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Geological factors controlling occurrence and distribution of arsenic in groundwaters from the southern margin of the Duero Basin, Spain

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ABSTRACT

Groundwater from springs and boreholes on the southern edge of the Cenozoic Duero Basin (DB) of Spain has concentrations of arsenic (As) which are commonly above the EC drinking-water limit of 10 µg/L, and reach observed values up to 241 µg/L. Groundwater compositions within the sedimentary aquifer vary from Ca-HCO₃ type, variably affected by evaporation and agricultural pollution at shallow levels, to Na-HCO₃ compositions in deeper boreholes of the basin. Groundwater conditions are mainly oxidising but reducing groundwaters exist in sub-basins within the aquifer, localised flow paths likely being influenced by basement structure. Arsenic concentrations are spatially variable, reaching up to 38 µg/L in springs of the Spanish Central System (SCS) basement aquifer and up to 62 µg/L in springs from the DB. Highest As concentrations are associated with the Na-HCO₃ compositions in deep boreholes (200–450 m depth) within the DB. These have high pH values (up to 9.6) can give rise to associated elevated concentrations of V and U (up to 64 µg/L and 30 µg/L respectively). In the deep borehole waters of the DB, oxidising flows derived from the mineralised igneous-metamorphic basement and discharging via major faults, are considered the origin of the higher concentrations. Compositions are consistent with desorption of As and other anionic species from metal oxyhydroxides in an oxic environment. Under locally reducing conditions prevalent in some low-flow parts of the DB, an absence of detectable dissolved As is coincident with low or undetectable SO₄ concentrations, and consistent with loss via formation of authigenic sulphide minerals. Mitigation measures are needed urgently in this semi-arid region where provision of alternative sources of safe drinking water is logistically difficult and expensive.

KEY WORDS: Arsenic, semi-arid region, water quality, hydrogeochemistry, water policy, environmental health.

1 Introduction

A number of European countries, including France, Greece, Hungary, Italy, Portugal, Romania and Spain, have groundwater with concentrations of As above the EC drinking-water limit of 10 µg/L. In Spain, problems related to the presence of As have increased significantly in recent years. This results from the change in EC regulations and corresponding change in the Royal Decree, RD 140/2003 (BOE 45, 2003), both of which reduced the limit from 50 µg/L to 10 µg/L in line with WHO recommendations (WHO, 2011). One of the worst-affected areas of Spain is located in the Cenozoic aquifers of the Duero Basin (DB), where As contamination was first detected during routine drinking-water surveillance (Fernández et al., 2004).

Groundwater is a vital resource in the semi-arid areas of the basin and is relied upon heavily for potable supply and agricultural production. In some areas of the basin, As concentrations in groundwater reach values up to several hundreds of µg/L (maximum observation 640 µg/L from a study by Sahún et al., 2004). This situation affects the groundwater used for drinking purposes in several townships of Segovia and Valladolid. On the southern edge of the basin, concentrations are generally lower, sometimes only slightly above the limit, but sufficient to invalidate its use for drinking water. The situation has been managed by the distribution of bottled water to the local population and more recently with the installation of water treatment plants which abstract water from nearby reservoirs. These inevitably lead to an increase in costs for users. The rising demands for drinking water often cannot be met by surface-water supplies alone.

The impact on health of As exposure from drinking water has not been defined for the region. No increased incidences of bladder or lung cancer have been noted in the districts of the DB (Lopez-Abente et al., 2006; Aragonés et al., 2009). However, Aragonés et al. (2009) found a clear geographic pattern of gastric cancer incidence in Spain, with highest incidence coinciding with the DB. While gastric cancer has not been clearly linked to As exposure, environmental exposure via drinking water was highlighted as one possible cause of the distributions observed.

The study area is located close to the central-southern edge of the Cenozoic Duero Basin (Figure 1a), where a major lithological contrast exists between the sedimentary basin and the igneous and metasedimentary basement of the Spanish Central System (SCS). The Spanish-Portuguese Duero river basin is located in the north-western part of the Iberian Peninsula and contains the largest of the peninsular rivers (572 km in Spanish territory). The basin has an area of 97,290 km² and groundwater is used mainly for public supply and irrigated agriculture.

The source of As in DB groundwater is established as natural (Barroso et al., 2002, García-Sánchez & Álvarez-Ayuso, 2003; Fernández et al., 2004; Sahún et al., 2003, 2004; García-Sánchez et al., 2005; Gómez et al., 2006; Pardo et al., 2008; Moyano et al., 2008; Delgado et al., 2009). Delgado et al. (2009) found arsenic contents of 10–50 mg/kg in the Neogene sediments of the basin. Sahún et al. (2003, 2004) and Gómez et

al. (2006) related the high concentrations of As in groundwater to the sediments of the Zaratán Facies (Middle Miocene) and proposed mobilisation of arsenic by desorption from Fe and Mn oxyhydroxides, under oxidising and alkaline conditions. García-Sánchez et al. (2005) linked the release to competition between HCO_3 and arsenate for sorption sites on oxyhydroxides under oxic conditions. Although these numerous studies have provided insights into the nature and distribution of the As problem in the region, the causes of the problem are not fully resolved.

The main objective of this paper is to identify the key geological factors controlling arsenic incorporation, mobility and distribution in the aquifers and to establish their impacts on water supply.

2 Geological and hydrogeological background

The study area is located where the northern edge of the Spanish Central System overthrusts the sediments of the Duero Basin (Figure 1b). The SCS is an intraplate Cenozoic thick-skin pop-up with an E-W to NE-SW main trend. This forms the most prominent topography in the interior of the Iberian Peninsula (Gómez Ortiz and Babín Vich, 1996; De Vicente et al., 2007). The northern edge of this structural unit is bounded by the Cenozoic DB which occupies a large area of the Iberian Peninsula. Sediment infill is continental and controlled by the tectonic activity of the margins. The basement is formed by Neoproterozoic to Mesozoic SCS rocks. Tectonic features comprise a pervasive fault network and the DB southern margin is generally tectonic. The Messejana-Plasencia basic dyke (MPD), a SW–NE slightly-curved alignment stretching more than 500 km, forms one of the principal structures of the Iberian Peninsula. The northern extreme of the dyke disappears under the Neogene cover of DB (Palencia et al., 2006). It can be assumed that the clear gravimetric and magnetic lineaments in the DB reflect unveiled basement structures that must also affect the sedimentary cover. This interpretation is supported by the tectonic control of numerous stratigraphic units (Alonso-Gavilán et al., 2004).

Metalliferous minerals on the north rim of the SCS include rare occurrences of lead, copper and uranium ore (Junta de Castilla y León and IGME databases) as well as ores of W, Sn, As, Au, Zn and Ag, along with fluorite and barite. Skarns include W, Cu, Zn, Sn and Fe; episyenites contain veins of W, Cu, Zn and Sn, and greisens contain W and Cu (Jiménez Benayas et al., 1997). Secondary arsenic minerals, including scorodite, have also been recorded in some areas of SCS (e.g. Barrios Sánchez et al., 2008; Murciego et al., 2009).

The DB is the most important aquifer of the region. The aquifer is mainly unconfined, though confined sections may be identified locally at depth, associated with overlying discontinuous clay horizons. The main recharge to the DB aquifer is via meteoric infiltration of $2.28 \times 10^8 \text{ m}^3/\text{year}$ (Sahún 2004) and, in natural conditions, the main discharge is the Duero river, which is the most important drainage channel of the

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basin. Abstraction is from boreholes with depths ranging from 50 m to 450 m (the most common depth range is 160–200 m). In recent decades, with the continued abstraction of groundwater, the water level has been declining. The rivers Zapardiel and Trabancos are ephemeral, flowing only due to surface runoff (Sánchez, 2006).

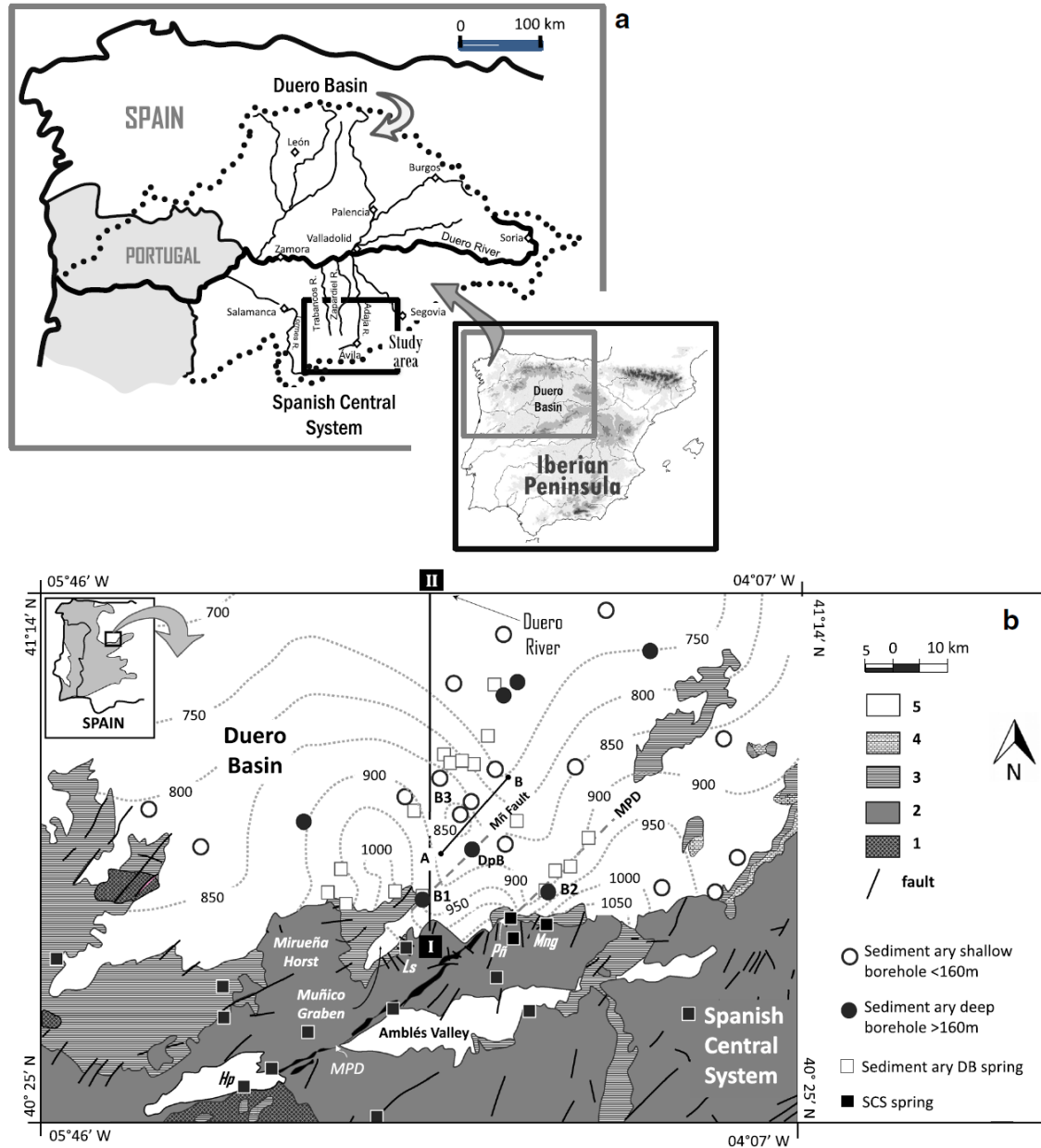


Figure 1. (a) Location of the Duero Basin and study area; (b) simplified map with the main geological and hydrogeological features, including piezometric surface. Geology: 1. Migmatite; 2. Granite; 3. Metasedimentary rocks; 4. Cretaceous carbonate; 5. Cenozoic and Quaternary sediments. MPD: Messejana-Plasencia dyke. rw: recharge water end member; hp: 'huevos podridos' spring; ls: 'la salud' spring. I-II Geological and hydrogeological cross-section, given in Figure 2a.

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The local climate is Mediterranean, although markedly continental. Temperatures average 10.5–12°C and annual rainfall is 600 mm. The lowest values (≤ 400 mm) are recorded in the south of the basin, in the rain shadow of the SCS. Winters are cold (average temperature in the winter months < 5 °C) and summers short and arid.

The general flow of groundwater in the study area is S-N, towards the Duero River (Figure 2a), although some anomalies can be identified in relation to basement structure and the probable creation of small isolated sub-basins or even perched aquifers. The groundwater piezometric surface (Figure 1b), particularly the 900 m.a.s.l. contour, shows a significant deflection near the prolongation of the major Muñico Fault (Mñ Fault) and Messejana-Plasencia dyke (MPD) systems. The groundwater contours reveal two important flow paths, linked to these fault structures originating in the SCS and extending into the sedimentary aquifer of the DB. The delineation of the subsurface faults is noted also by the location of the main spring waters in the study area. Further, an irregularity in water head is noted (850 m.a.s.l.; Figure 2b), probably again relating to the influence of the basement structure. Closely-spaced points have more than 100 m difference in piezometric level, which could be interpreted as a small perched aquifer associated with a horst structure.

3 Methods

In order to check for relationships between waters draining fissured aquifers of the SCS and sedimentary aquifers of the DB, water samples were taken in both environments from the study area: springs were sampled in SCS and both springs and boreholes in DB. Spring water samples ($n=32$) were collected during December 2010 and April 2011. Groundwaters from three boreholes in the DB aquifer (B1, B2, and B3) were sampled in November 2012. In each case, sampling took place during the rainy season.

Flowing spring samples were collected in a receptacle and field measurements taken rapidly to capture representative in-situ compositions. Samples from boreholes were taken from installed pumps or directly when artesian. Site locations were determined by Garmin GPS with UTM, which is accurate to around 5 m. On-site analysis included water temperature, pH, ORP (oxidation-reduction potential) and EC (electrical conductance, 25°C). For the first and third sampling period, a Hanna portable pH instrument (HI 9025C) was used, while a Thermo Scientific Orion 250A pH/Electrode was used for the second. The ORP electrode response was checked daily against fresh Zobell's solution. In all cases, field-measured ORP readings were corrected for the standard hydrogen electrode and Eh values are reported.

At each site, water samples were also collected for laboratory analysis. Samples for major and trace-element analysis were filtered (0.45 μm) on site into factory-new polyethylene bottles. Those collected for analysis of cations were acidified to 1% v/v with Suprapur® HNO_3 (65%) and analysed as soon as possible following collection. Unacidified groundwater samples collected for arsenic speciation were refrigerated at

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4°C and analyzed within one week of collection at the laboratories of the University of Valladolid. Chemical analyses from the first and third sampling campaign were carried out in the Instituto Geológico y Minero de España (IGME) laboratories and the second batch of samples was analysed in the British Geological Survey (BGS) laboratories. In the IGME laboratory, Ca and Mg were measured by AAS-CFA (Atomic Absorption Spectrophotometry-Continuous Flow Analysis), K and B were measured by ICP-AES, As and Sr by ICP-MS and lithium by AAS. Fluoride was determined by ion-selective electrode. In the BGS laboratories, major cations, SO₄ and trace elements including As were analysed by ICP-MS (Agilent 7500cx fitted with an Octopole Reaction System collision-cell interface). Chloride, NO₃ and F were determined by ion chromatography. Electrical charge imbalances were in all cases less than 3%.

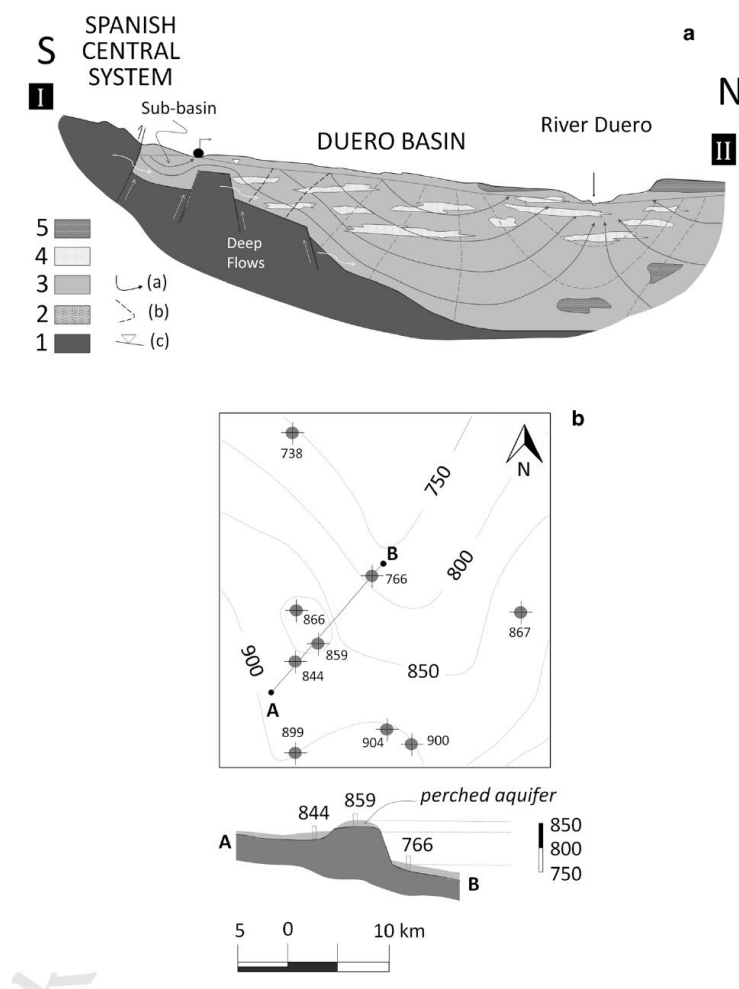


Figure 2. (a) Schematic geological and hydrogeological cross section of the contact zone between the Spanish Central System (SCS) (basement) and the southern edge of the Duero Basin (DB), and interpretation of groundwater flow (IGME, 2008; Sánchez, pers. commun., 2013). Presence of small sub-basins controlling local flow is also indicated. Legend: (1) impermeable basement; (2) gravel and conglomerate in arkosic sludge matrix; (3) Cenozoic sediment; (4) pans of sand and gravel; (5) clay and silt. a) flow line; b) equipotential line; c) piezometric surface. (b) Schematic interpretation of the anomaly outlining the piezometric isoline 850 m.a.s.l., detected against Mirueña Horst.

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Arsenic speciation was carried out on a small number of samples by HPLC-ICP-MS. Arsenite and arsenate ions were separated on an Agilent G3154A HPLC column before detection by an Agilent 7500 Series ICP-MS (Day et al., 2002; Milstein et al., 2002; Li et al., 2010; Komorowicz and Barańkiewicz, 2011). Concentrations of arsenic species in the water samples were quantified by interpolation in the respective linear calibration plots, obtained for concentrations 0.5-100 µg/L. Sample dilution was required in some cases.

In addition to the collected groundwater samples, 20 analyses of good quality (full analysis and analytical charge imbalances <5%) were selected for the defined study area from the water-quality network of the Duero River Basin District ('Confederación Hidrográfica del Duero', MAGRAMA). The data, considered representative of borehole water in the study area, derive from samples collected in 2008 (autumn and summer), 2009 (autumn), and 2010 (summer and winter).

4 Results

The chemical compositions of the groundwaters are mainly Ca-HCO₃, mixed-cation-HCO₃ and Na-HCO₃ types. Table 1 shows the main hydrochemical facies in the different environments and Figure 3 shows the distributions in a Piper diagram. Representative chemical analyses for groundwaters are shown in Table 2, and summary statistical data are summarized in Table 3.

4.1 SCS groundwater

Fifteen spring water points sampled in the northern sector of the SCS near the contact with Cenozoic DB sediments, indicate a large range in pH from slightly acidic to strongly alkaline (range 5.85–9.98). Carbonate reactions in the carbonate-rich aquifers are likely important processes, with generation of high pH values and presence of CO₃ in a minority of high-pH samples. The groundwaters are usually oxidising with redox potentials (Eh values) up to 473 mV. By contrast, two springs ('La Salud' (Ls) and 'Huevos podridos' (Hp) show much lower values (around 17 and 115 mV respectively) and are characterized by a smell of sulphide, in correspondence with low concentrations of SO₄ (<1 mg/L). The range in concentrations of sulphate for the springs is large (up to 148 mg/L, median 15 mg/L).

TDS values are in the range 38–1270 mg/L, the highest values located near the contact with DB. The hydrochemical facies of the SCS springs are Na-HCO₃ (46.5%), Ca-HCO₃ (46.5%) and Ca-Cl (7%) (Table 1). Sodium (6-106 mg/L, median 15 mg/L) is the most prevalent cation in the higher areas of the SCS. Under the oxic conditions, nitrate concentrations are high in some samples, with a variation between <0.5 mg/L and 113 mg/L (NO₃), and a median of 17 mg/L. Concentrations of Fe and Mn are correspondingly usually low (median values of 0.8 and 10 µg/L respectively).

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Table 1
Percentages of main hydrochemical facies.

Hydrochemical Facies	Spring waters In SCS	Spring waters In DB	Shallow Boreholes (DB)	Deep Boreholes (DB)
Bicarbonate waters	93%	64%	60%	60%
Chloride waters	7%	0%	27%	40%
Other	0%	36%	13%	0%
Calcium waters	53%	100%	54%	0%
Sodium waters	47%	0%	33%	100%
Other	0%	0%	13%	0%
Ca-HCO ₃ facies	46.5%	64%	46%	0%
Na-HCO ₃ facies	46.5%	0%	14%	60%
Na-Cl facies	0%	0%	27%	40%
Other	7%	36%	13%	0%

Table 2
Representative analyses of groundwaters from the study area.

Sample		'La Salud'	'Huevos Podridos'	Peñalba Pñ	Mingorría Mng	DB46	DB47	DB53	DB56	SB6	S21	DpB	B1	B2	B3
Groundwater type		Spring SCS	Spring SCS	Spring SCS	Spring SCS	Spring DB	Spring DB	Spring DB	Spring DB	Borehole MAGRAMA	Borehole MAGRAMA	Borehole MAGRAMA	Borehole DB	Borehole DB	Borehole DB
Borehole depth m	-	-	-	-	-	-	-	-	-	35	70	450	220	270	160
Spring elevation m	1183	1021	1064	1025	922	985	846	1032	-	-	-	-	-	-	-
Latitude °N	40.71	40.48	40.77	40.75	40.84	40.80	41.04	40.80	40.92	41.20	40.87	40.80	40.80	40.98	
Longitude °W	4.98	5.32	4.75	4.66	4.62	4.94	4.80	5.00	5.54	4.78	4.84	4.93	4.67	4.91	
Sample date	Dec-10	Dec-10	Apr-11	Apr-11	Apr-11	Apr-11	Apr-11	Dec-10	May-08	Dec-10	Jun-10	Nov-12	Nov-12	Nov-12	
Temperature °C	9.4	5.7	10.9	10.4	11.8	11.7	11.6	11.7	18.2	13.7	25.2	16	17	9.9	
SEC ^a	µS cm ⁻¹	260	391	946	1660	nd	nd	nd	556	497	188	674	347	310	257
pH	units	9.98	7.86	7.27	7.44	7.36	6.98	7.24	7.19	7.53	9.38	9.22	9.62	9.41	9.34
Eh	mV	17	115	390	397	400	421	404.9	409	nd	nd	nd	428	401	27
HCO ₃	mg l ⁻¹	99	99	317	532	158	288	250	286	191	70	276	252	189	109
CO ₃	mg l ⁻¹	nd	nd	nd	nd	<1	<1	<1	<1	nd	nd	nd	4.83	6.04	8.5
Cl	mg l ⁻¹	13.0	56.0	71.9	147	36.5	45.8	119.2	32.8	16.9	13.5	16.7	15	16	15
SO ₄	mg l ⁻¹	19.0	28.0	64.9	148	59.9	91.6	66.8	4.32	34.4	<1	33.6	22	22	17
NO ₃	mg l ⁻¹	<0.5	<0.5	72.5	113	132	118	146.1	16.3	27.1	<0.5	2.40	2	4	5
Ca	mg l ⁻¹	1.0	<1	120	130	68.2	135	132	57.3	45.6	2.80	<1	1	1	1
Mg	mg l ⁻¹	3.0	1.0	21.8	66.8	15.3	15.9	32.9	26.1	11.6	2.50	0.50	2	3	7
Na	mg l ⁻¹	51.0	89.0	38.4	106	43.3	32.4	24.2	16.4	25.8	25.5	139	118	91	50
K	mg l ⁻¹	<1	1.0	2.9	25.0	5.8	4.5	9.9	6.1	1.40	1.20	0.50	<1	2	<1
Facies		Na-HCO ₃	Na-HCO ₃	Ca-HCO ₃	MixCa- MixHCO ₃	Ca- MixHCO ₃	Ca- MixHCO ₃	Ca- MixHCO ₃	MixCa- MixHCO ₃	Ca-HCO ₃	Na-HCO ₃	Na-HCO ₃	Na-HCO ₃	Na-HCO ₃	Na-HCO ₃
F	mg l ⁻¹	6.9	14	0.32	<0.01	0.15	0.49	0.366	0.36	2.55	0.21	2.26	2.0	3.0	0.6
SiO ₂	mg l ⁻¹	31.6	30.1	34.3	29.4	37.4	47.2	52.3	9.99	nd	nd	nd	15.3	15.3	0.5
Sr	µg l ⁻¹	17.9	19.7	792	1310	652	971	1693	270	nd	nd	nd	nd	nd	nd
Mn	µg l ⁻¹	0.92	5.0	0.90	0.40	<0.2	0.40	<0.2	<0.2	10	4.00	1.0	0.71	0.57	6.46
Fe _T	µg l ⁻¹	2.3	nd	8.0	3.0	2.0	3.0	1.0	2.0	10	170	10	20	<15	42
Li	µg l ⁻¹	100	300	44	137	33	31	61	24.0	nd	nd	nd	nd	nd	nd
Mo	µg l ⁻¹	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.71	1.01	64.9
B	µg l ⁻¹	86	824	<10	72.0	<10	<10	<10	<10	nd	nd	nd	190	113	<100
V	µg l ⁻¹	nd	nd	7.10	19.8	6.70	18.7	13.9	0.20	nd	nd	nd	63.6	47.6	0.11
As	µg l ⁻¹	0.76	1.72	37.6	32.4	19.1	9.57	23.1	1.32	10.0	1.0	90	138	241	2.3
Se	µg l ⁻¹	nd	nd	0.90	0.40	1.00	0.90	0.70	0.30	nd	nd	nd	1.1	<0.5	<0.5
Y	µg l ⁻¹	nd	nd	0.02	0.02	0.02	0.01	0.019	0.03	nd	nd	nd	nd	nd	nd
U	µg l ⁻¹	nd	nd	10.3	21.4	12.9	2.86	12.3	15.7	nd	nd	nd	30.3	11.7	0.05
NH ₄	mg l ⁻¹	nd	nd	nd	nd	nd	nd	nd	nd	0.32	1.95	0.05	<0.05	<0.05	<0.05
TOC	mg l ⁻¹	nd	nd	nd	nd	nd	nd	nd	nd	0.60	1.10	0.25	0.6	0.7	1.01
Sl _{calcite}	units	0.06	-	0.12	0.46	-0.29	-0.16	0.08	-0.25	-0.08	0.04	-0.23	0.20	0.02	0.02
AsIII	µg l ⁻¹	-	-	-	-	-	-	-	-	-	-	-	12.5	5.9	0.5
AsV	µg l ⁻¹	-	-	-	-	-	-	-	-	-	-	-	125.5	235.1	1.8

^a SEC: specific electrical conductance
Sl_{calcite} has been calculated using Phreeqc.

^b nd: not determined

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Arsenic concentrations in the SCS springs vary over the range 0.1–37.6 µg/L, with a median value of 1.02 µg/L. The higher concentrations are present in oxidising waters; low concentrations characterise the reducing flows. Figure 4 shows the relationship between As, pH and concentrations of anions in the spring waters. In the SCS groundwaters, the large range in pH and alkalinity in particular is observed.

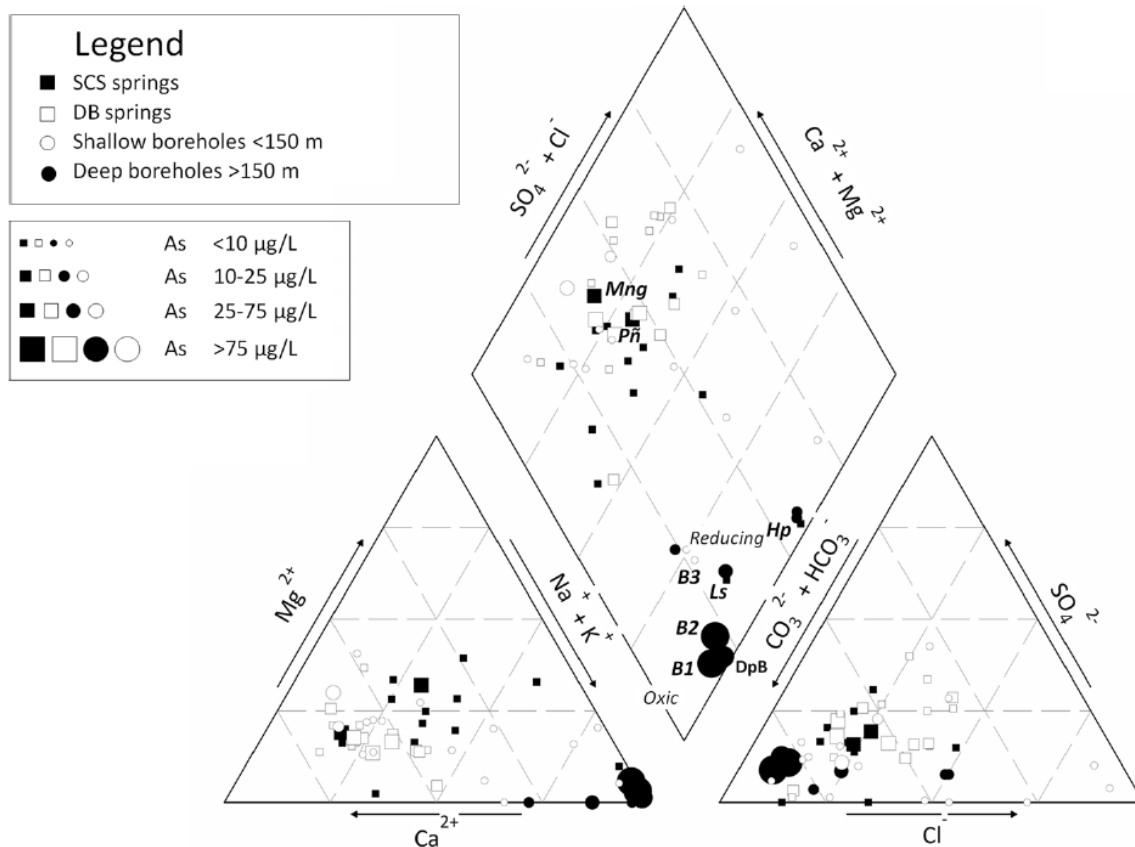


Figure 3. Piper diagram showing compositions of samples from springs and boreholes, together with As concentrations. Specific compositions of La Salud (Ls), Huevos podridos (Hp), Peñalba (Pñ) and Mingorría (Mng) springs and deep boreholes B1 and B2 are indicated. Symbol sizes denote As concentration ranges.

4.2 DB groundwater

DB spring water samples show a pH range of 6.15–7.99, which typically increases downgradient from the marginal areas to the basin plain. Saturation states with respect to calcite vary between -2.61 and 0.44. The springwaters are usually oxidising with high redox potentials (Eh values up to 484 mV). Concentrations of Fe and Mn are also low (<1-10 µg/L, <0.2-1.1 µg/L respectively) under the prevailing oxic conditions.

Values of TDS are generally higher than those found in the SCS springs (range 176-1130 mg/L). Higher TDS values are found mainly but not exclusively in discharge zones.

Concentrations of NO_3 are often high (up to 206 mg/L; Tables 2, 3b). Of the spring waters investigated, 88% exceed the EC and Spanish limit for NO_3 in drinking water (50 mg/L). Occurrence of high concentrations, above the concentrations expected from natural soil reactions, are likely to result from pollution and evaporation. Concentrations of sulphate are also generally higher than in springs from SCS (4–158 mg/L, median 54 mg/L); alkalinity is in the range 27–341 mg/L, median 171 mg/L.

The main hydrochemical facies of the DB springs is Ca-HCO_3 (64%). Calcium (27–195 mg/L, median 85 mg/L) usually correlates well with magnesium (2–33 mg/L, median 17 mg/L). Sodium has a range of 8–109 mg/L (median 38 mg/L).

Arsenic concentrations in the springs lie in the range 1–63 $\mu\text{g/L}$ (median 12.4 $\mu\text{g/L}$) and are spatially variable. Some high concentrations of uranium and vanadium are also observed (up to 55 $\mu\text{g/L}$ and 19 $\mu\text{g/L}$ respectively), consistent with the oxic conditions.

In the samples of groundwater from the boreholes, depths range from 23 m to 450 m (median 62 m), and all are completed within the DB sedimentary aquifer. The main hydrochemical facies of the shallow borehole groundwater (to 160 m) are Ca-HCO_3 (46%), Na-HCO_3 (14%) and Na-Cl (27%). For deep borehole groundwater (>160 m) the hydrochemical facies are Na-HCO_3 (60%) and Na-Cl (40%) (Table 1; Figure 3). The borehole groundwaters are commonly though not always oxidising. They have variable saturation states with respect to calcite ($\text{SI}_{\text{calcite}}$ -0.9–0.54), being most variable in shallow groundwaters (<40 m deep). Total dissolved solids range between 93 and 844 mg/L, the higher values resulting from evaporation under ambient semi-arid climatic conditions in the shallower boreholes.

Redox-sensitive elements have a large range of concentrations, though most reflect the dominance of oxic conditions in the borehole environment, particularly at shallower levels. Concentrations of NO_3 reach up to 195 mg/L, 20% exceeding the EC and Spanish limit for nitrate in drinking water. The highest NO_3 concentrations occur in boreholes with depth <40 m. The sample with the highest concentration also has a relatively high concentration of NH_4 (0.32 mg/L) and TOC (8.1 mg/L), suggestive of a pollutant origin. For the boreholes as a whole, concentrations of NH_4 lie in the range <0.1–2.9 mg/L and TOC values are 0.3–8.1 mg/L. Phosphate as PO_4 ranges from <0.1 to 0.5 mg/L and has no obvious depth relationship. Concentrations of dissolved Fe and Mn are <0.01–0.84 mg/L and <0.5–69 $\mu\text{g/L}$ respectively.

Dissolved As concentration in the borehole groundwaters reaches 241 $\mu\text{g/L}$, 60% of samples exceeding the 10 $\mu\text{g/L}$ EC drinking-water limit. Relatively high As concentrations (>10 $\mu\text{g/L}$) are found in shallow groundwaters (<40 m) but the highest are seen in deep (200–450 m) borehole waters. Here, arsenic concentrations of 90–241 $\mu\text{g/L}$ are observed. A broad positive correlation with pH is observed (Figure 4).

Giménez-Forcada, E.; Smedley, P.L. (2014). Geological factors controlling occurrence and distribution of arsenic in groundwaters from the southern margin of the Duero Basin, Spain. *Environ Geochem Health*. 36(6):1029-47. DOI: 10.1007/s10653-014-9599-2

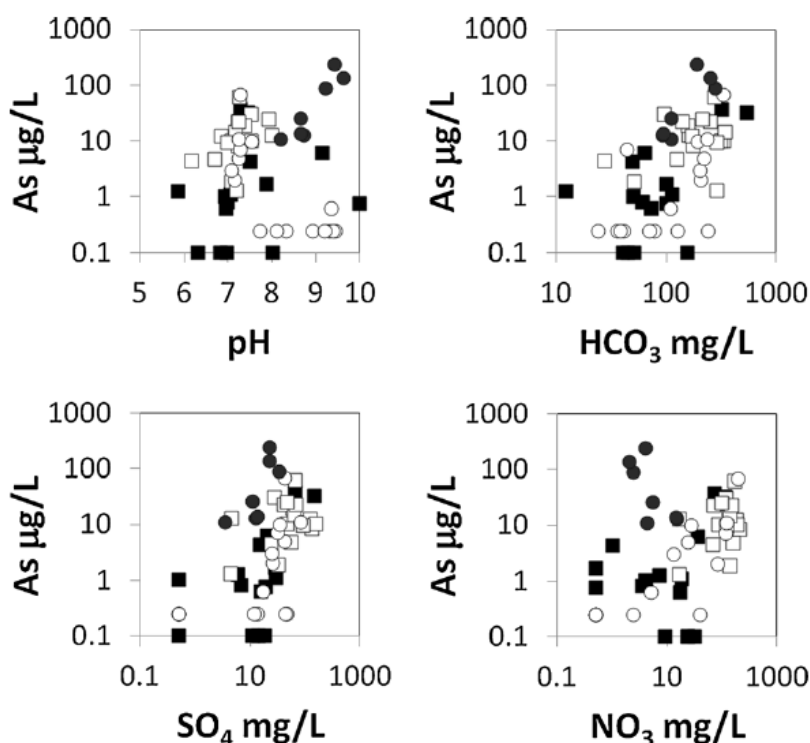


Figure 4. Relationship between As and pH, SO_4 , HCO_3 and NO_3 in groundwaters from the SCS and DB (symbols as in Figure 3 legend).

The deepest boreholes, B1, B2 and DpB, have groundwater pH values >9 (Figure 4) and samples B1 and B2 correspondingly contain CO_3 . Eh values (where measured) are >400 mV (Table 2), indicating oxic conditions. Concentrations of NO_3 are in the 2–4 mg/L range, which are low compared to the shallow groundwaters, but still indicative of oxic conditions. Other trace anion and oxyanion species also have relatively high concentrations in these groundwaters. Concentrations of fluoride are in the range 2–3 mg/L (Table 2). For boreholes B1 and B2 where trace-anion data are available, concentrations are respectively: uranium (30 µg/L, 12 µg/L), vanadium (64 µg/L, 48 µg/L), boron (190 µg/L, 113 µg/L) and molybdenum (1.7 µg/L, 1.0 µg/L).

4.3 Arsenic species

Figure 5a illustrates the thermodynamically predicted arsenic speciation for SCS and DB springs and for borehole B1 and B2, in an Eh–pH diagram for aqueous As species in the system As– O_2 – H_2O at 25°C and 1 bar total pressure (Brookins, 1988; Smedley and Kinniburgh 2002). A dominance of As(V) is indicated for all samples represented, although spring samples Hp and Ls (in which As concentration is below detection limit) lie close to the As(III) field and the uncertainty in speciation is greatest for these samples. The most thermodynamically stable As(V) species predicted for the pH and Eh ranges of the groundwater are HAsO_4^{2-} and, to a lesser extent, H_2AsO_4^- . A variation can

Giménez-Forcada, E.; Smedley, P.L. (2014). Geological factors controlling occurrence and distribution of arsenic in groundwaters from the southern margin of the Duero Basin, Spain. *Environ Geochem Health*. 36(6):1029-47. DOI: 10.1007/s10653-014-9599-2

be observed from acidic and more oxic waters (recharge areas in SCS) to alkaline and less oxidising waters (discharge areas in DB). The samples B1 and B2 are strongly alkaline and oxic, and have the highest observed As concentrations.

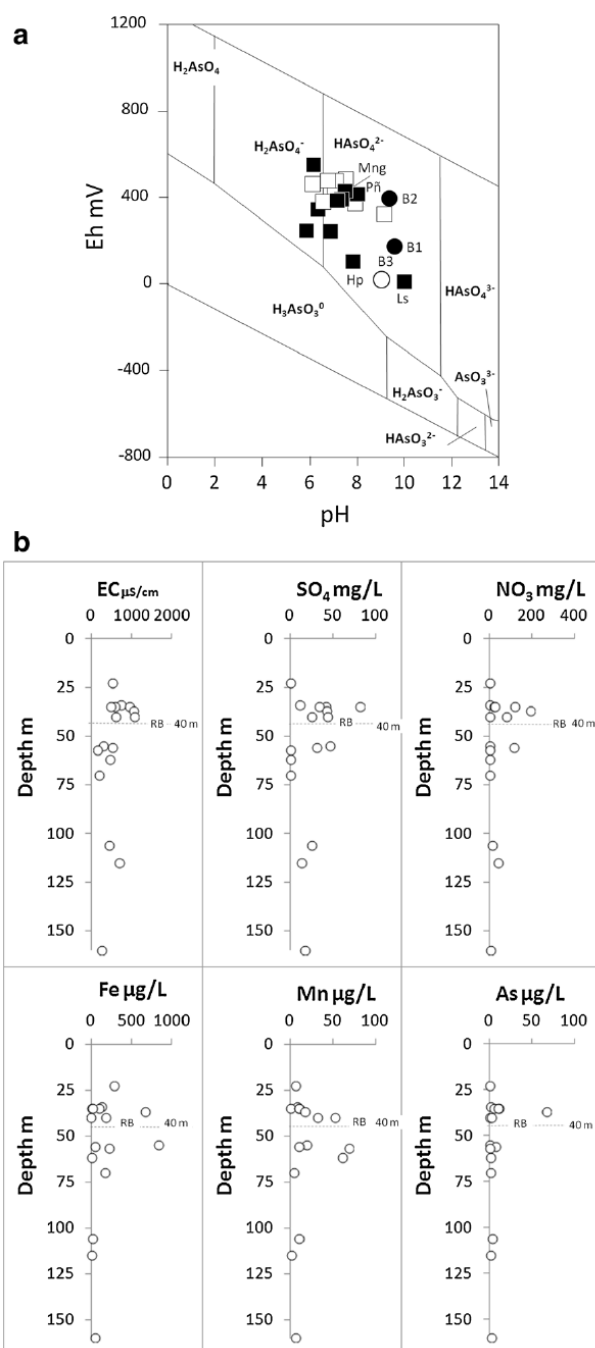


Figure 5. (a) Eh-pH diagram for aqueous As species in the system As–O₂–H₂O at 25°C and 1 bar total pressure (Smedley and Kinniburgh 2002); showing SCS springs, DB springs and boreholes B1 and B2. (symbols as in Figure 3). (b) Variation of several parameters with depth for shallow sedimentary boreholes (depths <160 m); RB (approximate redox boundary position according hydrochemical data

Giménez-Forcada, E.; Smedley, P.L. (2014). Geological factors controlling occurrence and distribution of arsenic in groundwaters from the southern margin of the Duero Basin, Spain. *Environ Geochem Health*. 36(6):1029-47. DOI: 10.1007/s10653-014-9599-2

These observations are supported by As speciation data from boreholes B1, B2 and B3 (Table 3c). These have As(III)/As_T ratios of 0.02, 0.09 and 0.22 respectively. Oxidic groundwater from boreholes B1 and B2 with high concentrations of As (138 µg/L, 241 µg/L respectively) are clearly dominated by As(V). The more reducing groundwater from borehole B3, with a lower concentration of As, has a higher proportion of As(III). Organic As species were undetected.

Table 3a
Summary statistical data for analytes in spring waters taken in the Spanish Central System.

Component	Units	Min	Max	Median	Mean [*]	Standard Deviation	10th centile	90th centile	n
Altitude	m	989	1536	1054	1118	155	995	1465	11
Eh	mV	17.4	473	354	314	143	36.9	469	11
T	°C	5.70	20.5	11.0	10.98	4.06	6.00	18.2	15
SEC	µS cm ⁻¹	85.6	1563	231	375	399	95.0	1242	15
pH	units	5.85	9.98	7.05	7.40	1.04	6.13	9.48	15
TDS	mg l ⁻¹	38	1266	159	269	318	61	932	15
Ca	mg l ⁻¹	<1	130	15.0	29.9	40.9	0.600	124	15
Mg	mg l ⁻¹	1.00	66.8	5.00	9.95	16.6	0.88	39.8	15
Na	mg l ⁻¹	6.00	106	15.0	28.7	30.7	7.15	95.6	15
K	mg l ⁻¹	<1	25.1	1.00	3.33	6.22	0.500	13.3	15
HCO ₃	mg l ⁻¹	12	532	63.0	117	136	28.8	403	15
Cl	mg l ⁻¹	3.00	147	13.0	29.6	38.6	3.40	102	15
SO ₄	mg l ⁻¹	<1	148	15.3	26.3	37.1	0.000	98.0	15
NO ₃	mg l ⁻¹	<0.5	113	16.8	23.9	31.0	0.25	88.6	15
F	mg l ⁻¹	<0.05	14.24	0.025	1.99	4.55	0.009	12.8	11
SiO ₂	mg l ⁻¹	13.20	34.3	25.4	24.1	7.22	13.8	33.7	11
Sr	µg l ⁻¹	<10	1310	63.6	279	395	5.00	999	15
Mn	µg l ⁻¹	0.030	39.7	0.805	6.02	12.9	0.039	35.6	12
Fe _T	µg l ⁻¹	<15	734	10.0	93.9	240	3.00	734	9
Li	µg l ⁻¹	<0.05	137	0.260	16.6	35.7	0.025	81.2	15
B	µg l ⁻¹	<10	135	50.0	52.5	41.5	5.00	135	9
As	µg l ⁻¹	0.09	37.6	1.02	5.90	12.0	0.126	34.5	15
U	µg l ⁻¹	0.002	21.4	0.190	6.38	9.47	0.002	21.4	5

^{*}Non-detects treated as half-detection-limit values

5 Discussion

5.1 Groundwater from springs

As observed in previous studies of spring waters in Ávila province, the concentration of arsenic generally is higher in groundwater from the DB aquifer than in the SCS basement (Giménez-Forcada et al., 2010a,b).

The highest values of arsenic in spring waters collected from the SCS are found in two springs located very close to the DB contact, in the locations of Peñalba (Pñ) and Mingorría (Mng). These are oxidising (Eh values 390 mV and 397 mV respectively) Ca-HCO₃ waters. They also have relatively high concentrations of uranium and vanadium, with uranium concentrations reaching among the largest observed in the spring-water dataset (21.4 µg/L). These can be considered dissolved species since the concentrations of Fe and Al are low (each less than 10 µg/L) and the colloidal contribution therefore negligible.

Giménez-Forcada, E.; Smedley, P.L. (2014). Geological factors controlling occurrence and distribution of arsenic in groundwaters from the southern margin of the Duero Basin, Spain. *Environ Geochem Health*. 36(6):1029-47. DOI: 10.1007/s10653-014-9599-2

Table 3b
Summary statistical data for analytes in spring waters taken in the Duero Basin

Component	Units	Min	Max	Median	Mean*	Standard deviation	10th centile	90th centile
Altitude	m	807	1032	915	909	65.9	818	1022
Eh	mV	386	484	409	429	36.6	389	483
pH	units	6.15	7.99	7.22	7.20	0.43	6.58	7.93
SEC	$\mu\text{S cm}^{-1}$	176	1133	528	610	262	255	983
Ca	mg l^{-1}	27	195	85.2	92.5	45.8	32.9	148
Mg	mg l^{-1}	1.83	32.9	16.9	17.1	8.57	5.01	29.4
Na	mg l^{-1}	8.20	109	38.4	43.3	25.1	14.8	82.7
K	mg l^{-1}	2.02	38.7	5.82	9.32	9.6	2.06	29.9
HCO ₃	mg l^{-1}	27.2	341	172	199	96.5	46.3	330
CO ₃	mg l^{-1}	<1	<1	-	-	-	-	-
Cl	mg l^{-1}	11.2	170	45.8	68.7	49.5	14.6	153
SO ₄	mg l^{-1}	4.33	158	54.1	61.4	43.5	4.53	138
NO ₃	mg l^{-1}	16.3	206	132	119	55.0	16.5	190
F	mg l^{-1}	0.07	0.49	0.26	0.26	0.12	0.08	0.41
SiO ₂	mg l^{-1}	9.99	52.3	36.8	36.1	13.2	11.7	51.9
Sr	$\mu\text{g l}^{-1}$	179	1893	652	801	507	252	1733
Mn	$\mu\text{g l}^{-1}$	<0.2	1.10	0.10	0.30	0.30	0.10	0.94
Fe _T	$\mu\text{g l}^{-1}$	<1	11.0	2.00	2.53	2.80	0.50	8.60
Li	$\mu\text{g l}^{-1}$	1.00	99.0	33.0	37.3	24.0	9.00	78.2
B	$\mu\text{g l}^{-1}$	<10	58.0	5.00	9.06	12.9	5.00	22.0
As	$\mu\text{g l}^{-1}$	1.32	62.5	12.4	16.2	14.7	1.76	37.4
V	$\mu\text{g l}^{-1}$	0.20	18.7	6.30	7.25	4.97	2.04	15.0
Se	$\mu\text{g l}^{-1}$	0.20	1.60	0.70	0.75	0.42	0.20	1.44
W	$\mu\text{g l}^{-1}$	0.03	4.24	0.05	0.36	1.01	0.03	1.33
U	$\mu\text{g l}^{-1}$	0.03	54.91	10.2	11.1	13.0	0.05	26.2

*Non-detects treated as half-detection-limit values; n=17

Reducing conditions occur in a minority of springs taken in SCS, as shown by 'La Salud' (*Ls*) and 'Huevos podridos' (*Hp*) springs (Figure 1b). In these, pH values are alkaline and the water is of Na-HCO₃ type. In both reducing springs, dissolved arsenic concentrations below detection limit and low SO₄ concentrations can be explained by sulphate-reducing conditions favouring production of solid iron sulphide, with resultant instability of dissolved As (Lowers et al., 2007).

In the SCS sector, spring waters are distributed linearly in association with the main family of faults (NE-SW, E-W, and NW-SE). The occurrence of arsenic is likely linked to weathering of vein-hosted sulphide mineralisation identified in the SCS range. Release from these arsenic-bearing sulphide minerals by oxidation is a likely process for generating dissolved As (e.g. Schreiber et al., 2003; Appleyard et al., 2006).

The influence of the crystalline basement in the general chemistry of DB groundwater is evidenced by the springs located along the extensions of fault lines within the Cenozoic sediments (Figure 6). For DB springs, carbonate and silicate weathering reactions generate the major-ion compositions observed, along with alkaline pH values. Trace elements that commonly accumulate in water through silicate and carbonate weathering reactions, such as Si (median 17 $\mu\text{g/L}$), Li (median 33 $\mu\text{g/L}$),

Giménez-Forcada, E.; Smedley, P.L. (2014). Geological factors controlling occurrence and distribution of arsenic in groundwaters from the southern margin of the Duero Basin, Spain. *Environ Geochem Health*. 36(6):1029-47. DOI: 10.1007/s10653-014-9599-2

Ba (median 117 µg/L), and Sr (median 652 µg/L), show good inter-element positive correlations (r for Ba–Sr 0.88; Si–Ba 0.64; Li–Sr 0.85; Si–Sr 0.73).

Table 3c
Summary statistical data for analytes in borehole waters from the Duero Basin (databases MAGRAMA 2008-2010, and boreholes B1, B2 and B3)

Component	Units	Min	Max	Median	Mean [*]	Standard Deviation	10th centile	90th centile	n
Well depth	m	23	450	62	134	129	34	380	23
Temperature	°C	10	25	15	15	4	10	19	22
SEC	µS cm ⁻¹	165	1066	497	524	252	216	1013	23
pH	units	7.07	9.62	8.64	8.39	0.90	7.18	9.43	23
TDS	mg l ⁻¹	93	844	328	354	178	135	643	23
HCO ₃	mg l ⁻¹	23.8	330	109	143	89	37	266	23
Cl	mg l ⁻¹	13.5	262	26	55	63	15	171	23
SO ₄	mg l ⁻¹	<1	82	22	23	20	1	45	23
NO ₃	mg l ⁻¹	<1	195	5	29	51	1	118	23
Ca	mg l ⁻¹	<1	137	13	36	40	1	100	23
Mg	mg l ⁻¹	<1	42	7	9	11	1	27	23
Na	mg l ⁻¹	7	139	38	54	39	15	124	23
K	mg l ⁻¹	<1	49.9	1.4	3.8	10.2	0.5	5.2	23
F	mg l ⁻¹	<0.5	3.0	0.3	0.6	0.9	0.1	2.4	23
Mn	µg l ⁻¹	<0.5	69.0	6.5	14.6	19.9	0.6	57.8	23
Fe _T	µg l ⁻¹	<10	840	50	140	210	5	520	23
As	µg l ⁻¹	<0.5	241	5.0	27.9	57.7	0.0	119	23
NH ₄	mg l ⁻¹	<0.05	2.9	0.1	0.5	0.9	0.0	2.4	23
NO ₂	mg l ⁻¹	<0.05	0.1	0.0	0.0	0.0	0.0	0.1	23
TOC	mg l ⁻¹	0.25	8.1	0.9	1.2	1.5	0.6	1.6	23
AsIII	µg l ⁻¹	0.5	12.5	5.9	6.3	6.0	0.5	12.5	3
AsV	µg l ⁻¹	1.8	235	126	121	117	1.8	235	3

* Non-detects treated as half-detection-limit values.

In the DB spring waters, concentrations of As, U and V are often relatively high although the correlations between them are weak (Pearson's correlation for As-V 0.20, As-U 0.11, V-U 0.36). Uranium shows a general positive correlation with alkalinity (r value for U-HCO₃ 0.62). The overall elevated concentrations As, V and U are consistent with the observations made by Sahún et al. (2004) and Gómez et al. (2006) in previous studies of the DB. These elements are stabilised in soluble form under oxic conditions as arsenate, vanadate and uranyl carbonate species (Langmuir, 1978; Smedley et al., 2005; Naeem et al., 2007). Around 6% of analysed samples collected in DB have U concentrations in excess of the WHO (2011) provisional guideline value for U in drinking water of 30 µg/L. Desorption of these trace elements from metal oxides and stabilisation in anionic and oxyanionic form under the ambient high-pH and oxic conditions is considered a likely process for release into solution. Ferric and aluminium are known to be disseminated in the sediments (Armenteros et al., 2002; Gómez et al., 2004; and Sahún et al., 2004). Additional recorded minerals in these aquifers include authigenic pyrite, iron-titanium oxides, authigenic illite, detrital grains of white mica, biotite and organomineral compounds, and these represent potential primary sources of these trace elements (Appelo and Postma, 2006; Seddique et al., 2008; Masuda et al., 2010).

Giménez-Forcada, E.; Smedley, P.L. (2014). Geological factors controlling occurrence and distribution of arsenic in groundwaters from the southern margin of the Duero Basin, Spain. *Environ Geochem Health*. 36(6):1029-47.
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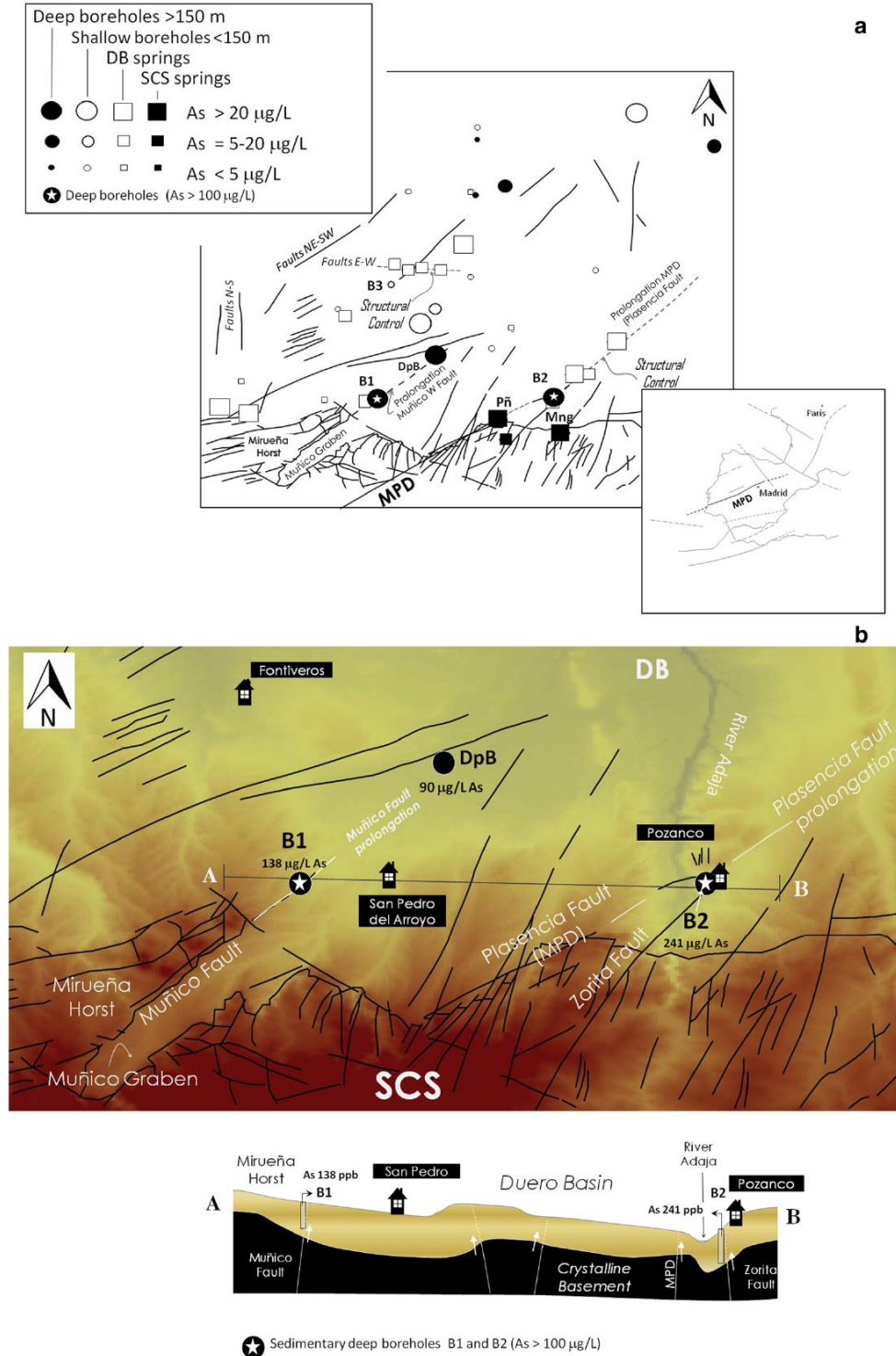


Figure 6. (a) Arsenic distribution in DB springs and boreholes in relation to the main fractures mapped by Simón (1996). (b) Topography of the area between Muñico Graben and Messegana-Plasencia dyke (Plasencia fault). The fault lines correspond to those mapped by Simón (1996). Deep boreholes B1 and B2 with the highest As concentrations are represented in a small cross sections.

5.2 Groundwater from boreholes

Arsenic-contaminated groundwater from the boreholes in the DB is also mainly associated with oxic and alkaline conditions, and as for the springs, arsenic release can be explained by desorption from metal oxides, as well as potentially from primary silicate minerals and sulphide ores.

Although factors such as pH and redox conditions play important roles in controlling the occurrence, distribution and mobility of arsenic in the groundwaters, the basement structure also exerts a significant control. The groundwater flow system in DB is influenced by the configuration of faults, which act as preferential flow zones in tectonic depressions (Vilanova et al., 2008), particularly those faults whose direction coincides with general flow path in the basin. In addition, horst and graben structures, orientated mainly NE-SW and E-W, can generate discrete hydrogeological cells.

Large variations in chemical quality occur in the aquifer, both spatially and with depth. In the shallow sedimentary aquifer (<40 m), evaporation appears to be an important factor. Evaporation can increase the concentrations of analytes including trace elements in the residual waters (e.g. Fujii and Swain, 1995; Welch and Lico, 1998; Smedley and Kinniburgh, 2002). The presence of soluble evaporite minerals may also enhance solute concentrations, although the distribution of evaporites within this sector of DB is noted to be limited.

Figure 5b shows trends in some solutes with depth for all samples from the study area for which depth information is available. For the shallow wells (<40 m), pollution, oxidising conditions and evaporation are likely factors controlling chemical composition. At 40–160 m depth, reducing conditions can be important in some samples and can affect the concentrations of As, as well as other redox-sensitive analytes (SO_4 , NO_3 , Fe and Mn; Figure 5b). The low concentrations of As observed at depth are consistent with As substitution into neoforming sulphide minerals under reducing conditions.

In deeper boreholes within the sedimentary aquifer (200–450 m), the dominant waters are sodium-bicarbonate facies with alkaline pH (>9) and high values of arsenic (up to 241 $\mu\text{g/L}$), associated with an oxidising environment. The most plausible hypothesis to explain this composition is the contribution of oxidising flows following the main direction of faults in DB. Faults behave as effective conduits for groundwater flow and influence the recharge of the basin. These deep flow paths (coming directly from the basement and also through the discontinuities within the sedimentary basin) can also transport dissolved As from As-enriched zones in the SCS, potentially enhanced from the DB sediments, under oxic and alkaline groundwater conditions.

Basement structure consists of an alternation of horsts and grabens, associated with late or post Variscan tectonism, the main fault orientations of which are NE-SW, $\text{N}0^\circ\text{--}10^\circ\text{E}$, and $\text{N}80^\circ\text{--}90^\circ\text{E}$ (Ubanell, 1985; Ares et al., 1995; Simon, 1996; Babín and Gómez, 1997; Herrero, 1999). These structures have their manifestation on the

basement surface as large lineaments or areas with a high density of smaller lineaments. The structural forms have determined subsequent sedimentation and lithological discontinuities (Colmenero et al. 2001; Armenteros et al. 2002; Alonso-Gavilán et al. 2004). These in turn control the hydrogeological and hydrochemical features in the basin (Marchán-Sanz et al., 2010).

The major fault structures appear to control the occurrence of dissolved arsenic in the groundwaters in this area of DB (Figure 6a). The clearest example is given by groundwaters extracted from the deepest boreholes DpB, B1 and B2, which have been drilled along the main fault lines, taking advantage of the direction of preferential recharge flows. These oxidising, alkaline, sodium-bicarbonate-dominated flows have relatively high concentrations of As, U, V and F, and (albeit with limited data) appear to have high percentages of As(V).

Figure 6b shows the location of the three boreholes with highest arsenic concentration, and their location with respect to the main faults, together with a cross section showing structural control. One of the boreholes (DpB) represents deep flows (90 µg/L As; MAGRAMA database). A concentration of 138 µg/L As is found in the deep borehole B1, drilled in the prolongation of Muñico Fault, and 241 µg/L As in borehole B2, near the junction between Zorita Fault and Messejana-Plasencia Dyke (known as Plasencia Fault when it reaches DB). All these boreholes have been drilled within the sedimentary filling of DB. Plotting the piezometric surface reveals that both are within lines of preferential flow (Figure 7). Borehole B2 is an artesian borehole drilled in the vicinity of the prolongation of the Messejana-Plasencia dyke (MPD), which can be considered as a very important path flow system, where the oxic recharge water seems to travel long distances rapidly, providing waters enriched in arsenic. The interpretation of Figure 7, showing the distribution of dissolved As in relation to the main structures of the area, provides an explanation for the patchy distribution of arsenic in the groundwaters of the study area. The maximum observed values are concentrated at the prolongation of Mirueña Horst and of the MPD and Zorita Fault. In both cases, the basin fill is thin, and the influence of crystalline basement structures therefore greater. These horsts have been denominated as areas of high As, relating to structural control in an oxidising environment ('OE-SC'; Figure 7). Conversely, lower As concentrations (<5 µg/L) are located in the depressed areas on both sides of prolongation of Mirueña Horst (one corresponds to the prolongation of Muñico Graben; Figure 7). Reducing conditions appear to be responsible. Such conditions, as evidenced by low concentrations of SO₄ and NO₃, and highest As(III)/As_T ratio (borehole B3 0.22) are consistent with sulphate reduction, likely microbially mediated. This can result in precipitation of solid sulphide minerals with consequent sequestration of As (low-As, reducing environment, deep control, 'RE-DC'; Figure 7). In several locations in this sector, relevant clayey horizons can be identified in the upper 100–150 m (ITGE, 1995), which could be responsible of slower flows and reducing conditions, particularly in sub-basin areas.

Giménez-Forcada, E.; Smedley, P.L. (2014). Geological factors controlling occurrence and distribution of arsenic in groundwaters from the southern margin of the Duero Basin, Spain. *Environ Geochem Health*. 36(6):1029-47. DOI: 10.1007/s10653-014-9599-2

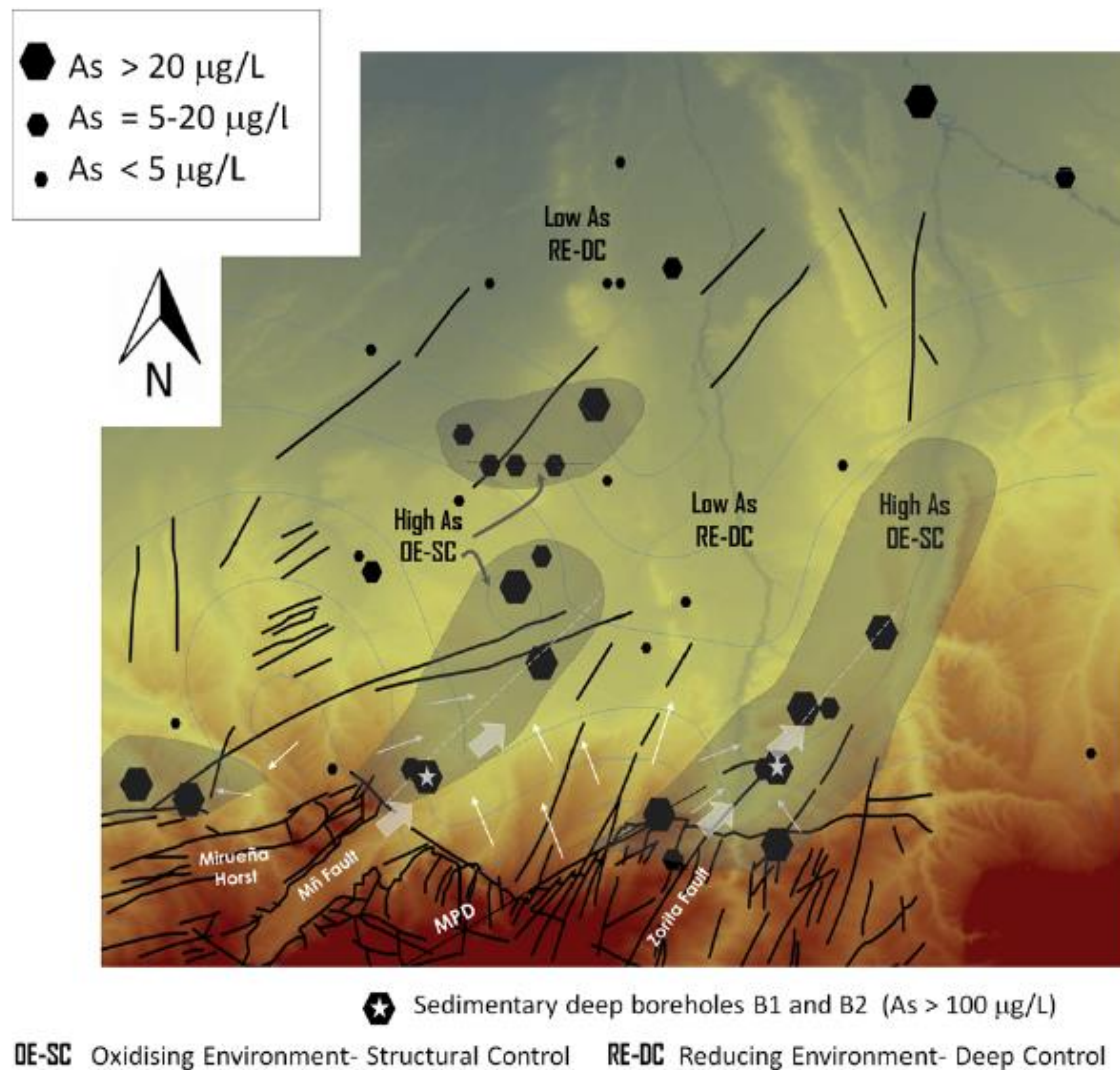


Figure 7. Arsenic distribution in groundwaters from the study area, adjacent to the main fractures. Blue contours indicate the piezometric surface. Symbol size reflects arsenic concentration.

The MPD–Zorita Fault and Muñico Fault must be considered as significant As inputs, capable of collecting and transmitting rapid flows and maintaining the oxygenated character of the recharged water. This natural groundwater flow regime is probably influenced further by flow induced by exploitation of boreholes drilled in the zone of influence of the faults.

6 Conclusions

The occurrence of arsenic in groundwaters from the southern margin of the Duero Basin is variable spatially and with depth. Relatively high concentrations of dissolved As

occur under oxic and alkaline conditions (pH 7–9.6) and the high concentrations are often accompanied by relatively high concentrations of U, V and F. Oxic and alkaline conditions occur both at shallow levels in springs and in boreholes at deeper levels (200–450 m depth) in the DB. The three-dimensional distributions of As in the DB are strongly controlled by basin structure. Basin morphology, prolongation of faults within the DB, particularly division of the underlying basement into blocks at its base, produces discrete hydrodynamic environments which result in spatial variations in hydrochemical composition. Fault zones with high permeability are particularly important preferential flow paths for oxic recharge water.

Under the oxidising conditions present in large parts of the DB aquifer, the mobility of As (as arsenate), is most likely promoted by desorption from metal oxyhydroxides in the sediments under high-pH conditions generated as a result of carbonate (and silicate reactions) in the sedimentary aquifer. Primary sulphides in the basement rocks however, are concluded to have been the primary mineral source.

In depressed areas, at levels deeper than about 40 m, reducing conditions indicated by low concentrations of dissolved SO_4 , generate correspondingly low concentrations of dissolved As. These are likely the result of As removal coincident with the neoformation of iron sulphides.

The results of this study can be of value to improve the management of groundwater resources in the area and perhaps in other sectors of DB where the problem is more severe.

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Giménez-Forcada, E.; Smedley, P.L. (2014). Geological factors controlling occurrence and distribution of arsenic in groundwaters from the southern margin of the Duero Basin, Spain. *Environ Geochem Health*. 36(6):1029-47. DOI: 10.1007/s10653-014-9599-2

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