where the EC measured value was 260 $\mu\text{S}/\text{cm}$ (Table 1; Fig. 2). The main temporal variations in EC values were observed in AG and number 5 samples from 2013 survey, and in MA and VI surface water samples from 2015 survey. Samples from the dry season often have a higher electrical conductivity than the corresponding samples from the rainy season.

Regarding PP and FB, they are the most mineralized waters of the study area. In general, in both samplings, an increase in salinity from southwest to northeast coinciding with increasing urbanization has been observed.

In the studied springs, the flow values measured in both samplings are lower in the dry season than in the rainy season. In 2013, the sampling included intermittent springs (Fig. 1c. sites 8, 9, 10, 11, 12 and 13). In these sites, there was no flow in the dry season, while in the rainy season it reached values between 9 L/s in the site 12 and 200 L/s in the site 9. In relation to perennial springs, those located in the forest area show seasonal variability: in MA the measured flow was 94 L/s in the dry season and 254 L/s in the rainy season, whereas in VI the flow varies between 14 and 60 L/s in the dry season and rainy season, respectively. The flows in the FB and PP springs located in the edge of the plain are constant, being about 210 and 240 L/s, respectively, during the year (SACMEX 2009).

In the dry season, groundwater temperatures range between 7 and 17 °C, and stream samples range between 10 and 15 °C. In the rainy season, groundwater temperatures range between 9 and 18.5 °C, and the temperature of stream samples ranges between 9.5 and 12 °C (Table 1).

Figure 3 and Table 2 show the statistic values calculated for major and minor chemical components, EC and pH values for all samples. In spring samples, the variables with

Table 1 Chemical and isotopic compositions of water samples and saturation indexes of selected mineral phases

Name	Elevation (masl)	Sampling date	Latitude	Longitude	EC ^(f) (μS/cm)	pH ^(f)	T ^{te} (°C)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	NO ₃ (mg/L)
2	3567	abr-13	19.206300	-99.299750	45	6.65	11.3	6.2	2.4	2.1	1.3	1.0	0.5
2	3567	ago-13	19.206300	-99.299750	50	6.32	s/d	11.7	3.3	4.8	2.0	1.3	ND
3	3466	abr-13	19.200150	-99.293680	50	6.78	17.1	4.7	2.1	2.2	1.7	1.6	0.0
3	3466	ago-13	19.200150	-99.293680	45	6.48	11.0	8.7	2.9	4.0	1.1	0.8	ND
4	3534	abr-13	19.207333	-99.296850	75	6.31	13.3	6.1	2.5	2.1	1.4	0.8	1.0
4	3534	ago-13	19.207333	-99.296850	60	6.09	11.5	12.4	4.4	5.4	1.8	1.0	4.4
5	3511	abr-13	19.206050	-99.295467	79	6.25	14.8	6.1	2.4	2.2	1.8	1.2	1.2
5	3511	ago-13	19.206050	-99.295467	50	6.72	12.7	11.8	3.5	4.7	1.3	0.7	ND
7	3471	abr-13	19.201800	-99.294300	60	6.82	15.2	5.1	2.2	2.3	1.5	1.3	0.3
7	3471	ago-13	19.201800	-99.294300	50	6.52	13.7	10.4	3.1	4.7	1.4	0.8	ND
8	3431	ago-13	19.197960	-99.287240	40	6.46	13.9	12.7	3.8	4.6	1.3	0.9	ND
9	3375	ago-13	19.186660	-99.281730	50	6.53	15.7	11.8	3.2	3.7	1.3	1.6	ND
10	3515	ago-13	19.202210	-99.297090	40	6.53	16.5	11.6	3.6	4.1	1.2	1.0	ND
11	3627	ago-13	19.207950	-99.302017	40	6.14	11.2	12.1	3.6	4.3	1.4	1.2	ND
12	3535	ago-13	19.207233	-99.296967	60	6.54	12.9	14.8	4.2	5.0	1.4	0.9	ND
13	3046	ago-13	19.209717	-99.216900	100	6.50	18.5	15.0	6.1	6.2	2.4	1.8	ND
AG	3547	abr-13	19.207300	-99.296780	260	6.66	17.0	6.2	2.6	2.2	1.3	0.7	1.0
AG	3547	ago-13	19.207300	-99.296780	60	6.15	12.6	11.3	3.1	5.4	1.5	0.8	ND
AG	3547	abr-15	19.207300	-99.296780	89	7.42	9.5	6.8	2.7	4.4	1.3	0.7	1.0
AG	3547	sep-15	19.207300	-99.296780	84	6.56		7.4	3.0	4.3	1.3	1.1	1.0
OA	3355	abr-13	19.203650	-99.242670	50	6.97	11.3	4.0	1.5	2.5	2.4	1.1	0.6
OA	3355	ago-13	19.203650	-99.242670	55	6.35	12.3	10.7	3.2	5.9	2.7	1.3	2.5
OA	3355	abr-15	19.203650	-99.242670	68	7.31	9.5	4.0	1.6	5.3	2.1	1.2	1.1
OA	3355	sep-15	19.203650	-99.242670	59	6.96	9.5	3.8	1.5	5.2	2.0	1.1	1.0
MA	3458	abr-15	19.216670	-99.283330	67	7.58	15.0	4.2	2.1	5.0	1.6	0.7	<0.26
MA	3458	sep-15	19.216670	-99.283330	52	6.80		3.7	1.8	2.8	0.9	0.7	0.5
VI	3545	abr-15	19.218833	-99.303000	68	7.64	10.0	4.9	2.1	3.4	1.0	0.5	0.4
VI	3545	sep-15	19.218833	-99.303000	49	6.96	9.5	3.9	1.8	2.3	0.7	0.5	0.1
PP	2305	abr-15	19.297361	-99.181667	243	7.74	14.0	13.2	7.7	18.3	3.9	11.2	31.6
PP	2305	sep-15	19.297361	-99.181667	237	6.37	16.6	13.1	8.6	17.8	3.8	11.6	36.3
FB	2313	abr-15	19.294167	-99.184444	179	7.38	17.0	10.5	5.7	11.6	3.3	4.1	16.7
FB	2313	sep-15	19.294167	-99.184444	208	6.75	14.1	10.4	7.5	12.7	3.3	7.5	21.9
Name	SO ₄ ²⁻ (mg/L)	HCO ₃ (mg/L)	F (mg/L)	Si (mg/L)	Al (mg/L)	δ ¹⁸ O (‰ SMOW)	δ ² H (‰ SMOW)	log PCO ₂ (atm)	Al	An	K-F	M	K
2	6.2	24.2											
2	6.9	58.1											
3	5.2	22.5											
3	6.9	42.0											
4	5.4	25.3											
4	6.1	71.0											
5	5.3	24.0											
5	5.1	69.4											
7	5.8	21.4											
7	6.3	48.7											
8	5.8	60.8											
9	5.5	61.6											

Table 1 continued

Name	SO ₄ ²⁻ (mg/L)	HCO ₃ (mg/L)	F (mg/L)	Si (mg/L)	Al (mg/L)	δ ¹⁸ O (‰ SMOW)	δ ² H (‰ SMOW)	log PCO ₂ (atm)	Al	An	K-F	M	K
10	6.7	55.8											
11	7.0	64.2											
12	6.2	71.2											
13	15.9	80.1											
AG	5.6	24.6											
AG	6.7	68.2											
AG	4.9	49.3	0.09	12.6		-15.7	-86	-4.0	-1.68	-2.92	0.33	4.57	5.84
AG	5.4	62.2	0.13	14.5		-11.2	-76						
OA	4.2	16.4											
OA	5.2	52.1											
OA	4.0	37.1	0.17	22.3		-15.8	-87	-4.0	-0.86	-2.66	1.28	5.63	6.52
OA	4.5	42.7	0.18	23.8		-11.0	-76						
MA	3.6	37.6	0.06	16.3		-14.6	-79	-4.3	-1.66	-3.05	0.31	3.72	4.95
MA	5.2	45.1	0.10	11.5	0.015	-10.2	-68						
VI	3.7	37.3	0.05	9.5		-14.6	-81	-4.3	-2.18	-3.29	-0.19	3.65	5.15
VI	5.6	42.7	0.14	10.1	0.059	-9.9	-67						
PP	24.2	67.3	0.29	20.4		-13.3	-75	-4.2	-0.76	-2.41	1.05	4.07	5.05
PP	25.6	36.6	0.37	21.5		-9.8	-66						
FB	15.4	52.7	0.29	19.1	0.072	-14.5	-79	-4.0	-0.91	-1.96	0.99	4.88	5.87
FB	18.2	46.4	0.32	21.6	0.007	-10.2	-70						

EC electrical conductivity, (f) field measured, ND not detected, Al albite, An anorthite, K-F K-Feldspar, M montmorillonite, K kaolinite

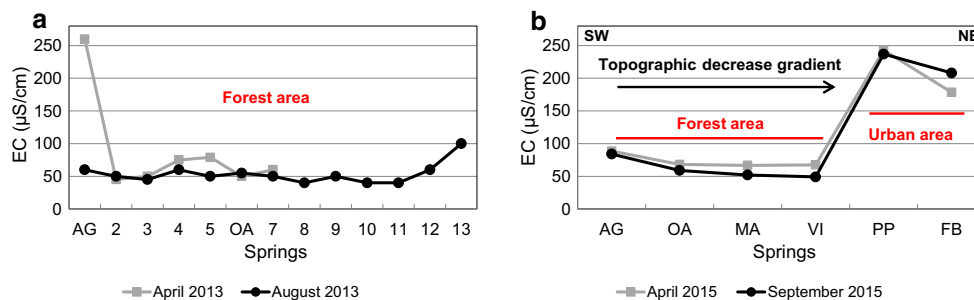


Fig. 2 a EC values measured in 2013 surveys. b EC values measured in 2015 surveys

the greatest variation are NO₃ and to lesser extent Ca, Na, HCO₃ and F, while pH is the variable with the lowest range. In stream samples, NO₃ is the variable with the greatest range as it occurs in the springs, while pH, and to lesser extent HCO₃, Mg and Ca are the variables with the lowest range.

Taking into account the values of the coefficient of variation of each variable analysed (Table 2), in spring samples Cl and NO₃ and to lesser extent Na and SO₄ show the higher values, while the pH value shows the lowest variation. In the case of stream samples, NO₃ shows the highest coefficients of dispersion, while the pH, Mg and HCO₃ show the lowest values.

Water chemical types: spatial and temporal variation

Samples from April 2013 are Ca/Mg-HCO₃ types, and the OA sample for this time is the less mineralized water (Fig. 4a). Even though samples from August 2013 have the same chemical type than April samples, all of them have higher contents of Ca and HCO₃ (Fig. 4b). Figure 4c, d shows samples from OA, AG, PP and FB springs, and MA and VI stream from April and September 2015 surveys, respectively. Samples from April 2015 evolve from Ca-HCO₃-Ca/Na-HCO₃ to NaCa-HCO₃/Na-HCO₃. In September 2015, the samples located in the high topographic sector

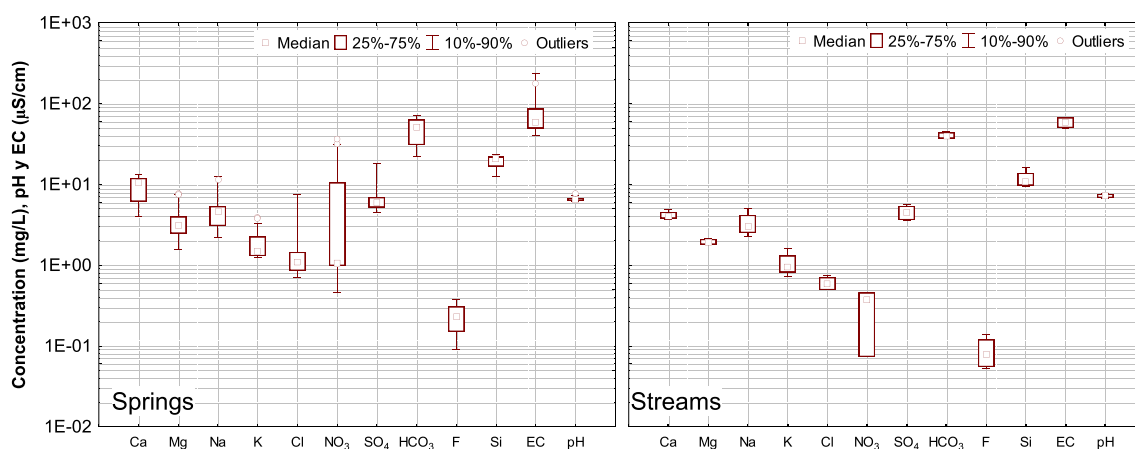


Fig. 3 Distribution of concentrations of major and minor components, EC and pH values

Table 2 Summary of statistical parameters for water samples

	<i>n</i>	Mean	Median	Min	Max	P25	P75	St.dev.	Coef.var.
<i>Springs</i>									
Ca (mg/L)	28	9.4	10.5	3.8	15.0	6.2	12.0	3.5	37.2
Mg (mg/L)	28	3.6	3.2	1.5	8.6	2.5	4.0	1.9	51.0
Na (mg/L)	28	5.6	4.6	2.1	18.3	3.1	5.4	4.3	75.7
K (mg/L)	28	1.9	1.5	1.1	3.9	1.3	2.3	0.8	42.6
Cl (mg/L)	28	2.2	1.1	0.7	11.6	0.9	1.5	2.9	136.6
NO ₃ (mg/L)	16	7.6	1.1	0.3	36.3	1.0	10.5	12.0	157.8
SO ₄ (mg/L)	28	8.2	6.0	4.0	25.6	5.2	6.9	5.9	71.4
HCO ₃ (mg/L)	28	48.4	50.7	16.4	80.1	30.9	63.2	18.5	38.2
F (mg/L)	8	0.23	0.23	0.09	0.37	0.15	0.31	0.10	43.79
Si (mg/L)	8	19.5	20.9	12.6	23.8	16.8	21.9	3.9	20.2
EC (μS/cm)	28	89	60	40	260	50	86	68	76
pH	28	6.65	6.54	6.09	7.74	6.36	6.80	0.41	6.15
<i>Streams</i>									
Ca (mg/L)	4	4.2	4.1	3.7	4.9	3.8	4.6	0.5	12.5
Mg (mg/L)	4	2.0	1.9	1.8	2.1	1.8	2.1	0.2	8.5
Na (mg/L)	4	3.4	3.1	2.3	5.0	2.5	4.2	1.2	35.1
K (mg/L)	4	1.1	1.0	0.7	1.6	0.8	1.3	0.4	36.9
Cl (mg/L)	4	0.6	0.6	0.5	0.7	0.5	0.7	0.1	20.8
NO ₃ (mg/L)	3	0.3	0.4	0.1	0.5	0.1	0.5	0.2	66.8
SO ₄ (mg/L)	4	4.5	4.5	3.6	5.6	3.6	5.4	1.0	22.9
HCO ₃ (mg/L)	4	40.7	40.1	37.3	45.1	37.5	43.9	3.9	9.5
F (mg/L)	4	0.09	0.08	0.05	0.14	0.06	0.12	0.04	45.76
Si (mg/L)	4	11.8	10.8	9.5	16.3	9.8	13.9	3.1	26.0
EC (μS/cm)	4	59	59	49	68	51	67	10	16
pH	4	7.24	7.27	6.80	7.64	6.88	7.61	0.43	5.93

n number of samples, *P* percentile, *St. Dev.* standard deviation, *Coef. Var.* coefficient of variation

in a forest area are the same water chemical type than in April 2015, while FB is NaMg-HCO₃ type and PP is Na-Cl type. In the upper area, VI and MA samples are less mineralized in the humid period, while FB and PP for the same date are more mineralized. The latter two samples have some differences in Na-Mg and Cl-HCO₃ contents.

Isotopic content of water

Stable isotopes contents have been measured in samples from September 2015. These contents are representative of the rainy season and vary between -11.2 and -9.8‰ for $\delta^{18}\text{O}$ and between -76 and -66‰ for $\delta^2\text{H}$. Figure 5 shows the

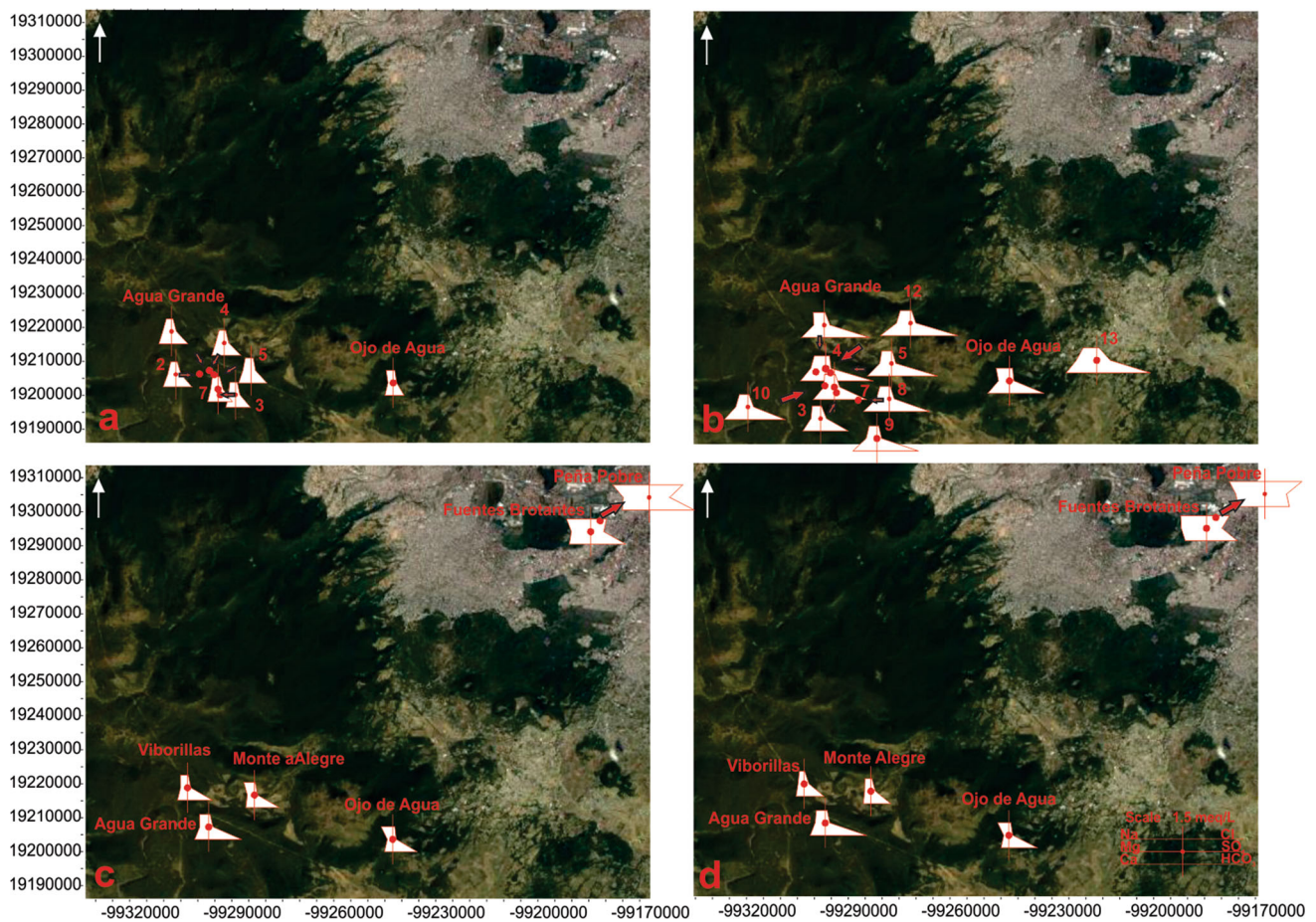


Fig. 4 Stiff diagrams of samples from two extreme hydrological conditions: dry season (April) and rainy season (August/September) for years 2013 and 2015. **a** April 2013; **b** August 2013; **c** April 2015; **d** September 2015

isotopic contents of spring and stream samples regarding the world (Craig 1961) and local (Cortez and Farvolden 1989) meteoric water lines. All samples show trends that are consistent with both meteoric lines suggesting that these waters have the same isotopic signatures of world and local precipitation and were not affected by any process, such as evaporation. In addition, they vary in a limited range, suggesting that the isotopic signature of recharge water is similar, that is to say they do not vary much in the study zone.

The chemical composition of water and its origin

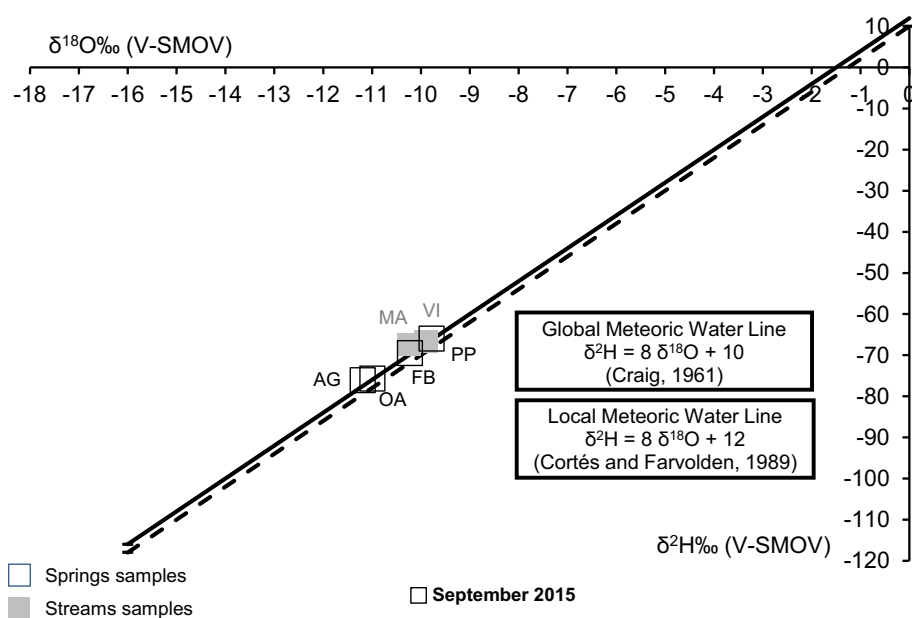
Groundwater chemistry is the result of the coupling of various physico-chemical processes such as: (1) the interaction, in forms of chemical reactions, between water and sediments or rocks; (2) the concentration of solutes by evaporation processes; (3) mixing processes between waters from different origin. The climatic, geological and geomorphological characteristics of the natural system constrain the occurrence of these processes (Edmunds et al. 2002).

In order to identify the hydrogeochemical processes that provide the chemical composition of water, the source of major

solutes was studied. The sources and processes proposed to explain the chemical composition of water are hypotheses that must be contrasted with hydrogeochemical modelling.

The main sources and processes contributing alkalinity to water are: atmospheric supply; edaphic CO₂ and silicate mineral dissolution; and organic matter decomposition from soils, landfill leachate and from urban wastewater. According to pH values measured in the field, all of them are under eight suggesting that the major part of alkalinity occurs as bicarbonate (Table 1).

The CO₂ concentrations were calculated with PHREEQC 3.0 code (Parkhurst and Appelo 2013) using field pH values and laboratory alkalinity contents. In the studied samples, CO₂ concentrations vary between 10^{-4.25} and 10⁻⁴ atm and are lower than the CO₂ rainwater concentration from unpolluted areas (approximately 10^{-3.5} atm). The low content in the case of VI, MA and PP samples could be due to the loss of CO₂ during sampling. Regarding bicarbonate contents, they increase from the upper to the lower topographic gradient, from 37 to 67 mg/L towards the urban area.

Fig. 5 Isotopic contents of water samples

The lower degree of mineralization, the temperature values and the isotopic contents observed in the samples suggest that the residence time of water from rainwater infiltration through soil and volcanic fractured rocks to the discharge on springs is very short. Therefore, the atmospheric supply and chemical reactions that occur in the first metre of the soil profile are important sources of solutes.

In volcanic rocks, silica minerals, such as albite, anorthite and K-feldspar, are very abundant. The effect of silicate dissolution on the water chemistry is the addition of cations and silica. Figure 6 shows that all samples in the study area are undersaturated with respect to albite and anorthite (Table 1), suggesting that water will actively dissolve these minerals which are important sources of Na and Ca. The AG, MA and VI samples are saturated with respect to K-feldspar, while OA, PP and FB are oversaturated. This suggests that K-feldspar dissolution is unlikely to occur and that this process is not a significant source of potassium for groundwater.

Figure 6 shows that the incongruent dissolution of albite and anorthite points out the probable formation of kaolinite except for the PP sample which is very close to the smectites stability limits. With respect to K-feldspar, all water samples are in equilibrium with kaolinite although there is no mineralogical data to confirm the presence of these clay minerals in the study area.

Another possible chemical process that can provide K and Mg to water is biotite dissolution. The product of this dissolution on the water chemistry is the addition of potassium, magnesium, silica and alkalinity. Figure 7a, b shows the relationship between Mg and K with Si. In VI and AG samples located in the upper sector of the study area, and in FB and PP samples located near Mexico City,

Si increases as Mg increases (Fig. 7a). This suggests that the dissolution of silicate minerals may be an important source of silica, while in the urban area the high magnesium contents could be indicating the presence of another source of this element such as human activities. The same behaviour is observed in relation with potassium content, suggesting that the samples located in the urban area are being affected by human activities such as waste disposal. In Fig. 7c, the samples placed on the line of dissolution of biotite suggest that this process is an important source of magnesium and potassium, mainly in the VI, AG, FB and PP samples, although in the latter two samples the presence of another source of these elements is not excluded.

Considering that nitrate is a good indicator of pollution in Fig. 8, the relationship between Mg and K with NO_3 is represented. Figures show the positive correlation between these solutes. FB and PP samples have the highest contents of these solutes, and both increase simultaneously with NO_3 , indicating that towards Mexico City water quality is being affected by human activities.

Regarding SO_4 and Cl contents, in all samples mainly those located in the forest area, the sources of these solutes seem to be from atmospheric deposition. In FB and PP samples, both contents increase simultaneously with NO_3 suggesting an additional source from anthropogenic activities, as occurs with Mg and K (Fig. 9).

Analysis of the temporal evolution of the chemical data

Figure 10 shows the temporal evolution of EC values and Cl, NO_3 , SO_4 , HCO_3 , Ca, Mg, Na and K for different time periods for the AG, VI and MA samples. These datasets

Fig. 6 *Left* saturation indexes of silica minerals versus pH values. *Right* location of the water samples in the mineral stability diagrams of albite, anorthite and K-feldspar (Modified from Tardy 1971)

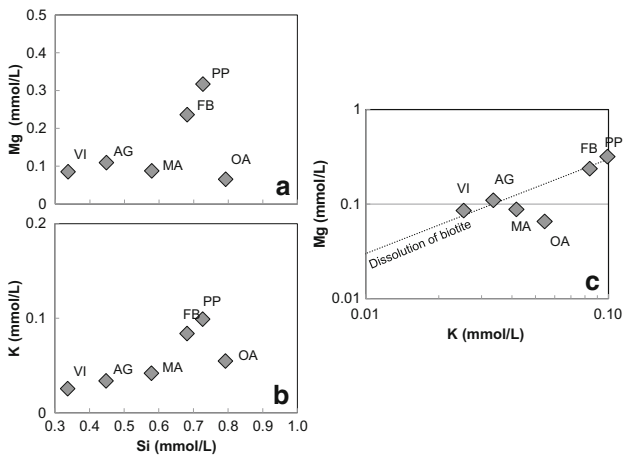
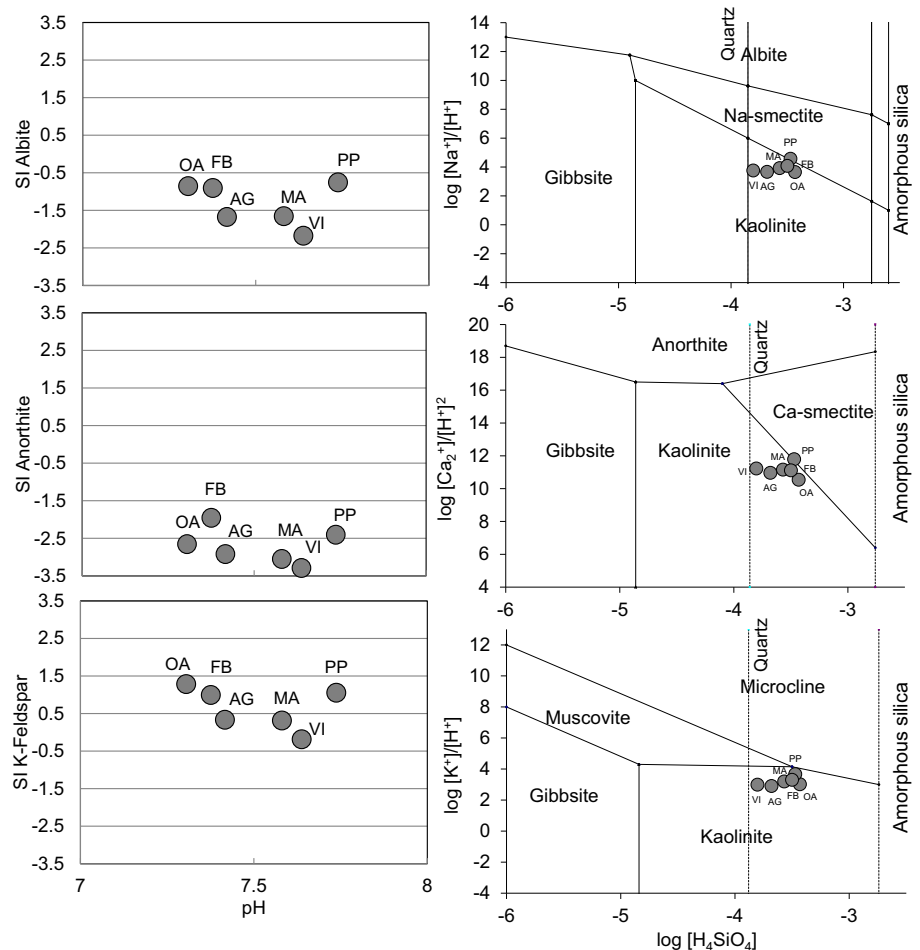


Fig. 7 **a** Relationship between Mg and Si content. **b** Relationship between K and Si content. **c** Relationship between Mg and K content

come from other sources of information, and in any case the flow values are known, which is a limitation in the data interpretation.

In AG, VI and MA samples, EC values show some temporal changes which vary between 50 and 100 $\mu\text{S}/\text{cm}$.

In these emplacements, there are a few EC data measured after 2004, at which time the PHES was implemented, but these values are similar to those measured before this date, with the exception of one value corresponding to AG, which has a EC value higher than 250 $\mu\text{S}/\text{cm}$.

In all samples, the concentrations of Cl and SO_4 behave similarly: all contents were higher before 2004, and after this date a slight decrease was observed. Chloride concentrations vary between 0.5 and 7 mg/L, while sulphate concentrations vary between 2.5 and 28 mg/L.

Large variations in nitrate concentrations were observed throughout the analysed period, although the concentrations were very low. The maximum measured value was 1 mg/L.

The HCO_3 concentrations varied between 17 and 68 mg/L and range in one order of magnitude, while concentrations of Cl, SO_4 , and NO_3 ranged over two orders of magnitude.

The contents of Ca, Mg, Na and K varied between 3 and 11, 1 and 6, 2 and 9 and 0.8 and 4 mg/L, respectively. In the three emplacements, studied cations show some temporal changes, mainly in Mg, Na and K contents.

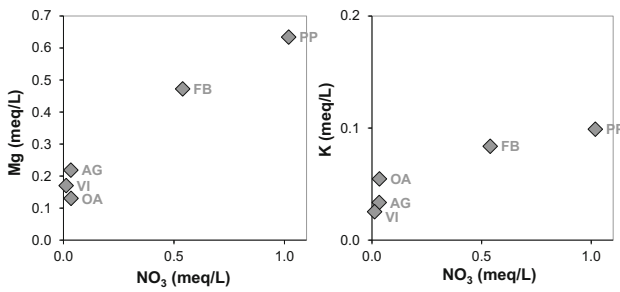


Fig. 8 *Left* relationship between Mg and NO₃ contents. *Right* relationship between K and NO₃ contents

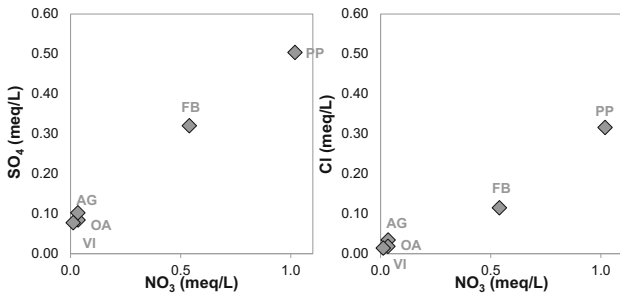


Fig. 9 *Left* relationship between SO₄ and NO₃ contents. *Right* relationship between Cl and NO₃ contents

Proposed upper limit of the natural background

As explained in “Materials and methods” section in this study, the 90th percentile is proposed as the upper limit of the natural chemical background of water in the study area (Table 3). The previous and current chemical data were considered for the calculation. Regarding the current chemical data (2013 and 2015 sampling) and in order to simplify the calculation and having seen that there are no major differences in the chemical compositions between water from springs and streams, the calculation was made by grouping all samples, since they all come from springs.

Discussion

Water salinity increases from southwest to northeast, towards the urban area. As indicated by the chemical composition and temperature values, in the forest area the low level of mineralization of water is due to the fast rate of flow through the fractured volcanic rocks. The high density of fractures of the bedrock constrain the residence time of water within the aquifer and the extent to which water–rock chemical reactions can take place.

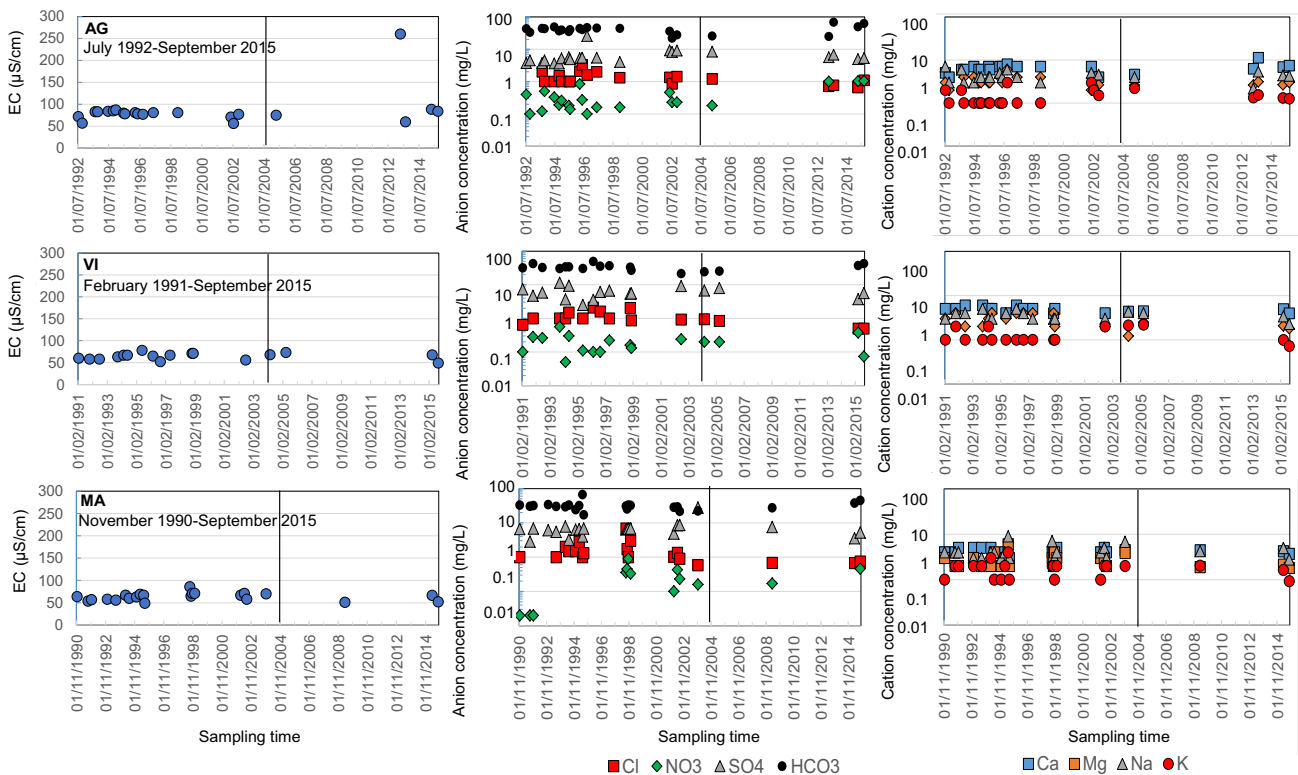


Fig. 10 Temporal evolution of EC, Cl, NO₃, SO₄, HCO₃, Ca, Mg, Na and K in samples from springs for different time periods

Table 3 Values of the 90th percentile of major chemical variables, EC and pH values for water

Parameter	<i>n</i>	90 percentile
Ca (mg/L)	81	11.6
Mg (mg/L)	81	4.0
Na (mg/L)	81	5.4
K (mg/L)	81	2.2
Cl (mg/L)	75	2.0
NO ₃ (mg/L)	61	1.0
SO ₄ (mg/L)	81	8.6
HCO ₃ (mg/L)	81	61.6
F (mg/L)	61	0.1
EC (μS/cm)	81	83
pH	81	7.70

According to the presence of minerals and the saturation indexes of water concerning them, silicate minerals dissolution can be a relevant source of sodium, calcium, magnesium, potassium, alkalinity and silica. Another important process is the edaphic CO₂ dissolution which provides alkalinity to water. The water chemical type in the upper part of the aquifer is Ca/Mg-HCO₃ and is associated with recent recharge water with a short residence time within the aquifer. The chemical composition of groundwater evolves from Ca/Mg-HCO₃ to Na-HCO₃ types along a groundwater flowpath, and near the urban area the composition of water becomes Na/Mg-HCO₃ and Na-Cl types.

This increase in salinity may be due in part to the increase in the residence time of water within the aquifer favouring the occurrence of chemical reactions. However, the effects of urbanization that is taking place where FB and PP samples are located seems to be mostly responsible for the increases in water salinity. The positive correlations between magnesium, potassium, chloride, sulphate and nitrate indicate that the chemical quality of water resources is being affected by human activities in this area.

According to Báez et al. (2009), the nitrate content measured in rainwater in Mexico City is 0.04 mg/L. The maximum nitrate content measured in the forest area is 4 mg/L, which is in accordance with natural contribution from atmospheric supply and organic matter dissolution. Towards the urban area, concentrations increase up to 36 mg/L. This increase is mainly due to the presence of areas subject to direct influx of wastewaters from septic tanks system and irregular waste disposal, which is consistent with that deduced by Jujnovsky et al. (2010) for the adjacent Magdalena River basin.

The large variation of concentrations of NO₃, Cl and, to a lesser extent Na and SO₄, in groundwater suggests that there are a number of sources and processes that

incorporate these components to water, indicating that there are likely to be anthropogenic sources for these chemical constituents. On the other hand, the low coefficients of dispersion of pH suggest that this variable is controlled by very few natural processes. The spatial variations in the chemical composition, the water temperature values, the main sources of solutes, and the deduced chemical processes are in agreement with those described by Edmunds et al. (2002) and Peñuela-Arévalo and Carrillo-Rivera (2013).

According to Birkle et al. (1998), 51% of precipitation in the Sierra de Las Cruces is lost by evapotranspiration, and this increases to about 70–80% of precipitation on the alluvial plain. Jujnovsky et al. (2012) estimated that evapotranspiration accounts for 40% of the annual rainfall for Magdalena River basin, which has similar characteristics to the study area. The isotopic data suggest that evaporation does not seem to be an important process and this observation is in agreement with the behaviour described by Ryan (1988), Cortez and Farvolden (1989) and Edmunds et al. (2002). The isotopic contents of samples from September 2015 are consistent with those measured by Cortez and Farvolden (1989), Cortez et al. (1989) and Peñuela-Arévalo and Carrillo-Rivera (2013) in this zone, and are close to the local and world meteoric lines, suggesting that the vertical infiltration of local rainfall through the fractured system is rapid.

Regarding temporal variations in the chemical composition of water, it was generally observed that during rainy season EC values of water located in the forest area were lower than those measured during the dry season. This observation is consistent with the seasonal rainfall and streamflow trends measured during this period which reach two or three orders of magnitude above those measured in April. The opposite behaviour is observed in samples located in the urban area. Given the characteristics of the places where the FB y PP samples were collected, this could be due to the contribution of water by the soil washing.

The chemical composition of springs located in the upper part of the watershed has not changed considerably over the past three decades, and there are no major discernible trends in the compiled water chemical data.

Given the increased deforestation and the population growth of Mexico City in the study area during the last decades, the fact that the chemical characteristics of water remain stable, or show a slight variation in the contents of some compounds, could be considered as a positive impact of the implementation of PHES programs. The rapid rate of flow of water through fractured volcanic rocks makes these areas highly vulnerable to pollution, while deforestation represents a high risk for the regulation of the seasonal flows and to maintain the recharge quality and rate of the

aquifer. Thus, the mechanism of the PHES, through which land owners receive compensation for forest conservation and give up other land uses, has become an environmental policy instrument that has contributed to maintaining the quality of the water and the provision of an environmental service.

Despite the low density of sample points, and although this is a preliminary study, the reference levels of the natural quality of the water provision environmental service proposed for the area are a useful tool in the assessment of the PHES program. This does not exclude the necessity of implementing a monitoring program for the springs, which should be carried out not only by the official institutions responsible for the resources management, but also in the participative social-academic schemes, considering the logistical and economic requirements that this task implies.

Conclusions

After a decade of implementing the PHES in the conservation soil of Mexico City, there is a need to assess the impact of this program beyond determining whether the program complies with its state aims and the perceptions that government agencies and the community have about the benefits in terms of the protection of water resources.

In this work, perennial and intermittent springs outcropping both in the forest area and in the urban area were studied. In the forest area, the water chemical type is Ca/Mg-HCO₃ and evolves towards the urban area to Na-HCO₃, Na/Mg-HCO₃ and Na-Cl types; in the same direction, water salinity increases from 40 to 100 μS/cm.

The origin of the chemical composition of water is due to the occurrence of chemical reactions between water and rocks, although the residence time of water within the aquifer is short. The main processes identified are: dissolution of the edaphic CO₂ and the silicate minerals. These hypotheses must be contrasted with hydrogeochemical modelling. The increase in salinity towards the urban area is partly due to the increase in the residence time of water within the aquifer favouring the occurrence of chemical reactions, but it is mainly due to the presence of effluents generated by human activities, which is supported by the positive correlations between magnesium, potassium, chloride, sulphate and nitrate. On the other hand, the high coefficients of variation of these variables support the fact that there are various sources and processes that incorporate these components to water. The existence of evaporation does not seem to be an important process that affects the chemical composition of water. The isotopic signature of recharge water is the same as the rainwater for that

region, indicating that vertical infiltration of local rainfall through the fractured volcanic rocks is rapid.

Some temporal variations were observed in the chemical composition of water. EC values in the forest area vary according to the rainfall regime; during the rainy season, water is less mineralized than during the dry season, but in samples located in the urban area, water is more salinized during the humid period probably due to soil washing by the surface runoff.

From the analysis conducted with chemical background data for some of the springs studied, no considerable temporal changes in the chemical composition of water in the last 30 years were observed, which, in part, can be attributed to the implementation of PHES for the water resources conservation in the forest area.

Whereas the recharge zone in the forest areas is being protected with the application of the PHES, those areas located at the edge of the plain require the application of mechanisms for their conservation. Considering the high vulnerability of these areas to pollution, and their relevance in the water provision service to the population of Tlalpan delegation and to the recharge of the ZMCM aquifer, the environmental policy mechanisms should integrate efficient urban drainage works and solid waste disposal.

Water chemistry is an important indicator of changes in water resources. In this way, baseline chemistry of the groundwater resources in the conservation soil area is a useful reference to assess pollution trends and monitor the impacts of the water management instruments, such as PES programs, with an acceptable degree of reliability.

Acknowledgements This research was supported by the projects 155039 Basic Science, 246947 National Problems and 260199 residential sabbatical, funded by the *Consejo Nacional de Ciencia y Tecnología* (CONACYT, México). The first and fifth authors were funded by the *Consejo Nacional de Investigaciones Científicas y Técnicas* (CONICET-Argentina) and by the *Consejo Nacional de Ciencia y Tecnología* (CONACYT, México), respectively. We also thank the San Miguel and Santo Tomas Ajusco communities, particularly Moisés Reyes Flores for their continued support, and Arturo Ramos for their assistance in carrying out Fig. 1. Finally, the authors thank the anonymous reviewers for their valuable contributions to the improvement of the manuscript.

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