# Distribution of arsenic in groundwater in the area of Chalkidiki, Northern Greece

A. Kouras [a], I. Katsoyiannis [b], D. Voutsa [a,*]

[a] *Environmental Pollution Control Laboratory, Department of Chemistry, Aristotle University, Thessaloniki 54 124, Greece*
[b] *Swiss Federal Institute for Aquatic Science and Technology, EAWAG, Ueberlandstrasse 133, CH-8600 Duebendorf, Switzerland*

## Abstract

An integrate study aiming at the occurrence and distribution of arsenic in groundwater in the area of Chalkidiki, Northern Greece has been carried out. Groundwater samples from public water supply wells and private wells were analysed for arsenic and other quality parameters ($T$, pH, EC, Ca, Mg, Na, K, Cl, $HCO_3$, $NO_3$, $SO_4$, B, Fe, Mn). Arsenic showed high spatial variation; ranged from 0.001 to 1.840 mg/L. Almost 65% of the examined groundwaters exhibit arsenic concentrations higher than the maximum concentration limit of 0.010 mg/L, proposed for water intended for human consumption. Correlation analysis and principal component analysis were employed to find out possible relationships among the examined parameters and groundwater samples. Arsenic is highly correlated with potassium, boron, bicarbonate, sodium, manganese and iron suggesting common geogenic origin of these elements and conditions that enhance their mobility. Three groups of groundwater with different physicochemical characteristics were found in the study area: (a) groundwater with extremely high arsenic concentrations (1.6–1.9 mg/L) and high temperature (33–42 °C) from geothermal wells, (b) groundwater with relatively high arsenic concentrations (>0.050 mg/L), lower temperatures and relatively high concentrations of major ions, iron and manganese and, (c) groundwater with low arsenic concentrations that fulfil the proposed limits for dinking water.
© 2007 Elsevier B.V. All rights reserved.

*Keywords:* Arsenic; Geothermal; Groundwater; PCA; Saturation index

## 1. Introduction

Due to severe problems of water stress and deterioration of water quality, there is high interest on the quality of groundwater all over the world. The quality of groundwater depends on the composition of recharging water, the mineralogy and reactivity of the geological formations in aquifers, the impact of human activities and the environmental parameters that may affect the geochemical mobility of certain constituents.

The presence of trace elements in groundwater is an important issue because it affects possible uses of water. Particularly, arsenic contamination of groundwater is of increasing concern due to high toxicity and widespread occurrence of this element [1,2]. Increased concentrations of arsenic have been determined in many areas all over the world such as, in South East Asia (Bangladesh, Vietnam, West Bengal–India, Nepal, Cambodia, Mongolia, China, Thailand, Pakistan, Taiwan) [3–8], in Central and South America (Argentina, Chile, Mexico) and in North America (USA and Canada) [9–14] and in Australia [15]. Elevated arsenic concentrations have also found in various European countries, i.e., Hungary, Romania, Italy, Greece, Spain, Finland, Germany [2,16,17]. In particular, elevated arsenic concentrations in groundwater have been reported for many areas in Greece probably due to natural enrichment from geothermal activities and/or pollution [18–21]. In order to minimize the possible risk from arsenic a parametric value of 10 µg As/L has been set for water intended for human consumption according to Directive 98/83/EC [22]. US-EPA also decided to move forward in implementing the same standard for drinking water [23], which is also the guideline value recommended by the World Health Organization [24].

After the implementation of the EC Directive, some municipalities in Greece had problems since the concentration of arsenic in groundwater did not fulfil the new standard. Scatter water quality data held by local authorities and organisations revealed the occurrence of arsenic in the area of Northern

Greece. An extended research project aiming at the investigation of quality of groundwater in the area of Chalkidiki, Northern Greece has been carried out during the period 2001–2004. This paper presents an integrated study on the occurrence and the distribution of arsenic in the area of Chalkidiki, Northern Greece. The concentrations of arsenic are discussed in relation to the other physicochemical parameters measured in groundwater. Correlation analysis and principal component analysis were employed to find out possible relationships among the examined parameters and groundwater samples. Saturation indices for selected minerals were also calculated.

## 2. Experimental

### 2.1. Area description

The study area is located in the west part of Chalkidiki, S-SE of the Katsika mountain up to the coastal area (Fig. 1). The area is under rapid urbanization and tourist development and there is increased need for large quantities for high quality drinking water. The agricultural activities in the area also demand high quantities of irrigation water. Due to overexploitation the water table is lowered and the water quality is deteriorated due to increased salinization, especially in coastal waters. The presence of elevated concentrations of arsenic and boron is also a significant problem [25,26].

The Katsika mountain and the area of Petralona are Karstic and present a very intense geomorphologic relief in contrast to the flat coastal area (Fig. 1). Mesozoic limestones are the main

rock type in this area, along with granites-granodiorites which are located on the northwestern part. The Neocene consists mainly of unconsolidated clastics, clays and marls. The Neocene sediments, in many cases, include ventricular intercalations of sands, marls, grits, travertine, limestone and conglomerates. The major area is characterized by the presence of thermal and mineral water springs [27,28].

### 2.2. Sampling and analysis

A spatial sampling strategy was applied so that the quality of groundwater can be represented accurately. The water samples were collected from 30 wells located from the level of the sea up to 240 m above the sea level. The wells were not liable to obvious local contamination. Ten of them are public water supply wells used mainly for drinking purposes, 18 private owned wells used manly for irrigation and domestic household supply and two are geothermal wells. Well depth varies from 10 to 300 m. Flow rates ranged from 2 to 600 m$^3$/h. Water samples have been collected during the period 2001–2004, through six sampling campaigns. All wells were pumped for 15 min to remove standing water from the casing and storage system prior to sampling. In order to ensure that all samples represent groundwater and not water from the well bore, water temperature, conductivity and pH were continuously monitored during the purging, and sample collection did not start until these parameters were stable.

Polyethylene bottles precleaned with $HNO_3$ were used for sample collection. All bottles were rinsed with deionised water. Temperature (*T*), pH and conductivity (EC) were measured in
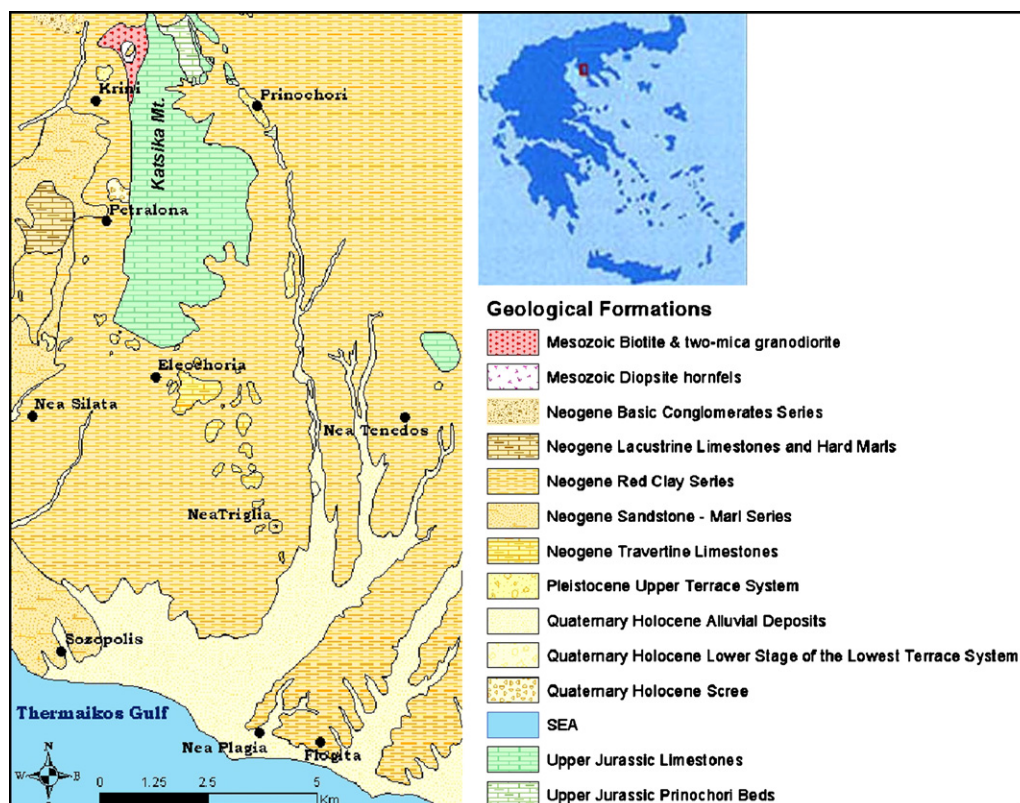


Fig. 1. Geological map of the studied area in Chalkidiki, Northern Greece.

Table 1
Physicochemical characteristics (mean values) of groundwater in the area of Chalkidiki, Northern Greece

| Sample ID | As (mg/L) | $T$ (°C) | pH | EC (μS/cm) | Ca (mg/L) | Mg (mg/L) | Na (mg/L) | K (mg/L) | $HCO_3$ (mg/L) | Cl (mg/L) | $SO_4$ (mg/L) | $NO_3$ (mg/L) | B (mg/L) | Fe (mg/L) | Mn (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.008 | 18.5 | 6.8 | 1556 | 110 | 72 | 132 | 4.45 | 635 | 135 | 49.2 | 66 | 1.50 | 0.230 | 0.039 |
| 1A | 0.074 | 21.4 | 6.7 | 1405 | 124 | 59 | 99 | 5.04 | 683 | 109 | 37.1 | 33 | 1.68 | 0.225 | 0.006 |
| 2 | 0.103 | 18.5 | 6.9 | 1514 | 113 | 77 | 110 | 5.76 | 647 | 152 | 32.4 | 54 | 2.12 | 0.148 | 0.008 |
| 2A | 0.035 | 18.3 | 6.4 | 1640 | 151 | 81 | 112 | 8.65 | 836 | 144 | 27.6 | 28 | 2.48 | 0.195 | 0.037 |
| 3 | 0.019 | 22.5 | 6.5 | 1240 | 112 | 55 | 95 | 3.88 | 677 | 84 | 24.9 | 5.4 | 2.06 | 0.210 | 0.030 |
| 3A | 0.028 | 20.3 | 6.7 | 1207 | 105 | 53 | 94 | 4.77 | 636 | 85 | 22.0 | 12 | 1.72 | 0.081 | 0.016 |
| 4 | 0.004 | 19.2 | 6.9 | 963 | 57 | 64 | 70 | 2.42 | 543 | 45 | 12.3 | 25 | 0.63 | 0.078 | 0.006 |
| 5 | 0.075 | 20.5 | 6.9 | 1431 | 112 | 79 | 91 | 4.72 | 626 | 123 | 31.6 | 53 | 1.51 | 0.350 | 0.009 |
| 6 | 0.438 | 20.2 | 6.9 | 1641 | 208 | 44 | 105 | 9.26 | 757 | 141 | 32.5 | 47 | 3.34 | 0.167 | 0.077 |
| 7 | 0.265 | 20.3 | 6.4 | 1483 | 172 | 42 | 98 | 8.06 | 674 | 129 | 30.8 | 30 | 2.63 | 0.172 | 0.020 |
| 8 | 1.730 | 33.0 | 6.3 | 2091 | 277 | 34 | 155 | 18.8 | 1011 | 202 | 25.9 | 0.4 | 6.04 | 0.468 | 0.013 |
| 9 | 0.008 | 20.2 | 7.5 | 720 | 40 | 60 | 33 | 0.98 | 397 | 29 | 35.9 | 0.3 | 0.12 | 0.063 | 0.004 |
| 10 | 0.022 | 21.3 | 7.7 | 810 | 43 | 56 | 47 | 1.22 | 378 | 65 | 23 | 8.6 | 0.52 | 0.090 | 0.016 |
| 10A | 0.013 | 21.3 | 6.9 | 780 | 33 | 51 | 67 | 1.32 | 385 | 53 | 17.4 | 1.4 | 0.21 | 0.069 | 0.004 |
| 11 | 0.003 | 21.0 | 7.3 | 1026 | 48 | 79 | 67 | 1.16 | 574 | 56 | 21.0 | 4.8 | 0.32 | 0.070 | 0.003 |
| 12 | 0.005 | 22.3 | 7.1 | 1017 | 53 | 72 | 73 | 1.68 | 554 | 62 | 22.4 | 7.4 | 0.48 | 0.063 | 0.003 |
| 13 | 0.010 | 22.8 | 7.3 | 1080 | 53 | 73 | 64 | 1.72 | 583 | 59 | 17.6 | 7.8 | 0.66 | 0.396 | 0.006 |
| 15 | 0.012 | 18.2 | 7.1 | 4400 | 217 | 278 | 289 | 6.70 | 542 | 984 | 371 | 142 | 2.70 | 0.048 | 0.004 |
| 15A | 0.003 | 17.6 | 7.0 | 878 | 51 | 87 | 21 | 0.90 | 570 | 26 | 8.9 | 3.4 | 0.10 | 0.032 | 0.003 |
| 17 | 0.001 | 15.8 | 6.7 | 1249 | 183 | 21 | 52 | 0.42 | 417 | 162 | 21.1 | 58 | 0.29 | 0.037 | 0.003 |
| 18 | 0.002 | 17.0 | 7.2 | 1080 | 130 | 47 | 58 | 3.6 | 567 | 56 | 69 | 0.4 | 0.98 | 0.030 | 0.003 |
| 19 | 0.002 | 20.6 | 7.4 | 805 | 136 | 14 | 27 | 1.52 | 412 | 33 | 22.3 | 36 | 0.16 | 0.011 | 0.002 |
| 20 | 0.141 | 17.7 | 6.3 | 1638 | 211 | 45 | 102 | 8.46 | 688 | 192 | 26.7 | 16 | 3.45 | 0.120 | 0.008 |
| 22 | 0.150 | 20.2 | 6.3 | 1450 | 189 | 38 | 100 | 9.69 | 720 | 137 | 22.5 | 5.1 | 3.44 | 0.075 | 0.050 |
| 14 | 1.795 | 40.7 | 6.3 | 1981 | 254 | 39 | 144 | 16.4 | 1043 | 166 | 28.4 | 0.2 | 4.07 | 0.396 | 0.006 |

Table 2
Summary statistics of physicochemical parameters in groundwater in the area of Chalkidiki Northern Greece

| Parameter | Units | Min | Max | Median | Mean | 10th | 90th | S.D. | CV[a] |
|---|---|---|---|---|---|---|---|---|---|
| $T$ | °C | 10.7 | 42.1 | 20.0 | 21.2 | 17.0 | 27.0 | 5.7 | 26.6 |
| pH | | 5.8 | 8.1 | 6.8 | 6.8 | 6.3 | 7.3 | 0.4 | 6.0 |
| EC | µS/cm | 700 | 5100 | 1400 | 1406 | 828 | 1970 | 631 | 45 |
| Ca | mg/L | 33 | 287 | 129 | 117 | 48 | 245 | 72 | 54 |
| Mg | mg/L | 6.3 | 322 | 59 | 62 | 32 | 83 | 41 | 67 |
| Na | mg/L | 19 | 341 | 92 | 94 | 31 | 151 | 50 | 53 |
| K | mg/L | 0.3 | 20 | 4.5 | 5.7 | 0.9 | 14 | 5.1 | 91 |
| HCO$_3$ | mg/L | 378 | 1035 | 592 | 623 | 415 | 816 | 161 | 26 |
| SO$_4$ | mg/L | 7 | 384 | 26 | 36 | 13 | 39 | 55 | 155 |
| Cl | mg/L | 24 | 1250 | 125 | 136 | 30 | 205 | 159 | 117 |
| NO$_3$ | mg/L | 0.02 | 184 | 24 | 29 | 0.45 | 60 | 30 | 105 |
| Mn | mg/L | 0.001 | 0.080 | 0.006 | 0.012 | 0.002 | 0.037 | 0.018 | 150 |
| Fe | mg/L | 0.011 | 0.460 | 0.079 | 0.110 | 0.033 | 0.400 | 0.097 | 88 |
| B | mg/L | 0.04 | 6.50 | 1.48 | 1.80 | 0.14 | 4.00 | 1.64 | 91 |
| As | mg/L | 0.001 | 1.843 | 0.013 | 0.311 | 0.002 | 1.741 | 0.604 | 194 |

[a] CV: S.D. × 100/mean.

the field. Upon reception in the laboratory water samples were filtrated through 0.45 mm membrane filters. Two aliquots, one acidified to pH < 2 with nitric acid and one unacidified, were stored at 4 °C before chemical analysis. Acidified aliquots were used for analysis of heavy metals. The water samples were analyzed for Ca, Mg, Na, K, HCO$_3$, Cl, SO$_4$, NO$_3$, Mn, As, Fe and B by employing standard titrimetric method (HCO$_3$, Ca, Mg), ion chromatography (Na, K, SO$_4$, Cl, NO$_3$), photometric (B), flame atomic absorption or graphite furnace atomic absorption (Fe, Mn) and flame atomic absorption/hydride generation (As) [29].

Quality control samples include replicates and field blanks. Replicate samples were collected immediately after the routine samples in the field using the same collection method and equipment. All difference measured in concentrations between replicate pairs were well within the precision of the method for all measured parameters. Analysis of blank samples did not show any inherent bias in the method of analysis for the trace elements and major ions. The accuracy of methods has been checked by standard solutions. Analytical errors were in the range of 5–10%. The anion/cation balance was <±4%.
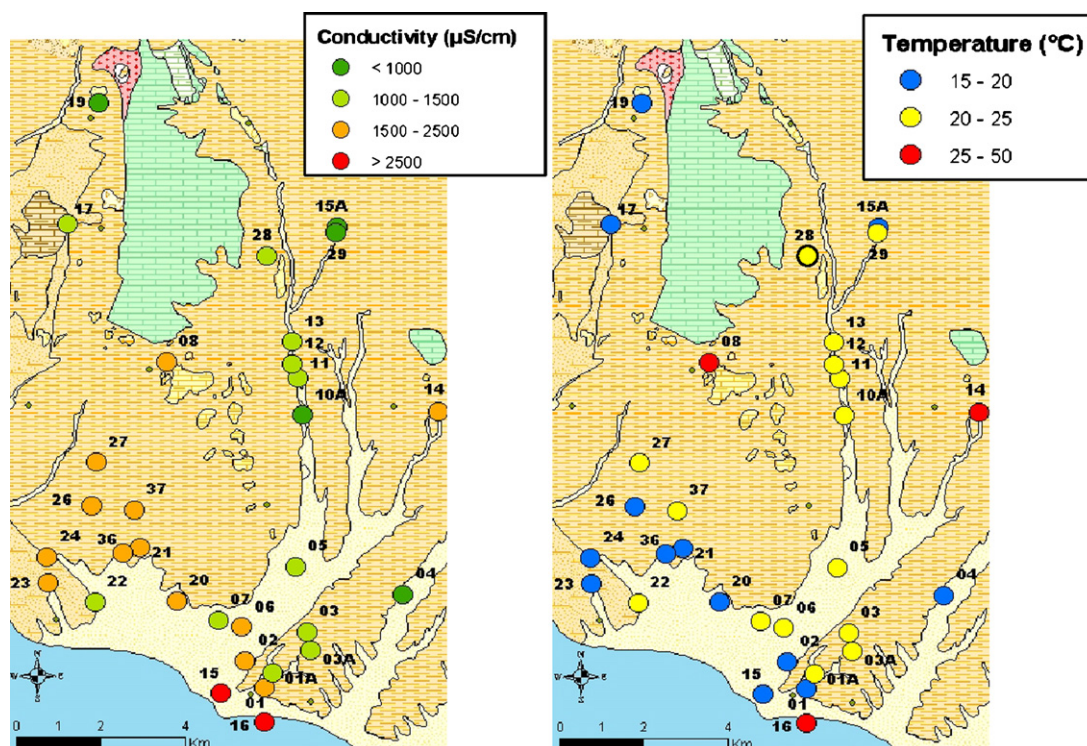


Fig. 2. Spatial distribution of temperature and conductivity in groundwater in the area of Chalkidiki, Northern Greece.

### 2.3. Data treatment—statistical analysis

All statistical analyses were performed with SPSS, Version 12.0 [30]. The examined parameters were tested for goodness of fit to normal distribution with Kolmogorov–Smirnov's test. All of them, except pH, were not normally distributed, thus, non-parametric tests were used to compare different groups and correlation of analysis. The Mann–Whitney $U$-test was employed to detect differences between two groups. The Kruskal–Wallis test was used for comparison of more than two groups. Spearman's rank correlation coefficient was used to measure the strength of the associations between arsenic concentrations and other parameters. A $p < 0.05$ was considered to indicate statistical significance. The saturation indices were calculated by PHREEQC using WATE4QF database.

## 3. Results and discussion

### 3.1. Physicochemical parameters

The quality characteristics (mean values of physicochemical parameters) of groundwater in the area of Chalkidiki, Northern Greece, are shown in Table 1. Summary statistical data for each parameter are shown in Table 2; the ranges are biased due to some extreme values measured in geothermal wells and in wells directly impacted by seawater intrusion. The pH values ranged from slightly acidic to slightly alkaline (5.8–8.1), with a mean value of 6.80. Electric conductivity (EC) was relatively high, ranging from 828 to 1970 μS/cm, with mean value 1406 μS/cm. The spatial distribution of conductivity is illustrated in Fig. 2. The higher values were observed at the coastal wells, suggesting influence of seawater. The temperature in groundwater ranged from 17 to 27 °C, mean temperature 21.2 °C. High temperatures were measured in geothermal wells (mean values: 33 °C in well no. 8 and 40.7 °C in well no. 14, Table 1) (Fig. 2). Bicarbonate was the dominant anion in groundwater, followed by chloride, sulphate or nitrate. Calcium and magnesium were the dominant cations in groundwaters; sodium exhibited significant contribu-
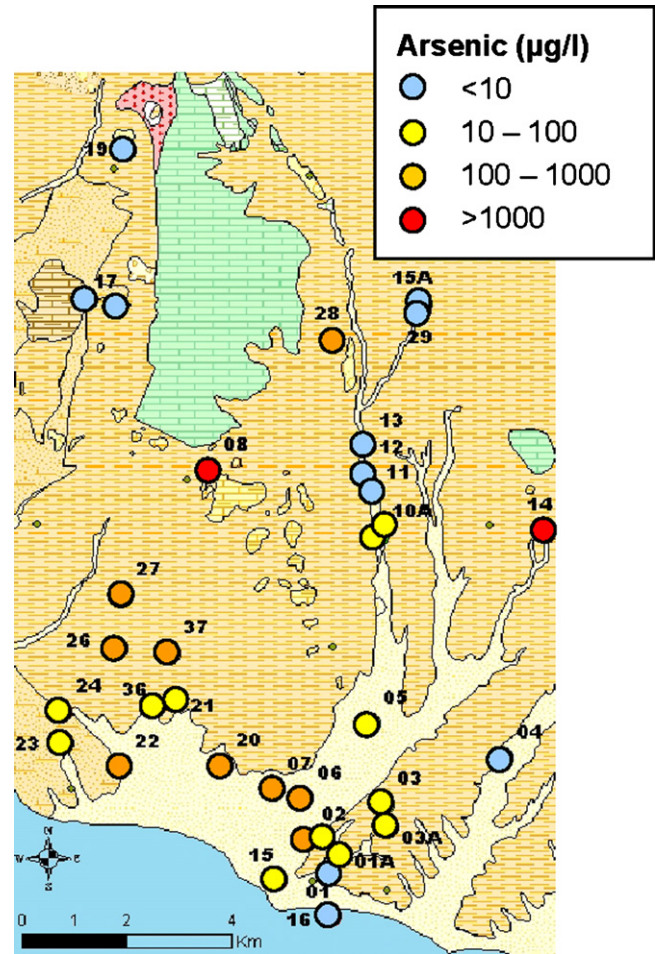


Fig. 3. Spatial distribution of arsenic in groundwater in the area of Chalkidiki, Northern Greece.

tion in some wells. Calcium and bicarbonate were also recorded as dominant ions in the majority of groundwater samples in the area of Thessaloniki, Northern Greece [31]. Groundwater samples were classified according to the dominant ions in four water types: Ca–Mg–HCO₃, Mg–Ca–HCO₃, Ca–Na–HCO₃ and

Table 3
Spearman's correlation coefficients[a]

|  | As | $T$ | EC | pH | Ca | Mg | Na | K | Cl | SO₄ | HCO₃ | NO₃ | B | Mn | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| As | 1.000 | | | | | | | | | | | | | | |
| $T$ | 0.053 | 1.000 | | | | | | | | | | | | | |
| EC | 0.721 | −0.282 | 1.000 | | | | | | | | | | | | |
| pH | −0.542 | 0.373 | −0.664 | 1.000 | | | | | | | | | | | |
| Ca | 0.505 | −0.319 | 0.759 | −0.645 | 1.000 | | | | | | | | | | |
| Mg | −0.197 | −0.100 | −0.154 | 0.395 | −0.626 | 1.000 | | | | | | | | | |
| Na | 0.792 | −0.131 | 0.860 | −0.618 | 0.525 | −0.092 | 1.000 | | | | | | | | |
| K | 0.905 | 0.015 | 0.781 | −0.587 | 0.674 | −0.271 | 0.845 | 1.000 | | | | | | | |
| Cl | 0.587 | −0.331 | 0.895 | −0.752 | 0.777 | −0.329 | 0.746 | 0.626 | 1.000 | | | | | | |
| SO₄ | 0.548 | −0.059 | 0.569 | −0.243 | 0.399 | −0.131 | 0.643 | 0.501 | 0.472 | 1.000 | | | | | |
| HCO₃ | 0.810 | −0.090 | 0.872 | −0.602 | 0.682 | −0.112 | 0.794 | 0.893 | 0.682 | 0.492 | 1.000 | | | | |
| NO₃ | 0.164 | −0.276 | 0.635 | −0.362 | 0.618 | −0.195 | 0.482 | 0.313 | 0.620 | 0.459 | 0.321 | 1.000 | | | |
| B | 0.872 | −0.059 | 0.868 | −0.695 | 0.711 | −0.251 | 0.858 | 0.957 | 0.775 | 0.457 | 0.915 | 0.310 | 1.000 | | |
| Mn | 0.860 | −0.179 | 0.770 | −0.580 | 0.509 | −0.180 | 0.794 | 0.832 | 0.589 | 0.502 | 0.790 | 0.328 | 0.820 | 1.000 | |
| Fe | 0.640 | 0.218 | 0.648 | −0.315 | 0.248 | 0.215 | 0.643 | 0.614 | 0.435 | 0.465 | 0.616 | 0.419 | 0.646 | 0.706 | 1.000 |

[a] Data from geothermal wells are not included.

Mg–Na–$HCO_3$. The concentration of nitrate ranged from 0.02 to 184 mg $NO_3$/L. The higher concentrations were observed in irrigation wells located at the SW part of the study area which is an intensively cultivated area. Nitrate pollution in groundwater of this area has been previously reported by Latinopoulos et al. [32]. Extremely high concentration of nitrate (142 mg $NO_3$/L) was found in a low depth (∼10 m) well (sample ID 15) suggesting direct impact from agricultural activities; this well also exhibited high values of conductivity, chloride, calcium, magne-

sium, sodium and potassium probably due to seawater intrusion since it is very close to the seashore.

### 3.2. Arsenic concentrations

The spatial distribution of arsenic in groundwater of Chalkidiki area, Northern Greece is illustrated in Fig. 3. The concentration of arsenic ranged from 0.001 to 1.843 mg/L (Table 2). Almost 65% of the examined wells exhibited arsenic
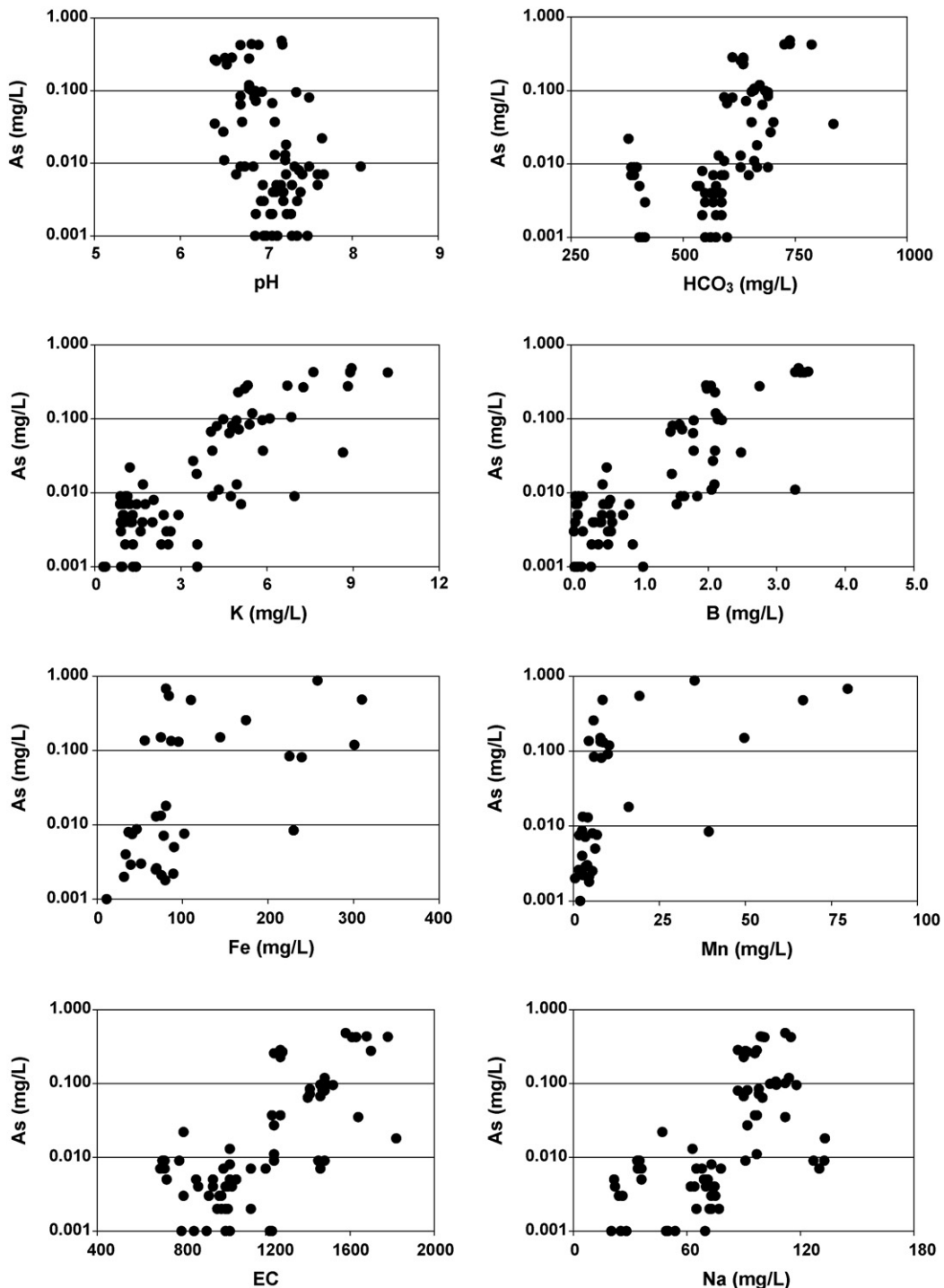


Fig. 4. Bivariate plots of arsenic with selected physicochemical parameters.

concentrations higher than the limit of 0.010 mg/L for drinking water (Table 1). The highest concentrations of arsenic were found in wells 8 and 14 (1.730 and 1.795 mg/L, respectively) where high temperatures were also measured (33 and 41 °C, respectively) (Table 1). Almost all the other physicochemical parameters (conductivity, calcium, chloride, carbonate, iron, sodium, potassium and boron) exhibited maximum values in these wells. On the contrary, the minimum concentrations of nitrates were determined in these wells. The occurrence of arsenic in geothermal waters is attributed to geogenic sources. High temperature as well as enrichment mechanisms such as evaporation, reductive dissolution of iron and manganese minerals and dissolution due to high carbonate concentration could probably affect the mobility of arsenic in these waters. Kartsic geothermal water percolates into the surrounding neogene sediments and contaminates the groundwaters in the coastal plains porous sediments [20]. Relatively high arsenic concentrations (0.040–0.237 mg/L) of geogenic origin have been also determined in deep wells in the major area of Thessaloniki, Greece, under reducing conditions [18].

The variation of arsenic concentrations in groundwater is an important consideration for monitoring, regulation, and treatment of arsenic as well as for environmental and health studies in regional scale [33]. Low temporal variation of arsenic was found during the sampling period, showing a variability of <20% for arsenic concentrations <5 μg/L due to increased analytical errors, and <7% for higher arsenic concentrations.

Spearman's correlation coefficients have been calculated to examine possible relationships among the measured parameters (Table 3). Arsenic concentrations are also plotted against selected physicochemical parameters (Fig. 4). Arsenic exhibited significant correlation with K, B, HCO₃, Na, EC, Mn and Fe. The wells with high arsenic content exhibited also high boron concentrations suggesting common origin of these elements [25]. This relationship between arsenic and boron in groundwater has also been observed by other investigators [34,35]. The relationship between arsenic and bicarbonate is also well documented because this ion can play an important role in the mobilization of arsenic through the competition for adsorption sites and through the formation of arseno-carbonate complexes [10,35,36]. Moreover, correlation between arsenic and iron or
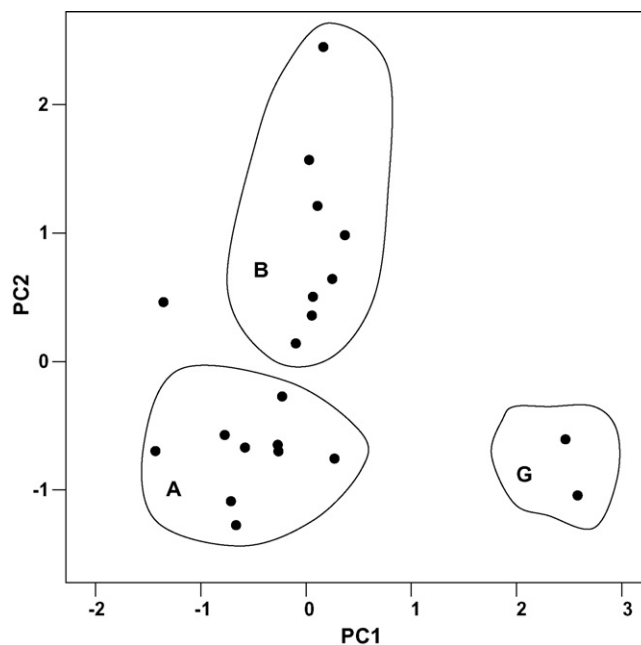


Fig. 5. First vs. second principal component from PCA analysis.

manganese is often observed in groundwater because, under certain conditions, the presence of Fe/Mn oxyhydroxides could lead to desorption of arsenic, iron and manganese [9,18,34]. The strong correlation of potassium with arsenic as well as with bicarbonate and sodium could be the result of a hydrochemical process such as hydrolysis of K-feldspars, which can lead to an increase of K, Na and HCO₃ in groundwater [4]. A weak negative correlation of arsenic with pH is presented in Fig. 5. However other investigators reported a positive correlation between arsenic and pH probably due to desorption processes at higher pH values [21,33]. In this study pH seems to have minimum effect; especially the geothermal wells with the highest arsenic concentrations exhibited the lowest pH values.

Using the analytical data from wells with different total arsenic concentration the saturation indices for selected minerals were calculated (Table 4). Groundwater is saturated with respect to iron minerals such as ferric oxides–goethite and hydroxides.

Table 4
Saturation indices for selected minerals

| Mineral | Sample 1 As: 0.008 mg/L | Sample 3A As: 0.028 mg/L | Sample 2 As: 0.103 mg/L | Sample 7 As: 0.265 mg/L | Sample 6 As: 0.438 mg/L | Sample 14 As: 1.795 mg/L |
|---|---|---|---|---|---|---|
| Calcite | −0.03 | −0.22 | −0.06 | −0.20 | 0.56 | 0.25 |
| Dolomite | 0.03 | −0.43 | 0.00 | −0.75 | 0.14 | 0.22 |
| Goethite | 8.11 | 7.30 | 8.16 | 7.12 | 8.26 | −6.80 |
| Fe(OH)₃ | 2.21 | 1.41 | 2.27 | 1.23 | 2.37 | 0.91 |
| Rhodocrocite | −1.13 | −1.88 | −0.93 | −1.78 | −0.69 | −1.41 |
| Siderite | −1.72 | −1.72 | −1.51 | −1.32 | −2.15 | −1.38 |
| MnOOH | −4.72 | −6.10 | −6.75 | −6.78 | −3.73 | −7.14 |
| Ca₃(AsO₄)·4H₂O | −14.08 | −14.08 | −12.24 | −11.69 | −9.17 | −9.74 |
| Mn₃(AsO₄)·8H₂O | −15.58 | −15.58 | −13.43 | −14.62 | −11.08 | −12.69 |
| FeAsO₄·2H₂O | −5.33 | −5.24 | −4.10 | −4.08 | −3.74 | −3.23 |
| PCO₂ | −1.09 | −0.87 | −1.03 | −0.58 | −1.21 | −0.17 |

However, groundwater is undersaturated with respect to manganese minerals, such as MnOOH, as well as with respect to carbonate minerals of iron and manganese, such as rhodocrocite and siderite. Groundwater with high arsenic concentrations showed positive saturation indices for calcite and dolomite indicating supersaturated groundwater with respect to these minerals. Calculated values of log $PCO_2$ are $>-2.0$, which according to Bhattacharya et al. [35] may be a consequence of input of organic matter from irrigation.

## 3.3. Principal component analysis

PCA is a powerful recognition technique that attempts to explain the variance of a large set of intercorrelated variables with a smaller set of independent variables-principal components. PCA has been frequently employed on large and complex water quality datasets obtained from monitoring studies surface or groundwaters [18,36,37]. PCA was used to compare the compositional patterns between the examined waters samples and to identify the factors influencing each one.

The treatment of dataset with PCA, after Varimax rotation, showed three factors interpreting the 83.2% of variance (Table 5). The first PC, accounting for 48.4% of the variance in the whole data set was correlated with $HCO_3$, As, B, Fe, K, $T$, Na and EC. The second PC, accounting for 17.4% of the total variance is strongly correlated positively with Ca and negatively with Mg. The third PC 17.4% is strongly correlated with $NO_3$ and $SO_4$. The PCA plot of PC1 against PC2 is illus-

Table 5
Varimax rotated factor matrix

|  | PC1 | PC2 | PC3 |
|---|---|---|---|
| As | 0.888 | 0.283 | −0.192 |
| $T$ | 0.846 | 0.052 | −0.373 |
| EC | 0.833 | 0.323 | 0.421 |
| pH | −0.608 | −0.562 | −0.188 |
| Ca | 0.617 | 0.716 | 0.249 |
| Mg | −0.025 | −0.886 | −0.056 |
| Na | 0.836 | 0.140 | 0.425 |
| K | 0.890 | 0.411 | 0.090 |
| Cl | 0.619 | 0.484 | 0.504 |
| $SO_4$ | 0.271 | −0.146 | 0.766 |
| $HCO_3$ | 0.935 | 0.192 | 0.111 |
| $NO_3$ | −0.233 | 0.017 | 0.841 |
| Mn | 0.119 | 0.286 | 0.589 |
| Fe | 0.854 | −0.208 | 0.116 |
| B | 0.826 | 0.453 | 0.207 |
| % Variance | 48.4 | 17.4 | 17.4 |

trated in Fig. 5. Three groups of wells are observed: group (G) with PC1 scores >0, group (A) with PC2 scores <0 and group (B) with PC2 scores >0. The physicochemical characteristics of each group are shown in Fig. 6. These groups of wells represent groundwater with significant different physicochemical characteristics, according to non-parametric test Kruskal–Wallis. The wells from group G (geothermal wells) exhibited the highest concentrations of As, $T$, $HCO_3$, EC, Ca and lower Mg, $NO_3$, and pH values. Groundwater samples from groups A and B did
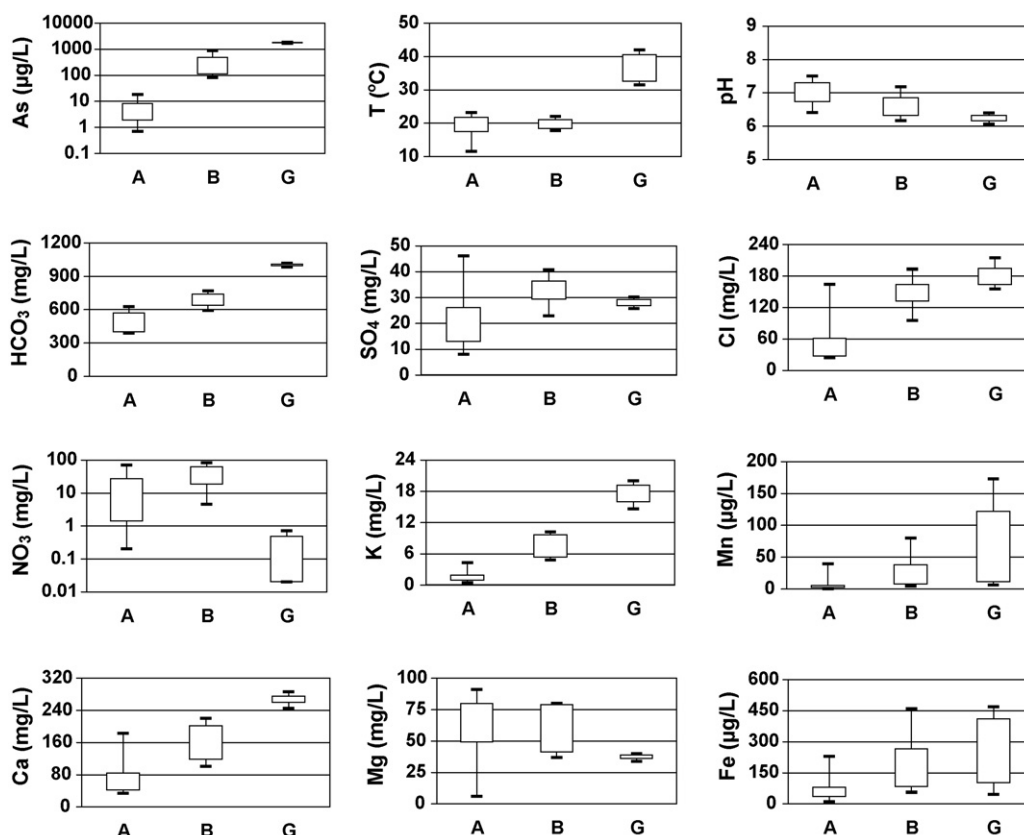


Fig. 6. Physicochemical characteristics of three groups resulting from PCA. Box plots represent min, max, 20th and 80th percentiles.

not show significant difference for $T$, Mg and $NO_3$, according to Mann–Whitney $U$-test. However, groundwater samples from group B exhibited relatively high concentrations of As ($>0.050$ mg/L), higher concentrations of $HCO_3$, EC, Ca, Na, K, Cl, $SO_4$, Fe and Mn and lower pH values whereas groundwater from group A exhibited lower arsenic concentrations (usually $<0.010$ mg/L), low concentrations of cations and anions, manganese and iron. Groundwater from group A is mainly of Mg–$HCO_3$ type, whereas groundwater in wells from group B is mainly of Ca–$HCO_3$ type.

## 4. Conclusions

This study presents the arsenic distribution in groundwater in the area of Chalkidiki, Northern Greece. Groundwater samples from public water supply wells and private wells were analysed for arsenic and other quality parameters ($T$, pH, EC, Ca, Mg, Na, K, Cl, $HCO_3$, $NO_3$, $SO_4$, B, Fe, Mn). Arsenic showed high spatial variation; ranged from 0.001 to 1.840 mg/L. Almost 65% of the examined wells exceeded the limit of 0.010 mg/L proposed for water intended for human consumption. Geothermal wells exhibited extremely high arsenic concentrations (1.6–1.9 mg/L) and high temperature (33–42 °C). Arsenic showed strong correlation with K, B, Na, $HCO_3$, EC, Mn and Fe. Iron, manganese, and bicarbonate are probably the key factors regulating arsenic concentration in groundwater. PCA has been employed and three groups of groundwater with different physicochemical characteristics are observed.

## Acknowledgements

## References

[1] C.K. Jain, I. Ali, Arsenic: occurrence, toxicity and speciation techniques, Water Res. 34 (2000) 4304–4312.

[2] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, Appl. Geochem. 17 (2002) 517–568.

[3] M. Berg, H.C. Tran, T.C. Nguyen, H.V. Pham, R. Schertenleib, W. Giger, Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat, Environ. Sci. Technol. 35 (2001) 2621–2626.

[4] H. Guo, Y. Wang, Geochemical characteristics of shallow groundwater in Datong basin, northwestern China, J. Geochem. Explor. 87 (2005) 109–120.

[5] R.T. Nickson, J.M. McArthur, B. Shrestha, T.O. Kyaw-Myint, D. Lowry, Arsenic and other drinking water quality issues, Muzaffargarh District, Pakistan, Appl. Geochem. 20 (2005) 55–68.

[6] T. Agusa, T. Kunito, J. Fujihara, R. Kubota, T.B. Minh, P.T.K. Trang, H. Iwata, A. Subramanian, P.H. Viet, S. Tanabe, Contamination by arsenic and other trace elements in tube-well water and its risk assessment to humans in Hanoi, Vietnam, Environ. Pollut. 139 (2006) 95–106.

[7] M.F. Hossain, Arsenic contamination in Bangladesh—an overview, Agr. Ecosyst. Environ. 113 (2006) 1–16.

[8] C.F. Harvey, K.N. Ashfaque, W. Yu, A.B.M. Badruzzaman, M.A. Ali, P.M. Oates, H.A. Michael, R.B. Neumann, R. Beckie, S. Islam, M.F. Ahmed, Groundwater dynamics and arsenic contamination in Bangladesh, Chem. Geol. 228 (2006) 112–136.

[9] M.J. Kim, J. Nriagu, S. Haack, Arsenic species and chemistry in groundwater of southeast Michigan, Environ. Pollut. 120 (2002) 379–390.

[10] M.J. Kim, J. Nriagu, S. Haack, Arsenic behaviour in newly drilled wells, Chemosphere 52 (2003) 623–633.

[11] S. Wang, C.N. Mulligan, Occurrence of arsenic contamination in Canada: sources, behavior and distribution, Sci. Total Environ. 366 (2006) 701–721.

[12] S. Haque, K.H. Johannesson, Arsenic concentrations and speciation along a groundwater flow path: the Carrizo Sand aquifer, Texas, USA, Chem. Geol. 228 (2006) 57–71.

[13] R.E. Price, T. Pichler, Abundance and mineralogical association of arsenic in the Suwannee Limestone (Florida): implications for arsenic release during water–rock interaction, Chem. Geol. 228 (2006) 44–56.

[14] S.C. Peters, J.D. Blum, M.R. Karagas, C.P. Chamberlain, D.J. Sjostrom, Sources and exposure of the new Hampshire population to arsenic in pubic and private drinking water supplies, Chem. Geol. 228 (2006) 72–84.

[15] S.J. Appleyard, J. Angeloni, R. Watkins, Arsenic-rich groundwater in an urban area experiencing drought and increasing population density, Perth, Australia, Appl. Geochem. 21 (2006) 83–97.

[16] D.K. Nordstrom, Worldwide occurrences of arsenic in groundwater, Science 296 (2002) 2143–2145.

[17] A. Aiuppa, R. Avino, L. Brusca, S. Caliro, G. Chiodini, W. D'Alessandro, R. Favara, C. Federico, W. Ginerva, S. Inguaggiato, M. Longo, G. Pecoraino, M. Valenza, Mineral control of arsenic content in thermal waters from volcano-hosted hydrothermal systems: insights from island of Ischia and Phlegrean fields (Campanian Volcanic Province, Italy), Chem. Geol. 229 (2006) 313–330.

[18] D. Voutsa, C. Samara, Th. Kouimtzis, Groundwater quality in the major industrial area of Thessaloniki, Greece. Part 2. Heavy metal distribution-source identification, Toxicol. Environ. Chem. 45 (1994) 105–119.

[19] M. Mitrakas, A survey of arsenic levels in tap, underground and thermal mineral waters of Greece, Fresen. Environ. Bull. 10 (2001) 717–721.

[20] K. Tyrovola, N.P. Nikolaidis, N. Veranis, N. Kallithrakas-Kontos, P.E. Koulouridakis, Arsenic removal from geothermal waters with zero valent iron-effect of temperature, phosphate and nitrate, Water Res. 40 (2006) 2375–2386.

[21] I.A. Katsoyiannis, A.A. Katsoyiannis, Arsenic and other metal contamination of groundwaters in the industrial area of Thessaloniki, Environ. Monit. Assess. 123 (2006) 393–406.

[22] EC, Directive related with quality of water intended for human consumption, 98/83/EC, 1998.

[23] EPA, Implementation guidance for the arsenic rule. Office of groundwater and drinking water. EPA report-816-D-02-005, Cincinnati, USA, 2002.

[24] WHO, Guidelines for drinking water quality Health Criteria and Other Supporting Information, vol. 2, 2nd ed., World Health Organisation, Geneva, Switzerland, 1996, pp. 940–949.

[25] E. Dotsika, Th. Kouimtzis, A. Kouras, D. Poutoukis, D. Voutsa, Hydrochemical and isotopical study for the origin of boron in the waste Chalkidiki area, in: Proceedings of Sixth Greek Hydrogeological Conference, Xanthi, 2002, pp. 347–352.

[26] W. Kloppmann, P. Negrel, J. Casanova, A. Gutierrez, C. Guerrot, M. Pennisi, G. Bianchini, M.N. Cerbai, A. Vengosh, I. Pankratov, A. Marei, E. Dotsika, D. Poutoukis, D. Voutsa, Th. Kouimtzis, A. Charalambides, P. Klose, A. Shathas, G. Huel, J. Baker, M. Priel, P. Glueckstern, E. Weinthal, Y. Parag, Boron contamination of water resources in the Mediterranean region: distribution, sources, social impact and remediation: the BOREMED project, in: Procceedings of the International Conference MONTPELLIER 2003 "Hydrology of the Mediterranean and the semi arid regions", Montepellier, (2003). France.

[27] H. Jackelen, E. Loehnert, A. Papakonstantinou, Natural tracers, chemical parameters and environmental isotopes, in groundwater of the western Chalkidiki peninsula Greece, in: Proceedings of the Fifth International Symposium on Underground Water Tracing, Athens, Greece, 1986, pp. 59–73.

[28] E.P. Lohnert, A. Papakonstntinou, Relationship between karst and porous aquifers on Chalkidiki peninsula Greece, in: Procceedings of the IAH 21rst Congress, Gulin, China, vol. XXI, 1988, pp. 321–326.

[29] APHA, AWWA, WPCF, Standard methods for the examination of water and wastewater, 16th ed., Washington DC, 1995.

[30] SPSS Base 12.0S for Windows; SPSS Inc.

[31] D. Voutsa, C. Samara, Th. Kouimtzis, Groundwater quality in the major industrial area of Thessaloniki, Greece. Part 1. Chemical composition-geochemical processes, Toxicol. Environ. Chem. 38 (1993) 145–156.

[32] A. Xefteris, P. Anastasiadis, P. Latinopoulos, Groundwater chemical characteristics in Kalamaria plain, Chalkidiki peninsula, Greece, Fresen. Environ. Bull. 13 (2004) 1158–1167.

[33] J.D. Ayotte, D.L. Montgomery, S.M. Flanagan, K.W. Robinson, Arsenic in groundwater in eastern New England: occurrence, controls and human health implications, Environ. Sci. Technol. 37 (2003) 2075–2083.

[34] P.L. Smedley, H.B. Nicolli, D.M.J. MacDonald, A.J. Baros, J.O. Tullio, Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina, Appl. Geochem. 17 (2002) 259–284.

[35] P. Bhattacharya, M. Claesson, J. Bundschuh, O. Sracek, J. Fagerberg, G. Jacks, R.A. Martin, A. Storniolo, M. Thir, Distribution and mobility of arsenic in the Rio Dulce alluvial aquifers in Santiago del Estero Province, Argentina, Sci. Total Environ. 358 (2006) 97–120.

[36] M.J. Kim, J. Nriagu, S. Haack, Carbonate ions and arsenic dissolution by groundwater, Environ. Sci. Technol. 34 (2000) 3094–3100;
D. Voutsa, E. Manoli, C. Samara, M. Sofoniou, I. Stratis, A study of surface water quality in Macedonia, Greece: speciation of nitrogen and phosphorus, Water Air Soil Pollut. 129 (2001) 13–32.

[37] V. Simeonov, J.A. Stratis, C. Samara, G. Zachariadis, D. Voutsa, A. Anthemidis, M. Sofoniou, Th. Kouimtzis, Assessment of the surface water quality in Northern Greece, Water Res. 37 (2003) 4119–4124.