Chemical analysis and nutritional assessment of trace elements in natural mineral waters bottled in Spain

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Analisis químico y valoración nutricional de elementos traza en aguas minerales naturales envasadas en España

Anàlisi química i valoració nutricional d'elements traça en aigües minerals naturals envasades a Espanya

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RESUMEN

Han sido analizadas las concentraciones de 26 elementos traza en 74 marcas de aguas minerales naturales (AMN) envasadas comercializadas en España. Fueron estudiados los siguientes elementos: Al, As, Sb, Ba, Be, B, Cd, Cs, Zn, Co, Cu, Cr, Sr, Fe, Li, Mn, Mo, Ni, Ag, Pb, Se, Tl, Ti, Th, U y V. Los elementos que tienen las concentraciones mediana más altas (100 a 0.42 µg / L) son Sr, Fe, B, Cr, Ba, Al, Zn, Ni, Se y Tl. Sobre la base de los análisis, la cantidad de Fe contenida en un litro de agua mineral natural es del 0.17 a 1.15% de la Cantidad Diaria Recomendada (CDR), la cantidad de Zn es del 0.007 a 0.033%, y la cantidad de Se es del 0.657 a 2.18%. En base a la relación valor máximo/valor mínimo, se establece una primera categoría de elementos con valores <100, que incluye a micronutrientes esenciales (Fe, Zn, Se, Ni y As) y a algunos elementos tóxicos (Pb, Cd y Sb). La segunda categoría (relación 100 a 400) incluye los micronutrientes Cu y Mo. La tercera categoría (relación > 400) incluye Mn, Cr, y B. La comparación de estas relaciones max/min con los obtenidos en un estudio europeo (Bertoldi et al.) muestra que para 4 elementos traza (Al, B, Zn y Li) los cocientes de estas relaciones tienen valores próximos a 1, El Cs tiene el valor más alto (1.8), y los restantes valores están comprendidos entre 0.6 (para Ba) y 0.09 (para V).

Palabras clave: Aguas minerales naturales (AMN); España; elementos traza; metales traza; análisis químico; valoración nutricional; análisis de alimentos; composición de alimentos; Cantidad Diaria Recomendada (CDR); Ingesta Diaria Dietética Segura y Adecuada Estimada **(IDDSAE)**.

SUMMARY

The concentrations of 26 trace elements in 74 brands of bottled natural mineral water (NMW) marketed in Spain were analysed. The following elements were studied: Al, As, Sb, Ba, Be, B, Cd, Cs, Zn, Co, Cu, Cr, Sr, Fe, Li, Mn, Mo, Ni, Ag, Pb, Se, Tl, Ti, Th, U, and V. Sr, Fe, B, Cr, Ba, Al, Zn, Ni, Se, and Tl have the highest median concentrations (100 to 0.42 mg / L). Based on our analysis, the amount of Fe in one litre of NMW is 0.17 to 1.15% of the Recommended Daily Amount, the amount of Zn is 0.007 to 0.033%, and the amount of Se is 0.657 to 2.18%. The first category includes spread values (ratio max / min <100), including essential micronutrients (Fe, Zn, Se, Ni, and As) and some toxic elements (Pb, Cd and Sb). The second category (100 to 400) includes the micronutrients Cu and Mo. The third category (> 400) includes Mn, Cr, and B. Comparing spread values, two studies (Bertoldi et al. and ours) show that 4 trace elements (Al, B, Zn, and Li) have values close to 1. Cs has the largest value (1.8), and the remaining values are between 0.6 (for Ba) and 0.09 (for V).

Keywords: Natural Mineral Waters (NMW); Spain; trace elements; trace metals; chemical analysis; nutritional assessment; food analysis; food composition; RDI; **ESADDI1**.

RESUM

Han estat analitzades les concentracions de 26 elements traça en 74 marques d'aigües minerals naturals (AMN) envasades, comercialitzades a Espanya. Els següents ele-

[1]NMW = natural mineral water; RDI = Recommended Daily Intake; ESADDI = Estimated safe and adequate daily dietary intake; ICP-MS = Inductively Coupled Plasma Mass Spectrometry; MDL = Method detection limit; MQL = Method detection quantification; CRM = Certified Reference Materials; RSD = Relative standard deviations; PV = Parametric values; E/S = Relationship (Europe / Spain).

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ments van ser estudiats: Al, As, Sb, Ba, Be, B, Cd, Cs, Zn, Co, Cu, Cr, Sr, Fe, Li, Mn, Mo, Ni, Ag, Pb, Se, Tl, tu, Th, U i V. Els elements que tenen les concentracions mitjana més altes (100-0,42 µg/L) són Sr, Fe, B, Cr, Ba, Al, Zn, Ni, Se i Tl. Sobre la base de les anàlisis, la quantitat de Fe continguda en un litre d'aigua mineral natural és del 0.17 a 1.15% de la Quantitat Diària Recomanada (CDR), la quantitat de Zn és del 0.007-0,033%, i la quantitat de Se és del 0657 a 2.18%.
D'acord amb la relació valor màxim/valor mínim, s'estableix una primera categoria d'elements amb valors <100, que inclou a micronutrients essencials (Fe, Zn, Se, Ni i As) i alguns elements tòxics (Pb, Cd y Sb). La segona categoria (relació 100 a 400) inclou els micronutrients Cu i Mo. La tercera categoria (relació> 400) inclou Mn, Cr, i B. La comparació d'aquestes relacions max/min amb les obtingudes en un estudi europeu (Bertoldi et al.) mostra que per 4 elements traça (A, B, Zn i Li) els quocients d'aquestes relacions tenen valors propers a 1, el Cs té el valor més alt (1.8), i els restants valors estan compresos entre 0.6 (per Ba) i 0.09 (per V).

Paraules clau: Aigües minerals naturals (AMN); Espanya; elements traça; metalls traça; anàlisi química; valoració nutricional; anàlisi d'aliments; composició d'aliments; Quantitat Diària Recomanada (CDR); Ingesta diària Dietètica Segura i Adequada Estimada **(IDDSAE)**.

INTRODUCTION

Natural mineral water is defined as a 'microbiologically wholesome water originating in an underground water table or deposit, and emerging from a spring tapped at one or more natural or bore exits (EC. 1996; 2003; 2009), with a distinguishing and constant chemical composition'. Trace elements from mineral water are easily assimilable by human body due to they are in liquid phase (Fairweather-Tait et al. 1992). Moreover, the beneficial health effects of natural mineral waters have been extensively studied.
There are a set of mineral elements (Ca, Mg, P, Fe, F, I, Zn, Se), which are known as essential or indispensable elements, that performs one or more physiological functions; when intake of these elements is low, deficiency symptoms develop but resolves after intake is increased (Bender et al. 1997). For elements that occur in trace amounts (Cu, Mn, Cr, Mo, V, Co), it is more difficult to assess deficiencies and accompanying symptoms. There is another group of mineral elements that appear to be required by the body (deficiency symptoms), although their physiological properties have not yet been established; thus, these elements have been classified separately and are known as "probably indispensable" (B, Ni, As, Sn, Si). The requirements and deficiency symptoms related to the remainder of the microelements or trace elements are unknown, and it is assumed that the minimum intake of these elements (through drinking water and foods) is generally sufficient, although these elements are also of special toxicological interest (Goodhart et al. 1987).
The term "*Recommended Daily Intake" (RDI)* (Wenlock et al.1992) refers to the average daily amount that a person must ingest to meet bodily requirements. The RDIs of each element are established by expert committees of international organisations (after extensive nutritional and clinical analyses). When an RDI cannot be assigned, an *ESADDI (estimated safe and adequate daily dietary intake)* is provided, which is a range between a minimum and a maximum value that ensures that bodily requirements are met and the risk of excessive intake, which could pose a toxicity risk for some elements (Cu, Mn, Cr), is limited.
In the last few years many studies have also focused on the elemental composition of bottled and some mineral waters in individual countries – such as Nigeria (Nkono & Asubiojo et al. 1997), Canada (Dabeka et al., 2002), Sweden (Rosborg et al., 2005), Greece (Soupioni et al., 2006; Karamanis et al., 2007), Italia (Naddeo et al. 2008, , Turkey (Baba et al. 2008; Güler et al. 2007;2008;) Estonia (Bityukova et al. 2010), Líbano (Semerjian et al. 2011), Arabia Saudí (Maqbool et al. 2009), Egipto (Mahmoud et al. 2001), United Kingdom (Farmer and Johnson 1985), Hungary (Ubul et al. 2010), Poland (Aleksander Astel et al., 2014), Norway, Sweden, Finland e Iceland (Björn et al., 2010), Portugal (Carla Lourenço et al., 2010), Slovenian (Mihael Brencic et al., 2010). As part of the European TRACE project (Tracing Food commodities in Europe, VI FP), a study (Bertoldi et al. 2011) surveying the chemical composition (39 parameters) of 571 mineral waters bottled and marketed in 23 European countries, particularly considering the legal limits and nutritional implications, has been conducted.
Given the geological processes are the most important factors controlling the source and distribution of chemical elements in natural waters, the importance of geochemical data must not be underestimated. A study on data on pH, conductivity and concentrations of 69 elements and ions from 186 bottled mineral waters of 158 different Italian name brands was performed (Cicchella, et al. 2010). In addition, the European Groundwater Geochemistry Project (Birke et al.2010) analysed a total of 1785 European bottled water samples. These bottled water samples were purchased throughout 40 European countries, and the samples were analysed for 71 chemical parameters.
The chemical composition of groundwater as a drinking water supply and possible source of mineral water bottled it has been also studied (Reddy et al. 2007; Shuixian 2013).
Spain is a particularly groundwater-rich European country, and the large variety of this groundwater depends on the rocks that constitute the aquifers. However, literature regarding the minerals contained in Spanish waters is minimal. A previous paper (Gutiérrez-Reguera et al. 2012) has described a hydrochemical study on the natural mineral waters bottled in Spain, establishing different classifications based on hardness, dry residues, etc.
The purpose of the present paper is to investigate the levels of mineral trace elements in brands of bottled water sold on the Spanish market. This study is necessary to characterise each bottled water and to assess its nutritional properties. The study involves 74 brands of NMWs registered in the Official Journal of the European Union (OJEU, 2012). It seeks to characterise and differentiate the waters according to their quality to assess the human health benefits of these minerals at their present concentrations. The trace metals selected for the study are of interest because of their nutritional value, their known role in certain functions of the body, their value to human health, and in some cases, their toxicity levels.

MATERIALS AND METHODS

Analysed samples and study area

Table 1 shows the 74 samples of NMW studied, indicating the springs of origin, places of bottling, the autonomous communities to which they belong, and the province of such communities. The distribution by communities is shown in Figure 1, in which Catalonia, Castilla La Mancha and Castilla y León head the list with 34 brands (approximately 46%), followed by Galicia, Andalucia and Valencia (approximately 34%). The spatial distribution is shown in Figure 2, which also illustrates the general lithology of the area(s) containing the springs corresponding to each province and the type of aquifers used in that area compared to the regional map (to relate these parameters to the mineral contents and their concentrations)

***Table 1** List of N.M.W. brands indicating the spring of origin, place of bottling, and the Community and Province they belong to.*

Nº	SOURCE OF ORIGIN	PLACE OF PACKAGING	PROVINCE	COMMUNITYY
1	Spring Bronchales3,Teruel	Bronchales Water, Inc., Bronchales (Teruel)	Teruel	ARAGÓN
2	Spring Water Rosal, Calera and Chozas (Toledo)	WaterCommercialRosalSL, Calera and Huts(Toledo)	Toledo	CASTILE LA MANCHA
3	NevadaSpringWater.	Marquis Waters, SL, Spot The Tesorillo, Albuñán (Granada)	Granada	ANDALUSIA
4	SpringWaterNevada,Granada.	By Marquis Waters SL,Spot The Tesorillo, Albuñán (Granada) toAspro dibeSCABalderrubio(Granada)	Granada	ANDALUSIA
5	Spring Aiguaneu, Espinelves (Girona)	packaged inthe MontsenyAiguaEspinelvesbySA toCAPRABO-SA, L'Hospitalet (Barcelona)	Girona	CATALUNYA
6	Spring ofSan Joaquin.	for El Corte Ingles, in Villa San Joaquin Huelmos de Cañedo, Valdunciel (Salamanca)	Salamanca	CASTILE AND LEÓN
7	Fontoiraspring.	In the Spring Fontoira, Aguas de Cospeito SL,Cospeito (Lugo).	Lugo	GALICIA
8	Fontoiraspring.	Water CospeitoS.L. (Lugo)	Lugo	GALICIA
9	Spring Source Arquillo Masegoso (Albacete). TheNatural PlaceArquillo.	By Aquadeus, SL, Robledo (Albacete)	Albacete	CASTILE LA MANCHA
10	SpringTheFirs, Arbucies (Girona)	Aquarel Ibérica SAN estlé, Barcelona	Girona	CATALUNYA
11	Spring The Jaras, Herrera Duque (Badajoz)	in the Fountain, Herrera Duke-Nestlé	Badajoz	EXTREMADURA
12	Spring Bezoya, Ortigosa del Monte (Segovia).	inthe spring by Leche Pascual group.	Segovia	CASTILE AND LEÓN
13	Spring Cabreiroá, Verin(Galicia)	ForCabreiroáWater, Inc., Verin(Ourense)	Ourense	GALICIA
14	Fuente blancas pring, Sierra de Segura, Sorihuela of Guadalimar(Jaén).	Aquifer International Holdings SA,themanan. Fuenteblanca, ArchbishopVillanueva(Jaén)	Jaén	ANDALUSIA
15	FuencislaSpring, San Antonio deRequena (Valencia).	for DIA, Inc., Getafe (Madrid).	Valencia	VALENCIA
16	Spring MontalvoV, Aldeatejada (Salamanca)	by Agropecuaria Los Escudos S.L. Aldeatejada(Salamanca)	Salamanca	CASTILE AND LEÓN
17	The Ideal Spring II, Valleseco (LasPalmas)	FirgasbottledwatersInc.(LasPalmas)	Las Palmas	GRAND CANARY
18	Spring FontNovaPla	bottledat source,by Exdema SA, Aiguamurcia (Tarragona)	Tarragona	CATALUNYA
19	Source of FontD'Or	Bottledat the Source for FontD'Or SA, Sant HilariSacalm (Girona)	Girona	CATALUNYA
20	Spring ofFont delRegas,Arbucies(Girona).	by Font of Regas, Inc., Arbucies (Girona).	Girona	CATALUNYA
21	FontSpringNatura, Loja (Granada)	By ParkDam, SA, Villa La Presa, Loja (Granada) - Sierra deLoja (Granada)	Granada	ANDALUSIA
22	SacalmSpring, Sant Hilarisacalm(Girona)	By Aguas FontVella and Lanjaron, SA, Urgell (Barcelona) - Groupe Danone.	Girona	CATALUNYA
23	Spring Siguenza, Moratoilla de Henares (Guadalajara)	by Aguas FontVella and Lanjaron, SA, Urgell (Barcelona) - Groupe Danone.	Guadalajara	CASTILE LA MANCHA
24	Spring Fontecabras, Jaraba(Zaragoza)	By Springs of Stone, SA, Villanueva de Gallego (Zaragoza)	Zaragoza	ARAGÓN
25	Spring Fontecelta, Fontecelta, SA, Sarria(Lugo)	By Fontecelta, Inc., Sarria (Lugo)	Lugo	GALICIA
26	Fontecelta spring.	In Spring Fontecelta, Sarria (Lugo)	Lugo	GALICIA
27	Spring Fontecelta, Sarria (Lugo).	By Fontecelta to Shopping Carrefour SA.	Lugo	GALICIA
28	Spring Fontecelta, Sarria(Lugo)	By Fontecelta, Inc., for Auchan Production	Lugo	GALICIA
29	Spring Fonteide	Packaging by Aguas del Valle de la Orotava SL, La Orotava (Tenerife)	Tenerife	GRAND CANARY
30	Spring Fonter, Amer (Girona)	by Aguas FontVella and Lanjaron, SA, Groupe Danone	Girona	CATALUNYA
31	Fuensanta of Buyeres	Bottled at source,by SAWater Fuensanta, FuensantaSpa, Nava (Asturias)	Asturias	ASTURIAS
32	SpringSourceArquilloMasegoso(Albacete). TheNatural PlaceArquillo.	Supermarkets DIAPortugal, Lisbon (Portugal).	Albacete	CASTILE LA MANCHA
33	Spring FountainVal 2	By Water Mondariz FountainVal, SA (Pontevedra)	Pontevedra	GALICIA
34	Sierra Spring WaterItem" TheMoreral" Fuente la Higuera(Valencia).	Mineral Water FontTeak, SA, Fuente la Higuera(Valencia).	Valencia	VALENCIANA
35	Spring The Narrow, Partida Villa-Gallur, Caudete (Albacete).	By DIALOREINVESTMANT S.L. for DIA	Albacete	CASTILE LA MANCHA
36	Spring Mountains, the Marquis Huerta (Cuenca)	By Light Source Management, SL, Huerta of the Marquis (Cuenca)	Cuenca	CASTILE AND LEÓN

Nº	SOURCE OF ORIGIN	PLACE OF PACKAGING	PROVINCE	COMMUNITYY
37	Source Spring Spring, San Antonio de Requena (Valencia)	By Natural Mineral Water San Benedtto SA, San Antonio de Requena (Valencia)	Valencia	VALENCIA
38	Source Spring Spring, San Antonio Requena (Valencia)	By San Benedetto Mineral Water, SA, San Antonio deRequena (Valencia)	Valencia	VALENCIA
39	Source Spring Spring, San Antonio de Requena (Valencia)	By Natural Mineral Water San Benedtto SA, San Antonio de Requena (Valencia)	Valencia	VALENCIA
40	Source Spring Spring, San Antonio de Requena (Valencia).	By San Benedetto Mineral Water, SA, San Antonio deRequena (Valencia).	Valencia	VALENCIA
41	Spring Fuentelajara, Belvis de la Jara(Toledo)	In Spring Fuentelajara, Belvis de la Jara(Toledo).	Toledo	CASTILE LA MANCHA
42	Spring Fuenteror, Barranco Madrelagua, Teror (Gran Canaria (LasPalmas) Fuente AgriaTeror	Terorpackaged by SAWater-Teror (GrandCanary)	Las Palmas	GRAND CANARY
43	Spring Fuentevera	Hinojosa-Down HouseCaleraand Huts (Toledo), for liquid foodsCommercial SA.	Toledo	CASTILE LA MANCHA
44	CaveSpring, Lebanza (Palencia)	SA water bottling Palentina	Palencia	CASTILE AND LEÓN
45	Spring Lizartza(Guipuzcoa)	In saluswater, SA, Tolosa (Guipuzcoa)	Guipuzcoa	PAIS VASCO
46	water from Sierra Nevada,Health Spring, Lanjaron (Granada)	by Aguas FontVella and Lanjaron, SA, Urgell (Barcelona) - Groupe Danone.	Granada	ANDALUSIA
47	ownspring water, The Cliffs of Higuela, Alburquerque(Badajoz).	By springs in Extremadura, SA, Badajoz.	Badajoz	EXTREMADURA
48	Spring Malavella	Spring and Bottled by Malavella SA, Caldes de Malavella (Girona)	Girona	CATALUNYA
49	Spring Valtorre	In Spring, by Valtorre Water SA-Belvís de la Jara (Toledo)	Toledo	CASTILE LA MANCHA
50	Spring MondarizIV, Spa Mondariz, Pontevedra	Mondariz Water Founta in Vall SA Mondariz (Pontevedra)	Pontevedra	GALICIA
51	Montepinosspring.	by CNavalpotroInc., Almazan(Soria).	Soria	CASTILE AND LEÓN
52	SpringMountPinos, Almazan (Soria).	for El Corte Ingles,Almazan (Soria).	Soria	CASTILE AND LEÓN
53	SpringMountPinos, Almazan (Soria).	for E lCorte Ingles,Almazan (Soria).	Soria	CASTILE AND LEÓN
54	SpringNature ,Finca laPandera, Los Villares (Jaén)	By Sierra de Jaén, SA, Finca La Pandera, Los Villares (Jaén)	Jaén	ANDALUSIA
55	SpringCamporrobles, Camporrobles (Valencia)	distributed by Leche Pascual Group, Inc.	Valencia	VALENCIA
56	The Canyons Spring, Ribera del Folgoso (Leon)	distributed by Leche Pascual group.	León	CASTILE AND LEÓN
57	SpringNeval, Moratalla (Murcia)	By AGUAMUR, SL, Finca El Chopillo, Moratalla (Murcia)	Murcia	MURCIA
58	SpringOrotana, Artana (Castellón), Sierra de Espadan	Bottled at source by SAWaterOrotana	Castellón	VALENCIA
59	Spring St. AntonII, Valleseco (Las Palmas)	Firgas bottled watersInc. (LasPalmas)	Las Palmas	GRAND CANARY
60	SantAniol de Finestres (Girona)	packaged in SantAniolAigua (Girona)	Girona	CATALUNYA
61	SantAniol de Finestres (Girona)	packaged in SantAniolAigua (Girona)	Girona	CATALUNYA
62	SantAniol de Finestres (Girona)	Packaged in SantAniolAigua (Girona)	Girona	CATALUNYA
63	Spring Sierra Cazorla,Archbishop Villanueva (Jaén)	For aquifer International HoldingsSA, the Archbishop Villanueva (Jaén).	Jaén	ANDALUSIA
64	Spring The Chumacero	Valencia de Alcantara, Caceres	Cáceres	EXTREMADURA
65	FountainWeeping	By Sierrade Jaen SA, Finca La Pandera,Valdepeña of Jaen, Los Villares (Jaén)	Jaén	ANDALUSIA
66		Spas and Water by Solan de Cabras,SL (Cuenca).	Cuenca	CASTILE LA MANCHA
67	Spring Fuencaliente of Solares	By Spring Fuencaliente, SA, Solares (Cantabria)	Cantabria	CANTABRIA
68	Telenospring, Palacios de la Valduerna(Leon).	By Lands and Building, SL, Palacios de la Valduerna (Leon).	León	CASTILE AND LEON
69	SpringValtorre	Valtorre in the spring, water Valtorre, SA, Villa La Torre,Belvis dela Jara (Toledo)	Toledo	CASTILE LA MANCHA
70	Spring Source ArquilloMasegoso (Albacete). The Natural Place Arquillo.	By Aquadeus, SL, Robledo (Albacete)	Albacete	EXTREMADURA
71	Spring VichyCatalan.	By SAVichyCatalan, Roger de Llúria.	Girona	CATALUNYA
72		Packed for compagnieFourniereVichy, Nestlé WatersEspagne (Barcelona)	Barcelona	CATALUNYA
73	Spring Fontalegre, Viladrau (Girona)	Nestle Waters to Spain,SA, Barcelona	Girona	CATALUNYA
74	Spring Vilas of Turbón, Las Villas del Turbón,Torrelarribera (Huesca)	Vilaswaters of TurbónInc. in the spring	Huesca	ARAGÓN

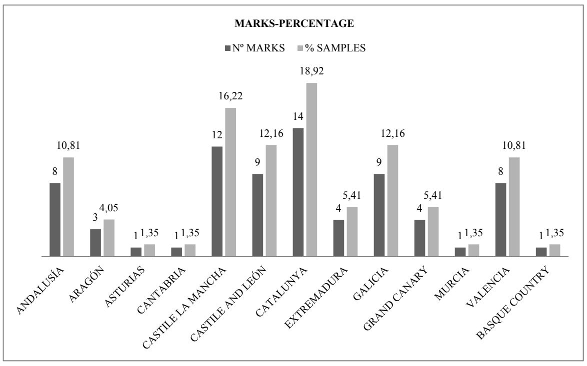

Fig 1. *Number of brands per communities and percentage.*

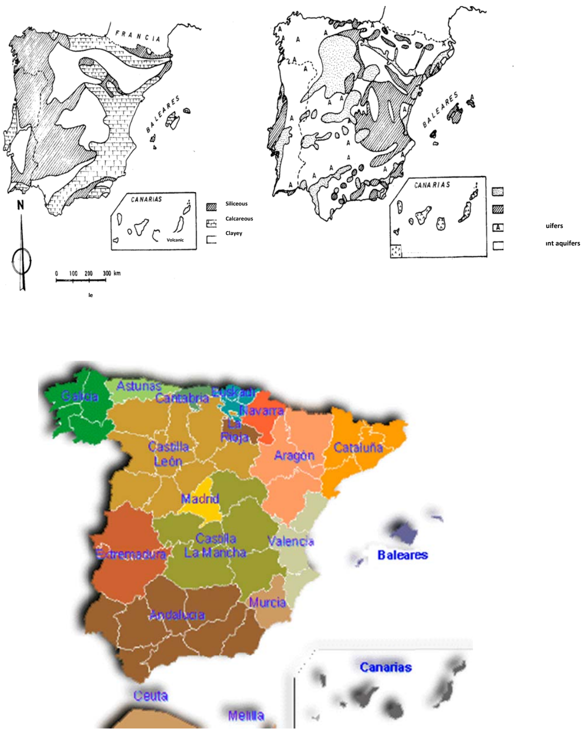

Fig 2. *Map of general lithology, aquifers synthesis and Autonomies of Spain.*

Analytical determination methods

Samples of bottled NMW were collected from shops and in some cases, were provided by the bottling companies. Prior to their analysis, the water samples were stored at 4ºC. Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, at the Research General Services of the University of Seville), the following elements were analysed: Al, As, Sb, Ba, Be, B, Cd, Cs, Zn, Co, Cu, Cr, Sr, Fe, Li, Mn, Mo, Ni, Ag, Pb, Se, Tl, Ti, Th, U and V.

An X7 SERIES ICP-MS Instrument (Thermo Elemental, USA) was used for the analysis of metals and metalloids. The detection limits of this analytical technique are usually low enough for accurate determination of the low-level range of elements in mineral water samples. The ICP-MS was used with a standard low-volume glass impact bed spray chamber (Peltier cooled at +3 °C), a concentric glass nebuliser and a Cetac ASX-500 autosampler (Cetac Technologies, USA). The operating conditions were optimised daily to obtain the highest sensitivities and S/N ratios. The transient signals were monitored and collected in the "TRA profile mode" using PlasmaLab (TM) software (Windows, 2000). The instrumental details and operating conditions are summarised in **Table 2**.

Table 2 *Instrumental characteristics and working conditions for ICP-MS method.*

Spectrometer	X7 SERIES ICP-MS, Thermo Elemental (U.K)
Rf power	1400 W
Lens	Infinity
Interface	Environmental- Ni cones
Detector	Simultaneous AutoRange Plus Peak jumping - 60 sweeps - 10 ms dwell/peak (58 s Total)
Spraychamber	Peltier cooled impact based, 3ºC
ICP	Solid State 27 MHz- 1200 (500*) W
Nebulizer	Concentric
Torch	1.5 mm (quartz)
Flow parameters (l min-1)	Plasma, 12.0 (14.0*) ; Auxiliary, 0.7 (1.0*); Nebuliser, 0.91.
Analytical masses (amu)	6Li, 9Be, 11B, 27Al, 47Ti, 49Ti, 51V, 52Cr, 55Mn, 56Fe, 59Co, 60Ni, 62Ni, 63Cu, 65Cu, 66Zn, 67Zn, 68Zn, 75As, 82Se, 87Sr, 88Sr, 95Mo, 97Mo, 98Mo, 106Cd, 107Ag, 108Cd, 109Ag, 111Cd, 114Cd, 121Sb, 123Sb, 133Cs, 135Ba, 137Ba, 203Tl, 205Tl, 208Pb, 232Th, 238U
Internal standard mass (amu)	45Sc, 115In, 159Tb, 209Bi

*Conditions for Al, V, Fe, Se, As, which form oxides.

Complete ICP-MS analyses were conducted according to the 200.8 US EPA method, with some modifications related to tuning and mass calibration. These adaptations were established from the 'Getting Started Guide for X Series ICP-MS' (Thermo Electron Corporation, 2004) and were restricted to the isotopes of interest. The tuning solution, which was used for instrument regulation prior to analysis, was prepared by mixing Be, Co, In, Ce, Ba and U (from Cromlab, Barcelona, Spain) in Suprapure® Nitric acid (2%) to produce a concentration of 10 μg L^{-1} of each element. The mass calibration solution, which was used prior to analysis to obtain a current mass calibration, was prepared from a multielemental standard of the following elements in Suprapure Nitric acid (2%, Merck): Li, Be, B, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sb, Cs, Ba, Tl, Pb, Th and U.

When the problem of interferences appeared, it was solved by the utilisation of equations of interference corrections (200.8 US EPA method).

Importantly, great care was taken to reproduce the sample matrix in all calibration and QC standards and to properly select the internal standards. It was necessary to clean the glass material with 0.2 N nitric acid for 24 h to minimise metal residues. Additional care was taken with regard to sample handling to avoid problems associated with contamination. Consequently, all reagents, materials and samples were handled within a vertical laminar airflow cabinet (Indelab, model IDL-48 V). The cabinet contained a high-efficiency particulate air HEPA filter that ensured air cleanliness class 100, according to Federal Standard 209E, and was located in an isolated dark room for the purpose of analytical weighing.

The analytical method's performance characteristics, such as trueness, precision, method detection limit (MDL) and quantification (MQL) and linearity within the calibration range, were tested. The accuracies of spectrometric determinations were established by international Certified Reference Materials (CRM). Experimental concentrations were obtained from 18 replicates over 6 days. Quality control samples were used according to the EPA protocol (section 9.0 of EPA 200.8:1994). CRM-TMDW (Trace Metals in Drinking Water Standard) from High Purity Standards (Charleston, United States), which is certified for trace metals in drinking water, was used to determine the accuracy of the US EPA method for rainwater by ICP-MS. The trueness of the method was evaluated via determination of specific elemental concentrations in the CRM. Recoveries (R) were calculated by dividing the mean value of the determined element by the certified value. The results (**Table 3**) demonstrate that the method presented optimum trueness, with values in the AOAC range.

Limits of detection and quantification were calculated using the standard deviations obtained from calibration curves. Limits of detection (**Table 3**) are quite low, enabling analyses of very low levels of metals and metalloids in drinking water. The MDL and MQL were calculated as the concentrations corresponding to a signal that was 3 and 10 times the standard deviation of the intercept, respectively. Linearity within the calibration range was calculated as $100(1 - s_b/b)$, where b is the slope of the calibration curve and s_b is its standard deviation. The ICP-MS calibration curves were linear for all elements analysed, generally obtaining values higher than 95.0% (Cuadros et al., 1996). As shown in **Table 3**, the linearities of aluminium, chrome, and iron were 97.4%, 97.8% and 95.7%, respectively, while the remaining elements had values higher than 98%. Each sample was analysed three times. From these replicates, the standard deviation for each element in each solution was calculated. For ICP-MS, an unweighted least-squares fit of the standard deviation to the concentration was then performed. Internal Standards are composed of Sc, In, Tb and Bi, which presented optimum accuracies (97.8-101.2%).

***Table 3** Recovery, linearity and sensitivity for ICP-MS method.*

Analyte	Concentration obtained±SD (µg L-1)	CRM concentration ±SD (µg L-1)	Recovery (%)	Linearity (%)	MDL (µg L-1)	MQL (µg L-1)
Be	20 ±0.10	19.2 ± 0.20	96.0	99.1	0.035	0.117
Al	120 ± 0.60	120.6 ± 1.33	100.5	97.4	0.409	1.36
Cr	20 ± 0.10	19.3 ± 0.09	96.5	97.8	0.042	0.140
Mn	40 ± 0.20	38.5 ± 0.45	96.3	98.7	0.035	0.117
Fe	100 ± 0.50	113.1 ± 2.38	113.1	95.7	2.87	9.57
Co	25 ± 0.13	24.6 ± 0.23	98.4	98.8	0.040	0.133
Ni	60 ± 0.30	53.8 ± 0.59	89.7	98.1	0.126	0.420
Cu	20 ± 0.10	18.5 ± 0.20	92.5	98.2	0.071	0.237
As	80 ± 0.40	80.6 ± 0.16	100.8	98.1	0.125	0.417
Se	10 ± 0.05	9.5 ± 0.19	95.0	98.2	0.463	1.54
Sr	250 ± 1.25	264 ± 1.85	105.6	99.4	0.035	0.117
Mo	100 ± 0.50	96.8 ± 1.07	96.8	99.3	0.062	0.207
Ag	2 ± 0.01	2 ± 0.03	100.0	99.5	0.052	0.173
Cd	10 ± 0.05	10.3 ± 0.17	103.0	99.4	0.053	0.177
Sb	10 ± 0.05	10.4 ± 0.07	104.0	98.1	0.048	0.160
Ba	50 ± 0.25	50 ± 0.04	100.0	99.5	0.083	0.277
Tl	10 ± 0.05	10 ± 0.01	100.0	99.5	0.045	0.150
Pb	40 ± 0.20	36.2 ± 0.29	90.5	99.1	0.135	0.450
U	10 ± 0.05	10.1 ± 0.18	101.0	99.8	0.053	0.177

SD standard deviation, CRM certified reference material

Treatment of Results

Diverse results treatment methods were used, involving basic statistical analyses of the analytical data obtained for the specific trace elements.

An analysis of statistical parameters was performed and included determining measures of variability or data dispersion, which indicate the degree to which the values are different or how they vary from one another. The values will be high when the data are very heterogeneous and low when the data are very homogeneous. This analysis of the statistical parameters also indicates measures of position, which describe the position of a data group in the number line (the data have a tendency to group around a certain point); based on this, a typical value that describes or summarises the entire dataset can be determined, depending on the study characteristic(s) and the selected sample(s).

All statistical parameters were calculated using Microsoft Office Excel 2007. This software was also used to perform diverse graphical representations, which were of great interest to the study.

RESULTS AND DISCUSSION

Analytical results

Table 4 shows all the analytical results that correspond to the components analysed in the 74 samples of natural mineral waters. Each value corresponds to the mean pertain to three determinations, and the median of relative standard deviations of the triplicates (%RSD) are shown at the end of the table.

Of all the trace elements studied, almost all the values were below the corresponding MDL for only 3 elements. *Cd* had only one value above its MDL, 3.61 µg/l in sample 6. Similarly, *Ag* also had only one value, 3.12 µg/l in sample 6; *Tl* had four values above its MDL: 0.079 µg/l in sample 2, 3.814 µg/l in sample 6, 0.156 µg/l in sample 71 and 0.207 µg/l in sample 72. When calculating the medians of these three elements (as well as the medians of other elements for which the values were below their MDLs), MDL values were used.

There were four trace elements with a value slightly above the PV in some samples; Sb, Fe, Mn and Se. Sb exceeded the PV in one of the samples, maybe due to the PET packaging (Birke et al., 2010). Fe exceeded the PV concerning spring water and drincking water in seven samples, whereas there were not PV for natural mineral water. Mn exceeded it in two samples and Se in one of the samples, the latter being an essential element for human health. For Se, 46 of the samples showed values below its MDL, and the rest varied between 0,524 µg/L and 4,135 µg/L, except for two high values.

Statistical analysis of the results

Statistical analyses of the results were performed in two stages: (1) at the global level, in which all results were considered; and (2) at the spatial level, in which the results obtained in the different communities were compared.

Global statistical analysis

Table 5 presents the basic statistical analyses of the analytical data obtained for the 74 samples. The table also includes the Method Detection Limit (MDL) values as well as the parametric values (PVs) required by Regulations (Council Directive 98/83/CE, November 3th of 1998, regarding Water Quality for Human Consumption).

Table 4 *Minority components and traces (trace elements) of the 74 samples collected from N.M.W.studied (µg/l).*

SAMPLE Nº	Al	As	Sb	Ba	Be	B	Cd	Cs	Zn	Co	Cu	Cr	Sr	Fe	Li	**Mn**	**Mo**	**Ni**	**Ag**	**Pb**	**Se**	**Tl**	**Ti**	**Th**	**U**	**V**
1	0.997	0.125	0.258	19.1	0.035	41.4	0.053	0.169	4.04	0.040	0.071	27.7	11.1	84.9	21.0	3.72	0.062	0.657	0.052	0.135	0.314	0.045	0.426	0.087	0.053	0.086
2	0.409	2.19	0.171	2.45	0.035	0.825	0.053	0.165	0.696	0.082	0.071	0.042	419	88.3	108	0.293	0.214	2.30	0.052	0.135	0.822	0.079	2.058	0.375	18.2	11.6
3	0.409	0.125	0.101	1.92	0.035	37.5	0.053	0.107	3.36	0.040	0.071	26.2	62.3	77.6	18.0	0.313	0.073	2.80	0.052	0.135	0.527	0.045	0.426	0.110	0.053	0.086
4	4.88	0.125	0.113	0.064	0.035	66.6	0.053	0.081	2.34	0.040	0.071	32.0	63.6	142	1.00	0.209	0.062	2.42	0.052	0.135	0.463	0.045	0.286	0.067	0.010	0.086
5	15.9	0.125	0.095	693	0.035	23.8	0.053	0.052	8.28	0.376	3.64	4.44	101	65.4	6.00	0.364	1.06	0.133	0.052	0.135	0.463	0.045	3.441	0.067	6.49	1.32
6	2.65	6.64	3.81	59.5	0.035	44.1	3.61	4.11	7.96	3.79	0.071	32.1	131	151	29.0	3.56	3.60	1.17	3.12	3.62	22.0	3.814	7.222	2.40	4.27	0.086
7	0.591	0.125	0.370	26.3	0.035	44.5	0.053	0.241	4.54	0.063	0.071	27.2	152	80.3	24.0	0.322	0.062	2.26	0.052	0.135	0.463	0.045	1.61	0.046	0.172	0.086
8	1.16	0.197	0.241	30.9	0.035	11.5	0.053	0.244	5.51	0.040	0.071	2.53	164	126	1.00	0.107	0.057	0.313	0.052	0.135	0.363	0.003	3.674	0.133	0.173	0.086
9	0.972	0.125	0.328	2.59	0.035	49.4	0.053	0.039	1.79	0.040	0.071	26.5	56.3	174	19.0	0.397	0.187	2.82	0.052	0.135	0.463	0.045	0.426	0.036	0.260	0.086
10	4.48	0.490	0.048	517	0.035	15.2	0.053	0.141	2.18	0.040	0.071	3.08	140	71.5	8.00	0.117	13.5	0.412	0.052	0.158	0.263	0.045	3.314	0.067	31.7	1.23
11	1.25	0.125	0.280	5.79	0.035	38.0	0.053	0.246	9.41	0.263	0.071	26.4	4.42	113	22.0	4.37	0.062	0.024	0.052	0.135	0.463	0.045	0.481	0.021	0.062	0.086
12	0.435	0.304	0.166	21.8	0.120	68.9	0.053	1.44	2.53	0.048	0.071	29.5	12.0	91.7	171	0.524	0.062	3.22	0.052	0.135	0.463	0.045	0.258	0.067	0.068	0.086
13	8.30	0.125	0.048	23.5	1.70	348	0.053	256	1.73	0.040	0.071	32.4	127	37.8	6090	4.32	1.54	2.91	0.052	0.135	0.463	0.045	5.212	0.084	0.375	0.086
14	0.412	0.125	0.081	0.664	0.035	82.5	0.053	0.390	1.73	0.065	0.071	30.6	47.8	354	18.0	0.312	0.116	2.68	0.052	0.135	0.463	0.045	0.426	0.067	0.322	0.086
15	15.7	1.26	0.048	0.083	0.035	5.70	0.053	0.045	0.696	0.413	0.071	0.042	32.1	558	24.0	1.30	0.062	6.22	0.052	0.135	4.14	0.045	0.426	0.067	0.053	0.086
16	5.34	0.125	0.180	20.3	0.035	47.3	0.053	0.041	3.84	0.076	0.071	27.9	155	42.1	9.00	0.175	0.062	2.40	0.052	0.135	0.469	0.045	0.426	0.067	1.52	0.086
17	13.6	0.125	0.127	75.7	0.146	44.9	0.053	0.111	7.61	1.89	3.87	5.81	484	260	7.00	251	0.597	0.759	0.052	0.135	0.463	0.045	11.32	0.067	0.075	43.4
18	96.0	0.125	0.195	47.8	0.035	54.6	0.053	0.123	10.5	1.18	6.85	6.54	1538	252	9.00	1.95	1.39	1.88	0.052	0.144	0.463	0.045	10.74	0.067	1.68	0.086
19	81.8	0.125	0.178	18.6	0.035	23.0	0.053	0.147	5.75	0.750	5.19	5.18	50.8	94.8	1.00	1.17	1.84	0.583	0.052	0.085	0.463	0.045	8.281	0.067	9.42	0.086
20	0.504	0.125	0.048	22.9	0.035	44.4	0.053	0.421	2.78	0.049	0.071	27.5	155	107	37.0	0.243	7.51	2.76	0.052	1.24	0.463	0.045	0.426	0.067	143	0.086
21	0.409	0.125	0.148	4.90	0.035	50.7	0.053	0.258	3.02	0.093	0.071	27.9	392	131	36.0	0.319	1.48	2.66	0.052	0.135	0.463	0.045	0.426	0.067	0.727	0.086
22	2.37	0.125	0.213	29.0	0.035	48.0	0.053	0.102	2.30	0.063	0.071	28.9	72.4	134	32.0	0.165	11.5	2.92	0.052	0.135	0.894	0.045	1.898	0.067	9.94	0.086
23	2.27	0.125	0.463	5.14	0.035	51.5	0.053	0.302	2.22	0.096	0.071	27.5	98.1	135	22.0	0.417	0.069	2.38	0.052	0.135	0.627	0.045	0.426	0.067	0.712	0.086
24	3.27	0.125	0.085	16.7	0.035	62.8	0.053	0.431	3.58	0.148	0.071	27.8	672	173	56.0	0.381	0.190	2.13	0.052	0.135	0.463	0.041	0.426	0.067	1.15	0.086
25	6.54	1.18	0.327	5.20	0.035	410	0.053	103	2.34	0.040	0.071	27.4	167	103	1141	1.02	0.255	2.31	0.052	0.135	2.17	0.045	1.95	0.067	0.053	0.086
26	1.97	0.125	0.291	4.73	0.035	414	0.053	122	2.56	0.041	0.071	27.4	174	106	1141	0.510	0.597	2.54	0.052	0.135	0.463	0.045	1.12	0.067	0.053	0.086
27	5.80	0.596	0.149	2.48	0.035	435	0.053	107	1.87	0.040	0.071	29.0	123	99.6	1171	0.340	0.546	3.12	0.052	0.135	1.30	0.045	1.42	0.067	0.053	0.086
28	6.48	0.319	0.158	2.18	0.035	424	0.053	100	2.72	0.040	0.071	27.9	162	90.3	1207	0.245	0.143	3.01	0.052	0.135	0.570	0.045	1.28	0.067	0.048	0.086
29	2.92	0.192	0.156	0.083	0.035	25.5	0.053	0.135	0.696	0.083	0.071	5.49	26.5	191	1.00	0.131	2.13	0.56	0.052	0.135	0.463	0.045	6.26	0.067	0.065	65.9

SAMPLE Nº	Al	As	Sb	Ba	Be	B	Cd	Cs	Zn	Co	Cu	Cr	Sr	Fe	Li	**Mn**	**Mo**	**Ni**	**Ag**	**Pb**	**Se**	**Tl**	**Ti**	**Th**	**U**	**V**
30	16.7	0.125	0.261	16.2	0.035	69.0	0.053	0.283	18.7	4.04	0.071	28.7	59.9	108	27.0	27.0	0.062	1.07	0.052	0.135	0.463	0.045	0.426	0.067	0.053	0.086
31	3.96	2.53	1.72	42.9	0.035	159	0.053	3.83	13.9	0.129	0.071	30.1	1061	81.4	30.0	0.605	0.062	0.54	0.052	0.135	0.463	0.045	1.95	0.067	0.092	0.086
32	1.98	0.125	0.314	1.73	0.035	62.1	0.053	0.128	1.94	0.040	0.071	27.8	43.6	211	20.0	0.389	0.062	3.10	0.052	0.135	0.463	0.045	0.426	0.067	0.213	0.086
33	4.52	0.125	0.230	3.58	0.035	62.2	0.053	1.89	19.3	0.040	0.071	32.0	160	150	43.0	0.497	0.062	2.09	0.052	0.135	0.463	0.045	1.33	0.067	0.115	0.086
34	4.15	0.125	0.128	11.1	0.035	94.4	0.053	0.203	2.05	0.280	0.909	27.9	1841	166	45.0	0.388	1.26	1.58	0.052	0.135	1.25	0.045	0.426	0.067	1.70	0.086
35	1.65	0.125	0.048	4.92	0.035	74.1	0.053	0.141	1.70	0.040	0.071	29.0	181	201	30.0	0.390	0.168	2.83	0.052	0.135	1.17	0.045	0.426	0.067	0.492	0.086
36	4.11	0.125	0.068	2.77	0.035	51.0	0.053	0.084	27.6	0.074	0.071	28.3	113	149	19.0	0.143	0.062	2.54	0.052	0.135	0.463	0.045	0.426	0.067	0.329	0.086
37	1.34	0.125	0.293	24.3	0.035	66.1	0.053	0.086	2.87	0.187	0.071	28.6	349	126	21.0	0.341	0.147	1.88	0.052	0.135	0.463	0.045	0.426	0.067	0.631	0.086
38	4.99	0.125	0.127	27.1	0.035	65.2	0.053	0.114	1.92	0.249	0.071	28.4	408	138	24.0	0.362	0.061	1.73	0.052	0.135	0.463	0.045	0.426	0.067	0.754	0.086
39	4.53	0.148	0.102	15.6	0.035	66.2	0.053	0.125	2.01	0.183	0.071	28.7	337	150	25.0	0.379	0.067	2.31	0.052	0.135	1.48	0.045	0.426	0.067	0.628	0.086
40	2.56	0.309	0.102	9.36	0.035	96.1	0.053	0.318	1.93	0.149	0.071	28.7	296	180	26.0	0.268	0.441	2.16	0.052	0.135	0.602	0.045	0.426	0.067	0.503	0.086
41	4.61	0.806	0.153	10.5	0.035	48.7	0.053	0.280	2.57	0.040	0.071	29.2	100	203	73.0	0.303	0.062	2.63	0.052	0.135	0.463	0.045	1.66	0.067	1.69	0.086
42	15.1	1.07	0.048	0.083	0.035	0.825	0.053	0.045	0.696	0.565	0.071	0.042	13.0	625	1.00	1.79	0.062	5.56	0.052	0.135	2.88	0.045	0.426	0.067	0.053	36.3
43	2.02	4.02	0.986	0.083	0.035	47.5	0.053	0.039	4.52	0.040	0.071	30.9	27.6	115	23.0	0.264	0.062	1.99	0.052	0.135	0.463	0.045	4.70	0.067	2.87	0.086
44	4.31	0.125	0.375	8.40	0.035	2.82	0.053	0.051	0.377	0.040	0.071	1.62	39.6	72.0	1.00	0.009	0.033	0.16	0.052	0.135	0.038	0.045	0.655	0.086	0.035	0.086
45	4.09	0.125	0.595	4.16	0.035	43.7	0.053	0.360	2.68	0.303	0.543	27.3	1191	67.2	25.0	0.413	0.062	1.56	0.052	0.135	0.367	0.045	0.426	0.067	0.267	0.086
46	3.58	0.404	0.356	26.8	0.035	44.9	0.053	1.33	2.33	0.107	0.071	27.4	107	57.1	34.0	0.117	0.510	2.11	0.052	0.135	0.463	0.045	0.426	0.067	0.242	0.086
47	1.71	7.98	0.100	10.4	0.035	43.3	0.053	0.209	16.9	0.627	12.8	28.4	11.3	77.8	21.0	16.9	0.220	0.776	0.052	0.135	1.67	0.045	0.426	0.067	0.083	0.086
48	22.7	0.125	0.048	14.5	0.035	43.2	0.053	0.042	9.36	0.368	4.02	4.57	281	62.2	1160	0.412	0.240	0.341	0.052	0.147	0.463	0.045	3.57	0.067	0.607	0.086
49	6.71	0.781	0.167	8.40	0.035	243	0.053	32.1	2.39	0.040	0.071	28.8	133	127	58.0	0.359	0.062	2.93	0.052	0.135	0.463	0.045	1.58	0.067	0.998	0.086
50	5.04	0.439	0,248	9.07	0.089	63.1	0.053	9.17	10.4	3.16	0.071	29.3	104	141	490	0.270	0.062	2.82	0.052	0.135	0.896	0.045	0.642	0.067	0.395	0.086
51	4.31	0.120	0.097	379	0.035	46.7	0.053	0.045	3.88	0.086	0.071	28.1	130	52.6	27.0	0.396	0.062	2.49	0.052	0.135	1.16	0.045	0.426	0.067	0.650	0.086
52	5.13	0.125	0.148	334	0.035	47.4	0.053	0.045	3.23	0.088	0.071	28.1	118	35.1	28.0	0.381	0.062	2.67	0.052	0.135	0.463	0.045	0.426	0.067	0.613	0.086
53	4.85	0.777	0.048	602	0.035	42.6	0.053	0.052	4.59	0.119	0.071	27.5	123	20.3	28.0	0.427	0.062	2.46	0.052	0.135	3.39	0.045	0.426	0.067	0.585	0.086
54	3.35	0.125	0.089	1.61	0.035	45.9	0.053	0.045	2.26	0.416	0.071	28.5	183	95.6	19.0	0.363	0.062	2.61	0.052	0.135	0.463	0.045	0.426	0.067	0.116	0.086
55	4.82	0.125	0.111	0.164	0.035	52.1	0.053	0.061	1.90	0.058	0.071	27.6	66.4	101	18.0	0.410	0.062	2.90	0.052	0.135	0.463	0.045	0.426	0.067	0.037	0.086
56	5.74	0.305	0.331	3.20	0.035	48.5	0.053	0.172	1.54	0.040	0.071	28.0	101	125	63.0	1.24	0.396	3.17	0.052	0.135	0.463	0.045	0.426	0.067	0.213	0.086
57	5.62	0.643	0.104	10.5	0.035	63.5	0.053	0.195	3.32	0.150	0.071	28.6	231	149	24.0	0.366	1.62	2.64	0.052	0.135	0.709	0.045	0.426	0.067	1.79	0.086
58	24.6	0.125	0.196	127	0.035	55.9	0.053	0.097	11.6	0.399	4.12	5.23	58.8	192	1.00	0.504	0.320	0.065	0.052	0.135	0.463	0.045	3.12	0.067	0.989	5.30
59	11.0	0.125	0.191	0.083	0.035	27.6	0.053	0.040	0.090	0.300	3.61	8.37	101	208	1.00	0.274	0.512	0.131	0.052	0.135	0.463	0.045	8.39	0.067	0.041	22.1
60	24.2	0.125	0.048	14.6	0.035	44.8	0.053	0.049	9.92	0.397	4.07	5.14	280	136	1.00	0.500	0.226	0.327	0.052	0.141	0.463	0.045	3.44	0.067	0.581	0.086
61	18.9	0.125	0.048	38.8	0.035	32.8	0.053	0.059	42.5	0.620	5.14	3.88	283	27.9	1.00	7.34	0.178	3.47	0.052	0.135	0.463	0.045	2.66	0.067	0.558	0.086
62	36.5	0.125	0.048	14.7	0.035	56.3	0.053	0.083	3.51	0.631	4.69	4.50	258	27.5	5.00	1.695	0.430	0.917	0.052	0.049	0.463	0.045	4.68	0.067	0.56	0.086

SAMPLE Nº	Al	As	Sb	Ba	Be	B	Cd	Cs	Zn	Co	Cu	Cr	Sr	Fe	Li	Mn	Mo	Ni	Ag	Pb	Se	Tl	Ti	Th	U	V
63	5.42	0.125	0.149	2.18	0.035	66.7	0.053	0.122	1.85	0.143	0.755	28.7	83.7	170	1.00	0.188	0.062	2.31	0.052	0.135	0.463	0.045	0.426	0.067	0.374	0.086
64	4.22	5.12	0.12	1.15	0.035	45.5	0.053	0.349	4.29	0.040	0.071	27.7	7.22	79.3	22.0	8.03	0.062	0.071	0.052	0.135	0.650	0.045	0.426	0.067	0.154	0.086
65	4.48	0.125	0.255	0.318	0.035	50.8	0.053	0.028	2.59	0.062	0.071	30.1	206	101	1.00	0.365	0.062	2.51	0.052	0.135	0.463	0.045	0.426	0.067	0.125	0.086
66	5.32	0.109	0.56	5.02	0.035	49.5	0.053	0.101	1.78	0.040	0.071	28.4	144	155	20.0	0.369	0.068	2.81	0.052	0.135	0.996	0.045	0.426	0.067	1.55	0.086
67	5.79	0.125	0.346	13.9	0.035	59.8	0.053	0.444	2.55	0.124	0.071	30.0	250	75.1	12.0	0.251	0.269	2.02	0.052	0.135	0.463	0.045	0.293	0.067	0.821	0.086
68	4.32	0.722	0.216	23.1	0.035	49.8	0.053	0.050	4.38	0.091	0.071	27.6	162	37.4	19.0	0.135	0.062	2.51	0.052	0.135	0.524	0.045	0.426	0.067	1.62	0.086
69	4.70	0.982	0.15	4.39	0.035	47.8	0.053	0.317	2.05	0.040	0.071	27.7	77.0	145	61.0	0.380	0.062	3.15	0.052	0.135	1.72	0.045	0.426	0.067	1.09	0.086
70	3.92	0.111	0.082	0.083	0.035	51.8	0.053	0.063	1.29	0.164	0.071	28.2	46.6	164	20.0	0.381	0.062	3.05	0.052	0.135	0.677	0.045	0.426	0.067	0.251	0.086
71	0.250	6.53	0.106	88.8	0.035	208	0.053	20.5	3.55	0.040	0.071	36.7	537	12.9	3011	0.177	10.1	2.71	0.052	0.135	9.00	0.156	5.28	0.067	0.095	0.086
72	1.74	1.48	0.489	52.6	0.035	148	0.053	147	0.71	0.164	0.071	5.23	945	19.9	2671	151	0.710	1.22	0.052	0.135	1.20	0.207	6.84	0.089	0.041	0.086
73	1.73	0.125	0.235	94.2	0.035	55.2	0.053	0.095	5.33	0.045	0.071	28.8	142	66.5	1.00	0.561	10.8	2.39	0.052	0.135	0.463	0.045	0.248	0.067	10.5	0.086
74	10.4	0.193	0.126	6.62	0.035	10.2	0.053	0.096	0.696	0.122	0.071	0.637	128	67.5	1.00	0.186	0.090	0.197	0.052	0.135	1.50	0.045	1.76	0.337	0.156	0.086
RSD (%)	6.4	4.1	0.8	1.0	3.7	0.6	3.2	0.1	3.5	6.5	9.6	1.5	0.1	5.3	3.2	1.2	2.8	5.0	1.3	2.4	5.1	1.3	12.7	2.7	3.6	2.6

RSD= Median Relative Standard Deviation for triplicate.

In general, except for Cr, Fe and Ni (for which coefficients of variation are below 1 and median values are very similar to mean values), data dispersions are very high for all trace elements (coefficients of variation above 1). Thus, the median value could be used to represent each dataset, although its value may be very different from the mean value, because the median values generally do not substantially change. In some cases, unique extreme values distort the dataset; thus, the median value is more representative.

Spatial variation analysis

The graphs in **Figure 3** show the relationships among median values of trace element concentrations, in µg/l, at both national and regional levels. Comparative analyses were based on median values, as data dispersions are quite high. The trace elements with higher median concentrations are as follows: Sr and Fe (with concentrations above 100 µg/l); B and Cr (with concentrations between 50 and 27 µg/l); Ba and Al (with concentrations between 10 and 4 µg/l); Zn and Ni (with concentrations between 2.6 and 2.3 µg/l); and Se and Ti (with concentrations between 0.46 and 0.42 µg/l). The remainder of the trace elements are present at much lower concentrations (between 0.135 and 0.035 µg/l), with many values below their MDL values. As a result, no variation was found among communities.

Fig 3. Median concentrations of the different trace elements at both national and regional levels.

In summarising the plethora of data/results contained in these trace-element graphs, we highlight several points of interest:

In regard to essential nutrient microelements with known RDIs, the median values obtained for *Fe* are relatively homogeneous (between 67 and 117 µg/l), with high values between 148 and 234 µg/l. The highest median values obtained for **Fe** (above 150 µg/l) pertained to the communities of the Canary Islands, Valencia, Castilla La Mancha and Murcia, while Castilla y León contained the lowest median values of *Fe.* The median values obtained for **Se** were also very homogeneous, with the lowest being 0.463 (its MDL for 9 communities). Other values that should be highlighted are as follows: Murcia (0.709), Extremadura (0.664), Castilla La Mancha (0.545) and Valencia (0.533). In contrast, the median values obtained for *Zn* were very heterogeneous (between 0.7 and 6.9 µg/l), with values ranging from 0.696 in the Canary Islands to 13.930 in Asturias-Cantabria.

Relating the essential nutrient microelements with unknown RDIs but with known ESADDIs, almost all *Cu* concentrations obtained were below its MDL, with Catalonia at 1.856 and Canary Islands at 1.840. *Mn* values were very low (reaching levels below 0.4 µg/l), with Extremadura having an outlying value of 6.196 and all other communities having values between 0.251 and 1.033. Except for the communities of Murcia, Catalonia and Cantabria, which show more heterogeneous values, *Mo* values were also very low (around 0.062-0.1 µg/l). *Cr* values were very homogeneous (around 28-30 µg/l), with only two very low values (corresponding to Catalonia (5.206) and the Canary Islands (5.648)). In this regard, it is worth highlighting Murcia (1.616) and Catalonia (1.221), which were followed distantly by the Canary Islands (0.555). All other values for Cr are very low (around 0.062-0.1 µg/l). Contrary to this values, *Co* values were very dispersed (between 0.04 and 0.43 µg/l), with maximum values pertaining to the Canary Islands and Catalonia.

Concerning microelements that are possibly essential trace elements, all values obtained for *Ni* varied widely (between 0.5 and 3 µg/l) and were greater than its MDL. *B* had very homogeneous median values (between 26 and 60 µg/l), with two well-differentiated, high values for Galicia and Asturias. *As* also had homogeneous values, between 0.125 (its MDL in 7 communities) and 0.64 µg/l, with two high, differentiated values in Extremadura and Asturias.

Finally, Sb, Pb and Cd were considered as non-essential microelements with toxic effects in tolerable doses. As a slightly toxic element, *Sb* had very low and homogeneous values (between 0.11 and 0.6 µg/l). Of particular interest, Asturias had the highest value (1.7 µg/l), which was nearest the PV of Sb (5 µg/l). As a moderately toxic element, all median values obtained for *Pb* were below its MDL. Last, as a very toxic element, *Cd* had median values below its MDL.

Hydrogeochemical study

In a previous work (Gutiérrez-Reguera et al., 2012), a study of physicochemical characteristics (general parameters and major components) of bottled mineral waters of Spain was carried out. Based on the data obtained in this previous work, and in order to facilitate the realization of a hydrogeochemical assessment, the median values of general parameters and major components were shown in **Figure 4**. To summarize, it may be noted the following:

a) The water pH varied between 7.6 and 8.3 (neutral waters-slightly basic waters); the redox potential varied between 194 and 227 mV (oxidizing waters), and total dissolved solids (TDS) values indicated that they were low mineral concentration waters.

b) Regarding anions, the bicarbonates varied between the very low value found in Extremadura (6.40 mg/L) and the highest (352.15 mg/L) in Baleares. Sulphates values were between Extremadura (4.90 mg/L) and Murcia (62.00 mg/L). Chlorides were between Aragon (3 mg/L) and Balearic Islands (64 mg/L). Fluorides ranged between Murcia (0.06 mg/L) and Castilla y León (0, 50 mg/L), being values well below 1.5 mg/L (limit value to be shown on labels) in all cases. Nitrates concentrations were also well below 50 mg/L, parametric value for this anion, varying between Catalonia (1.50 mg/L) and Castilla y León (15.80 mg/L). Finally for SiO2, the data varied between Murcia (1.95 mg/L) and Canary Islands (85.70 mg / L).

c) Respecting cations, calcium were between Extremadura (6.14 mg/L) and Valencia (88.70 mg/L). Magnesium values were between Extremadura (1.50 mg/L) and Murcia (35 mg/L) and sodium ranged between Aragon (1.50 mg/L) and Canary Islands (41.75 mg/L).

Fig 4. Representation of median values of each community, general parameters and major components.

In addition, Table 6 shows the categories of the 74 samples, based on their hydrochemical facies, hardness and mineralization. From this study it was deduced that:

a) Regarding hydrochemical facies, 43.2% were Ca-HCO_3, 25.7% Ca-Mg-HCO_3, 16.2% Na-K-HCO_3, and 5.4% Mg-Na-K-HCO_3. Aditionally other values that should be highlighted were 2.7% for Na-K-Cl and 2.7% for Ca-SO_4 and Ca-Mg-$SO_{4.}$

b) According the hardness, 43.2% were very hard water and 27% hard water. Only 14.9% were soft water and slightly hard water respectively.

c) In relation to the total dissolved solids , 87.8% were low mineral concentration water. On the other hand, only 5.4% were very low mineral concentration water, 4.1% high mineral concentration water and 2.7% moderated mineral concentration water.

Concerning trace elements, it should be indicated the following:

a) Sr showed values above 1000 µg/L in samples 34 and 45, which had Ca-SO_4 and Ca-Mg-SO_4 facies, very hard water and moderated mineral concentration. These samples corresponded to limestone soils and calcareous, sandstone aquifers.

b) As had high values compared to the others in samples 43, 47 and 64, which were Na-K-Cl and Ca-Na-K-Cl facies and soft waters. Sample 64 was very low mineral concentration water, whereas the others were low mineral concentration waters. All pertained to siliceous soils and detritic, fissured aquifers.

c) Sample 6 showed high concentrations for As, Sb, Cd, Co, Ag, Pb, Se, Tl and Ti with regard to the others, being Ca-HCO_3 facies, hard, low mineral concentration water. Regarding the lithology, soils were siliceous and clayey, while aquifers were mainly detritic or isolated aquifers.

d) Cs and Ti had high values compared to the others in samples 13 and 72, with Na-K-HCO_3 facies, very hard, high mineral concentration water. These samples came from siliceous soils and calcareous, fissured aquifers.

e) Zn, another essential element, showed results very heterogeneous, ranging from 0.696 µg/L (its MDL) to 27.55 µg/L, emphasizing the sample 61 with the highest value. This sample was Ca-HCO_3 facies, very hard, low mineral concentration water, from siliceous soils and from isolated aquifers and porous, fissured aquifers.

f) Al had highest values in samples 20 and 21, which had Ca-HCO_3 facies, hard and very hard water respectively, low mineral concentration waters. These samples pertained to siliceous, calcareous soils and fissured, porous aquifers.

g) The highest concentrations in Ba corresponded to the samples 5, 10, 51, 52 and 53. These samples were Ca-HCO_3 facies, hard and very hard, low mineral concentration waters. These corresponded to siliceous and calcareous soils and fissured, porous aquifers.

h) Co showed its highest values in the samples 6, 30 and 50, that were Ca-HCO_3 and Na-K-HCO_3 facies, hard and soft respectively, low mineral concentration waters. These came from siliceous, clayey soils and isolated, porous aquifers.

3.4. Nutritional assessment analysis

Considering a daily intake of 1 litre of natural mineral water, we determined the amounts of characteristic minerals administered to the body, determining the percentage in terms of each mineral's RDI or ESADDI.

For each bottled water, a mineral concentration was determined by either approximating the average of all values (for weak mineralisation waters, due to the large number of samples) or determining a characteristic maximum or mean value (for those waters for which there are few samples regarding mineralisation levels).

Table 7 highlights some characteristic examples of different bottled waters, according to mineralisation type, with respect to the contribution a mineral water may make to a person's mineral consumption. For majority components, the mineral concentration increases from very weak to strong, but no increase (or decrease) is observed for minority or trace components.

Fe has an RDI ranging from 12 – 15 mg in women and 10 - 12 mg in men. Given the median value of *Fe* in water from Castilla La Mancha (150.05 µg/l between samples 181 and 188), bottled water from this region constitutes 1 to 1.25% of its RDI in women and 1.25 to 1.5% of its RDI in men.

For *Zn*, for which the highest median concentration value was obtained in Asturias, (13.93 µg/l), an intake of 1 litre of this bottled water would constitute between 0.093% of its RDI in men and 0.116% of its RDI in women. *Zn* has an RDI of 12 mg in women and 15 mg in men.

For Se, Murcia stands out with the highest value; the intake of 1 litre of this water would cover between 1.3% in women and 1% in men of its RDI. *Se* has an RDI of 55 µg/day for women and 70 µg/day for men. Thus, the intake of 1 litre of sample-21 water from Castilla y León, which has a concentration of 22.02 µg/l (the highest value), would constitute between 31.5 and 40% of its RDI, which is a very high value.

Cu's highest value was obtained for the community of Catalonia, from which the intake of 1 litre would only constitute 0.06 to 0.13% of its ESADDI. The RDI of *Cu* is not well known, but its ESADDI is 1.5 - 3 mg in adults and 0.7 - 2 mg in children. Using water from Extremadura (sample 141), which has a concentration of 12.84 µg/l (among the highest), the intake of 1 L constitutes 0.01284 mg of Cu, between 0.9 and 0.43% of its ESADDI.

For Mn, with a concentration of 250.9 µg/l, the intake of 1 litre of water would constitute 12.5 – 5% of its ESADDI, a very high value.No RDIs are known for *Mn*, but it has an ESADDI interval between 2-5 µg/day in adults. Thus, for 1 litre of sample-1, from Aragón, which has a concentration of 3.72 µg/l, the *Mn* contribution , constitues between 186 and 74.4% of its RDI.

There are also no RDIs for **Cr**, but it has an ESADDI interval between 50 - 200 µg/day in adults. Thus, selecting the mean value of 28 µg/l in water, therefore it would constitute between 14 - 56% of the ESADDI.

For *Fe*, the intake of 1 litre of water from the Canary Islands (234.3 µg/l) would constitute between 1.56 and 1.95% of its RDI in women and between 1.95 and 2.34% in men.

Comparative analyses with mineral waters of other European countries

The analytical results obtained in the present research study were compared to those published by Bertoldi et al. in the paper "Survey of the chemical composition of 571 European bottled mineral waters" (2011). For each element, the minimum, maximum, median and *spread* values (maximum/minimum ratios) were reported in **Table 8**. Those minimum values that were undetectable were expressed as below the MDL. The spread value of an element that was not detectable in all samples was calculated using that element's MDL as the minimum value.

Maximum, minimum and median values

The minimum values are always below the MDL values in the analysis of European waters, whereas in the analysis of Spanish waters there are two elements, Sr and Fe, for which the minimum values (4.415 and 12.89, respectively) are above the MDL values. The E/S proportion of minimum values is above 1 for every element studied excepting Cd, Li, Tl and U (which have values near 1) and Pb (0.4).

In almost all cases, the maximum values obtained in the present study are significantly lower than those reported for Europe. E/S values are high, except for Co, Li and V (which have values near 1) and Cd, Pb, Tl and U (which have values below 1). In every case, these maximum values are lower than the maximum values permissible under legal regulations.

With regard to median values, there are 6 elements (Cd, Cu, Pb, Se, Tl and V) that, in both studies, had values below their MDLs. Regarding E/S proportions, there are 6 elements with E/S values near 1 (B, Cd, Co, Ni, Tl and U), whereas Al, Cs, Li and Pb have values below 1, and other Ba, Zn, Cu, Mo, Se and V have values well above 1.

Spread values

In addition to absolute values, E/S proportions have been calculated. There are 3 elements with values near 1 (Al, Zn and Li), while B and Cs exhibited higher values (1.5 and 1.8). All other values are below 1, from 0.6 for Ba and 0.09 for V. Regarding absolute *spread* values, we can establish the following intervals, which will allow a better comparison among the data: low (<100), medium (between 100 and 400) and high (>400). We analysed these values according to the types of microelements considered in the discussion of results in the previous section:

In regard to essential nutrient microelements with known RDIs, Fe is one of two elements (the other is Sr) that have minimum values above their MDLs (12.89 µg/l in the case of Fe); thus, its spread occurs at one of the lowest values (48). In the previous analysis of European waters, no data regarding Fe are reported. Zn also shows a low value, 61, which is consistent with the European value, 55. Se, however, has a much higher value than that reported for the European study (47.56 versus 9.0), because its minimum value is much lower in the present study (although both are registered as low). In conclusion, these three elements exhibit lower spread values, which is consisted with the European data.

Relating to essential nutrient microelements with unknown RDIs but with known ESADDIs, Cu has a mean value of 181, higher than that of the European study (68, considered low). Mn has one of the highest values, 7169, which is consistent with the European value of 3429, one of the highest in that study. In the Spanish study, Cr has a high value as well (874); Cr was not analysed in the European study. However, in the present study, Mo has a mean value of 217, while the European value is 113. Co has a spread value of 101 versus a low value (34) in the European study. In conclusion, in the Spanish study, there are two elements (Cu and Mo) in the second interval and another two (Mn and Cr) in the third interval. However, in the European study, Cu is in the low interval, and Mn is in the high interval.

Concerning microelements that are possibly essential trace elements, in the first group, Ni exhibits low values in both (Spanish and European) studies. B exhibits high values (527 and 782) and should be framed within the third group of elements (which have spreads above 400). On the other hand, As has a value of 64 in the present study, and it was not analysed in the European study.

Finally, in regard to non-essential microelements with toxic effects in tolerable doses, Sb should be framed within the first group (it was not analysed in the European study), whereas Pb and Cd should be in the first group, consistent with the lowest values detected in the European study.

CONCLUSIONS

1. Chemical analyses of the NMWs of Spain indicate that the elements Sr, Fe, B, Cr, Ba, Al, Zn, Ni, Se and Tl have the highest median concentrations, with the values of other elements being very low.

2. With respect to analyses per autonomous communities, Fe, Se, Mn, Cr and V show very homogeneous values among communities, with the following exceptions: Fe in the Canary Islands (which presents a value above

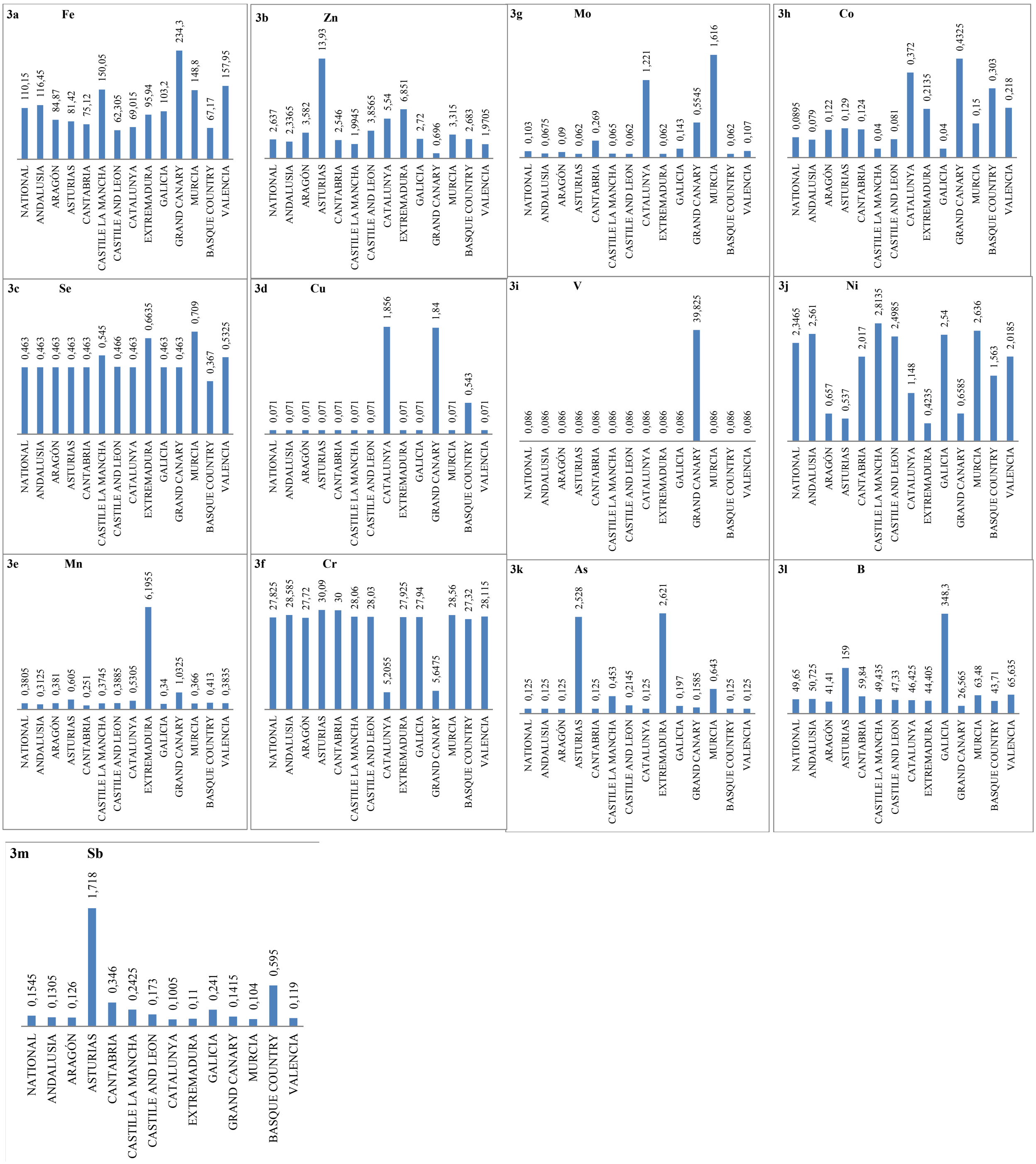

***Fig 3**. Median concentrations of the different trace elements at both national and regional levels.*

its PV), Mn in Extremadura (with a value of 6.196), Cr in Catalonia and the Canary Islands (with very low values, around 5 µg/l), and V in the Canary Islands (with a value of 39.825). The rest of the elements show dispersed values, which indicate variable types of waters, with regard to their trace elements, with Zn exhibiting a high value of 14 µg/l in Asturias.

3. There are four trace elements that show values slightly above the PV in some samples; Fe, Mn and Se. Fe exceeded the PV in four samples (it exceeds the PV concerning drincking water, whereas there is not PV for natural mineral water). Mn exceeded it in two samples and Se in a sample.

4. The hydrogeochemical study carried out reveals that:

The most of the samples are bicarbonated (Ca-HCO_3, Ca-Mg-HCO_3, Na-K-HCO_3 and Mg-Na-K-HCO_3 facies in this order). Only 5.4% are chlorinated (Na-K-Cl) or sulphated (Ca-SO_4 and Ca-Mg-SO_4).

Regarding the hardness, 43.2% are very hard waters and 27% hard waters. Only 14.9% are soft waters and moderately hard waters respectively.

In relation to total dissolved solids, 87.8% are low mineral concentration waters. Only 5.4% are very low mineral concentration, 4.1% high mineral concentration and 2.7% moderated mineral concentration waters.

Sr shows values above 1000 µg/L in two samples with Ca-SO_4 and Ca-Mg-SO_4 facies respectively, very hard, mode-

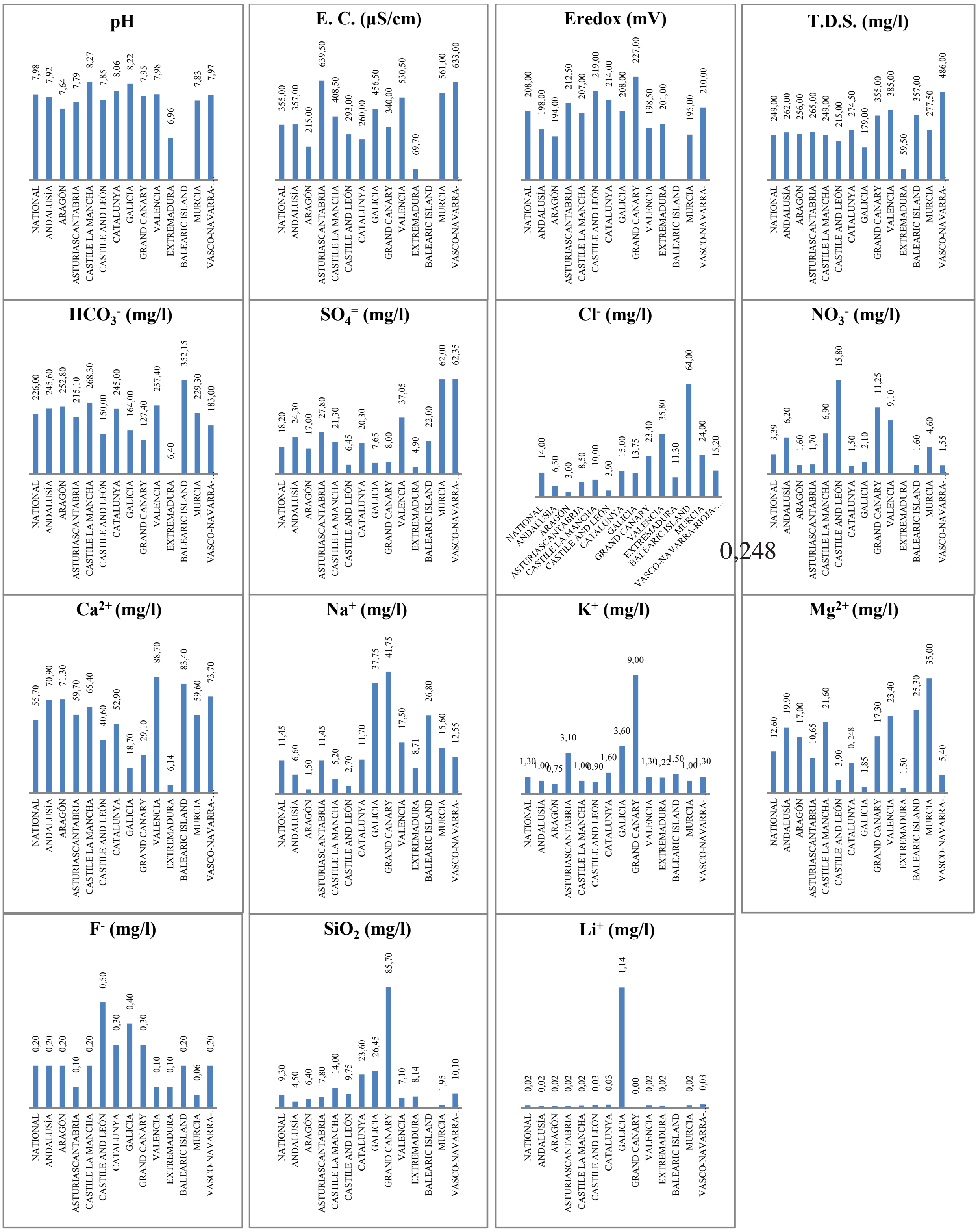

Fig 4. *Representation of median values of each community, general parameters and major components.*

rated mineral concentration waters, from limestone soils and calcareous, detritic aquifers.

As presents the highest values in three of the samples which are chlorinated (Na-K-Cl and Ca-Na-K-Cl), from siliceous soils and detritic, fissured aquifers.

The highest concentrations in As, Sb, Cd, Co, Ag, Pb, Se, Tl and Ti corresponds to a sample with Ca-HCO_3 facies, hard, low mineral concentration water coming from siliceous, clayey soils and basically detritic aquifers or isolated aquifers.

Cs and Ti have high values in two samples with Na-K-HCO_3 facies, very hard, high mineral concentration waters, corresponding to siliceous soils and calcareous, fissured aquifers.

Table 5 Statistical parameters of trace elements of the 74 samples of N.M.W. bottled in Spain.

ELEMENTARY STATISTICS/PV	200	10000	5	1000		1000	5				2000	50	
MDL	0.409	0.125	0.048	0.083	0.035	0.825	0.053	0.045	0.696	0.04	0.071	0.042	0.035
TRACE ELEMENTS	Al	As	Sb	Ba	Be	B	Cd	Cs	Zn	Co	Cu	Cr	Sr
Nº OF DATA	74	74	74	74	74	74	74	74	74	74	74	74	74
MAXIMUN	96.0	7.98	3.807	693	1.70	435	3.61	257	42.5	4.04	12.8	36.7	1841
MINIMUN	0.409	0.125	0.048	0.083	0.035	0.825	0.053	0.045	0.696	0.040	0.071	0.042	4.42
AMPLITUDE	95.6	7.86	3.759	693	1.66	434	3.56	257	41.8	4.00	12.8	36.6	1836
MEDIAN	4.40	0.125	0.155	10.5	0.035	49.7	0.053	0.141	2.64	0.089	0.071	27.8	130
MEAN	8.24	0.732	0.265	50.4	0.060	79.3	0.101	12.4	5.07	0.338	0.871	22.3	234
STANDARD DEVIATION(s)	15.1	1.55	0.479	130	0.193	96.9	0.413	41.3	6.58	0.749	2.11	11.1	332
VARIANCE(s2)	228	2.42	0.229	16959	0.037	9381	0.171	1709	43.4	0.561	4.44	124	10994
COEFFICIENT OF VARIATION(s/P)	1.83	2.12	1.805	2.58	3.18	1.22	4.09	3.33	1.30	2.21	2.42	0.498	1.42

ELEMENTARY STATISTICS/PV	200		50		20		10	10					
MDL	2.87	0.001	0.035	0.062	0.126	0.052	0.135	0.463	0.045	0.426	0.067	0.053	0.086
TRACE ELEMENTS	Fe	Li	Mn	Mo	Ni	Ag	Pb	Se	Tl	Ti	Th	U	V
Nº OF DATA	74	74	74	74	74	74	74	74	74	74	74	74	74
MÁXIMUN	625	6090	251	13.5	6.22	3.12	3.62	22.0	3.81	11.3	2.40	143	65.9
MÍNIMUN	12.9	1.00	0.035	0.062	0.126	0.052	0.135	0.463	0.045	0.426	0.067	0.053	0.086
AMPLITUDE	612	6089	251	13.4	6.09	3.07	3.49	21.6	3.77	10.9	2.33	143	65.8
MEDIAN	110	22.5	0.380	0.103	2.35	0.052	0.135	0.463	0.045	0.426	0.067	0.374	0.086
MEAN	130	267	6.83	1.07	2.05	0.093	0.197	1.17	0.100	1.91	0.108	3.61	2.61
STANDARD DEVIATION(s)	99.1	871	33.8	2.72	1.19	0.356	0.423	2.72	0.438	2.54	0.274	17.0	10.3
VARIANCE(s2)	9811	758013	1142	7.39	1.43	0.127	0.179	7.41	0.192	6.44	0.075	290	105
COEFFICIENT OF VARIATION(s/P)	0.763	3.25	4.95	2.54	0.581	3.82	2.14	2.33	4.38	1.33	2.52	4.72	3.94

MDL = Method Detection Limit; PV = Parametric Value

Zn shows the highest concentration in a sample with Ca-HCO_3, very hard, low mineral concentration water, from siliceous soils and isolated, porous, fissured aquifers.

The highest concentrations in Al has been found in two samples with Ca-HCO_3 facies, hard and very hard respectively, low mineral concentration waters, coming from siliceous, calcareous soils and fissured, porous aquifers.

Concerning Ba, five of the samples have the highest values. These samples are Ca-HCO_3 facies, hard and very hard, low mineral concentration waters, from siliceous, calcareous soils and porous, fissured aquifers.

Co shows their highest concentrations in three of the samples, with Ca-HCO_3 and Na-K-HCO_3 facies, hard and soft respectively, low mineral concentration waters, coming from siliceous, clayey soils and isolated porous aquifers.

5. Regarding the contributions of natural mineral waters to bodily minerals, nutritional assessment analyses reveal quite a variable range, because there is a wide variety of trace-element concentrations based on their RDIs or ESADDIs. Using the median concentration values of trace elements, it is possible to calculate the mean percentages of RDI that would be contributed by the intake of 1 litre of each natural mineral water; in this regard, the values obtained for the different communities are quite variable. For example, according to **Table 7**, Fe varies from 0.17% to 1.15%, Zn varies from 0.007 to 0.033%, Cu varies from 0.0024 to 0.428%, Mn varies from 0.0076 to 6.024%, Mo varies from 0.0248 to 2%, Se varies from 0.657 to 2.18%, Cr varies from 13.5 to 64% and Co varies from 4.5 to 15.15%.

6. Comparing these values with those obtained in the European study reveals similar values for B, Cd, Co, Ni, Tl and U. On the other hand, values obtained in Spanish bottled waters for Al, Cs, Li and Pb are higher than those obtained in the European study, whereas European bottled waters present higher median concentrations for Ba, Zn, Cu, Mo, Se and V.

7. In addition, the samples are classified according to their spread values (that is, the proportion of maximum and minimum values). The first category (values below 100) includes the essential micronutrients Fe, Zn, Se, Ni and As, in addition to a couple elements with toxic effects (Pb and Cd); the second category (values between 100 and 400) contains the micronutrients Cu and Mo, the third category (values above 400) includes the micronutrients Mn, Cr and B.

8. A comparison of spread values from both studies reveals that there are 4 elements with values near 1 (Al, B, Zn and Li), whereas Cs has a higher value (1.8). The rest of the values are below 1 and are between 0.6 for Ba and 0.09 for V.

Table 6 *Classification of samples based on their hydrochemical facies, hardness and mineralization.*

CATEGORY	SAMPLES	%	Nº SAMPLES
HYDROCHEMICAL FACIES			
Ca-HCO3	2, 5, 6, 7, 8, 10, 11, 16, 19, 20, 21, 22, 23, 30, 31, 36, 37, 38, 39, 40, 44, 46, 51, 52, 53, 55, 60, 61, 62, 68, 73 and 74	43.2	32
Ca-Mg-HCO3	1, 3, 4, 9, 14, 15, 17, 18, 24, 32, 35, 54, 56, 57, 58, 63, 65, 66 and 70	25.7	19
Na-K-HCO3	12, 13, 25, 26, 27, 28, 29, 42, 48, 50, 71 and 72	16.2	12
Ca-Na-K-HCO3	33	1.4	1
Mg-Na-K-HCO3	41, 49, 59 and 69	5.4	4
Na-K-Cl	43 and 47	2.7	2
Ca-Na-K-Cl	64	1.4	1
Cl-Ca-Na-K-HCO3	67	1.4	1
Ca-SO4	45	1.4	1
Ca-Mg-SO4	34	1.4	1
HARDNESS			
SOFT (≤ 50 mg/L CaCO3)	1, 11, 12, 29, 43, 47, 48, 50, 64, 68, 71	14.9	11
MODERATED (50-100 mg/L CaCO3)	3, 4, 19, 25, 26, 27, 28, 33, 42, 59, 73	14.9	11
HARD (100-200 mg/L CaCO3)	5, 6, 7, 8, 10, 13, 16, 20, 22, 30, 41, 44, 46, 49, 54, 56, 58, 65, 69, 74	27	20
VERY HARD (200-1000 mg/L CaCO3)	2, 9, 14, 15, 17, 18, 21, 23, 24, 31, 32, 34, 35, 36, 37, 38, 39, 40, 45, 51, 52, 53, 55, 57, 60, 61, 62, 63, 66, 67, 70, 72	43.2	32
TOO HARD (≥ 1000 mg/L CaCO3)	--	0	0
MINERALIZATION			
VERY WEAK (TDS≤50 mg/L)	1, 12, 64, 68	5.4	4
WEAK (TDS=50-500 mg/L)	2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 33, 34, 35, 36, 37, 38, 39, 40,41, 42, 43, 44, 46, 47, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 65, 66, 67, 69, 70, 71, 73, 74	87.8	65
AVERAGE (TDS=500-1500 mg/L)	34, 45	2.7	2
STRONG (TDS≥1500 mg/L)	13, 48, 72	4.1	3

Table7 *RDIs/ESADDIs percentages covered by the intake of 1 liter of NMW according to the element concentration.*

ELEMENTS/ CONTRI-BUTIONS NUTRITION	EXAMPLES TYPES MIN-ERALISATION	RDA or ESADDI	mg/l of element	NUTRITIONAL-CONTRIBUTION / Lwater. %of RDA.
	very weak		7	0.23 to 1.4
	weak	500 to	20	0.67 to 4
SODIUM	average	3000 mg	100	2 to 20
	strong		1.200	24 to 240
	very weak		0.5	0.025
POTASSIUM	weak	2000 mg	0.9	0.045
	average		3.5	0.175
	strong		78	3.9
	very weak		5	0.5 to 1
CALCIUM	weak	500 to	70	7 to 14
	average	1000 mg	100	10 to 20
	strong		120	12 to 24
	very weak	350 mg	3	0.9 to 1.07
MAGNESIUM	weak	man,	20	5.7 to 7.14
	average	280 mg	49	14 to 17.5
	strong	woman	50	14.3 to 17.9
	very weak	10 mg	0.08	0.53 to 0.8
IRON	weak	man,	0.115	0.77 to 1.15
	average	15 mg	0.067	0.45 to 0.67
	strong	woman	0.025	0.17 to 0.25
	very weak	4 mg	0.1	2.5 to 3.3
	weak	man,	0.2	5 to 6.7
FLUORIDE		3 mg		
	average	woman	2.1	52.5 to 70
	strong		7	175 to 233.3
	very weak	15 mg	0.004	0.03 to 0.033
		man,		
ZINC	weak	12 mg	0.0026	0.017 to 0.022
	average	woman	0.0027	0.018 to 0.023
	strong		0.001	0.007 to 0.008
	very weak	ESADDI	0.000071	0.005 - 0.0024
COPPER	weak	1,5 - 3	0.01284	0.856 - 0.428
	average	mg	0.000543	0.036 - 0.018
	strong		0.000071	0.005 - 0.0024
	very weak		0.0037	0.148 - 0.074
	weak	ESADDI	0.00038	0.0152 - 0.0076
MANGANESE		2,5 - 5		
	average	mg	0.00041	0.0165 - 0.00826
	strong		0.15	6.024 - 3.012
	very weak		0.000062	0.083 - 0.0248
	weak	ESADDI	0.0001	0.133 - 0.04
MOLYBDENUM		75 - 250		
	average	µg	0.000062	0.083 - 0.0248
	strong		0.0015	2 - 0.6
	very weak	70 µg	0.00065	0.929 to 1.18
SELENIUM	weak	man,	0.00046	0.657 to 0.84
	average	55 µg	0.00037	0.529 to 0.67
	strong	woman	0.0012	1.714 to 2.18
	very weak	ESADDI	0.027	54 - 13.5
CHROME	weak	50 - 200	0.0278	55.6 - 13.9
	average	µg	0.0273	54.6 - 13.65
	strong		0.032	64 - 16
	very weak		0.000091	4.55
COBALT	weak	2 µg vit	0.00009	4.5
	average	B12	0.000303	15.15
	strong		0.000164	8.2

ESADDI = Estimated Safe and Adequate Daily Dietary Intake; RDA=Recommended Daily Amount.

Table 8 *Comparative study between the analytical European data (E) reported by Bertoldi, D. et al. (2011) and the results obtained in 74 Spanish mineral waters of this work (S).*

TRACE ELEMENT (µg/l)	MINIMUN			MAXIMUN			MEDIAN			SPREAD		
	EUROPE	SPAIN	E/S	EUROPE	SPAIN	E/S	EUROPE	SPAIN	E/S	EUROPE	SPAIN	E/S
Al	< 1.5	< 0.409	3.7	420	96.0	4.4	< 1.5	4.40	0.3	280	235	1.2
As		< 0.125			7.98			< 0.125			64	
Sb		< 0.048			3.807			0.154			79	
Ba	< 0.37	< 0.083	4.5	1873	693	2.7	30.0	10.5	2.9	5131	8352	0.6
Be		< 0.035			1.70			< 0.035			49	
B	< 7	< 0.825	8.5	5313	435	12.2	33.8	49.7	0.7	782	528	1.5
Cd	< 0.05	< 0.053	0.9	0.69	3.61	0.2	< 0.05	< 0.053	0.9	13	68	0.2
Ce	< 0.05			0.70			< 0.05			14		
Co	< 0.11	< 0.04	2.8	3.79	4.04	0.9	< 0.11	0.089	1.2	34	101	0.3
Cs	< 0.05	< 0.045	1.1	519	257	2.0	0.05	0.141	0.4	10380	5704	1.8
Zn	< 4.7	< 0.696	6.8	260.0	42.4	6.1	< 4.7	2.64	1.8	55	61	0.9
Cu	< 1.6	< 0.071	22.5	112	12.4	8.7	< 1.6	< 0.071	22.5	68	181	0.4
Cr		< 0,042			36.7			27.8			874	
Sr		4.415			1841			130			417	
Fe		12.89			625			110			48	
La	< 0.05			1.15			< 0.05			23		
Li	< 0.06	< 0.06	1	5456	6090	0.9	11.5	22.0	0.5	87524	101500	0.9
Mn	< 0.6	< 0.035	17.1	1938	251	7.7	< 0.6	0.380	1.6	3429	7169	0.5
Mo	< 0.34	< 0.062	5.5	37.8	13.5	2.8	0.38	0.103	3.7	113	217	0.5
Nd	< 0.05			0.82			< 0.05			16		
Ni	< 1.9	< 0.126	15.1	30.3	6.22	4.9	< 1.9	2.35	0.8	16	49	0.3
Ag		< 0,052			3.12			< 0.052			60	
Pb	< 0.05	< 0.135	0.4	0.44	3.62	0.1	< 0.05	< 0.135	0.4	8.7	27	0.3
Rb	< 0.05			1010			2.47			20195		
Se	< 5.5	< 0.463	11.9	49.3	22.0	2.2	< 5.5	< 0.463	11.9	9.0	48	0.2
Sm	< 0.05			0.13			< 0.05			2.6		
Tl	< 0.05	< 0.045	1.1	1.32	3.81	0.3	< 0.05	< 0.045	1.1	26	85	0.3
Ti		< 0.426			11.3			< 0.426			27	
Th		< 0.067			2.39			< 0.067			36	
U	< 0.05	< 0.053	0.9	72.2	143	0.5	0.33	0.374	0.9	1443	2692	0.5
V	< 1	< 0.086	11.6	66.0	65.9	1.0	< 1	< 0.086	11.6	66	767	0.09
Yb	< 0.05			0.31			< 0.05			6.2		

E/S = Europe/Spain values ratio; Spread = maximum/minimum values ratio.

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