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Arsenic, antimony and other toxic elements in the drinking water of Eastern Thessaly in Greece and its possible effects on human health

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Abstract Twenty-six groundwater samples were collected from the Eastern Thessaly region and analysed by ICP-ES for these elements: Al, As, P, Pb, Zn, Mn, Fe, Cr, Sb, Cu, Na, Br, Cl, Si, Mg, Ag, Be, Bi, Dy, Er, Eu, Au, Ge, Ho, In, Ir, Os, Pt, Re, Rh, Ru, Lu, Hf, Hg, Tm, Zr and Nb. The objectives of the study were to assess the level of water contamination with respect to the EC and the USEPA health-based drinking water criteria. The geology of the studied area includes schists, amphibolites, marbles of Palaeozoic age, ophiolites, limestones of Triassic and Cretaceous age, Neogene and Quaternary deposits. The element ranges for groundwater samples are: Al 7–56 μ g l⁻¹, As 1–125 μg 1⁻¹, Br 6–60 μg 1⁻¹, Cl 500–25,000 μg 1⁻¹, Cr 1–6 μg 1⁻¹, Cu $1-15 \mu g l^{-1}$, Fe $10-352 \mu g l^{-1}$, Mg 2,940–40,100 µg l⁻¹, Mn 0–8 µg l⁻¹, Na 3,650–13,740 µg l⁻¹, P 20–48 µg l⁻¹, Pb 0–7 µg l⁻¹, Sb 0–21 µg l⁻¹, Si 3,310–13,240 µg l⁻¹ and Zn 7–994 μ g l⁻¹. The results of groundwater analyses from the region of Eastern Thessaly showed elevated concentrations of As and Sb. Factor analysis explained 77.8% of the total variance of the data through five factors. Concentration of Br, Cl, Mg, Na and Si is directly related to the presence of saltwater in the aquifer, so grouping of these variables in factor 1 probably reflects the seawater intrusion. Al, As and Sb are known to form complexes in the

environment, so grouping of these elements in factor 2 indicates their similar geochemical behaviour in the environment. The high negative loading of Mn in factor 2 indicates the presence of manganese oxideshydroxides in the study area. Pb and Zn are associated together in sulphide mineralisation; so grouping of these elements in factor 3 reflects the sulphide mineralization paragenesis in the Melivoia area. P and Cu are associated together in phosphate fertilizers; so grouping of these variables in factor 4 could be related to agricultural practices. Cr, Fe, Mn and Mg are associated together in iron and manganese oxides-hydroxides and the weathering products of the olivine of the ultrabasic rocks; so grouping of these elements in factor 5 reflects the lithology of the area. There is a natural contamination of groundwaters with elevated concentrations of As and Sb due to the presence of the arsenopyrite and stibnite mineralisation in the Melivoia, Sotiritsa and Ano Polydendri areas. Contamination over the health-based drinking water guidelines given by EC and EPA has been investigated from nine sampling sites out of 26 of Eastern Thessaly region.

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Introduction

Arsenic (As) is present usually in small amounts in all water, soil, rocks and air (Onishi 1969). Arsenic exists in oxidation states of -3, 0, +3, and +5. In water, in reducing conditions, it is more likely to be present as arsenite with an oxidation state of +3. However, if the water is oxygenated, it is more likely to be present as arsenate with an oxidation state of +5 (International Programme on Chemical Safety, 2001). Natural waters contain low levels of arsenic, in the As (V) form as H₂AsO₄ and as As (III) in As(OH)₃ (Cox 1997).

The most common As mineral is arsenopyrite. According to Goldschmidt (1954), arsenic is common in galena, pyrite, chalcopyrite but very rare in sphalerite. The chemical behaviours of As and antimony (Sb) are similar and both these elements form oxyanions in water and are chalcophilic group V metalloids (Wilson et al. 2004). Antimony is considered to be carcinogenic and toxic in a manner similar to arsenic (Gebel 1997).

Carcinogenecity in humans due to the ingestion of As-contaminated groundwater is currently regarded as one of the major health problems in Banvgladesh, China and Taiwan (Tseng et al. 1968; Islam et al. 2000; Guo and Tseng 2000; Chakraborti et al. 2003; Watanabe et al. 2004; Sun 2004; Paul 2004). Smith et al. (2000) reported that the serious arsenic disaster in Bangladesh is considered to be the world's biggest mass poisoning, and the situation in regions in West Bengal, India has been equated with the Chernobyl calamity (Post Conference Report 1995). An epidemiological study (Tseng et al. 1968; Tseng 1977) carried out to investigate the exposure of humans to high concentrations of As in drinking water from southwest Taiwan, showed that there is a relationship between skin cancer, keratosis and Blackfoot disease or a type of gangrene and high concentrations of As in drinking water. Paul (2004) reported that there are some similarities between arsenic poisoning and HIV/AIDS. In both, symptoms appear after a few years, victims of both suffer from a host of opportunistic diseases and frequently experience social discrimination.

The main objectives of the study were: (a) to assess the degree of arsenic and antimony contamination in groundwater; (b) to define the spatial distribution of heavy metals and other elements in groundwater with an emphasis on toxic elements (As and Sb); (c) to identify the most heavily polluted areas for environmental protection and remediation; and (d) to assess the regional geochemistry of the aquifer system and to delineate the factors controlling their geochemical variability.

Study area

Geographical location and physiography

The study area is situated in the eastern part of the Larisa town, central Greece (Fig. 1), about 400 km north of Athens. It extends parallel to the western coast of the Aegean Sea lying between the latitudes 39°40′ and 39°52′ and longitudes 22°45′ and 22°55′. The relief of the region is quite plain with mountains and low hills. Agricultural activity is intense with apple trees grown all over. Chestnut trees and vegetables are also grown quite densely. Kisavos Mountain lies west to the studied area while low hills surround its northern and southern part. Most of the surface is covered by forest.

Geology and mineralisation

The rocks of the Eastern Thessaly area belong to the Pelagonian zone and the Eohellenic tectonic nappe (Migiros 1983; IGME 1984, 1987). The Pelagonian zone in the study area consists mainly of white grey, medium to thick-bedded, karstic marbles. The Eohellenic tectonic nappe in the Melivoia and Karitsa area consists of serpentinites, metamorphic basic ophiolitic rocks (amphibolites and prasinites) and metamorphic rocks of sedimentary origin (mica–chlorite schists and quartz–chlorite–mica schists) of the Palaeozoic age.

The Quaternary sediments of the area studied consist of unconsolidated material with sand and rounded and angular pebbles in the torrent beds, and alluvial sediments. The Neogene sediments are composed of marly limestones, marls, and conglomerates.

The serpentinites consist mainly of antigorite. The amphibolites consist mainly of glauconitized actinolite and plagioclases. The main mineralogical constituents of prasinites are plagioclases, actinolite and epidote while chlorite, sericite, titanite and Fe-oxides and hydroxides occur in small proportions (Institute of Geology and Mineral Exploration 1984). Eastwards of the studied area, there are many occurrences of iron oxides-hydroxides with copper, antimony and arsenic mineralisation (Fig. 1). Copper occurs as malachite, antimony as stibnite and arsenic as arsenopyrite. Manganese and iron oxides are present in the southeast part of the studied area. Malachite $[Cu_2(CO_3)(OH)_2]$, stibnite (Sb_2S_3) , and arsenopyrite (FeAsS) occur within the metamorphic rocks of the basement and the ophiolithic complex (Migiros 1983). No mining activity has been reported in the whole mineralised area.

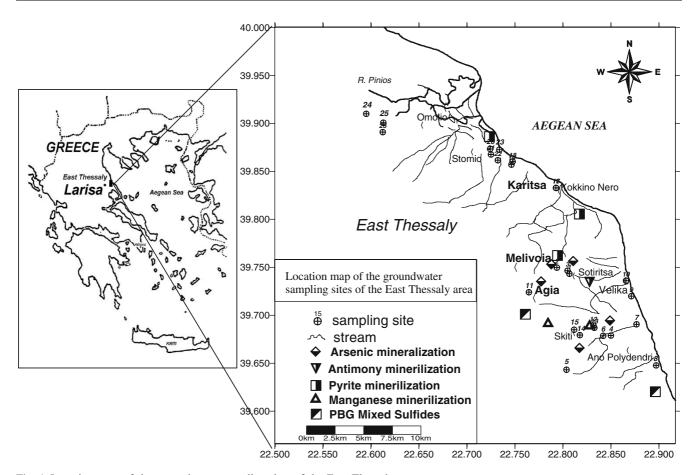


Fig. 1 Location map of the groundwater sampling sites of the East Thessaly area

Methodology

Water sampling and preparation

A total of 26 water samples were collected covering an area of approximately 100 km². All the water samples were taken during the period December 2003–February 2004. The sampling sites are shown on the location map (Fig. 1).

Water samples were obtained from springs, drillings and wells, the only available source for sampling. The hydrogeological characteristics and locations of groundwater sampling sites of the Eastern Thessaly area are shown in Table 1.

All possible precautions were taken during collection and handling of samples to minimise contamination. The water samples were directly collected in polyethylene bottles. Water pH was measured immediately after collection using a pH paper and the redox potential was measured in the field using an YSI Model 63 Eh-meter calibrated with Hach Solution. Two hundred millilitres of each sample was vacuum filtered through a 0.45 µm

pore size membrane filter and acidified to a final concentration of about 1% nitric acid and then stored in a polyethylene container. Exposure of the samples to air was minimised when filtering the samples to reduce the possibility of oxidation. The temperature of all samples stored in the fridge was maintained between 0 and 4°C.

Chemical analysis

Chemical analyses were performed at the Laboratory of Economic Geology and Geochemistry of the Geology Department, National and Kapodistrian University of Athens and the ACME Analytical Laboratories Ltd, Canada. All samples were analysed for As by Atomic Absorption Spectroscopy (AAS/Perkin Elmer 1100B) with a Mercury Hydride System (MHS 10/Perkin Elmer). The following elements were analysed by Inductively Coupled Plasma Emission Spectroscopy (ICP/ES): Al, Pb, Zn, Mn, Fe, Cr, Sb, Cu, Na, Br, Cl, Si, Mg, Ag, Be, Bi, Dy, Er, Eu, Au, Ge, Ho, In, Ir, Os, Pt, Re, Rh, Ru, Lu, Hf, Hg, Tm, Zr and Nb. The trace elements: Ag,

Be, Bi, Dy, Er, Eu, Au, Ge, Ho, In, Ir, Os, Pt, Re, Rh, Ru, Lu, Hf, Hg, Tm, Zr and Nb in all groundwater samples were not detected. Analytical precision was calculated from these duplicate samples and it was found to meet international standards.

Statistical analysis

The study focused on 15 elements—Al, As, Br, Cl, Cu, Fe, Mg, Mn, Na, P, Pb, Sb, Si, Zn and Cr on the basis of specific interest related to the lithology and the ore composition of the area. The software Microsoft[®] Excel for Windows and SPSS[®] 8.0 for Windows was used for data analysis.

The statistical technique of R-mode factor analysis was used for the interpretation of the geochemical data. Factor analysis aims to reduce the complex pattern of correlations among many variables to simpler sets of

 Table 1
 Hydrogeological characteristics and locations of ground-water sampling sites of the Eastern Thessaly area

Sampling site	Location	Type of sampling site	Dominant formation
1	Sotiritsa	Drilling	Marbles
2	Sotiritsa	Spring	Marbles
3	Sotiritsa	Drilling	Hydrothermal altered metamorphic rocks
4	Sotiritsa	Spring	Hydrothermal altered metamorphic rocks
5	Ano Polydendri	Spring	Hydrothermal altered metamorphic rocks
6	Skiti	Well	Weathered metamorphic rock
7	Skiti	Drilling	Hydrothermal altered metamorphic rocks
8	Ano Polydendri	Spring	Metamorphic rocks
9	Sotiritsa	Drilling	Hydrothermal altered metamorphic rocks
10	Velika	Drilling	Hydrothermal altered metamorphic rocks
11	Agia	Drilling	Marbles
12	Skiti	Spring	Marbles
13	Skiti	Spring	Marbles
14	Skiti	Spring	Marbles
15	Skiti	Spring	Hydrothermal altered metamorphic rocks
16	Kokkino Nero	Spring	Marbles
17	Karitsa	Spring	Marbles
18	Karitsa	Spring	Marbles
19	Karitsa	Drilling	Marbles
20	Stomio	Drilling	Metamorphic rocks
21	Stomio	Drilling	Metamorphic rocks
22	Stomio	Drilling	Metamorphic rocks
23	Stomio	Spring	Metamorphic rocks
24	Omolio	Spring	Metamorphic rocks
25	Omolio	Spring	Metamorphic rocks
26	Omolio	Well	Weathered metamorphic rock

relationships between fewer variables (Davis 1973; Alexakis and Kelepertsis 1998; Kelepertsis et al. 2001). A varimax rotation was applied to the initial factor loadings in order to maximise the variance of the squared loadings (Harmon 1976).

Results

The range and the mean values of the results of chemical analyses are shown in Table 2 in comparison with the Parametric Values given by the EC (1998) and the maximum contaminant levels and secondary maximum contaminant levels given by the EPA (2001) for drinking water. From this table, it is obvious that only As mean value (12 μ g l⁻¹) exceeds the Parametric Value given by the EC (1998) and the maximum contaminant level given by the EPA (2001) for drinking water. The As concentrations vary between 1 and 125 μ g l⁻¹. Fe mean value (93 μ g l⁻¹) does not exceed the Parametric Value given by the EC (1998) and the maximum contaminant level given by the EPA (2001) for drinking water. The Fe concentrations vary between 10 and 352 μ g l⁻¹.

The correlation coefficient matrix for the water data is shown in Table 3. Principal component factor analysis with a varimax rotation was subsequently applied to the data in order to create factors each representing a cluster of interrelated variables within the data set. The proportion of the variance explained by five factors, the rotated factor loadings and the communalities are presented in Table 4.

Classed post plots of geochemical distribution were created in Surfer®7 for Windows using kriging as the interpolation method. The classed post maps were projected on the simplified topographical map using Surfer®7 for Windows in order to visualise the spatial relationship between the arsenic and antimony concentration and the various sources of contamination in the study area. These maps are presented in Figs. 2 and 3, respectively.

Discussion

Assessment of groundwater pollution

The redox potentials and pH for the East Thessaly sampling sites are the principal parameters that control speciation of As and Sb in the study area. Water pH for East Thessaly sampling site samples varies between 6.0 and 6.6, while Eh ranges from +0.572 to +0.612 V (Table 2). The above-measured Eh-pH conditions plotted in a diagram depicted by Vink (1996) suggest that antimony in the water samples of East Thessaly should be principally as SbO_{3(aq)} and arsenic as

Table 2 Summary of the chemical composition of groundwaters sampled in East Thessaly, Greece, in comparison with secondary and risk-based drinking water criteria and the percentage of Eastern Thessaly's groundwater exceeding these criteria (n=26)

				Risk-based drinking water criteria				Percentage of Eastern Thessaly's groundwater exceeding criteria		
	Mean	Minimum	Maximum	Parametric value (EC ^a)	MCL (USEPA ^b)	SMCL (USEPA ^b)	EC	MCL (USEPA ^b)	SMCL USEPA ^b)	
pН	6.4	6.0	6.6	None	None	6.5–8.5	NA	NA	42.3	
Eh (V)	0.602	0.572	0.612	None	None	None	NA	NA	NA	
Al $(\mu g l^{-1})$	17	7	56	200	None	5-200	0	NA	0	
As $(\mu g l^{-1})$	12	1	125	10	10	None	23	23	NA	
Br ($\mu g 1^{-1}$)	32	6	60	None	None	None	NA	NA	NA	
Cl $(\mu g l^{-1})$	12	500	25,000	250,000	None	250,000	0	NA	0	
$Cr (\mu g L^{-1})$	2 3	1	6	50	100	None	0	0	NA	
Cu ($\mu g L^{-1}$)	3	1	15	2,000	None	1,000	0	0	0	
Fe $(\mu g l^{-1})$	93	10	352	200	None	300	3,6	NA	1	
$Mg (\mu g 1^{-1})$	13,710	2,940	40,100	None	None	None	ΝA	NA	NA	
Mn ($\mu g l^{-1}$)	2	0	8	50	None	50	0	NA	0	
Na $(\mu g l^{-1})$	7,748	3,650	13,740	200,000	None	None	0	NA	NA	
$P(\mu g l^{-1})$	25	20	48	None	None	None	NA	NA	NA	
Pb $(\mu g l^{-1})$	1	0	7	10	15	None	0	0	0	
Sb $(\mu g l^{-1})$	2	0	21	5	6	None	15.4	15.4	NA	
Si $(\mu g l^{-1})$	8,203	3,310	13,240	None	None	None	NA	NA	NA	
$Zn (\mu g l^{-1})$	85	7	994	None	None	5,000	NA	NA	0	

NA not applicable

^aThe EC has not yet established risk-based drinking water criteria for Br, Mg, P, Si and Zn

arsenates $H_2AsO_{4(aq)}^-$ and $HAsO_{4(aq)}^{2-}$. These inorganic species of arsenic are more toxic than the organic forms and are regarded to be one of the most serious drinking water pollutants (Smedley and Kinniburgh 2002; Impellitery 2004).

It was found that arsenic, antimony and iron contents in groundwater exceed the critical level of the EC and EPA drinking water standard (As: $10 \mu g l^{-1}$, Sb: $6 \mu g l^{-1}$, Fe: $300 \mu g l^{-1}$). According to the chemical analyses, contamination over the critical level is observed in nine sampling sites out of 26 in the Eastern

Thessaly area. Contamination of As (sampling sites: 3, 4, 5, 9, 10, 15), Sb (sampling sites: 4, 5, 6, 7) over the risk-based drinking water criteria given by the EC (1998) and EPA (2001) of the Eastern Thessaly groundwaters was observed. The EC and USEPA have not yet established health-based drinking water guidelines for Fe; however, sampling site 23 exceeds the USEPA secondary criteria.

Despite the relatively low positive (+0.38) correlation coefficient between As and Sb (Table 3), two groundwater samples (sampling sites 4 and 5) out of 26

Table 3 Correlation coefficient matrix for Eastern Thessaly groundwater elements (n = 26)

	Al	As	Br	Cl	Cr	Cu	Fe	Mg	Mn	Na	P	Pb	Sb	Si	Zn
Al	1														
As	0.70	1													
Br	0.14	0.19	1												
C1	0.16	0.24	0.92	1											
Cr	-0.32	-0.20	-0.25	-0.29	1										
Cu	0.29	0.28	0.15	0.22	-0.11	1									
Fe	0.03	0.05	-0.14	-0.16	0.36	-0.05	1								
Mg	0.30	0.18	0.56	0.50	0.24	0.17	0.02	1							
Mn	-0.05	-0.17	-0.04	-0.14	0.19	-0.02	0.46	0.32	1						
Na	0.15	0.11	0.92	0.91	-0.33	0.23	-0.24	0.54	-0.19	1					
P	0.00	-0.06	-0.11	0.02	-0.05	0.41	-0.02	-0.13	-0.21	0.04	1				
Pb	0.09	-0.01	-0.33	-0.18	0.02	0.23	0.07	-0.16	-0.08	-0.14	0.62	1			
Sb	0.26	0.38	0.17	0.17	-0.21	-0.17	0.03	0.06	-0.24	0.20	0.00	-0.09	1		
Si	0.39	0.29	0.61	0.56	-0.25	0.31	-0.01	0.37	-0.05	0.61	0.17	-0.08	0.29	1	
Zn	-0.10	-0.09	-0.39	-0.25	0.08	0.14	0.00	-0.21	-0.10	-0.21	0.58	0.96	-0.13	-0.22	1

^bThe USEPA has not yet established secondary or risk-based drinking water criteria for Br, Mg, Na, P and Si

Table 4 Varimax rotated component loadings of five factors and percent of variance explained for 15 groundwater elements of Eastern Thessaly area

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Al	0.090	0.743	0.008	0.469	0.060
As	0.095	0.804	-0.027	0.239	0.022
Br	0.944	0.111	-0.214	-0.012	-0.080
C1	0.927	0.139	-0.067	0.015	-0.159
Cr	-0.146	-0.431	-0.049	-0.049	0.632
Cu	0.236	0.053	0.250	0.680	-0.068
Fe	-0.179	0.223	0.091	-0.095	0.734
Mg	0.694	0.041	-0.089	0.225	0.493
Mn	-0.024	-0.921	-0.033	-0.087	0.789
Na	0.940	0.070	-0.044	0.093	-0.233
P	0.064	0.059	-0.013	0.884	-0.047
Pb	-0.122	0.047	0.963	0.120	0.065
Sb	0.147	0.719	-0.053	-0.281	-0.135
Si	0.553	0.357	-0.139	0.529	-0.113
Zn	-0.186	-0.113	0.951	0.024	-0.065
Percent of variance explained	30.3	15.7	12.4	10.9	8.5

exceeded both the EC and EPA health-based drinking water guidelines. The As and Sb concentrations of the groundwaters studied show a wide range (As: $1-125 \mu g l^{-1}$, Sb: 0.1–21 $\mu g l^{-1}$). High values of As and Sb were detected in the groundwater samples from the Sotiritsa and Ano Polydendri areas (sampling sites: 3, 4, 5, 6, 7, 9, 10, 15) while very low values were detected in the groundwater samples from the Karitsa, Stomio and Omolio areas (sampling sites: 16–26). By looking at the hazard zonation map (Fig. 2), arsenic contaminated groundwaters are recorded in an area lying between Melivoia, Ano Polydendri and Velika and this is due to the presence of arsenic, antimony and pyrite mineralisation which is a natural source of contamination. No sulphide mineralisation was found in the Karitsa and Omolio areas. Antimony contaminated groundwaters are recorded in an area lying between Velika, Skiti and Ano Polydendri (Fig. 3) and this is due to the presence of antimony and arsenic mineralisation which is a natural source of contamination.

Fig. 2 Hazard zonation map indicating As-health risk sites of groundwaters of the East Thessaly area (Greece)

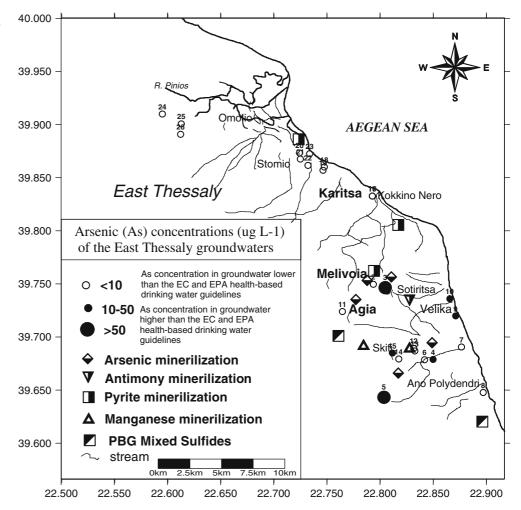
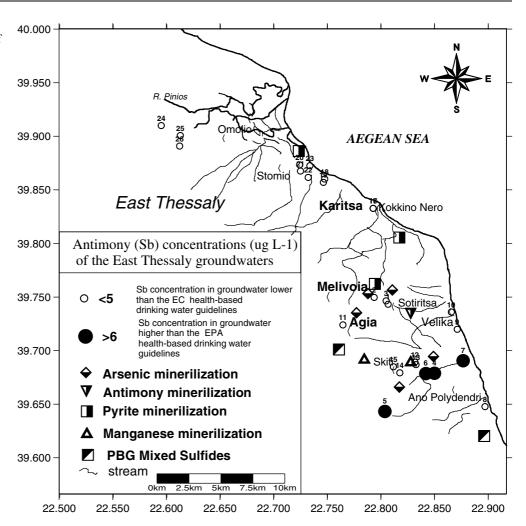


Fig. 3 Hazard zonation map indicating Sb-health risk sites of groundwaters of the East Thessaly area (Greece)



From Table 3, it is shown that the elements Br, Cl, Mg, Na and Si are strongly intercorrelated and associated with the seawater intrusion. The correlation coefficient As/Al is significant and very strong (+0.70). This observation indicates complex in the environment between As and Al. A recent environmental study carried out by Smith et al. (2002) showed that As complexes with Al. The correlation coefficient Pb/Zn is significant and very strong (+0.96); this observation indicates common sources for these metals.

In the present study, the element distribution in the groundwater samples of the Eastern Thessaly area is explained in terms of five factors, which explain 77.8% of the total variance of the data set (Table 4). Factor 1, accounts for 30.3% of the total data variability and shows high positive loadings for Br, Cl, Mg, Na and Si. This factor can be attributed to seawater intrusion in the area.

Factor 2 is a dipolar factor with high positive loadings of Al, As and Sb and high negative loading for Mn. This factor accounts for 15.7% of the total variance, indicating

complexes formations between Al, As and Sb. Also Smith et al. (2002) and Wilson et al. (2004) reported that As and Sb have strikingly similar geochemical behaviours in the environment and both complex with Al. As and Sb participates in the chemistry of arsenopyrite and stibnite, respectively, which form with chalcopyrite and pyrite the sulphide mineralisation paragenesis in the Melivoia area (Migiros 1998). Al was released during the alteration of the metamorphic rocks the "host of the mineralisation" by acid hydrothermal solutions and complexed with As and Sb. The positive loadings on these elements is opposed by high negative loading on Mn, clearly indicating the manganese oxides-hydroxides are antipathetically related to the sulphide mineralisation and the hydrothermally altered zones. Factor 3, contributes 12.4% and shows high positive scores of Pb and Zn, reflecting the known sulphide mineralisation in the rocks of the area. The sulphide mineralisation in the Eastern Thessaly is reported by Migiros (1998). Factor 4, accounting for 10.9% of the total variability, is a factor with high positive loading for P and Cu and median positive loading for Si.

According to Kabata Pendias et al. (1992), P and Cu are associated together in phosphate fertilizers; so grouping of these variables in factor 4 could be related to agricultural practices.

Factor 5, contributes 8.5% of the total data variability and shows positive loadings of Cr, Fe and Mn with a median contribution of Mg. The variability of the elements in this factor can easily be attributed to the known iron and manganese oxides—hydroxides and the weathering products of the olivine of the ultrabasic rocks, which are present in the area; therefore, factor 5 can be characterized as "lithogenic".

Effects of As toxicity on human

The waters of three arsenic contaminated sampling sites 4, 9, 10 is used for drinking and irrigation purposes in the Eastern Thessaly area. The highest As concentration of groundwater was recorded in the Sotiritsa area (sampling site 3). The As concentration (125 μ g l⁻¹) of groundwater of the sampling site 3 exceeds the critical level of 103 μ g l⁻¹ reported by Anawar et al. (2002). The groundwater of that sampling site can possibly produce dermatological diseases if it is used for drinking purposes.

However, the exposure time to develop arsenicosis varies from case to case reflecting its dependence on arsenic concentration in food and water, genetic variant of human being, nutritional status and compounding factors (Anawar et al. 2002). Chronic arsenic exposure, which causes skin pigmentation, inability to walk and deliberating pain, may not be diagnosed until exposure has occurred for several years (EPA 2002; McLellan 2002). According to Dhar et al. (1997) arsenic-affected patients show leucomelanosis, keratosis, gangrene, skin cancer and melanosis. Also, Ramirez-Solis et al. (2004) reported that long-term exposure to arsenic in drinking water has been linked to cancer of lungs, nasal passages, bladder, kidney, skin, liver and prostate in humans.

Conclusions

The results of groundwater analyses from the region of Eastern Thessaly showed elevated concentrations of As and Sb. Contamination over the health-based drinking water guidelines given by EC and EPA has been recorded in nine sampling sites out of 26 of Eastern Thessaly area. Arsenic and antimony contaminated groundwaters were recorded in an area lying between Melivoia, Velika, Ano Polydendri and Skiti area, this is due to the presence of arsenopyrite, stibnite and pyrite mineralisation which is a natural source of contamination. Concentrations of As and Sb below the health-based water guidelines have been measured in the remaining 17 sampling sites of Eastern Thessaly area. These sampling sites were recorded in metamorphic formations and carbonate rocks without any trace of mineralisation.

Factor analysis proved a successful method for grouping the elements according to their sources and provided evidence about their anthropogenic or natural origin. The factor analysis applied on the data explained 77.8% of the total variance of the data set through five factors. The first factor is that the Br-Cl-Mg-Na-Si grouping of the variables reflects the presence of seawater in the aquifer. The second factor is the "mineralisation factor" and accommodates elements (As, Sb, Al, Mn) that relate to the sulphide and manganese mineralisation and the hydrothermally altered zones. The spatial interpretation of this factor signified the natural origin of As and Sb in the Eastern Thessalv ground waters. The third factor accommodated elements that related to the oxidation products of galena and sphalerite. The fourth factor is an "anthropogenic factor" and accommodates elements (Cu, P) that occur together in phosphate fertilizers. Finally, the fifth factor is a "lithogenic factor" and accommodates elements (Cr, Fe, Mn, Mg) that relate to the known iron and manganese oxides-hydroxides and the weathering products of the olivine of the ultrabasic rocks, which are present in the area.

Presently, in Eastern Thessaly area, more than 5,000 people, drink water containing As and Sb above the EC and USEPA guidelines on health. Strategies to protect Eastern Thessaly's drinking waters from As and Sb natural contamination must be studied, developed and quickly implemented.

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References

Alexakis D, Kelepertsis A (1998) The relationship between the chemical composition—quality of ground waters and the geological environment in the East Attiki area, Greece. Mineral Wealth 109:9–20

Anawar HM, Akai J, Mostofa KM, Safiullah S,Tareg SM (2002) Arsenic poisoning in groundwater: health risk and geochemical sources in Bangladesh. Environ Int 27(7):597–604 Chakraborti D, Mukkerjee SC, Pati S, Sengupta MK, Rahman MM,Chowdhury U, Lodh D, Chanda CR, Chakraborti AK, Basu GK (2003) Arsenic groundwater contamination in Middle Ganga Plain, Bihar, India: a future danger? Environ Health Perspect 111(9):1194–1201

- Cox PA (1997) The elements on Earth. Inorganic chemistry in the environment. Oxford University Press, Oxford
- Davis SN (1973) Statistics and data analysis in Geology. Wiley, New York
- Dhar RK, Biswas BK, Samanta G, Mandal BK, Chakraborti D, Roy S, Jafar Islam A, Ara GA, Kabir S, Wadud Khan A, Akther Ahmed S, Abdul Hadi S (1997) Groundwater arsenic calamity in Bangladesh. Curr Sci 73(1):48–59
- EC (1998) Council Directive (98/83/EC) of 3 November 1998 on the quality of water intended for human consumption. Offic J Eur Commun, L 330
- EPA (2001) Rules and Regulations Federal Register, Vol.66, No.14, January 22, 2001
- EPA (2002) IRIS Summary—arsenic Inorganic; CASRN7440–38–2. Available: http://www.epa.gov/iris/subst/0728.htm
- Gebel T (1997) Arsenic and antimony:comparative approach on mechanistic toxicology. Chem Biol Interact 107:131–144
- Goldschmidt VM (1954) Geochemistry. Clarendon, Oxford
- Guo HR, Tseng YC (2000) Arsenic in drinking water and bladder cancer: comparison between studies based on cancer registry and death certificates. Environ Geochem Health 22:83–91
- Harmon H (1976) Modern factor analysis, 3rd edn. University of Chicago Press, Chicago
- Impelliteri C (2004) Effects of pH and competing anions on the speciation of arsenic in fixed ionic strength solutions by solid phase extraction cartridges.

 Water Res 38:1207–1214
- IGME. Ayia-Panayia Ayias sheet (1984) Geological Map 1:50.000. Department of Geological maps of IGME, Athens, Greece

- IGME. Karitsa sheet (1987) Geological Map 1:50.000. Department of Geological maps of IGME, Athens, Greece
- Islam Riajul MD, Salminen R, Lahermo PW (2000) Arsenic and other toxic elemental contamination of groundwater, surface water and soil in Bangladesh and its possible effects on human health. Environ Geochem Health 22:33–53
- International Programme on Chemical Safety (2001) Environmental health criteria 224. Arsenic and arsenic compounds. WHO, Geneva
- Kabata Pendias A, Pendias H (1992) Trace elements in soils and plants. CRC Press, Boca Raton
- Kelepertsis A, Alexakis D, Kita I (2001) Environmental geochemistry of soils and waters of Susaki area, Korinthos, Greece. Environ Geochem Health 23:117–135
- McLellan F (2002) Arsenic contamination affects millions in Bangladesh. Lancet 359(9312):1127
- Migiros G (1983) Geological structure of the Lower Olymbous area, Thessaly, Greece. PhD Thesis, University of Patras
- Migiros G (1998) The mineral wealth of Thessaly (Central Greece). Geotectonic setting—resource development. Mineral Wealth 108:15–26
- Onishi H (1969) In: Wedepohl KH (eds) Hand book of geochemistry, vol II (2) Springer, Berlin Heidelberg New York
- Paul BK (2004) Arsenic contamination awareness among the rural residents in Bangladesh. Soc Sci Med 59:1741–1755
- Post Conference Report (1995) Experts opinion, recommendation and future planning for groundwater problem of West Bengal. In: International conference on Arsenic in groundwater: cause, effect and remedy, School of Environmental Studies, Jadavpur University, Kolkata, India, 6–8 February 1995

- Ramirez-Solis A, Mukopadhyay R,Posen BP, Stemmler TL (2004) Experimental and theoritical characterization of arsenite in water: insights into the coordination environment of As–O. Inorg Chem 43(9):2954–2959
- Smedley PL, Kinniburgh DG (2002) A review of the source, behaviour and distribution of arsenic in natural waters.

 Appl Geochem 17:517–568
- Smith AH, Lingas EO, Rahman M (2000) Contamination of drinking water of arsenic in Bangladesh. A public health emergency. Bull WHO 78:1093–1103
- Smith E, Naidu R, Alston AM (2002) Heavy metals in the environment Chemistry of inorganic Arsenic in soils:II Effect of Phosphorus, Sodium, and Calcium on Arsenic sorption. J Environ Qual 31:557–563
- Sun G (2004) Arsenic contamination and arsenicosis in China. Toxicol Appl Pharmacol 198:268–271
- Tseng WP, Chu HM, How S, Fong JM, Lin CS, Yeh S (1968) Prevalence of skin cancer in an epidemic area of chronic arsenism in Taiwan. JNCL 40:435–463
- Tseng WP (1977) Effects of dose response relationships on skin cancer and blackfoot disease with arsenic. Environ Health Perspect 19:109–119
- Vink B (1996) Stability relations of antimony and arsenic compounds in the light of revised and extended Eh-pH diagrams. Chemical Geol 130:21–30
- Watanabe C, Kawata A,Sudo N, Sekiyama M, Inaoka T,Bae M, Ohtsuka R (2004) Water intake in an Asian population living in arsenic-contaminated area. Toxicol Appl Pharmacol 198:272–282
- Wilson NJ, Craw D, Hunter K (2004)
 Antimony distribution and environmental mobility at an historic antimony smelter site, New Zealand. Environ Pollut 129:257–266