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Geochemistry of stream sediments as a tool for assessing contamination by Arsenic, Chromium and other toxic elements: East Attica region, Greece

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Abstract: Geochemistry of surface hyporheic stream sediments, multivariate statistics and GIS database proved successful tools for assessing toxic element contamination in East Attica region. The objectives of this study were to assess the degree of contamination and to describe the surface hyporheic stream sediment geochemical variations in relation to geology, lithology and anthropogenic activities of East Attica region. The type of methodology used in this study consists of chemical analysis, pH evaluation, mineralogical analysis, cumulative probability plots, factor analysis, GIS database and comparison of the stream sediment contents with standards and levels recorded in the literature. The results of the study about stream sediments of East Attica region are presented. Cumulative probability plots in combination with spatial representation provided a clearer answer to the East Attica threshold question. The threshold values of East Attica streams are: As 20 mg kg^{-1}, Cd 0.3 mg kg^{-1}, Co 13 mg kg^{-1}, Cr 225 mg kg^{-1}, Cu 17 mg kg^{-1}, Mn 400 mg kg^{-1}, Ni 120 mg kg^{-1}, Pb 40 mg kg^{-1}, Sb 0.8 mg kg^{-1} and Zn 70 mg kg^{-1}. Relationships between various elements have been identified from factor analysis and reflect genetic associations. Factor analysis of the stream sediment data establishes eigenvalues that account for 85.8 % of the total variance and separates elements into three factors: Factor 1, an association of As, Ba, Cd, Fe, Cu, Fe, K, Mn Pb, Sb and Zn; Factor 2, an association of Co, Cr, Cu, Fe, Mg and Ni; and Factor 3, an association of Al, As, Ba, Co, Cu, Fe, K, Mn and Sb. A GIS elaboration showed the spatial relationship between high positive factor scores and presence of ore deposits and anthropogenic contamination. The sulphide and manganese-iron mineralization, small bodies of metabasic rocks and ophiolite fragments within Neogene-Quaternary deposits are the main components of toxic elements in East Attica surface hyporheic stream sediments. The composition of stream sediment is modified by contribution of various anthropogenic sources. There is both natural and anthropogenic input of As in East Attica streams, while there is a natural contamination of surface hyporheic stream sediments of East Attica region where natural elevated Cr and Ni surface hyporheic stream sediments contents exceed the Soil Guideline Values established by the Environment Agency.

Keywords: environmental geochemistry, factor analysis, hyporheic stream sediment, Arsenic, Chromium, threshold, Attica

1. INTRODUCTION

Stream sediments are mixtures of sediments, soils and rocks from the drainage basin upstream of the collection site (Mikoshiba et al., 2006). The term 'hyporheic zone', is used to refer to the zone adjacent and beneath to a stream or a river in which surface water interacts with groundwater (Smith, 2005). Moreover, the quality of groundwaters reflects input from the atmosphere, the water-rock-sediment-soil interactions as well as from anthropogenic contaminant sources. Stream sediments are usually considered as a sink for trace metals, but they can also act as sources of metals depending on the change of the environmental conditions (Segura et al., 2006). Then, trace metals are able to move towards the water column affecting the groundwater quality. Stream sediment analysis can be used to estimate point sources of contamination that, upon being discharged to surface waters, are rapidly adsorbed by particulate matter, thereby escaping detection by water monitoring (Förstner, 2004). Furthermore, stream sediment geochemistry data was used by Marini et al. (2001) to predict, at least partly, the chemical compositions of groundwater at Bisagno Valley.

According to Förstner (2004) and Smith (2005) the study of the geochemistry of the hyporheic zone sediments and the study of surface water-groundwater interactions should play a significant role in the holistic stream-basin approach of the Water Framework Directive (WFD; Council Directive 2000/60/EC).

Alexakis (2002) studied the geochemistry of major, minor and trace elements in East Attica groundwaters. According to Alexakis (2002) the East Attica groundwater are presently under threat from both anthropogenic (extensive agriculture, urban development, historical mining, industrial activities) and natural (lithology, sulphide and manganese-iron mineralization) pressure. Recent years environmental-geochemical studies that took place at the broader area of Lavrio revealed high concentrations of toxic elements in soils, groundwaters and near-shore surface sea sediments (Alexakis and Kelepertsis, 1998; Alexakis, 2002; Demetriades et al., 1996; Kelepertsis and Alexakis, 2004; Stamatis et al., 2001; Tristan et al., 1999). According to epidemiological study (Makropoulos et al., 1991) the broader area of Lavrio is classified, from an environmental point of view, as a high risk area. While a Geochemical Baseline Programme have been performed by Salminen et al. (2005) in order to provide high quality environmental geochemical baseline data for Europe, relatively little sediment geochemical analysis has been made on the streams in Greece and especially on the streams in East Attica region. No previous studies have been carried out on sediment contents in Rafina, Keratea-Artemis, Erasinos, PortoRafti and Kalivia streams.

The present research deals with the geochemical characteristics of East Attica surface hyporheic stream sediments. The purpose of this article is: (a) to describe the sediment geochemical variations in relation to geology, lithology and anthropogenic activities of East Attica region, (b) to focus on the application of stream sediment geochemistry as a tool to consider that any element concentration above a defined threshold concentration is directly attributed to anthropogenic activities, (c) to record the present quality status of the stream sediments in an area of booming development outskirts of Athens, (d) to compare element concentrations in the surface hyporheic sediment of East Attica region with standards for sediment and levels recorded in the literature, and (e) to identify any possible link between elevated threshold element values of East Attica streams and element concentrations in East Attica groundwaters recorded by previous studies.

2. STUDY AREA

2.1 Geographical location and geology

The study area is located between latitudes 37°28 and 38°02 and longitudes 23°50 and 24°05 and covers about 380 km^2. The southernmost sampling site is approximately 35 km and the northernmost 50 km from Athens, the capital of the Greek Republic (Fig.1). It includes the cities of Pallini, Rafina, Spata, Koropi, Markopoulo, Kalivia, Keratea and Lavrio. The area studied extends from Pendeli Mountain in the north to the city of Lavrio in the south, from the city of Paiania in the west to the Aegean Sea coastline in the east. The relief of the East Attica region is quite plain with hills.

The geological structure of East Attica region is dominated by two main units (Fig. 1): (a) the crystalline basement (Paleozoic-Upper Cretaceous), and (b) the Neogene-Quaternary deposits. The crystalline basement is composed of metamorphic rocks (marbles, schists and phyllites). The schists and phyllites are intercalated with quartzite and quartzite schists; small bodies of ophiolites, basic and metabasic rocks are also occasionally present in the schists and phyllites (Demetriades et al., 1996; Lozios, 1993; Papadeas, 2002; Pe-Piper and Piper, 2002; Stamatis et al., 2006). The Neogene-Quaternary deposits consist of marls, clays, conglomerates, ophiolite fragments, sandstones and other coarse unconsolidated sediments (Jacobshagen, 1986; Klisiouni, 1998; Pavlopoulos, 1997; Stamatis et al., 2006). The Pb-Ag-Zn massive sulphide mineralization of the broader area of Lavrio is composed of Ag-bearing galena (PbS), pyrite (FeS_2), sphalerite (ZnS), arsenopyrite (FeAsS) and chalcopyrite ($CuFeS_2$). Apart from the primary mineralization there are many secondary minerals (fluorite, barite, carbonates and quartz). Manganese-iron deposits occur peripherally to the massive sulphide mineralization. The Fe-Mn minerals were subsequently oxidized to pyrolusite and limonite

(Demetriades et al., 1996). The sulphide mineralization occurs within the marbles and close to their contact with schists, and also inside schists and marbles (Alexakis and Kelepertsis, 1998; Marinos and Petrascheck, 1956; Stamatis et al., 2006).

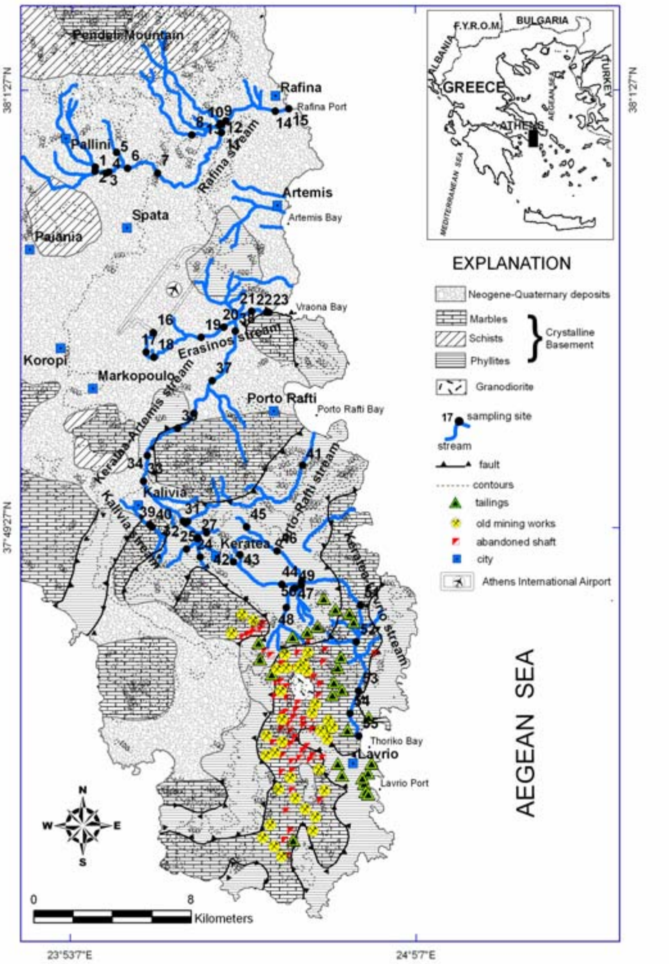

Figure 1. A simplified geological map of the East Attica region (modified from Jacobshagen, 1986), showing surface hyporheic stream sediment sampling sites

2.2 Drainage pattern

The limited permeability, characterizing the phyllites, schists and Neogene-Quaternary deposits, results in high run off. This is reflected in the drainage pattern development, which is of the dendritic type. The East Attica region is drained by six principal seasonal streams: the Rafina, the Erasinos, the Keratea-Artemis, the Porto Rafti, the Kalivia and the Keratea-Lavrio streams. All the streams studied, except the Kalivia stream, joins the sea along to the western coast of the Aegean Sea (Fig. 1). Some of the tributaries of the above seasonal streams have had no water flow for many months. During the winter period the heavy rainfalls causes a manifold increase in the runoff. Most of the East Attica stream sediments are transported during high stream discharge, in the winter period.

2.3 Anthropogenic activities in East Attica region

The East Attica region is characterized by extensive anthropogenic activities. The land in Rafina, Spata, Artemis, Markopoulo and Keratea areas is characterized by intensive construction works and intensive agricultural activities, especially olive oil trees, vegetables and vineyards. Dense highway network, small industries, the establishments of the Athens International Airport "Eleftherios Venizelos" (AIA), waste water treatment plants, the Athens racetrack and the 2004 Olympic Equestrian Centre are some of the types of land use taking place in the Spata, Artemis and Markopoulo areas. Lavrio is one of the most ancient mining districts in the world. In the Lavrio area extensive Ag-galena mining has occurred since 3000 B.C. up to the 1980s. Moreover, a huge amount of toxic waste produced from mining and smelting activities of Ag-galena including slags, tailings and low grade ore, were deposited in piles around Lavrio area, near the coastline, or even dumped into the sea representing a considerable threat for the environment. According to Tristan et al.(1999) and author observations, it is obvious that a large part of the residential area of Lavrio is situated over slags and contaminated soil, while olive trees and vineyards are mainly grown over the flotation residues.

3. MATERIALS AND METHODS

3.1 Sampling and preparation

A total of 55 surface hyporheic sediments (0-10 cm) were sampled in East Attica streams in December 2006 - January 2007 (Fig. 1). Sampling procedures are from Salminen et al. (2005). Sampling density is calculated to be about one site per 7 km^2. Since, some tributaries of the above seasonal streams have had no water flow for many months; the stream bed was covered by fallen bank material. The fallen bank material has been removed by digging and the stream sediment was sampled with extreme care. Over 5 kg of bulk surface hyporheic sediment sample were collected in order to ensure that sufficient fine-grained material would be available for analysis. Surface hyporheic sediment samples were collected using a polypropylene tool and stored into clean polyethylene (PE) bags. During the sampling process simultaneous site surveys carried out in order to provide site specific information relating to anthropogenic activities near the sampling points. Each bulk sediment sample actually represents the average of several surface hyporheic stream sediment sub-samples which were collected from 5-10 points over a stream stretch of ~50 m, preferably in its central part.

The surface hyporheic stream sediment samples were dried at room temperature (< 25^{o}C) for several days and sieved firstly to < 2.00 mm and secondly to < 0.2 mm, using nylon sieve cloth. The finer fraction (< 0.2 mm) was pulverized in an agate mortar to < 0.075 mm in order to ensure homogeneity and stored in polyethylene jars. Contact with metals was avoided throughout these operations to exclude metal contamination.

3.2 Evaluation of pH

The evaluation of pH was performed in duplicates according to the method described by ISRIC (2002). About 3.00 g of the pulverized surface hyporheic stream sediment sample were mixed with 7.5 mL of deionized water in polythene tubes. The tubes were capped and the mixtures were shaken for 2 hours on a KIKA KS 250 mechanical shaker at 250 motions per minute. Before opened the tubes for measurement, the tubes were shaken by hand twice. The electrode was immersed in the upper part of the supernatant and the pH was measured by a pre-calibrated pH meter using a JENWAY model 3040.

3.3 Chemical analysis

The homogenized < 0.075 mm stream sediment fraction was treated with a 4-acid (HNO_3, $HClO_4$, HF and HCl) digestion technique. The solutions were analyzed for Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn by atomic absorption spectroscopy (AAS) using a Perkin Elmer model 1100B at the

Laboratory of Economic Geology and Geochemistry of the National and Kapodistrian University of Athens and for Ag, Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, K, La, Li, Mg, Mo, Na, Nb, P, Rb, S, Sb, Sc, Sn, Sr, Ta, Th, Ti, U, V, W, Y and Zr by inductively coupled plasma mass spectrometry (ICP-MS) at the ACME Analytical Laboratories Ltd, Vancouver, Canada (ISO 9002 Accredited Co). The Nationals Institute of Standards and Technology geochemical reference samples were used to monitor the chemical analyses. Montana soil reference samples SRM 2710 and SRM 2711 were routinely analyzed to determine analytical errors (accuracy 5-10%). Duplicate measurements were conducted for 10% of the analyzed sediment samples (precision 2-3%). Chemical analysis data for 55 surface hyporheic sediment samples were compiled from this dataset, for the purposes of the present geochemical study.

3.4 X-Ray Diffraction (XRD) analysis

Seventeen (17) pulverized (< 0.075 mm) representative stream sediment sub-samples were made into pressed powder pellets for XRD analysis in an automated Siemens D5005 Diffractometer with Cu-Kα radiation (40kV-40mA), where each sample was scanned from 2^o to 65^o 2θ with a 0.04 second step. The software code EVA®2.2 for Windows was used for the evaluation of the diffraction patterns. XRD analysis was performed at the Laboratory of Economic Geology and Geochemistry, National and Kapodistrian University of Athens.

3.5 Scanning Electron Microscope (SEM) analysis

The SEM analysis was used as a complementary technique with XRD analysis. Eight (8) representative stream sediment pulverized (< 0.075 mm) sub-samples were examined by using a scanning electron microscope (SEM) JEOL JSM-5600. The qualitative analysis of some spots of the sediment samples was performed by using an Energy Dispersive X-ray detector (EDX) OXFORD LINK™ ISIS™ 300. The SEM working conditions were the following: acceleration voltage 20 kV, beam current 0.5 nA, beam diameter <2 μm and acquisition time 50 sec. The SEM analysis were performed on a resin/impregnated carbon coated samples at the Laboratory of Economic Geology and Geochemistry, National and Kapodistrian University of Athens.

3.6 Statistical analysis

Statistics is used to study the geochemical data distribution and to study relationships between the East Attica stream sediment contents. The software codes Microsoft® Excel, MINITAB® and SPSS® 13.0 for Windows were used for the statistical analysis.

The univariate summary statistics of the East Attica streams geochemical dataset (41 elements) and pH are calculated. The statistical analyses showed that all the element data, except Fe data, are positively skewed indicated in the summary statistics by the arithmetic mean > median and a logarithmic (base 10) transformation were applied to normalize this effect.

The East Attica stream sediment data was inspected for evidence of extreme or outlying values by using Tukey boxplots (Tukey, 1977) and a data subset for threshold calculation were prepared with these values omitted. Boxplot provides a graphical data summary relying solely on the inherent data structure, while outliers are detected as single values. Reimann et al. (2005) reported that one of the best graphical displays of geochemical distribution is a cumulative probability plot (CDF), originally introduced to geochemists by Tennant and White (1959), Sinclair (1974) and Rose et al. (1979). One of the main advantages of CDF diagrams is that each single data value remains clearly visible and extreme outliers are detectable as single values. According to Reimann et al. (2005) the graphical inspection using CDF diagrams and geographical displays to isolate sets of background data is far better suited for estimating the thresholds, action levels (e.g. maximum admissible concentrations) or clean up goals in environmental legislation. Threshold values by definition are regarded as the practical upper limits of the natural background populations (Rose et al., 1979). The knowledge of threshold values of chemical elements in East Attica surface hyporheic stream sediments is necessary before the sediment can be declared to be contaminated.

Owing to the great number of chemical variables, East Attica stream sediment data were processed by the statistical techniques of R-mode factor analysis, applying the Varimax-raw rotational technique with Kaiser Normalization, in order to determine inter-element relationships and common origin of the elements. The multivariate statistics analysis was applied on fifteen (15) elements- Al, As, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Sb and Zn on the basis of specific environmental interest related to the lithology, the ore composition and the type of anthropogenic activities of the East Attica region. Since East Attica streams geochemical parameters are log-normally distributed, then R-mode factor analysis have to be applied on the log-transformed data matrix (55 x 15) of element concentrations (Davis, 1973; Rose et al., 1979).

3.7 Map presentation and use of GIS

In this study, simplified digital geochemical maps were created using geographic information system ArcView 8.2 GIS® software (ESRI). Field data of stream sediment sampling sites were recorded in the field by using a Garmin eMap Geographical Position System (GPS), this data have been also plotted on additional information layer of the GIS. The geochemical maps were coupled with boxplots in order to have an improved insight to the data structure. The post plots for selected elements were classed according to its original Tukey boxplot (Tukey, 1977) and the threshold value. The element data values were divided into four classes as follows: (a) minimum to threshold value, (b) threshold value to upper hinge, (c) upper hinge to upper whisker, and (d) upper whisker to maximum. The classed post plots of element concentrations were projected on the digital map using graduated size symbols which are designed to highlight both background (+ symbols) and anomalous (circle symbols) values. A GIS procedure known as "natural breaks" that identifies gaps in ordered data to aid factor scores class selection is used. The spatial database was completed by projecting the factor score values distribution on the maps using graduated size symbols which are designed to highlight both high and low factor scores.

4. RESULTS

Table 1 presents univariate summary statistics (n=55) of the East Attica streams geochemical full dataset (41 elements content) and pH values. The trace elements Au, Be and Bi in all surface hyporheic stream sediment samples (n=55) were not detected. Surface hyporheic sediments pH values of the East Attica streams ranged from 7.5 to 8.9, while the mean pH is 8.1.

The seventeen (17) surface hyporheic East Attica stream sediment samples are dominated by Albite ($NaAlSi_3O_8$), Calcite ($CaCO_3$), Chlorite ($(Mg,Fe)_5(Al,Si)_5O_{10}(OH)_8$), Illite ($2K_2O.3MgO.Al_2O_3.24SiO_2.12H_2O$) and Quartz ($SiO_2$). Talc ($Mg_3(Si_4O_{10})(OH)_{2/3}MgO.4SiO_2.H_2O$) was detected in the following surface hyporheic sediment sampling sites: Rafina stream (sampling sites: 4, 10), Erasinos stream (sampling site: 16) and Keratea-Artemis stream (sampling sites: 49, 52, 53, 54), while Montmorillonite ($(Na,Ca)_{0.3}(Al,Mg)_2Si_2O_{10}(OH)_2.nH_2O$) has been detected only in Erasinos surface hyporheic stream sediments (sampling sites 16 and 18). Muscovite ($H_2KAl_3(SiO_4)_3$) has been identified in the following surface hyporheic sediment sampling sites: Rafina stream (sampling sites: 4, 5, 7), Kalivia stream (sampling site 39) and Keratea-Lavrio stream (sampling sites: 52, 53, 54, 55). No Fe-Mn oxides or hydroxides were detected in the studied surface hyporheic stream sediment samples by XRD.

The SEM observation and microanalysis results indicated that the eight selected surface hyporheic sediments of East Attica consist of Albite ($NaAlSi_3O_8$), Calcite ($CaCO_3$), Chlorite $(Mg,Fe)_5(Al,Si)_5O_{10}(OH)_8$, Chromite ($FeO{\cdot}Cr_2O_3$), Illite ($2K_2O{\cdot}3MgO{\cdot}Al_2O_3{\cdot}24SiO_2{\cdot}12H_2O$), Hematite($Fe_2O_3$), Fe-oxy-hydroxides, Litharge (PbO), Quartz (SiO_2) and anthropogenic grains of weathered metallurgical slag, containing Cu, Pb, Si and Zn. The qualitative microanalysis of selected bright particles in back scattered mode indicated that clay particles often appear coated with Fe-oxy-hydroxides, enriched in As, Cu and Zn.

The varimax rotated factor loadings, communalities and the proportion of variance explained are tabulated in Table 2.

Table 3 presents median, mean and threshold values (n=55) of the elements As, Cd, Co, Cr, Cu, Mn Ni, Pb, Sb and Zn in comparison with chemical analysis results obtained by other studies in order to gather preliminary information about the level of contamination in surface hyporheic sediments of East Attica region. Arsenic, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn and Zn East Attica surface hyporheic stream sediment contents were compared against background concentrations of elements (Turekian and Wedepohl, 1961; Salminen et al., 2005). The surface hyporheic stream sediment As, Cd, Cr, Ni and Pb concentrations were also assessed using the Environment Agency's screening method. Since the surface hyporheic sediments are an integral and dynamic part of drainage basins reflecting the average chemical composition of the surface materials (soils, sediments and rocks), the sediment element concentration may be compared against the Soil Guideline Values (SGVs) for residential and allotments land uses established by the Environment Agency (2002a, b, c, d, e). These standards can be used to assess the risks posed to human health from exposure to soil contamination in relation to land-use (Environment Agency, 2002a, b, c, d, e).

The classed post plots were coupled with boxplots for helping to understand the geochemical data (Fig. 3, 4). In order to visualize the spatial relationship between the chemical variations in the surface hyporheic stream sediments and the lithology, as well as the various sources of contamination in East Attica area, the classed post maps of factor scores were created (Fig. 4, 5, 6). The threshold values of the East Attica surface hyporheic stream sediments were extracted from the CDF diagrams by using criteria as breaks and inflection points (Fig.7).

5. DISCUSSION

5.1 Sediment quality assessment

The mean concentrations of As, Cd, Cr, Ni, Pb, Sb and Zn in the surface hyporheic stream sediment samples of East Attica region were significantly higher than those in average shale (Turekian and Wedepohl, 1961); while median contents of As,Cr,Ni,Pb and Sb in the East Attica surface hyporheic sediments were higher than these in average shale (Table 3).

The percentage proportions of the East Attica hyporheic stream sediment samples exceeding the SGVs established by the Environment Agency for residential land uses with plant uptake and allotments are 61%, 3.6%, 81%, 90.9% and 10.9% for As, Cd, Cr, Ni and Pb, respectively (Table 3).

The percentage proportion of the studied hyporheic stream sediment samples exceeding the SGVs for residential land uses without plant uptake are 61%, 0%, 63.6%, 85.5% and 10.9% for As, Cd, Cr, Ni and Pb, respectively (Table 3).

The pH values in surface hyporheic stream sediment of East Attica region were near neutral to alkaline (Table 1), probably as a result of the strong buffering capacity of the carbonates in the sediment fraction.

Table 1. Summary of univariate statistics of East Attica stream sediments geochemical dataset (n=55)

	Units	Detection Limit	Minimum	Maximum	Mean	Median	Sdev	Skewness
Ag	mg kg^{-1}	0.1	0.1	9.6	0.44	0.10	1.3	6.6
Al	wt%	0.01	2.02	5.98	3.62	3.61	0.8	0.6
As	mg kg^{-1}	1	8	272	41.8	24	51.9	3.1
Au	mg kg^{-1}	0.1	-	<0.1	-	-	-	-
Ba	mg kg^{-1}	1	64	781	199	156	157.8	2.8
Be	mg kg^{-1}	1	-	<1	-	-	-	-
Bi	mg kg^{-1}	0.1	-	<0.1	-	-	-	-
Ca	wt %	0.01	3.70	24.83	12.22	12.06	4.2	0.4
Cd	mg kg^{-1}	0.1	0.2	19.4	1.11	0.30	3.0	5.1
Ce	mg kg^{-1}	1	18	51	33	33	7.2	0.1
Co	mg kg^{-1}	0.2	4.4	39.2	18.5	17.5	7.3	0.7
Cr	mg kg^{-1}	0.1	52	1399	285.8	220.9	233.7	2.4
Cu	mg kg^{-1}	0.1	8.8	80.2	31.96	27.7	15.1	1.3
Fe	mg kg^{-1}	100	7600	41800	27169	27300	8051.5	-0.2
Hf	mg kg^{-1}	0.1	0.2	1.1	0.4	0.4	0.2	1.2
K	wt%	0.01	0.31	1.46	0.74	0.71	0.2	0.8
La	mg kg^{-1}	0.1	9.9	29.4	18.39	18.10	4.1	0.3
Li	mg kg^{-1}	0.1	11.1	44.1	24.74	23.90	7.6	0.6
Mg	mg kg^{-1}	100	4300	42500	16083	12400	10012	1
Mn	mg kg^{-1}	1	271	2673	716	610	451.2	2.9
Mo	mg kg^{-1}	0.1	0.2	2.1	0.74	0.60	0.4	1.5
Na	wt%	0.001	0.31	1.83	0.85	0.83	0.3	0.7
Nb	mg kg^{-1}	0.1	2.2	9.8	5.57	5.40	1.8	0.2
Ni	mg kg^{-1}	0.1	33.2	512.3	172.04	145.70	116.9	1.3
P	mg kg^{-1}	10	170	9630	633	430	1247	7
Pb	mg kg^{-1}	0.1	17.0	2611.2	217.32	48.20	511.5	3.4
Rb	mg kg^{-1}	0.1	12.7	65.2	34.62	33.60	10.2	0.5
S	wt%	0.1	0.1	0.4	0.12	0.10	0.1	3.2
Sb	mg kg^{-1}	0.1	0.2	28.9	3.54	1.60	5.7	3.0
Sc	mg kg^{-1}	1	3	13	8.33	8.00	2.2	0.0
Sn	mg kg^{-1}	0.1	0.5	3.9	1.8	1.7	0.7	1.2
Sr	mg kg^{-1}	1	64	582	166	141	106.4	2.5
Ta	mg kg^{-1}	0.1	0.2	0.7	0.46	0.45	0.1	0.1
Th	mg kg^{-1}	0.1	2.4	6.8	4.33	4.30	1.0	0.6
Ti	mg kg^{-1}	10	820	5440	2288	2190	909	1
U	mg kg^{-1}	0.1	0.3	2.5	0.72	0.70	0.4	2.5
V	mg kg^{-1}	1	26	121	66	63	19.3	0.3
W	mg kg^{-1}	0.1	0.2	4.0	0.5	0.4	0.5	6.0
Y	mg kg^{-1}	0.1	6.5	17.1	12.1	11.9	2.2	0.2
Zn	mg kg^{-1}	1	23	1331	169.98	92.00	234.2	3.4
Zr	mg kg^{-1}	0.1	3.1	73.2	13.30	10.60	10.5	3.7
pH			7.5	8.9	8.2	8.1	0.3	0.1

5.2 Surface hyporheic stream sediment mineralogy

XRD analysis results support the high Cr, Mn, Ni and Zn contents in the Erasinos surface hyporheic stream sediments by the presence of Montmorillonite which shows CEC values, varying between 800 and 1200 mg kg^{-1} (Appelo and Postma, 2005), and act as a metal adsorber.

According to the SEM image analysis, the Rafina and Erasinos surface hyporheic stream sediment clay particles (Illite, Chlorite) appear coated with Fe-oxy-hydroxides and despite the low CEC and low sorption of Illite and Chlorite, they act as carriers of As, Cu and Zn adsorbed onto the coating films of Fe-oxy-hydroxides (Fig.8). SEM analysis results support the high Cr content (1399 mg kg^{-1}) in the hyporheic stream sediment of Rafina stream (sampling site 7) by the presence of Chromite grains ($FeO{\cdot}Cr_2O_3$). The high Cu, Pb and Zn contents in the surface hyporheic stream sediment of Keratea-Lavrio stream are supported by the presence of anthropogenic grains of metallurgical slag determined by SEM analysis.

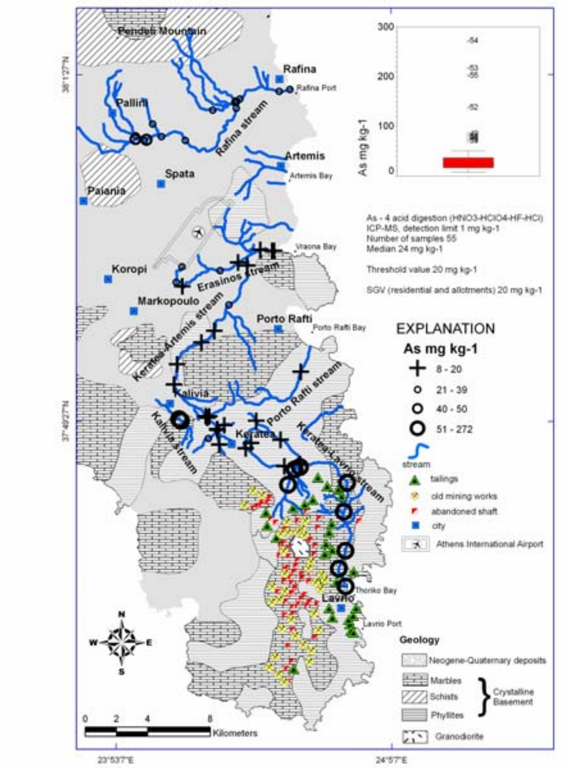

Figure 2. Symbol map of As concentrations in the surface hyporheic sediment of East Attica streams in comparison with geology (the symbols are designed to highlight both high and low values)

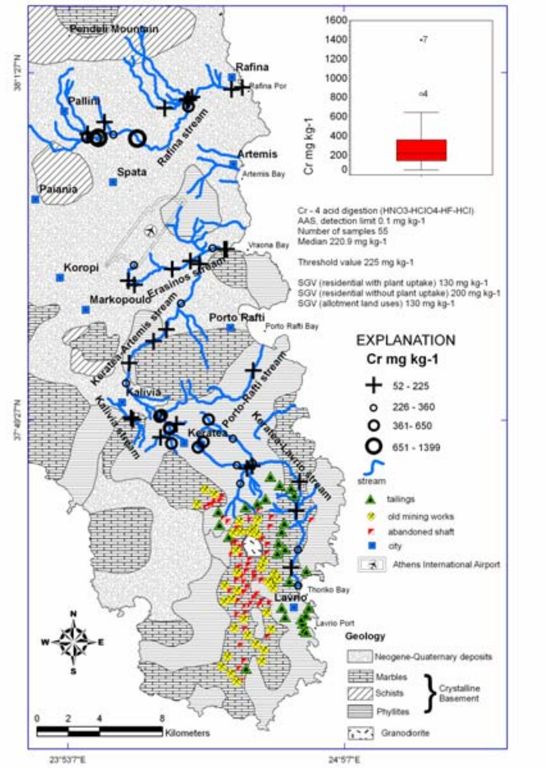

Figure 3. Symbol map of Cr concentrations in the surface hyporheic sediment of East Attica streams in comparison with geology (the symbols are designed to highlight both high and low values)

5.3 Regional geochemical signatures in relation to geology and anthropogenic activities

The As and Cr stream sediment geochemical maps were inspected in the light of known natural and anthropogenic processes. High As contents (circle symbols in Fig.2) varying between 51 and 272 mg kg^{-1} were recorded in stream sediment samples collected along the Kalivia stream and the southern part of Keratea-Lavrio stream, especially close to the old mining works and tailings. These As positive anomalies are associated with sulphide mineralization and anthropogenic activities. Sampling sites with anomalous As stream sediment contents, ranging from 21 to 39 mg kg^{-1} occur along the Erasinos and the Rafina stream; while sediment sampling sites with As content varying between 40 and 50 mg kg^{-1} were recorded along the western part of the Rafina stream. Due to the absence of sulphide mineralization in the areas of Rafina and Spata, these As positive anomalies are possibly associated with application of fertilizers and As-rich agricultural chemicals which are widely used in Rafina and Spata cultivated land. Moreover, Klissiouni (1998) reported that As contents in Spata soils ranges from 8 to 355 mg kg^{-1}; while the high As soil content cannot be correlated to the geological bedrock of the Spata area. The high As soil contents are attributed to the application of fertilizers and metal-rich agricultural chemicals in the Spata cultivated land.

Anomalous Cr concentrations (circle symbols in Fig.3) varying between 361 and 650 mg kg^{-1} were recorded in the part of Keratea-Artemis stream that extends from Keratea city in the south to the city of Kalivia in the north, as well as in the northern part of Keratea-Lavrio stream. The highest Cr content is recorded in stream sediments collected along the Rafina stream (sampling sites: 4,7), while the Cr content in sediments collected along the western part of Rafina stream varying between 226 and 360 mg kg^{-1}. These Cr positive anomalies are attributed to metabasic rocks, ophiolites and ophiolite fragments within Neogene and Quaternary deposits. Chromium content of Erasinos surface hyporheic stream sediments ranges from 226 to 360 mg kg^{-1}. The Erasinos Cr positive anomalies are associated with ophiolite fragments within Neogene-Quaternary deposits and presence of Montmorillonite which act as Cr adsorber.

Table 2. Varimax rotated component loadings of three factors and variance explained for 15 elements of East Attica surface hyporheic stream sediments (n=55). All data were logarithmically transformed prior to factor analysis. Loadings below ±0.260 are not shown

Variable	*Factor 1*	*Factor 2*	*Factor 3*	*Communality*
Al			*0.896*	*0.867*
As	*0.761*	*-0.275*	*0.421*	*0.831*
Ba	*0.845*		*0.286*	*0.842*
Cd	*0.927*			*0.867*
Co		*0.825*	*0.489*	*0.933*
Cr		*0.835*		*0.715*
Cu	*0.487*	*0.647*	*0.436*	*0.847*
Fe	*0.263*	*0.396*	*0.838*	*0.928*
K	*0.325*		*0.841*	*0.861*
Mg		*0.834*	*0.418*	*0.717*
Mn	*0.750*			*0.797*
Ni		*0.950*		*0.944*
Pb	*0.927*			*0.907*
Sb	*0.897*		*0.306*	*0.904*
Zn	*0.904*			*0.903*
Variance	*5.69*	*3.91*	*3.26*	*12.86*
% Variance	*37.9*	*26.1*	*21.8*	*85.8*

High Cr contents in soils and groundwaters of East Attica region have also been recorded by other studies (Klissiouni, 1998; Alexakis and Kelepertsis, 1998; Alexakis, 2002). Klissiouni (1998) reported high Cr contents in Spata and Markopoulo soils ranging from 34 to 413 mg kg^{-1}. According to Klissiouni (1998) the Spata and Markopoulo soil enrichment in Cr is due to the presence of ophiolites in the composition of phyllites and due to the presence of ophiolite fragments within Neogene-Quaternary deposits.

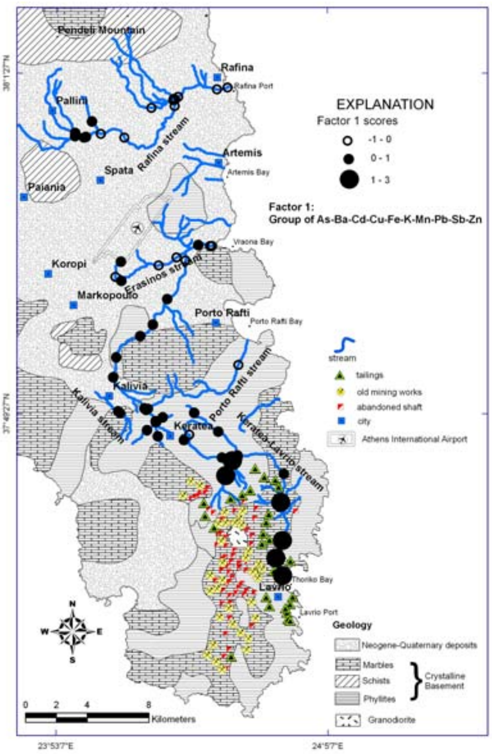

Figure 4. Graduated symbol plots of Factor 1 scores in comparison with geology

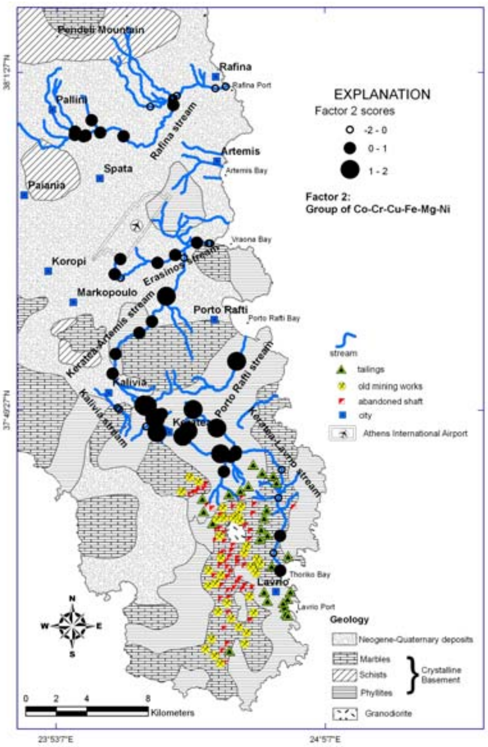

Figure 5. Graduated symbol plots of Factor 2 scores in comparison with geology

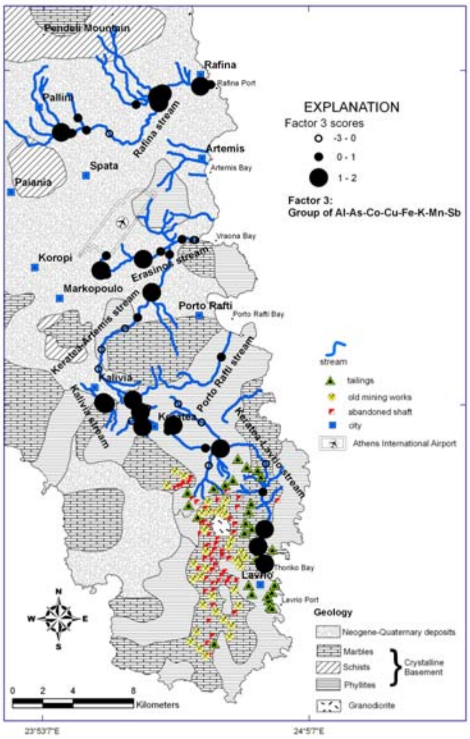

Figure 6. Graduated symbol plots of Factor 3 scores in comparison with geology

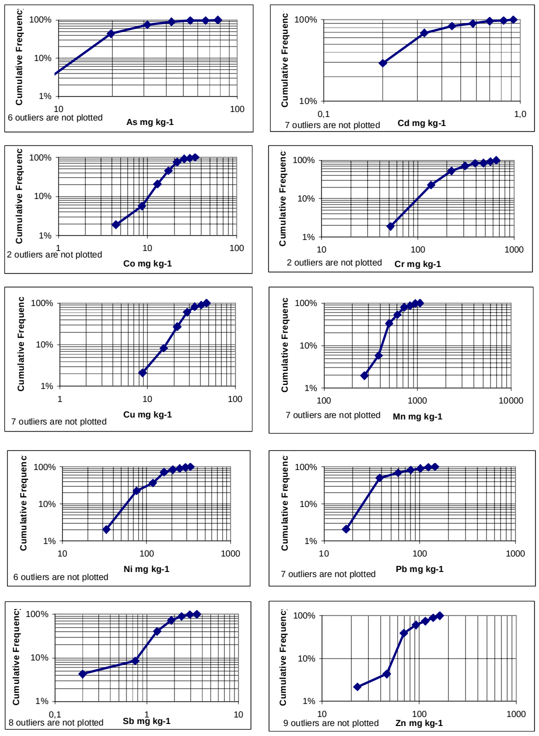

Figure 7. CDF diagrams of the East Attica surface hyporheic stream sediment data (n=55)

Alexakis (1998, 2002) reported that Cr content in Spata-Keratea-Lavrio groundwaters varies between 27 and 90 μg L^{-1}; while 26% of the Spata-Keratea-Lavrio groundwater samples exceeded the risk-based drinking water criteria of 50 μg L^{-1} given by the Council Directive 98/83/EC (1998).

The spatial distributions of the elements Al, As, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Sb and Zn were compacted in the scores of the first, second and third components of a multivariate analysis (factor analysis) implemented on the chemical analysis data of the East Attica surface hyporheic stream sediment samples. In the present study, the element distribution in the surface hyporheic stream sediments of the East Attica region is explained in terms of three factors, accounting for 85.8 % of the total variance of the geochemical dataset (Table 2).

Factor 1, explaining 37.9 % of the total variability, is a factor with high positive loadings (>+0.750) for As, Ba, Cd, Mn, Pb, Sb and Zn, moderate positive loadings for Cu (+0.487), K (+0.325) and low positive loading for Fe (+0.263). These elements occur in the known Pb-Ag-Zn massive sulphide mineralization and Fe-Mn mineralization and mining and smelting wastes; therefore Factor 1 is directly attributed to natural and anthropogenic contamination sources.

Factor 2 accounts for 26.1% of the total variance explained, is a dipolar factor and show high positive loadings (> +0.647) for Co, Cr, Cu, Mg and Ni, moderate positive loading (+0.396) for Fe and moderate negative loading (-0.275) for As. These elements occur in the known small bodies of ophiolites, basic and metabasic rocks (Papadeas, 2002; Pe-Piper et al., 2002); therefore Factor 2 is directly attributed to natural contamination sources and mainly the weathering products of the metabasic rocks, ophiolites and ophiolite fragments within Neogene-Quaternary deposits.

Factor 3, accounts for 21.8% of the total variance and shows high positive loading (≥+0.838) for Al, Fe and K, and median positive loading ranging from +0.286 to +0.489 for As, Ba,Co, Cu, Mn and Sb. Aluminum, Fe and K are known to occur together in Illite, Chlorite and Muscovite. Arsenic, Ba, Co, Cu, Fe and Mn are associated together in fertilizers, agricultural chemicals, manure, sludge and wastewater (Kabata-Pendias et al., 1992; Shomar et al., 2005); therefore Factor 3 indicates that elements with anthropogenic origin such as As, Ba, Co, Cu, Mn and Sb are associated with clay minerals (Illite, Chlorite and Montmorillonite) and Fe-oxy-hydroxide coating films, which act as elements adsorbers. Iron was believed to originate from both natural and anthropogenic sources, while according to Bradl (2004) Fe oxides are among the most important sinks for Cu in soils. According to Galan et al. (2003) and Lazzari et al. (2004), Fe-oxides and hydroxides may occur along or form thin coating films for clays and other minerals, acting as carriers of element contaminants. Factor 3, portrays the anthropogenic input and adsorption of As, Co, Cu and Mn by clay minerals (Illite, Montmorillonite and Chlorite) and Fe-oxy-hydroxides coating films.

Table 3. Mean, median and threshold values (mg kg-1) of East Attica surface hyporheic stream sediments (n=55) in comparison with SGVs (Environment Agency, 2002a, b, c, d, e) and element contents obtained by other studies (1 Turekian and Wedepohl, 1961; 2 Salminen et al., 2005; 3 Environment Agency Soil Guideline Values (SGV) with respect to land use, 2002a, b, c, d, e)

	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Sb	Zn
This study, median	24	0.3	17.5	220.9	27.7	610	145.7	48.2	1.6	92
This study, mean	41.8	1.1	18.5	285.8	31.9	716	172	217.3	3.5	169.9
Threshold values	20	0.3	13	225	17	400	120	40	0.8	70
Average shale [1]	13	0.3	19	90	45	850	68	20	1.5	95
Mean sediment [2]	10.2	0.53	11.1	96.3	22.8	706	36.5	39.4	1.08	122
SGVs (Residential with plant uptake) [3]	20	8	-	130	-	-	50	450	-	-
Percentage proportion (%) of East Attica's stream sediment samples exceeding the SGVs for Residential land use with plant uptake	61.0	3.6	-	81.0	-	-	90.9	10.9	-	-
SGVs (Residential without plant uptake) [3]	20	30	-	200	-	-	75	450	-	-
Percentage proportion (%) of East Attica's stream sediment samples exceeding the SGVs for Residential land use without plant uptake	61.0	0	-	63.6	-	-	85.5	-	10.9	-
SGV (Allotments) [3]	20	8	-	130	-	-	50	450	-	-
Percentage proportion (%) of East Attica's stream sediment samples exceeding the SGVs for Allotments	61.0	3.6	-	81.0	-	-	90.9	-	10.9	-

Figure 4 presents the spatial distribution of Factor 1. Higher positive scores (>+1) correspond to higher As, Ba, Cd, Cu, Fe, K, Mn, Pb, Sb and Zn surface hyporheic stream sediment concentrations. Surface hyporheic sediment samples collected along the southern part of Keratea-Lavrio stream revealed the heaviest load of the above elements because it flows through the historical mining sites and the smelter areas at Lavrio. Surface hyporheic stream sediment samples collected along the Rafina, Erasinos, Keratea-Artemis, Porto-Rafti and Kalivia streams present the lowest load of the above elements due to the lack of sulphide and iron-manganese mineralization.

Figure 5 shows the spatial variability of the Factor 2 score values. Higher positive scores (>+1), correspond to higher Co, Cr, Cu, Fe, Mg and Ni surface hyporheic stream sediment concentrations. The higher positive Factor 2 scores are observed in the part of Keratea-Artemis stream that extends from Keratea city in the south to the city of Kalivia in the north, as well as in the northern part of Keratea-Lavrio stream and in the Porto-Rafti stream, demonstrating Factor 2 association with phyllites and the small bodies of metabasic rocks and ophiolites. The sampling sites with the lower factor scores (factor scores < 0) lie in the mouth of Rafina stream as well as in the southern part of Keratea-Lavrio stream.

The significant element contamination input of Keratea-Lavrio stream to the Thoriko Bay and Lavrio Port marine environment was recorded by near-shore bottom sea sediments geochemical studies (Kelepertsis and Alexakis, 2004; Zotiadis, 2004). The concentrations of the elements in the Thoriko Bay and Lavrio Port near-shore bottom sea sediments range as follows: As (6-7616 mg kg^{-1}), Co (2-35 mg kg^{-1}), Cd (0.4-44 mg kg^{-1}), Cr (3-197 mg kg^{-1}), Cu (7-360 mg kg^{-1}), Ba (26-454 mg kg^{-1}), Fe (0.23-15.94 %), Mn (174-10795 mg kg^{-1}), Ni (6-139 mg kg^{-1}), Pb (83-6791 mg kg^{-1}) and Zn (51-9930 mg kg^{-1}) indicating natural variation and terrestrial toxic element input.

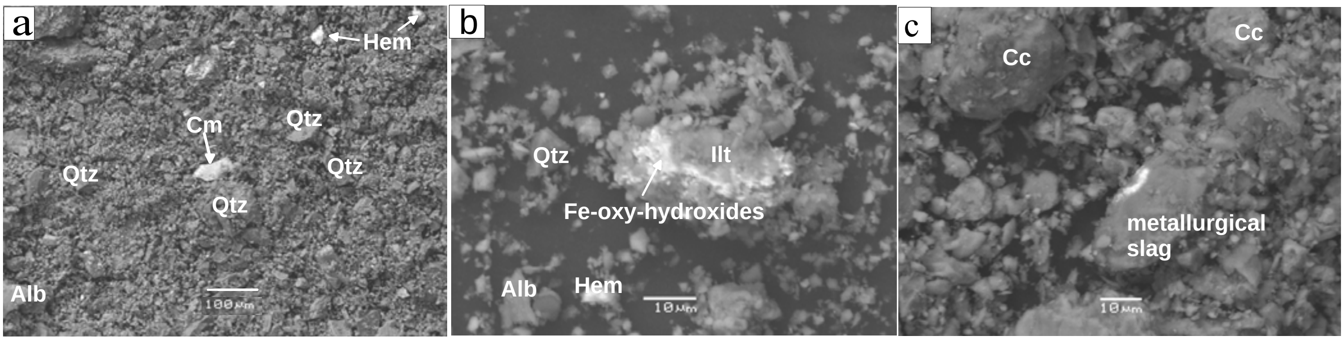

Figure 8. SEM images of surface hyporheic sediment samples of East Attica streams showing: (a) Chromite (Cm), Hematite (Hem) and Quartz (Qtz), (b) Calcite (Cc), Hematite (Hem) and typical aggregates of Chlorite (Chl) coated with Fe-oxy-hydroxides rich in As, Cu and Zn, (c) Hematite (Hem), Quartz (Qtz) and Illite (Ilt) coated with Fe-oxy-hydroxides rich in Cu, and (d) Calcite (Cc) and anthropogenic grain of metallurgical slag rich in Si, Pb, Cu, and Zn

Figure 6 shows the spatial variability of Factor 3. Higher positive scores (> +1), correspond to higher Al, As, Ba, Co, Cu, Fe, K, Mn and Sb surface hyporheic stream sediment concentrations. The higher positive Factor 3 score values (>+1) are mainly observed in the sediment samples collected along the Rafina stream, the southern part of Keratea-Lavrio stream, the Erasinos and the southern part of Keratea-Artemis stream, demonstrating Factor 3 association with cultivated areas of Rafina, Spata, Artemis, Keratea and Lavrio and intensive agricultural practices and wastewater discharge in the Erasinos stream.

Application of fertilizers and agricultural chemicals (pesticides, herbicides and fungicides) as well as the wastewater discharge of treatment plants is a common anthropogenic source of As, Ba, Co, Cu, Fe, Mn and Sb contamination worldwide (Alloway, 1995; Rose et al., 1979; Mandal et al., 2002; Robinson et al., 2006; Shomar et al., 2005). Furthermore, elevated As concentrations in stream sediments from agricultural areas in New England, USA, have previously been reported by Robinson and Ayuso (2004), demonstrating anthropogenic origin and application of pesticides. Moreover, according to Shomar et al. (2005) the enrichment of soils with Fe, Cu, Pb and Zn by the application of fertilizers and fungisides showed similar contents with soils affected by wastewater. According to Alloway (1995) soil levels of As, Cu and Co are affected by crop and soil treatments including fungisides, fertilizers and sewage sludges. Alloway (1995) reported that agricultural soils have generally been less badly affected by As build up than aquatic sediments and that the mobility of the As in aquatic sediments appears to have been reduced by the presence of Fe oxides.

The intensive agricultural practices applied in the Spata, Artemis and Keratea cultivated areas have been also recorded by the high nitrate (NO_3^-) and phosphate (PO_4^{3-}) contents in groundwaters, ranging from 61 to 265 mg L^{-1} and 0.01 to 6.75 mg L^{-1}, respectively (Alexakis, 2002; Stamatis et al., 2006).

6. CONCLUSIONS

The mean contents of As, Cd, Cr, Ni, Pb, Sb and Zn in the surface hyporheic sediment samples collected along East Attica streams were both significantly higher than these in average shale and than these reported in the stream sediments of Europe.

Small bodies of metabasic rocks, ophiolites and ophiolite fragments within Neogene-Quaternary deposits are the natural Cr contamination source for the surface hyporheic stream sediments, soils and groundwaters of Spata, Markopoulo and Keratea areas. The results of this study are in good agreement with the results of a groundwater geochemical survey in East Attica region, establishing a direct link between the Cr contents in the system rocks-soil-sediment and the Cr content in East Attica groundwaters.

High Cr contents in surface hyporheic stream sediments, soils and groundwaters of East Attica constitute a natural case of contamination, perhaps with some minor undetected anthropogenic input. East Attica region is a special case where natural elevated Cr surface hyporheic stream sediments concentrations exceed the Soil Guideline Values established by the Environment Agency. A GIS elaboration showed the spatial relationship between high Cr surface hyporheic stream sediment contents, small bodies of metabasic rocks, ophiolites and ophiolite fragments within Neogene-Quaternary deposits.

The surface hyporheic sediment samples of East Attica streams are dominated by Albite, Calcite, Chlorite, Illite, Muscovite and Quartz. Talc and Montmorillonite were also determined by XRD analysis; while Chromite grains, Litharge, anthropogenic metallurgical slag grains, and clay minerals coated with Fe-oxy-hydroxide films were detected by SEM analysis.

The main elements released at the Keratea-Lavrio stream upon weathering of the mineralized rocks, ore deposits, metabasic rocks and mining-metallurgical wastes are: As, Cd, Cu, Cr, Fe, Mn, Ni, Pb, Sb and Zn. The results of this study verify the importance of stream geochemical surveys in order to identify the terrestrial contamination sources and stream transported contamination to marine environment. The Keratea-Lavrio stream constitutes a distinct point of toxic elements contamination source of the Thoriko Bay marine environment.

R-mode factor analysis of the East Attica surface hyporheic stream sediments geochemical dataset, explaining the 85.8% of the total variability, showed the presence of three groups of associated elements. The group of As-Ba-Cd-Cu-Fe-K-Mn-Pb-Sb-Zn, named Factor 1, is related to natural/geological (Pb-Zn and Fe-Mn mineralization,) and anthropogenic (old mining works, smelting wastes, tailings) contamination sources of these elements. The group of Co-Cr-Cu-Mg-Ni, named Factor 2, is related to natural/lithological contamination sources. The group of Al-Fe-K with weak contribution of As-Ba-Co-Cu-Fe-Mn-Sb named Factor 3, is possibly related to clay minerals, Fe-oxy-hydroxides coating films and application of fertilizers and metal-rich chemicals in cultivated areas.

Factor analysis proved a successful tool for the identification of factors controlling the geochemical data variability, while GIS database, evidencing spatial relationships, was found to be very useful in the confirmation of East Attica's stream sediment geochemical interpretation of the statistical output.

The sulphide mineralization, manganese-iron mineralization, metabasic rocks and ophiolites are the main components of elements in East Attica surface hyporheic stream sediments. The composition of stream sediment is modified by contributions from various anthropogenic sources (tailings, smelting operations, old mine workings, metal-rich agricultural chemicals and fertilizers). The modification degree of the East Attica chemical sediments composition is different at each sampling site due to different magnitude of source contribution at each site.

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