

Natural baseline quality of Madrid Tertiary Detrital Aquifer groundwater (Spain): a basis for aquifer management

M. Elvira Hernández-García · Emilio Custodio

Abstract The Madrid Tertiary Detrital Aquifer is one of the largest and most important aquifers of Spain. This paper assesses the most relevant controls on the natural baseline quality and the dominant chemical processes within the aquifer. The hydrochemistry of the groundwater is variable despite the relative uniformity of the detrital sediments. The natural baseline is expressed as a range of values that are controlled by lithological and hydrological factors; spatial variations of groundwater chemistry are related to changes in rock type, water-rock interaction and the residence time of groundwater. The fundamental chemical processes within the Arkosic aquifer are hydrolysis of silicates, dissolution of carbonates, dissolution of evaporites (only in the vicinity of the transitional facies), ion exchange, neoformation of clays, precipitation of silica as cement, and precipitation of carbonates due to increasing temperature along the downward pathways. Some chemical and physico-chemical parameters like pH, dissolved oxygen, and hardness, and several elements like calcium, sodium, magnesium, silica, and arsenic show an evolutionary trend according to groundwater flow path. A gradual increase in arsenic concentration from recharge areas to discharge areas is observed; it is the main natural water constituent that deteriorates the quality of the

fresh Madrid groundwater as a drinking water supply. The occasionally elevated arsenic concentrations originate from natural sources. The concentration and mobility of arsenic seems to be controlled by pH-dependent anion exchange processes resulting from the evolution to Na-HCO₃ water.

Keywords Baseline quality · Geochemical processes · Hydrochemistry · Naturally occurring arsenic · Madrid Aquifer, Spain

Introduction

The EU research project called BaSeLiNe (EC EVK1-CT-1999-0006) aims to establish criteria for defining natural groundwater quality baselines and to develop a standardized Europe-wide approach which may be used in the application of the Water Framework Directive to define good chemical status of a water body due to natural circumstances, especially for the Groundwater (Daughter) Directive under preparation.

For the purpose of the BaSeLiNe project, the baseline concentration of a substance in groundwater may be defined as the concentration of a given element, species, or chemical substance present in solution which is derived from natural geological, biological, or atmospheric sources. The baseline chemistry of groundwater therefore represents pristine water without any trace of human impact. Several aquifers in Europe have been selected to show how baseline quality can be defined, under different circumstances.

The Madrid Aquifer offers the opportunity to investigate changes in the chemical characteristics of groundwater related to lithological and hydrological controlling factors. Spatial variations occur due to changes in rock type, the residence time of groundwater within the aquifer and water-rock interaction.

The focus of the study is on natural variations in water quality within the Madrid Tertiary Detrital Aquifer, that is, the freshwater part of the Tertiary sediments (detrital facies). The higher salinity waters within the transitional and chemical facies have been excluded.

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Perhaps the main water constituent that deteriorates groundwater quality as a drinking water supply is arsenic. It is considered to be natural and therefore baseline. Previous studies carried out by the first author in 1997 revealed high arsenic concentrations in some water supply wells in Madrid city (Hernández-García 1999). The arsenic concentrations exceeded the maximum level established by the current Spanish standards for drinking water (50 µg/L). Those results were probably the first report of high arsenic in the Madrid Tertiary Detrital Aquifer. Furthermore, in early 2004 the European Directive 98/93/CE on the quality of water for human consumption will come into effect in Spain. This Directive will establish a maximum contaminant level for arsenic in drinking water of 10 µg/L; consequently, the number of water supply wells affected by excessive concentrations of arsenic will be increased substantially.

The study area

The sedimentary basin of Madrid is a large tectonic depression (6,000 km²) filled with continental deposits of Tertiary age. The boundaries of the basin (Fig. 1) are the

Central System (Guadarrama Range and Somosierra Range) to the north-northwest, the Toledo Mountains to the south, and the Altomira Range to the east-southeast. The rivers Jarama, Guadarrama and Alberche drain the basin; all of them are tributaries to the Tagus (Tajo) River. Manzanares and Henares are other important rivers; both are tributaries to the Jarama River (Fig. 2A).

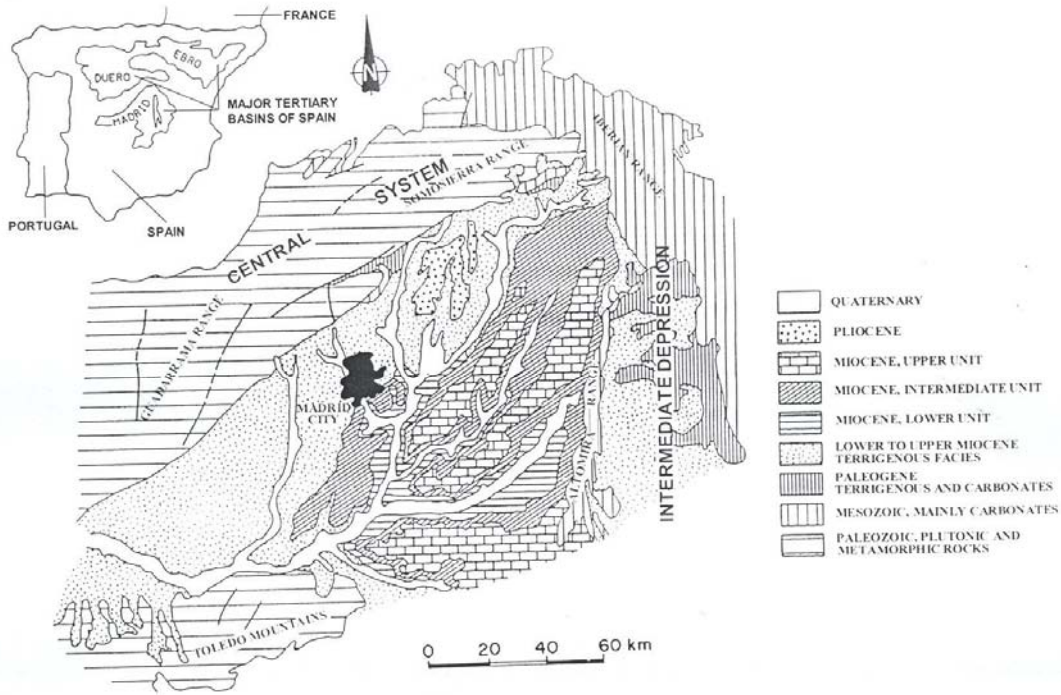
Altitudes of the Madrid Aquifer range from 650–800 m at the groundwater divides (interfluvies) and 470–600 m at the valleys. The altitudes of the surrounding mountains range from 1,000–2,400 m.

Average rainfall is between 400–500 mm/yr, and up to 2,000 mm/yr in the mountains, where part of it is as snow lasting several months; the period of July–August is dry (Hernandez-Garcia and Llamas 1995).

The aquifer system is mainly made up of detrital deposits (arkosic sands). The core area for evaluating the regional baseline groundwater quality will be the outcrop area of the detrital sediments inside the Madrid Region (around 2,500 km²). Madrid City is included in the study area (Fig. 2A). Selected data from water wells from this region are used to provide areal coverage.

The Madrid Aquifer contains high quality groundwater. The available fresh groundwater stored is at least 20,000 hm³ (1 hm³ ≡ 10⁶ m³) (Llamas and others 1996). This aquifer was declared a strategic resource for Madrid's drinking water supply in the Water Plan of the Tagus Basin (Confederación Hidrográfica del Tajo 1997). The Water Plan defines and establishes a protection area for the aquifer. Inside this protection area groundwater

Fig. 1 The sedimentary basin of Madrid and its boundaries (modified from Alonso Zarza and others 1989)



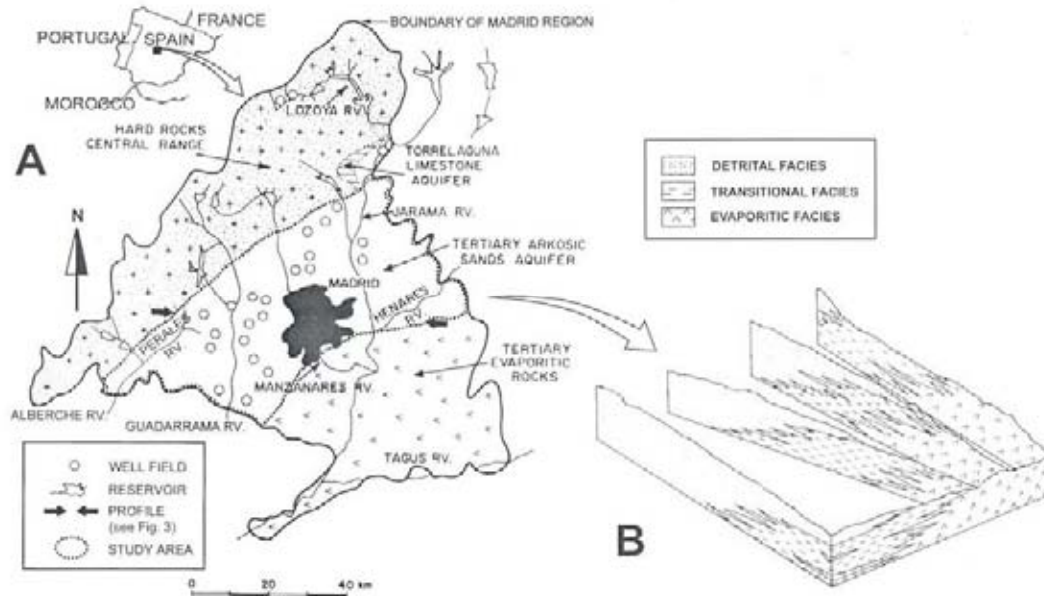


Fig. 2
 A Schematic map of the Madrid region's hydrogeological units and elements of the water supply system (modified from Llamas and others 1996). The broken line indicates the limits of the area considered in this paper. B Tridimensional diagram showing the spatial relations between facies in the sedimentary basin of Madrid. Facies are gradually related through lateral changes (modified from IGME 1989a)

resources are reserved to supply the needs of Madrid during periods of drought.

Madrid's public water supply company, called Canal de Isabel II (CYII), is responsible for the water supply of 95% of the population of the Madrid region (about 5 million inhabitants).

The great majority of the water supplied by CYII comes from fifteen surface reservoirs with a total capacity of 960 hm³. The well fields of CYII are only exploited during periods of drought. The remaining 5% of the population of the Madrid region use groundwater for their water supply. The Madrid Aquifer provides them with good quality potable water for drinking, agricultural, and stockbreeding use, as well as for industry. The public organization called Confederación Hidrográfica del Tajo (Tajo Water Authority, Ministry of the Environment) is responsible for licensing abstractions to supply these needs.

Background for the baseline of the Madrid Aquifer

An understanding of the groundwater system being studied requires information on the geology and the hydro-

geology of the system, to provide the physical framework and the background hydrogeochemistry.

Geology

The sedimentary basin of Madrid can be defined as a large intermontane tectonic depression. The structure of the basement derives from horst-graben dynamics related to the Alpine orogeny evolution of the Iberian Peninsula (Vegas and Banda 1982), which reactivated Late Hercynian fractures. The structure of the shallow basement shows preferential directions NE-SW, E-W, and NW-SE, which affects the deposition and can be seen on the sedimentary cover. Some segments of the Pliocene and Quaternary fluvial network match these structural features (Martín Escorza 1976; Capote and Fernández-Casals 1978).

The sedimentary basin of Madrid is filled with continental deposits of Tertiary age. Sediments are detrital (arkosic sands, silts and clays like smectite, illite, kaolinite, sepiolite, and palygorskite) in the vicinity of the surrounding mountains (mainly granitic rocks and schists). These detrital facies form the Madrid Tertiary Detrital Aquifer. Evaporites (gypsum, halite, polyhalite, thenardite, glauberite) and limestones (chemical facies) occur toward the centre of the basin. Between these two types of sediments there is a transitional facies, where micaceous sands, clays (smectite and sepiolite), amorphous silica, marl, limestone and gypsum are common. Facies are gradually related through lateral changes (Junco and Calvo 1984). The spatial relations between facies are shown in Fig. 2B.

The aquifer system is mainly composed of quasihorizontal lenses of arkosic sands surrounded by clay and silt. Smectite, kaolinite and illite appear to be the most common minerals in the clay fraction (IGME 1989b). These continental sediments that form the aquifer were

deposited by the coalescence of alluvial fans from the Central Range and the Toledo Mountains in the framework of a dry and warm climate during the Tertiary age (López Vera 1977; Calvo Sorando and García Yagüe 1985). The thickness of the Tertiary deposits usually exceeds 1,000 m and may be up to more than 3,000 m in the deepest parts (Cadavid 1977; Fig. 3).

Hydrogeology

Four main hydrogeological units can be distinguished in the Madrid region (Fig. 2A):

1. Central Range (3,000 km²) formed mainly by basement (low permeability) Paleozoic age schists and granitic rocks.
2. Cretaceous limestones (200 km²) forming isolated aquifers; the only relevant one is the Torrelaguna Limestone Aquifer, which is directly connected to the Jarama River.
3. Tertiary arkosic sands (2,600 km² inside the region; total outcrop area 6000 km²) which form the Madrid Tertiary Detrital Aquifer; this sedimentary basin behaves as a medium-to-low permeability formation; it is a key element for the Madrid water supply system.
4. Tertiary evaporites (2,300 km²) of low permeability, containing high salinity groundwater, even brine.

The Madrid Tertiary Detrital Aquifer can be considered regionally as an heterogeneous, anisotropic water-table aquifer. The estimated recharge is around 100–200 hm³/yr (Llamas and López Vera 1975). On a local scale, hydraulic

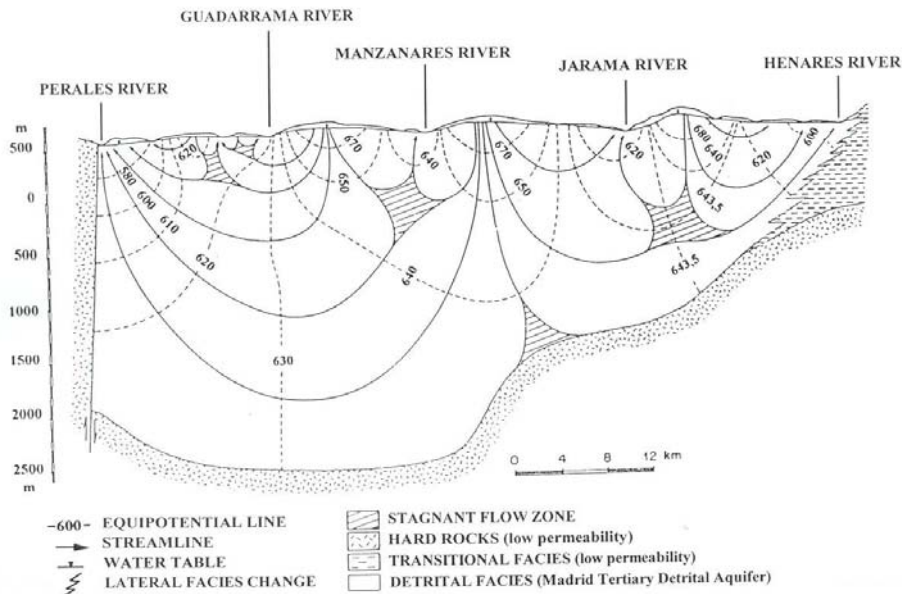
conductivity changes sharply in a random fashion, but on a regional scale statistical studies have shown a pattern in these changes which can be related to the geology. As a first approximation, a homogeneous, anisotropic hydraulic conductivity is assumed. Horizontal conductivity is about 0.10–0.25 m/day; vertical conductivity seems to be 50–200 times smaller (Martínez Alfaro 1980).

Since the 1970s (Llamas and López Vera 1975) it has been recognized that Madrid Aquifer recharge is mainly produced by infiltration of rainwater falling directly on the Tertiary interfluvies. The discharge occurs at the valley bottoms. Local, intermediate and regional flow systems corresponding to Tóth's scheme (Tóth 1963) seem to be present. In agreement with Hubbert's theory (Hubbert 1940), hydraulic head decreases with depth in the recharge areas, and increases with depth in the discharge areas. This conceptual model was initially based on conventional regional studies of the piezometric levels. Later on it was checked by means of several digital flow models (Carrera and Neuman 1982).

Mathematical models (finite-difference digital models) show water residence times that are usually less than five to ten thousand years for groundwater flowing through the upper part of the aquifer (up to 500 m deep), but may become hundreds of thousands of years when the flow paths correspond to intermediate or regional flows (Llamas and Martínez Alfaro 1981). Groundwaters with very different residence times in the aquifer converge in the discharge areas. According to Fernández Uribe and others (1985) the flow system explains the possible existence of water samples with abnormal geochemical characteristics corresponding to stagnant flow zones (Fig. 3). The two-dimensional vertical cross-section models of Llamas and Martínez Alfaro (1981) and López-Camacho

Fig. 3

Cross-section showing the undisturbed groundwater flow pattern in the Madrid Basin (modified from Herráez and Llamas 1982). See Fig. 2 for location



and López García (1979), and the three-dimensional digital flow models of Carrera and Neuman (1982), Martínez Alfaro (1982), and Virgós and others (1983) seem to confirm the existence of regional flows. Such models indicate that most of the natural recharge (up to 85–90%) follows local flows in the uppermost part of the aquifer (approximately up to 500 m deep).

Figure 3 shows the flow system obtained for a steady state vertical profile that is approximately perpendicular to the contour lines of the upper limit of the regional saturated zone.

Background hydrogeochemistry

Groundwater obtains its chemical and physico-chemical characteristics in three hydrochemical environments: a) rainfall; b) the unsaturated zone, and; c) the saturated zone.

Data on the chemical composition of the rainwater are scarce in the research area but there is information for localities not far away. Within the Madrid urban area, data show a salinity increase (mainly SO_4^{2-}) due to the burning of heating fuel and due to combustion engines (Fernández Patier and others 1989; Table 1). Nevertheless, the impact of this polluted rain on the Madrid Aquifer has not yet been detected in exploitation wells (Fernández Uría and others 1985) as vertical penetration velocity of rainfall water is typically less than 0.3 m/yr according to recharge rate and groundwater content, when considering diffuse flow. Most diffuse contaminants are still in the upper few tens of metres in the recharge areas and affect only the shallow screens of wells, although this may be a significant contribution. Deeper penetrations are possible in multi-screened wells or through unprotected well annuli if groundwater head decreases with depth. The excess of SO_4^{2-} relative to seawater also shows the important continental contribution of salts, and an excess of Na^+ is explained by the hydrolysis of silicate dust by acidic rain, which also contributes high concentrations of Ca^{2+} from carbonate dust grains. In Madrid, the 1988 chloride mean value was around 0.6 mg/L (Table 1). The chloride concentration of rainwater due to evapotranspiration increases the content by 15–20 times. There is information on rainwater composition for localities close to Madrid. In San Pablo de los Montes (Toledo), the chloride median value for the period 1984–2000 was around 0.7 mg/L, and in El Casar (Guadalajara), the chloride median value for the period June 2001–July 2002 was 0.8 mg/L; the ion ratio $r\text{Cl}^-/r\text{Br}^-$ median value (r means concentration in meq/L) in El Casar for the same period is 456, with a maximum mean value of 980 in spring, the rainy season.

The unsaturated zone in the interfluvies is around 50 m thick. Its upper part is covered with vegetated soil over most of the area. The remainder of the area is built-up. It is well recognized that the soil exerts a strong influence on the chemistry of the water that infiltrates through it, mainly because of the PCO_2 increase. In Madrid soils, the PCO_2 ($10^{-1.5}$ bar) is estimated to be about one hundred times higher than that of rainwater. The fundamental chemical processes within the unsaturated soil are: a) dissolution of evaporites, if any exist (only in the transitional and chemical facies); b) hydrolysis of silicates, and; c) dissolution of carbonates. Dissolution of evaporites does not increase the DIC (total dissolved inorganic carbon) but the hydrolysis of silicates in an open system (constant PCO_2 in the soil gas) increases the DIC; the dissolution of carbonates increases the DIC even in a system closed to CO_2 . ^{18}O and ^2H values for infiltrated water remain constant through the unsaturated zone (Fernández Uría and others 1985).

The saturated zone is considered a closed system in relation to CO_2 . There are no known sources of deep CO_2 or oxidizable organic matter. Besides, the three processes described for the unsaturated zone can be relevant here too: the neoformation of clays, the precipitation of silica as cement, and the precipitation of carbonates due to increasing temperature along the downward pathways (Fernández Uría and Llamas 1983). With regards to isotopic characteristics (Herráez 1983), no significant changes are expected in the initial values of ^{18}O and ^2H during the groundwater transit through the saturated zone. Changes in the values of ^{13}C and ^{14}C may be observed as a consequence of the previously mentioned reactions between water and aquifer matrix, and ^{14}C values decrease in groundwater with a long residence time in the aquifer. The initial composition of the infiltrated groundwater was studied during the 1980s by sampling small springs and dug wells (Toves Argüello 1983; Sahuquillo Poveda 1984). The commanding factor in this case seems to be the lithology of the recharge area. In the arkosic sands, hydrolysis of silicates and dissolution of small amounts of carbonates prevail. These waters are of the calcium-bicarbonate type; the DIC does not usually exceed 3.5 mmol/L; saturation indices (log) with respect to calcite and dolomite are negative; silica concentration is high (30–50 mg/L). In the transitional facies, dissolution of carbonates and some evaporites is more important than silicate hydrolysis. Waters are of the calcium-magnesium-bicarbonate type; typically the DIC is greater than 8 mmol/L; waters are supersaturated with respect to calcite and dolomite. In the evaporitic facies waters are of the

Table 1
Mean rainwater chemical composition data for the Madrid City area (mg/L). Data from 1988 (Fernández Patier and others 1989)

Season	N° of analysis	Cl^-	NO_3^- -N	SO_4^{2-} -S	Na^+	K^+	Mg^{2+}	Ca^{2+}
Winter	7	0.49	0.13	2.01	1.04	0.08	0.26	3.89
Spring	31	0.53	0.45	1.3	0.59	0.11	0.15	2.63
Summer	9	0.58	0.58	2.35	0.62	0.11	0.32	5.48
Autumn	13	0.66	0.16	1.49	0.61	0.17	0.35	3.55
Total	60	0.57	0.33	1.56	0.62	0.13	0.25	3.35

calcium-magnesium-sulphate type and the salinity is high (up to 5000 $\mu\text{S}/\text{cm}$).

The geochemical evolution of water within the saturated zone was evaluated during the 1980s and 1990s by sampling water wells with depths between 50–600 m (Rubio 1984; Fernández Uría 1984; Yélamos 1986; Molina 1989; Coletto 1994; Hernández-García 1999). The spatial variations of water isotopes were studied during the 1980s by Herráez (1983) and Fernández Uría and others (1984). Groundwater within the relatively uniform sediments of the detrital facies of the Madrid Aquifer has significantly variable chemical characteristics. To explain such variation, three main controlling factors have been considered: a) the lithology of the unsaturated recharge area; b) the flowpath length and the residence time of groundwater along the streamlines, and; c) the lithology of the aquifer matrix. In summary, and according to those authors, three main geochemical groups of groundwaters can be distinguished (their characteristics are defined in Table 2):

1. Recharge waters in detrital facies.
2. High residence time waters within detrital facies.
3. High residence time waters within detrital and transitional facies.

According to Table 2, the ^{18}O and ^2H contents from deep wells in the discharge areas (high residence time waters) are smaller than those from the interfluvial areas (recharge waters). Besides, the ^{14}C results show that the samples taken from the discharge areas are older. Herráez (1983) suggested that the lighter and older waters are palaeowaters; in other words water infiltrated during a cooler period.

BaSeLiNe sampling

A total of 61 groundwater samples and 166 solid samples were taken in the year 2000 in the Madrid area. The collection was carried out by the first author of this paper in the framework of a research contract between the Department of Geodynamics (Complutense University, Madrid, Spain), and the Geological Survey of Spain (Instituto Geológico y Minero de España, IGME), in part to additionally support the BaSeLiNe project. The analytical results from the data set were used for deriving baseline conditions. Field analyses of unstable parameters

(temperature, electrical conductivity, pH, redox potential and dissolved oxygen) were also carried out.

The groundwater samples were collected from water supply wells. Sampling and preservation in the field were performed following a specific methodology (Scalf and others 1981; Coletto and Maestro 1988; Krajca 1989; ITGE 1997). The water was passed through a 0.45 μm filter before analysis. Water samples were collected in 1 L pre-washed polyethylene bottles. Water samples for the determination of cations and heavy metals were preserved in the field with suprapure HNO_3 to $\text{pH}<2$. Water samples for the determination of anions and silica were preserved at 4 °C. The chemical analyses were performed at the Laboratory of the IGME; the samples were analysed for a full range of inorganic species and parameters: TDS (total dissolved solids), COD (chemical oxygen demand), CO_3^{2-} , HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- , NO_2^- , NH_4^+ , SiO_2 , PO_4^{3-} , Ca^{2+} , Na^+ , Mg^{2+} , K^+ , Al , Ag , As , Sb , Br^- , Ba , B , Cd , Co , Cr , Cu , Fe , Mn , Hg , Ni , Pb , Se , Sr , Tl , V , F , Li , Zn . The As, Se, Hg, Sr, Tl and Li were analysed by atomic absorption spectrometry with hydride generation. The Cl^- and Br^- were determined by high performance liquid chromatography (HPLC). The rest of the elements were analysed using inductively coupled plasma with mass spectrometry (ICP-MS).

Water samples are from wells and have been taken after a sufficient pumping time. Typically wells are multiscreened and obtain groundwater from a wide range of depths. This means that samples are a mixture of different waters. Results cannot be ascribed to a unique depth and they do not necessarily show that the water is at equilibrium with the minerals.

Results and discussion

Analytical results: summary of statistics

Table 3 shows a selection of analytical results for the groundwater samples. A summary of statistics for Madrid groundwater is given in Table 4. Chemical and physico-chemical parameters, major elements and trace metals are shown with maxima, minima, mean, standard deviation, median, 10th percentile and 90th percentile values calculated from all of the data (61 samples).

The major ion chemistry of the groundwater in the Madrid Tertiary Detrital Aquifer is summarised in a boxplot in

Table 2
Main groundwater geochemical groups from the Madrid Aquifer, and their characteristics

Water category	Geological facies	Water type	pH	EC $\mu\text{S}/\text{cm}$	HD meq/L	SiO_2 mg/L	DIC mmol/L	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	^{14}C pmc
Recharge	Detrital	Ca- HCO_3	<8.3	<500	<5	>20	<3.5 (*)	~ -7.5	~ -49	75
High residence time	Detrital	Na- HCO_3	>8.3	<600	<1	<20	<3.5 (*)	~ -9.0	~ -62	<40
High residence time	Detrital + Transitional	Mg-Na- SO_4 -Cl	>8.3	>1500	<24	>40	>3.5	~ -9.0	~ -62	<40

EC=electrical conductivity; HD=hardness; DIC=dissolved inorganic carbon; (*) except in the vicinity of the transitional facies

Table 3
Selected analytical data from the 61 groundwater samples from the Madrid Tertiary Detrital Aquifer

Municipality	Well depth (m)	Temp. (°C)	pH	EC (µS/cm)	O ₂ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	HCO ₃ ⁻ (mg/L)	CO ₃ ²⁻ (mg/L)	NO ₃ ⁻ (mg/L)	Na ⁺ (mg/L)	Mg ²⁺ (mg/L)	Ca ²⁺ (mg/L)	K ⁺ (mg/L)	As (mg/L)	V (mg/L)	F (mg/L)	B (mg/L)	Fe (mg/L)	Mn (mg/L)
Humanes	119	19.2	7.61	825	7	93	88	202	0	88	144	15	32	5	<0.010	0.00142	<0.5	0.01	<0.1	<0.025
Cubas	200	19.6	8.14	759	8	76	106	190	0	24	134	6	31	4	0.011	0.00204	0.9	0.04	<0.1	<0.025
Brunete	50	17.4	7.37	1293	7	97	330	282	0	120	154	58	164	8	0.010	0.00361	<0.5	0.03	<0.1	<0.025
Villamanta	112	17.7	7.44	383	8	53	6	121	0	32	19	8	56	1	<0.010	0.00262	<0.5	0.01	<0.1	<0.025
Sevilla la Nueva	160	19.9	6.96	412	7	26	4	163	0	8	39	8	27	2	<0.010	0.00182	<0.5	0.01	<0.1	<0.025
Villaviciosa de Odón	50	14.7	6.87	487	4	74	33	172	0	11	22	7	72	1	<0.010	0.00255	<0.5	0.01	<0.1	<0.025
Villa del Prado	115	17.7	6.85	587	7	87	19	86	0	132	49	14	67	1	<0.010	<0.001	<0.5	0.21	1.24	1.03
Torrejón de la Calzada	60	16.9	7.23	936	6	123	124	318	0	96	82	52	113	4	0.015	0.01317	<0.5	0.09	<0.1	<0.025
Torrejón de Velasco	16	19.0	7.82	1192	7	50	252	404	0	180	18	112	137	10	0.038	0.06528	0.87	0.03	<0.1	<0.025
Villanueva del Pardillo	180	19.0	8.34	307	7	24	8	146	3	5	56	5	13	0	0.013	0.00913	0.58	0.01	0.11	<0.025
Pozuelo de Alarcón	497	19.9	7.8	258	6	15	3	151	0	6	41	8	15	1	<0.010	0.00528	<0.5	0.01	<0.1	<0.025
Paracuellos de Jarama	115	17.2	8.4	343	7	15	5	212	0	12	92	2	5	1	<0.010	0.00635	<0.5	0.02	<0.1	<0.025
Daganzo	126	16.8	7.48	743	7	65	13	344	0	24	46	28	86	1	0.014	0.00945	0.71	0.01	<0.1	<0.025
Alcobendas	200	19.9	7.63	431	9	17	27	213	0	22	47	8	48	2	0.039	0.0156	<0.5	0.02	<0.1	<0.025
Arroyomolinos	265	23.5	9.05	424	4	17	58	165	9	5	102	1	6	1	0.036	0.02833	0.73	0.04	<0.1	<0.025
Villaviciosa de Odón	140	18.7	8.57	355	11	22	37	160	2	9	77	2	11	1	0.016	0.0335	0.55	0.02	<0.1	<0.025
	140	16.7	7.19	258	9	50	138	200	0	54	42	10	116	1	<0.010	0.00499	0.52	0.01	<0.1	<0.025
	300	20.6	7.12	447	6	44	4	216	0	6	54	4	45	2	<0.010	0.00193	<0.5	0.01	<0.1	<0.025
Villa del Prado	300	17.1	6.86	549	4	66	44	213	0	8	33	7	92	1	<0.010	0.00439	<0.5	<0.005	<0.1	<0.025
San Sebastián de los Reyes	120	20.4	8.94	411	5	37	52	131	7	5	108	1	2	0	0.091	0.07497	<0.5	0.03	0.14	<0.025
San Sebastián de los Reyes	300	18.2	7.87	291	7	14	3	182	0	7	37	4	35	1	0.037	0.00738	<0.5	0.01	<0.1	<0.025
San Agustín de Guadalupe	500	17.3	7.66	307	6	18	10	174	0	7	47	4	26	1	0.027	0.00749	<0.5	0.01	<0.1	<0.025
Madrid	250	25.3	7.9	442	6	28	27	233	0	5	89	4	23	2	0.03	0.00536	<0.5	0.02	<0.1	<0.025
Madrid	560	20.5	7.63	324	7	16	6	174	0	11	52	5	21	1	0.033	0.01021	<0.5	0.01	<0.1	<0.025
San Sebastián de los Reyes	70	17.9	7.77	293	9	10	3	185	0	8	21	5	42	1	0.026	0.00717	<0.5	0.01	<0.1	<0.025
Golmenar Viejo	160	16.4	7.9	257	8	14	5	154	0	4	34	3	30	1	0.079	0.01224	<0.5	0.01	<0.1	<0.025
San Agustín de Guadalupe	90	16.2	7.96	249	9	12	3	157	0	3	31	3	30	1	0.084	0.01193	<0.5	0.01	<0.1	<0.025
Paracuellos de Jarama	280	16.9	7.91	273	8	16	3	152	0	6	21	3	40	1	0.063	0.00618	<0.5	0.01	<0.1	<0.025
Alcobendas	350	23.3	8.12	312	8	16	10	174	0	4	55	3	16	1	0.045	0.00604	0.53	0.02	<0.1	<0.025
San Sebastián de los Reyes	165	16.2	8.03	808	9	58	176	278	0	20	141	16	60	6	0.037	0.01695	1.45	0.09	<0.1	<0.025
Villanueva de la Cañada	160	19.3	7.85	322	7	15	5	195	0	6	33	4	44	1	0.015	0.00745	<0.5	0.01	<0.1	<0.025
Pozuelo de Alarcón	250	19.3	8.05	276	5	8	5	181	0	5	44	4	22	1	0.045	0.00904	<0.5	0.01	<0.1	<0.025
Pozuelo de Alarcón	450	22.2	8.95	348	8	30	47	107	12	4	94	1	2	0	0.027	0.01721	<0.5	0.02	<0.1	<0.025
Gamarmá de Esteruelas	428	19.6	7.64	225	7	11	8	124	0	11	29	4	21	1	<0.010	0.00356	<0.5	0.01	<0.1	<0.025
Batres	171	23.1	8.06	239	8	13	5	129	0	6	45	2	10	1	0.013	0.01468	<0.5	0.01	<0.1	<0.025
San Sebastián de los Reyes	196	19.9	8.32	402	6	15	73	177	4	3	99	3	10	1	0.034	0.03767	0.92	0.03	<0.1	<0.025
Villanueva de la Cañada	250	18.6	8.53	332	5	16	28	174	7	2	91	1	6	1	0.065	0.03162	1.05	0.03	<0.1	<0.025
Pozuelo de Alarcón	175	18.5	8.3	306	7	17	13	191	6	8	80	3	14	1	0.04	0.02433	0.81	0.02	<0.1	<0.025
Batres	170	18.8	8.7	318	7	26	13	173	7	7	86	2	8	1	0.031	0.03504	<0.5	0.01	<0.1	<0.025
San Sebastián de los Reyes	220	20.5	8.43	414	6	24	76	164	3	7	102	3	13	1	0.027	0.04699	<0.5	0.03	<0.1	<0.025
San Sebastián de los Reyes	190	19.3	7.8	299	5	15	16	179	0	10	34	5	38	1	0.025	0.00703	<0.5	0.01	<0.1	<0.025
Paracuellos de Jarama	337	21.6	8.36	264	6	11	10	167	3	3	54	2	14	1	0.053	0.01648	<0.5	0.01	<0.1	<0.025
Madrid	95	18.5	8.52	367	7	22	18	199	6	5	38	3	30	1	0.02	0.00712	<0.5	0.01	<0.1	<0.025
Madrid	83	17.2	8.46	346	7.2	27	5	199	3	7	102	1	1	1	0.051	0.01741	0.5	0.04	<0.1	<0.025
El Casar de Talamanca	255	17.0	7.51	498	6	40	87	188	0	37	38	18	69	1	0.016	0.00379	<0.5	0.02	<0.1	<0.025
Valdeolmos	197	17.3	8.55	1016	7	135	260	193	2	3	280	6	10	2	<0.010	0.00312	1.66	0.11	<0.1	<0.025
Valdeolmos	476	21.5	7.54	345	7	22	20	193	0	8	36	8	42	2	<0.010	0.00354	<0.5	0.01	<0.1	<0.025
Valdeolmos	448	22.2	7.92	434	7	31	34	213	0	9	92	3	25	1	0.03	0.01138	0.68	0.03	<0.1	<0.025

Table 3
(Contd.)

Municipality	Well depth (m)	Temp. (°C)	pH	EC (µS/cm)	O ₂ (mg/l)	Cl ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	CO ₃ ²⁻ (mg/l)	NO ₃ ⁻ (mg/l)	Na ⁺ (mg/l)	Mg ²⁺ (mg/l)	Ca ²⁺ (mg/l)	K ⁺ (mg/l)	As (mg/l)	V (mg/l)	F (mg/l)	B (mg/l)	Fe (mg/l)	Mn (mg/l)
Alejalá	160	17.4	7.76	823	6	55	208	274	0	45	141	42	45	3	<0.010	0.02148	1.37	0.98	<0.1	<0.035
de Heras																				
Mosárid	200	17.0	7.01	322	7	15	47	125	0	39	19	8	48	1	<0.010	0.00184	<0.5	0.01	<0.1	<0.035
	252	17.8	7.3	447	7	40	85	185	0	35	40	16	71	1	<0.010	0.00378	0.57	0.03	<0.1	<0.035
	244	17.5	7.36	479	7	33	101	166	0	50	34	15	74	2	<0.010	0.00367	<0.5	0.01	<0.1	<0.035
	220	17.4	7.93	412	6	26	81	156	0	15	106	2	14	1	0.045	0.01124	0.11	0.12	<0.035	<0.035
	220	17.2	8	743	6	56	209	168	0	18	149	11	38	2	<0.010	0.0055	1.72	0.16	<0.1	<0.035
	220	17.2	7.25	377	7	30	47	141	0	33	24	11	54	1	<0.010	0.00182	<0.5	0.01	<0.1	<0.035
	360	17.8	7.55	337	6	23	35	166	0	16	15	10	56	1	<0.010	0.00106	<0.5	0.01	<0.1	<0.035
	164	15.6	8.7	332	8	20	60	149	8	2	105	1	3	1	0.089	0.02609	6.5	0.04	<0.1	<0.035
	80	18.0	8.91	403	6	28	104	156	11	3	127	1	3	1	0.077	0.03945	1.17	0.09	<0.1	<0.035
	245	17.5	8.56	443	7	27	85	169	4	3	114	1	8	1	0.071	0.03154	1.5	0.13	<0.1	<0.035

EC=electrical conductivity

Fig. 4. Figure 5 shows a cumulative probability plot for selected major elements of groundwater in the aquifer. Both figures show a wide range in concentrations, reflecting water mixtures (waters flowing within detrital, transitional and even evaporitic facies).

Hydrochemical characteristics of the Madrid Aquifer

Indicators of pollution

Three indicator inorganics are used to show the magnitude of modern contamination: nitrate, phosphate, and chemical oxygen demand (COD). Nitrate mean value is high (22 mg/L) which indicates human influence from agriculture, livestock and urban areas (leakages from damaged sewerage systems and septic tank effluents) in the water mixture. According to Custodio and Llamas (1983) the natural level of nitrate in groundwater is typically less than 10 mg/L NO₃⁻. Higher concentrations often indicates polluted groundwater, although the limit can be higher in arid lands. Around 35% of the groundwater samples contain concentrations above 10 mg/L NO₃⁻. The remainder of the samples correspond to high residence time dominated water mixtures that are free of human influence. Evapoconcentration of rainwater may produce up to 30 mg/L NO₃⁻, but most of this N is absorbed by plants, as intense arid condition recharge is not expected. The phosphate mean value is low (0.1 mg/L), and the great majority of the samples show concentrations lower than 0.5 mg/L; only one sample that was taken in an urban area shows an anomalous phosphate concentration (1.32 mg/L). COD mean value is 1.1 mg/L O₂, and the maximum value is 1.9 mg/L O₂. These values do not show a significant anthropogenic signal of oxidizable organic compounds, compatible with the high dissolved O₂ concentrations (4–11 mg/L) and oxidizing underground environment.

Hydrochemical properties of the groundwaters

Data from Tables 3 and 4 show that Ca²⁺, Na⁺ and HCO₃⁻ are the major constituents of the Tertiary detrital groundwaters. Mg²⁺, SO₄²⁻ and Cl⁻ are frequent in Tertiary transitional and Tertiary evaporitic groundwaters. The origin and distribution of these constituents is discussed further below.

As shown in Fig. 6, the rCl⁻/rBr⁻ ion ratio (r=concentrations in meq/L), when plotted against chloride for natural waters (without pollution), may help to identify groundwater origin. The marine value is 655±4; waters within detrital facies show lower values, and waters within detrital and transitional facies (even evaporitic facies, note the black dot in the upper right hand corner) show values close to or higher than marine; it is really possible that the dissolution of halite (a common mineral in the transitional and evaporitic facies) is increasing the rCl⁻/rBr⁻ ion ratio until values reach even higher than marine levels. Silica is always present, and the concentration ranges from 12–65 mg/L. Water mineralisation is low to moderate, in the range of 225–1300 µS/cm (at 25 °C) electrical conductivity. The temperature ranges from 15–17 °C if the well depth is less than 200 m, and up to 23 °C if the well

Table 4
Summary of chemical and physico-chemical parameters, and major element and trace metal concentrations, for the Madrid Aquifer

Parameters	Units	Minimum	Maximum	Mean	SD	Median	10thP	90thP
T	(°C)	14.7	25.3	18.7	2.1	18.2	16.8	21.6
pH		6.85	9.05	7.89	0.56	7.89	7.19	8.56
EC	(µS/cm)	225	1293	451	233	367	264	808
O ₂	(mg/L)	4	11	7	1	7	5	8
COD	(mg/L O ₂)	0.3	1.9	1.1	0.3	1.0	0.7	1.6
Ca ²⁺	(mg/L)	1	164	38	35	30	5	74
Na ⁺	(mg/L)	15	280	70	47	52	22	127
Mg ²⁺	(mg/L)	0	112	10	17	4	1	16
K ⁺	(mg/L)	0	10	2	2	1	1	3
HCO ₃ ⁻	(mg/L)	86	404	185	54	174	131	223
CO ₃ ²⁻	(mg/L)	0	12	2	3	0	0	7
SO ₄ ²⁻	(mg/L)	3	330	56	72	27	4	138
Cl ⁻	(mg/L)	8	135	28	23	20	10	56
NO ₃ ⁻	(mg/L)	1	180	22	34	8	3	50
PO ₄ ³⁻	(mg/L)	BDL	1.32	0.11	0.19	0.07	0.00	0.24
SiO ₂	(mg/L)	11.8	65.2	29.3	12.4	28.2	14.1	43.8
Fe	(mg/L)	BDL	1.24	0.03	0.16	0.00	0.00	0.00
Mn	(mg/L)	BDL	1.03	0.02	0.13	0.00	0.00	0.00
Li	(mg/L)	BDL	0.24	0.04	0.06	0.00	0.00	0.10
Cu	(mg/L)	BDL	BDL	-	-	-	-	-
Zn	(mg/L)	BDL	2.81	0.50	3.25	0.00	0.00	0.20
Ni	(mg/L)	BDL	0.059	0.001	0.008	0.000	0.000	0.000
Ba	(mg/L)	BDL	0.167	0.005	0.028	0.000	0.000	0.000
Sr	(mg/L)	BDL	4.27	0.16	0.60	0.00	0.00	0.52
F	(mg/L)	BDL	2.00	0.34	0.54	0.00	0.00	1.17
Br	(mg/L)	BDL	0.299	0.122	0.067	0.095	0.066	0.243
B	(mg/L)	BDL	0.21	0.03	0.04	0.01	0.01	0.09
Pb	(mg/L)	BDL	0.04	0.00	0.01	0.00	0.00	0.00
Cr	(mg/L)	BDL	BDL	-	-	-	-	-
Cd	(mg/L)	BDL	BDL	-	-	-	-	-
As	(mg/L)	BDL	0.091	0.025	0.026	0.024	0.000	0.063
Se	(mg/L)	BDL	BDL	-	-	-	-	-
Al	(mg/L)	BDL	BDL	-	-	-	-	-
Hg	(mg/L)	BDL	BDL	-	-	-	-	-
Ag	(mg/L)	BDL	BDL	-	-	-	-	-
Co	(mg/L)	BDL	BDL	-	-	-	-	-
Sb	(mg/L)	BDL	BDL	-	-	-	-	-
V	(mg/L)	BDL	0.052	0.015	0.017	0.009	0.002	0.036
Tl	(mg/L)	BDL	BDL	-	-	-	-	-

T=temperature, EC=electrical conductivity, COD=chemical oxygen demand, SD=standard deviation, 10thP=10th percentile, 90thP=90th percentile, BDL=below detection limit

depth is more than 200 m. This is compatible with a mean soil temperature of about 15 °C and a normal vertical gradient of 30 °C/km. A 2,417 m deep exploratory well in Tres Cantos, in the NE of Madrid, produced water of 87 °C (and TDS of 40,000 mg/L). Relatively warm waters indicate the sample is mostly deep water, and therefore little affected by anthropogenic contamination. The pH ranges from neutral (around 7) to alkaline (up to 9).

Most of the trace metals analysed (Fe, Mn, Cu, Zn, Pb, Cr, Ni, Cd, Sb, Se, Hg, Ag, Ba, Co, Sr, Tl and Al) are below the detection limit in the majority of the samples. Conversely, As, B, F, Li, Br and V are detectable in almost all of the samples (see Tables 3 and 4). The As concentrations are especially noteworthy, in a great number of cases exceeding the acceptable levels for drinking water. Eighteen percent of the samples analysed show As concentrations higher than 50 µg/L, the maximum level established by the current Spanish standards for drinking water; 64% of the samples show values higher than 10 µg/L, the maximum level specified by the European Directive 98/93/

CE. Remaining trace metals that are present in Madrid groundwaters (B, F, Li, Br, V) occur at concentrations below the drinking water limits.

Geochemical controls and the chemical evolution of the groundwaters in the Madrid Aquifer

Control of major components

In the detrital facies, the sodium and calcium controls are silicate hydrolysis reactions (hydrolysis of albite, anorthite, and intermediate terms); calcium and sodium concentrations up to 100 and 120 mg/L (respectively) can be found, exceeding sulphate and chloride concentrations. In the active part of the aquifer it is assumed that carbonates have already been leached and are absent. This may not be true in the deepest, low flow paths. The magnesium controls are magnesium and ferro-magnesium silicate hydrolysis reactions (biotites, illites, and so on); in general, magnesium values are less than 20 mg/L. The origin of potassium is mainly silicate hydrolysis reactions (biotites, moscovites,

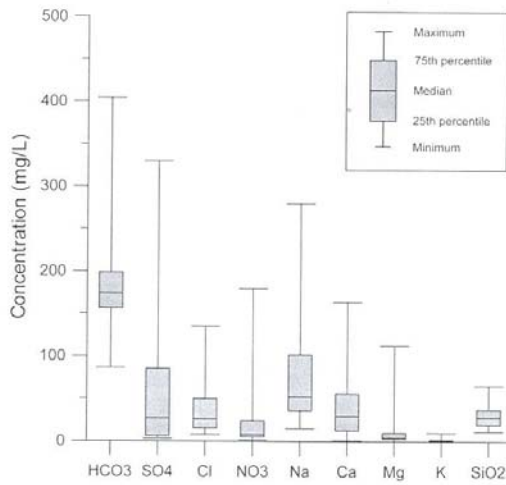


Fig. 4
Boxplot of concentrations of selected elements in the groundwater samples from the Madrid Tertiary Detrital Aquifer

orthose, microcline, and so on); its presence is not relevant in Tertiary detrital groundwaters (the mean value is 2 mg/L, because of its tendency to be absorbed during clay neof ormation (montmorillonite to illite transformation). The concentration of the bicarbonate anion can be explained as a result of the chemical reaction between soil CO₂ and water (the carbonates are absent); bicarbonate concentrations are typically less than 200 mg/L. Sulphate and chloride are mostly those contributed by rain. In the transitional facies, the main calcium controls are dissolution of evaporites and carbonates; calcium

concentrations in the range of 100–160 mg/L are frequent. The main sodium control is the dissolution of evaporites (halite); sodium values up to 300 mg/L have been observed in the mixtures. The magnesium controls are magnesium and ferro-magnesium silicate hydrolysis reactions (magnesium smectites, biotites, and so on), and the dissolution of magnesium carbonates (dolomite and magnesite); magnesium concentrations range from 30–110 mg/L. The origin of the potassium cation is silicate hydrolysis reactions (biotites) and perhaps the dissolution of potassium salts; potassium values range from 3–10 mg/L. Bicarbonate occurs as a result of the chemical reaction between CO₂ and water and the dissolution of carbonates (calcite and dolomite); bicarbonate concentrations are in the range 200–400 mg/L. Sulphate is mainly due to the dissolution of gypsum, anhydrite and polyhalite; sulphate values up to 350 mg/L have been observed. The main chloride control is the dissolution of evaporites (halite); chloride concentrations range from 50–150 mg/L.

Groundwater chemistry evolution

Spatial variations in the chemical characteristics of Madrid groundwaters are related to lithological and hydrological controlling factors: changes in rock type, residence time of groundwater within the aquifer, and water-rock interaction. A trilinear plot of major elements (Fig. 7) allows recognition of groundwater chemical types and the presence of any chemical evolutionary trends that may exist during processes of water-rock interaction.

According to this plot, the predominant groundwater types in the Tertiary arkosic sands aquifer are calcium bicarbonate and sodium bicarbonate. The arrow shows a water softening evolution trend from calcium bicarbonate to sodium bicarbonate types.

The groundwater types of calcium bicarbonate-sulphate, magnesium bicarbonate-sulphate, sodium

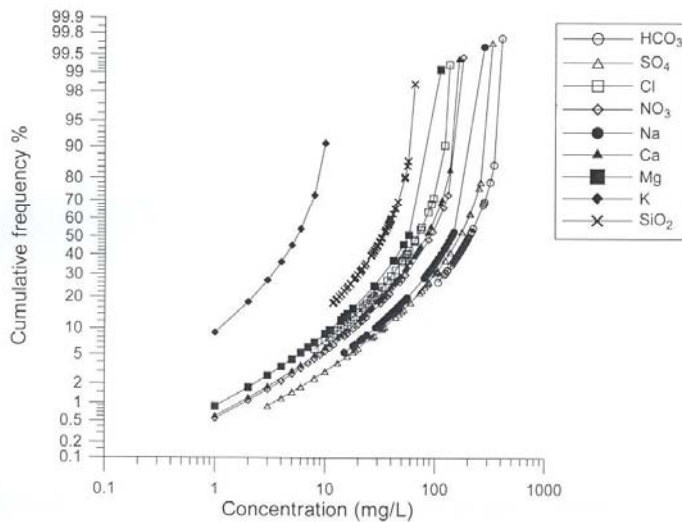


Fig. 5
Cumulative frequency plot for selected elements in the groundwater samples from the Madrid Tertiary Detrital Aquifer

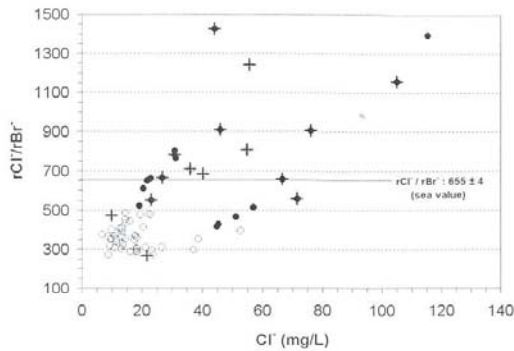


Fig. 6

Plot of the $r\text{Cl}^-/r\text{Br}^-$ ion ratio (r means concentration in meq/L) against chloride concentration for the Madrid Tertiary Detrital Aquifer. White dots: groundwater within detrital facies; black dots: groundwater within detrital and transitional facies; crosses: polluted groundwater

bicarbonatesulphate, and sodium bicarbonate-chloride are less frequent. These groundwater types represent high residence time waters within detrital, transitional and even evaporitic facies.

Two main geochemical groups of groundwaters and their characteristics are defined for the Madrid Detrital Aquifer:

- *Calcium bicarbonate type groundwaters*. These represent the recharge (low residence time) waters in detrital facies, found in shallow wells in the interfluvial zones.
- *Sodium bicarbonate type groundwaters*. These represent high residence time waters within the detrital facies:

- a) in shallow and deep wells in the discharge areas, and
- b) in deep wells (>400 metres deep) in the interfluvial zones.

Some of the most important characteristics are given in Table 5.

Data from groundwater in the Na-HCO_3 areas present Na^+/K^+ (meq/L) ratios higher than 100, being much lower those of the Ca-HCO_3 areas. If K^+ is controlled by clay neoformation reactions, this means that Na^+ is incorporated into water in the Na-HCO_3 areas.

The scatter diagram of Fig. 8 shows a negative correlation between pH and calcium. The correlation coefficient is -0.7 . Calcite saturation indices are plotted versus pH in Fig. 9. Taking into account deviations due to water mixing in the wells, it seems that the water tends to be at equilibrium with calcite along the flow path (increasing pH) except at the lower pH values, the recent recharge waters where possible carbonates are already leached by groundwater flow.

The scatter diagram of Fig. 10 shows a positive correlation between pH and cation exchange ratio, with a correlation coefficient of $+0.7$. Consequently, the general trend is toward a dominance of alkaline ions (mostly Na^+) from the recharge areas to the discharge areas, in such a way that sodium concentrations tend to increase along the groundwater flow path as calcium and magnesium concentrations decrease; only initially the ratio is held at about 0.5.

Apart from the pH, hardness, and the major elements calcium, sodium and magnesium, other groundwater constituents that show an evolutionary trend according to groundwater flow path are dissolved oxygen, silica and arsenic. The mild consumption of oxygen in oxidation processes (traces of organics, sulphides) seems to be the

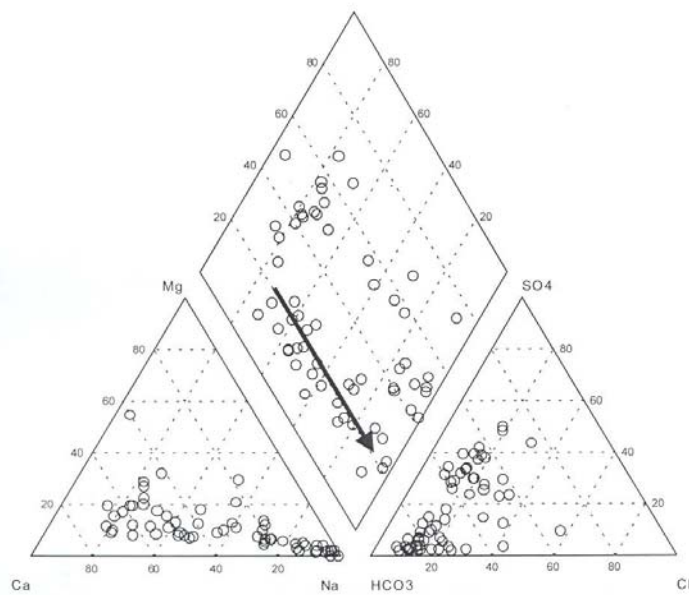


Fig. 7

Trilinear plot of major elements in the groundwater samples from the Madrid Tertiary Detrital Aquifer

Table 5
Most important characteristics of the two main groundwater types of the Madrid Tertiary Detrital Aquifer

Water type	pH	EC $\mu\text{S/cm}$	Na^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	HD meq/L	Redox
Ca- HCO_3	~ 7 (< 8.3)	< 500	< 30	40–100	< 20	< 5	oxidizing
Na- HCO_3	> 8.3	< 600	40–120	1–40	~ 1	< 1	oxidizing

EC=electrical conductivity, HD=hardness

main reason for the decrease in O_2 that has been observed from recharge areas (7–11 mg/L) to discharge areas (4–6 mg/L). The silica concentrations also decrease from recharge areas (20–65 mg/L) to discharge areas (8–15 mg/L). The scatter diagram of Fig. 11 shows the negative correlation between pH and silica (correlation coefficient of -0.7); the most probable explanation of the decreasing trend, especially at the upper pathways, may be the neoformation of clays and/or simple precipitation of silica as cement. Supporting the hypothesis, the scattered diagram of Fig. 12 also shows a negative correlation between pH and magnesium (correlation coefficient of -0.6). Sepiolite saturation indices are plotted versus pH in Fig. 13; it seems that the water tends to be at equilibrium with sepiolite (c =crystalline) along the flow path (increasing pH). Short groundwater flow paths in the detrital area preserve recharge water conditions, modified by the results of silicate weatherings, as carbonates are assumed to be previously leached. The penetration of anthropogenic pollutants is limited by the slow movement in an open system to surficial recharge. This means that only shallow groundwaters and short-time residence spring water will show contamination, except for the short-circuit effect of wells with downward decreasing head. The same is valid for longer flow paths, but in this case it has been shown in the previously mentioned studies that water is isotopically lighter, corresponding to cooler periods or to recharge at higher altitude, moving through the subhorizontal coarse discontinuous layers from piedmont interfluvial areas to the basin valleys. The difference of 1.5‰ (Table 2) means an elevation difference of about 500–700 m. However, the evolution to high pH and high alkaline ion ratio groundwaters does not seem to be explained by only silicate weathering processes and carbonate and silica precipitation. Cation exchange is a possible explanation; however, as the ground is not in cationic equilibrium with the groundwaters present, this means groundwater has a very low renovation rate, or a very long residence time, in agreement with the results of mathematical models. It is not well known if similar effects could be obtained from precipitation of solutes due to temperature changes, which may go in the opposite way.

Near the transitional facies, evaporite salts are mostly held in the low permeability layers, which explain why they have not been fully leached and diffuse slowly to the renovated coarse layers.

Presence of As, and the main factors that control the mobility of As in groundwaters

Figure 14 shows an arsenic contour map in $\mu\text{g/L}$. A gradual increase of arsenic concentration from recharge areas (values $< 10 \mu\text{g/L}$) to discharge areas (values up to

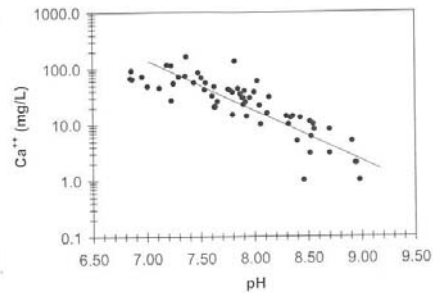


Fig. 8
Plot of calcium concentration versus pH for the Madrid Tertiary Detrital Aquifer. The correlation coefficient is -0.7

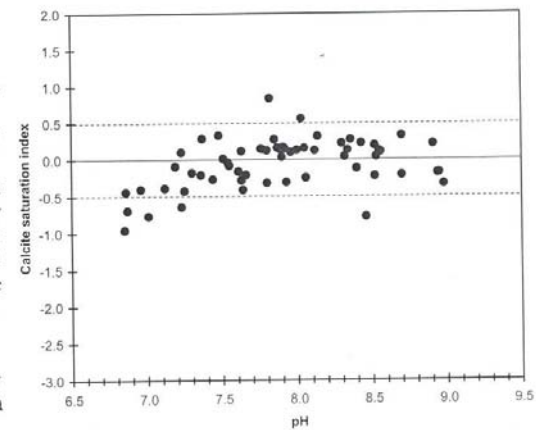


Fig. 9
Calcite saturation indices versus pH for the Madrid Tertiary Detrital Aquifer. Saturation indices have been calculated using the WATEQ4F code (Ball and Nordstrom 1991)

91 $\mu\text{g/L}$) is observed. High arsenic concentrations are also common in groundwaters sampled in deep wells in recharge areas. In general, high arsenic concentrations seem to be frequent in groundwaters with high residence time. Therefore, the arsenic contamination phenomenon in groundwaters of the Madrid Tertiary Detrital Aquifer result from natural causes.

The scatter diagrams of Figs. 15 and 16 show a positive correlation between As and pH (correlation coefficient of $+0.5$), and between As and the alkaline to earth-alkaline ion ratio (correlation coefficient of $+0.4$). The correlations are not high but may be considered significant as the

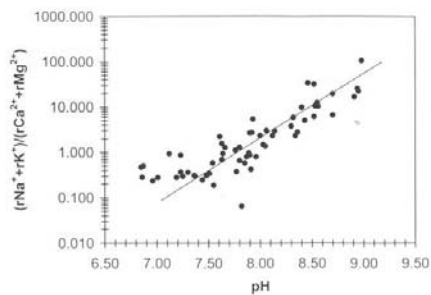


Fig. 10
Plot of the alkaline to earth-alkaline ion ratio versus pH for the Madrid Tertiary Detrital Aquifer. The correlation coefficient is about +0.7

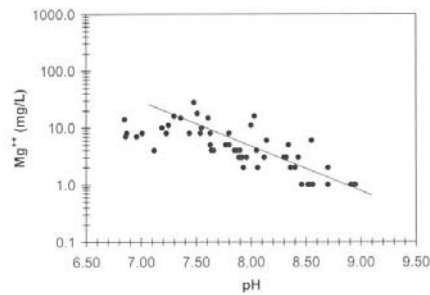


Fig. 12
Plot of magnesium versus pH for the Madrid Tertiary Detrital Aquifer. The correlation coefficient is -0.6

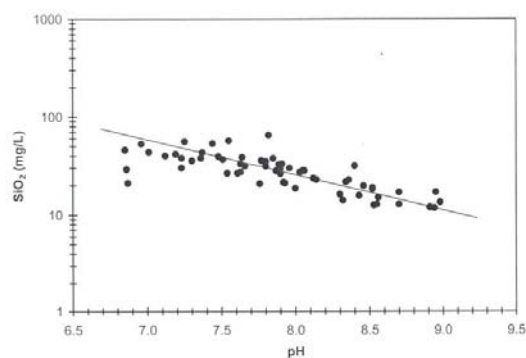


Fig. 11
Plot of dissolved silica concentration versus pH for the Madrid Tertiary Detrital Aquifer. The correlation coefficient is -0.7

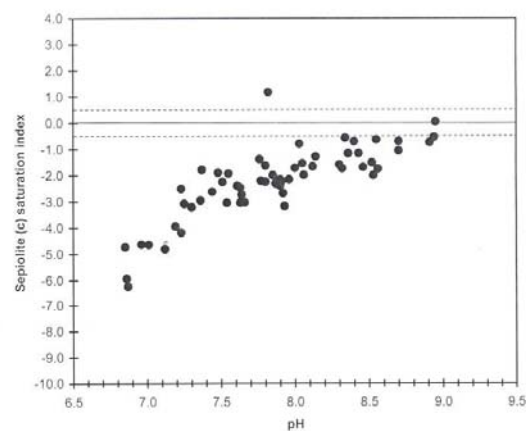


Fig. 13
Sepiolite (c) saturation indices versus pH for the Madrid Tertiary Detrital Aquifer. Saturation indices have been calculated using the WATEQ4F code (Ball and Nordstrom 1991)

number of points is reduced and samples are obtained from multiscreened wells. According to these positive correlations, it is possible that the concentration and mobility of As could be controlled by the same processes leading to the alkaline conditions in the aquifer. Nevertheless, the correlation between As and the well depth is near zero (Fig. 17). It seems that the values of the two variables have no relation, possibly due to the multiscreened nature of the wells sampled, which does not allow the application of a sure depth to the water samples. From the scatter diagrams made to analyse the association between As and minor constituents and trace metals, only As-V, As-F and As-B scatter diagrams show a positive correlation. These results are very interesting, because in aqueous systems the dominant forms of As, V, F and B are anionic complexes (Hem 1989) that can be easily exchanged for the OH^- ion (Boyle and others 1998). The correlation of As with V is especially noteworthy, with a correlation coefficient of +0.6 (Fig. 18). Consequently, the release of naturally-occurring arsenic to groundwater could also be controlled by anion exchange processes from sorbed As. The same mechanism could be controlling the mobility of V.

The most probable sources of arsenic are the basin-fill sediments, which are derived from the igneous and metamorphic rocks of the surrounding mountains. In the mineralised areas of the Central Range, arsenic occurs as arsenopyrite. Arsenic in source areas was presumably oxidised to soluble arsenic (anionic complex forms) before transport into the basin or, if after transport, before burial. At the low pH values that characterise the oxidation of As-bearing sulphide minerals, clay minerals such as kaolinite and smectite (Frost and Griffin 1977), and Fe and Al oxyhydroxides (Pierce and Moore 1982) are strong adsorbers of the arsenite (III) and the arsenate (V) forms of As. This is research still to be completed in the Madrid Tertiary Basin sediments. A similar process is expected for V, but starting from a different geochemical environment. The fine fraction of sediments may exceed 20 ppm As. This is an important natural source. Under favourable conditions, arsenic may be mobilised and enter the natural water system. As pH increases

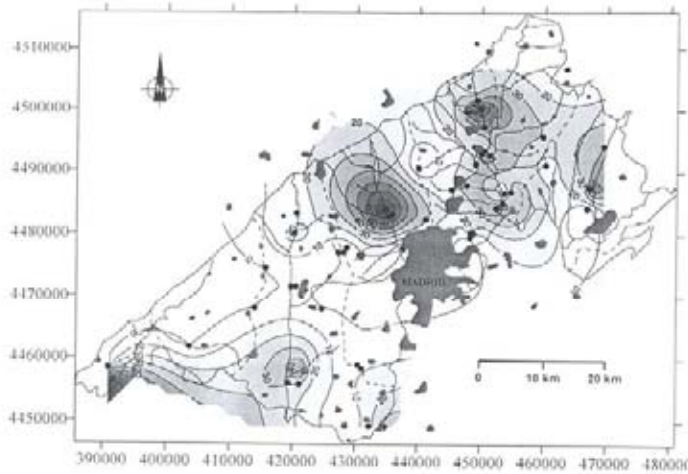


Fig. 14
Isoconcentration map of As ($\mu\text{g/L}$) in groundwater from wells of the Madrid Tertiary Detrital Aquifer (modified from Hernández-García and Fernández Ruiz 2002). Grey-filled contours: As contours; boundary line: study area; black dots: water wells; grey areas: urban areas; solid lines: rivers and streams; broken lines: interfluvies; numbers on the margin: Universal Transverse Mercator (UTM) coordinates

downflow, arsenic may be desorbed from clays (probably as an anion exchange process with OH^- ions) and/or from the Fe and Al oxyhydroxides, and enters the aqueous phase. However, arsenic release could also be affected by dewatering and fluctuating water-table levels in areas of high groundwater withdrawal rates. The heavy exploitation of water supply wells produces a water-table drawdown, which may be up to 100–200 m in parts of the study area, although a detailed survey of the water table is not available. The dewatered zone is consequently filled with air, carrying with it atmospheric oxygen, which favours the oxidation of arsenic-bearing sulphides that could be present in the dewatered sediments. Afterwards, when the water table goes up during the periods without groundwater exploitation, the oxidised arsenic may be released into the groundwater. During the next groundwater exploitation period, high concentrations of arsenic could be obtained from the upper screened part of these wells. This process has been observed in other aquifers by Paul and De (2000), and Schreiber and others (2000). This hypothesis is not rejected, although the existence of sulphides in such sediments and under oxidising conditions is doubtful. Further investigations are needed to examine the occurrence of arsenic in the aquifer sediments.

Conclusions: summary of the baseline quality

The Madrid Tertiary Detrital Aquifer is one of the largest and most important aquifers of Spain. This aquifer contains high quality groundwater and plays an important role in providing reserves to supply the needs of Madrid during periods of drought.

The natural baseline quality is expressed as a range of values which are controlled by lithological and

hydrological factors. Spatial variations occur due to changes in rock type, water-rock interaction, and the residence time of groundwater within the aquifer.

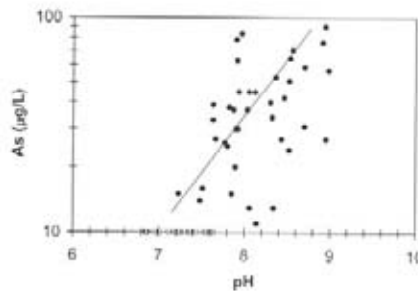


Fig. 15
Plot of total arsenic versus pH for the Madrid Tertiary Detrital Aquifer. The correlation coefficient is +0.5. White dots toward the lower left hand corner are samples with less than 10 $\mu\text{g/L}$ As

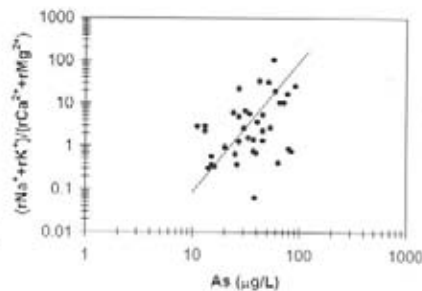


Fig. 16
Plot of the alkaline to earth-alkaline ion ratio versus total arsenic concentration for the Madrid Tertiary Detrital Aquifer. The correlation coefficient is +0.4

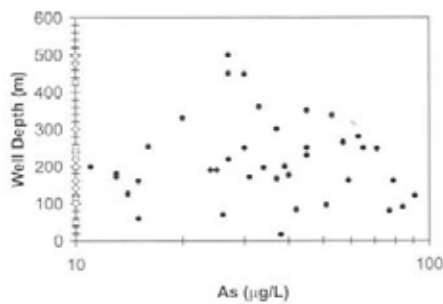


Fig. 17
Plot of total arsenic concentration versus well depth for the Madrid Tertiary Detrital Aquifer. The correlation coefficient is -0.1 . White dots on the extreme left are samples with less than $10 \mu\text{g/L}$ As

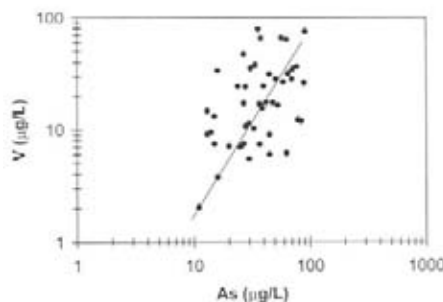


Fig. 18
Plot of total vanadium concentration versus total arsenic concentration for the Madrid Tertiary Detrital Aquifer. The correlation coefficient is $+0.6$

Human impacts are visible in the presence of indicator contaminants such as nitrate. However, the artificial contaminants are still in the upper part of the sediments and their appearance in drinking waters can be easily avoided if the water wells are constructed with a properly sanitary top protection (a 20 m cement seal may be enough). Perhaps the main water constituent that deteriorates groundwater quality for drinking water supply is arsenic. The presence of elevated arsenic concentrations is considered to be due to natural processes. High arsenic concentrations appear in groundwaters with high residence time; that is, they occur in groundwaters characterised by a) high pH values (values between 8.3 and 9) and the resulting occurrence of the CO_3^{2-} anion, b) high sodium concentrations, and c) low calcium, magnesium and silica concentrations. The concentration and mobility of arsenic seems to be controlled by hydrogeochemical processes leading to high pH values and high alkaline to earth-alkaline ion ratios. In fact, the groundwaters that display high concentrations of arsenic also show high levels of vanadium, fluoride and boron, whose stable forms in aqueous systems are anionic complexes. The groundwater quality in the Madrid area below the upper zone affected by anthropogenic activity is controlled by water-rock natural reactions which depend on

geochemical evolution that takes place along flow pathways. The naturally occurring arsenic in Madrid groundwater does not mean an immediate threat to public supplies, as the company responsible for Madrid's drinking water supply is ready to apply treatment to remove arsenic from drinking water. However, the presence of arsenic means an immediate threat to local supplies. The private or community owners of water wells affected by this toxic element might connect to the general supply systems, or apply treatments to remove the As at a rather high cost and with the need to safely dispose of treatment wastes.

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