# Factors controlling major ion and trace element content in surface water at Asprolakkas hydrological basin, NE Chalkidiki: Implications for elemental transport mechanisms

**E. Kelepertzis[1], A. Argyraki, E. Daftsis**

[1] Corresponding author: Section of Economic Geology and Geochemistry, Faculty of Geology and Geoenvironment, National and Kapodistrian University of Athens, Panepistimiopolis, Zographou 157 84, e-mail: kelepert@geol.uoa.gr

**Abstract** Chemical characteristics of stream water at Asprolakkas hydrological basin were determined in February 2009 in order to examine the main factors controlling the hydrogeochemistry of the drainage system. A total of 20 surface water samples were collected and analyzed for the major ions K, Na, Ca, Mg, $HCO_3$, $SO_4$ and the trace elements Fe, Pb, Zn, Mn, Cu, Ni, As, Sb, Mo and Ba. The application of R-mode factor analysis revealed that the polymetallic carbonate replacement type sulfide deposits, together with the porphyritic intrusions and the associated porphyry copper style mineralization, occurring in the studied area, impose fundamental control on the water chemistry. A third influencing factor includes the parameters As and $HCO_3$ and is attributed to the competitive behavior of As and bicarbonate ions, for filling in available absorption space on Fe(III) oxides. SEM-EDS methods, performed on retained filters from the filtration of representative water samples, showed that Pb is mainly transported by fine particulate matter. The chemical elements Mn, Zn, Mo and Sb are predominantly present as dissolved free ions, and correlate strongly with the electrical conductivity of the water samples.

## 1 Introduction

Mineral deposit regional geology and geochemical processes are fundamental controls on the surface water quality (Kelley and Taylor 1997). Apart from the very mobile and bioavailable dissolved forms of trace metals, suspended particulate matter and colloids are significant metal carrier phases. Colloids are particles that have at least one dimension in the size range of 1-1000 nm, and due to their small size they have a large specific surface area. These physical properties make colloids to have a significant impact on the transport of trace metals through sorption

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mechanisms (Kretzscmar and Schäfer 2005). They are also believed to be as reactive as suspended particulates and as mobile as dissolved solutes.

The present study aims to investigate the main factors that govern the hydrogeochemistry of running streams located at the mineralized wider area of Stratoni in NE Chalkidiki peninsula. Some general surface water quality characteristics and transport mechanisms of potentially toxic elements are also discussed.

## 2 Description of the study area

Geologically the study area consists of the metamorphic rocks of Vertiskos and Kerdylian geotectonic units, separated by the NW-SE trending Stratoni-Varvara fault (Fig. 1).

The main lithological types are represented by gneiss and amphibolites while Kerdylian sequence also comprises several marble horizons (Kockel et al. 1977), outcropping at the northern part of the area. The lower part is underlain by alluvial and Pleistocene deposits. The rocks have been intruded by Tertiary magmatic calc-alkaline granitoids, represented by the Stratoni granodiorite and the porphyritic intrusions of Skouries and Fisoka. Various ore deposits in the area are strongly related to the Tertiary intrusive bodies, including the Pb-Zn-Ag carbonate hosted replacement ore bodies of Madem Lakkos and Mavres Petres, the Piavitsa mixed sulfide and manganese ore deposits and the porphyry Cu-Au deposits at Skouries and Fisoka areas (Kalogeropoulos et al. 1989, Eliopoulos and Economou-Eliopoulos 1991).

The region is characterized by semi mountainous relief, typically around 300 m ASL, and by a well developed dendritic style drainage network. The average pluviometry in the catchment area is 650 mm and the flow rates of the streams present strong variations. From a hydrological point of view, the studied streams are flowing within the sub-basins of Piavitsa, Kerasia and Kokkinolakkas (Fig. 1). They all discharge (their waters) in Asprolakkas stream which has an E-W direction flowing towards the north part of Ierissos Gulf.

The current mining activity carried out in the Kassandra metallogenic province is represented by the exploitation of the Mavres Petres sulphide ore deposit whereas one of the future mine development plans is the Skouries project.

## 3 Sampling and analytical procedure

Water sampling was carried out in February 2009 under high flow conditions. A total of 20 samples were collected, preferably near stream confluences (Fig. 1).

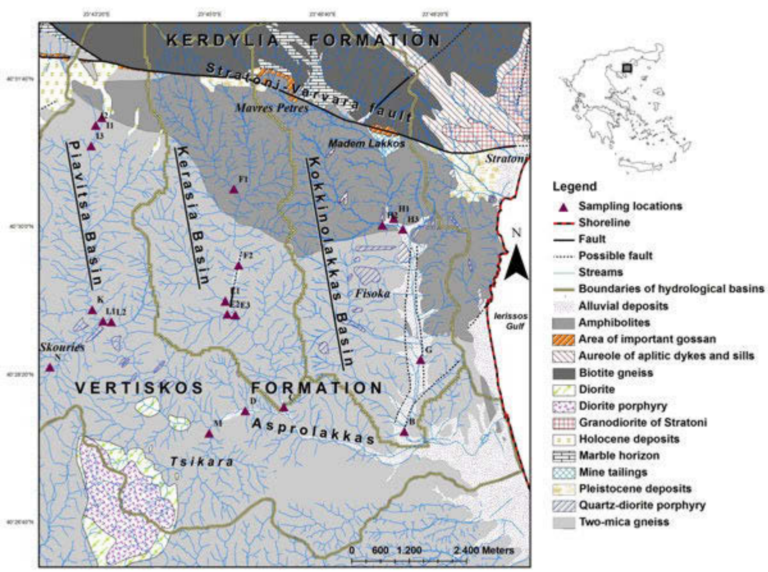



**Fig. 1.** Geological map of the study area showing sampling locations and hydrological catchments (after Kockel et al. 1977).

Special care was taken in order to ensure that the majority of streams that contribute to Asprolakkas hydrogeochemistry was sampled. Sample N represents water discharged by the old exploration adit of Skouries deposit.

Major physicochemical parameters such as pH and electrical conductivity were determined in the field. Samples were filtered with 0.45 μm membrane filter for the analysis of anions ($HCO_3^-$, $SO_4^{2-}$). Moreover, samples for major cations ($K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$) and metals (Fe, Pb, Zn, Mn, Cu, Ni, As, Sb, Mo, Ba) were filtered immediately in the field through 0.45 μm Millipore filters and acidified down to pH<2. Potassium, Na, Ca and Mg concentrations were determined by Inductively Coupled Plasma Emission Spectroscopy (ICP/AES) and $SO_4$ was measured gravimetrically as $BaSO_4$ (Laboratory of Quality Control of "Hellas Gold SA" at Stratoni). Heavy metals and metalloids were measured by Atomic Absorption Spectroscopy and Inductively Coupled Plasma Mass Spectroscopy (ICP/MS) at the Laboratory of Economic Geology and Geochemistry (Faculty of Geology and Geoenvironment, University of Athens) and the ACME Analytical Laboratories Ltd of Kanada. Quality control was performed by analysis of certified reference materials for trace element content verifying the good accuracy of the analytical results.

In order to identify metal bearing phases that are transported with the water flow as suspended particulate matter and colloidal particles with size greater than 0.45 μm, the filters retained by the filtration of 3 representative samples were examined by scanning electron microscope (SEM), equipped with an energy dispersive X-Ray spectrometer for microanalysis (EDS, Oxford LINK ISIS 300).

# 4 Results and Discussion

## 4.1 General water quality characteristics

A summary of the basic statistics of the chemical characteristics for the collected waters is shown in Table 1. The pH values remain constant for all the streams, displaying neutral to slightly alkaline conditions. Potassium and Na are found in low concentrations, deriving from the dissolution of biotite/muscovite and albite respectively, abundant in the geological formations of the study area. Chemical parameters such as Ca, Mg, $HCO_3$, $SO_4$, Fe, Pb, Zn, Mn, Ni, As and Sb present great variability among the examined samples.

**Table 1.** Basic descriptive statistics of the measured parameters for the collected waters from Asprolakkas watershed (February 2009).

| | Number of samples | Mean | Median | Standard deviation | Min | Max |
|---|---|---|---|---|---|---|
| pH | 20 | 8.1 | 8.1 | 0.2 | 7.6 | 8.5 |
| EC (μS/cm) | 20 | 602 | 463 | 314 | 328 | 1416 |
| K (mg/L) | 20 | 3 | 3 | 2 | 1 | 8 |
| Na (mg/L) | 20 | 13 | 13 | 4 | 7 | 20 |
| Ca (mg/L) | 20 | 79 | 64 | 44 | 40 | 191 |
| Mg (mg/L) | 20 | 25 | 17 | 17 | 11 | 68 |
| $HCO_3$ (mg/L) | 20 | 169 | 172 | 40 | 79 | 230 |
| $SO_4$ (mg/L) | 20 | 165 | 82 | 207 | 28 | 705 |
| Fe (μg/L) | 11 | 80 | 13 | 159 | 10 | 681 |
| Pb (μg/L) | 20 | 13 | 9 | 12 | 3 | 57 |
| Zn (μg/L) | 20 | 200 | 14 | 386 | 4 | 1150 |
| Mn (μg/L) | 20 | 1151 | 35 | 2443 | 3 | 7899 |
| Cu (μg/L) | 20 | 2 | 2 | 1 | 1 | 5 |
| Ni (μg/L) | 12 | 17 | 7 | 18 | 0.5 | 50 |
| As (μg/L) | 20 | 28 | 19 | 28 | 4 | 130 |
| Ba (μg/L) | 20 | 13 | 15 | 8 | 2 | 30 |
| Mo (μg/L) | 20 | 4 | 0.6 | 5 | 0.5 | 14 |
| Sb (μg/L) | 20 | 4.1 | 2.5 | 5 | 0.5 | 16 |

Kelepertzis et al. 2010 studied surface water quality within the Asprolakkas watershed during one hydrologic year and reported that each one of the studied basins displays its own hydrogeochemistry and dissolved contaminant concentrations. Samples H1, H3, G and B from Kokkinolakkas were plotted in the region of

$Ca-SO_4$ water type on a Piper diagram, reflecting the influence of the polymetallic sulfide deposits exploited at Mavres Petres and Madem Lakkos areas.

On the contrary, stream waters from Kerasia and Piavitsa fall within the Ca-$HCO_3$ type and present significantly lower Ca, Mg, $SO_4$, Zn, Mn, Ni and Sb values. Sample M drains the geological formations comprising the diorites and diorite porphyries southwards of Asprolakkas stream, and as a result it displays a $Ca-SO_4$ water type (Kelepertzis et al. 2010). Both of Piavitsa and Kerasia water samples are characterized by Pb and As values higher than the European Union limits (EU Council Directive 98/83/EEC). The geochemical behavior of those elements is discussed later.

Iron concentrations for a noticeable number of samples are below the detection limit of the analytical technique (10 μg/L), whereas the measured concentrations in all the collected waters are considered low. This is expected bearing in mind the slightly alkaline pH conditions prevailing in the studied drainage system. A few isolated elevated Fe values (samples H1, H3 and F2) are possibly explained by the presence of Fe rich colloids that passed through the used 0.45 μm pore-size membranes filters (Kimball et al. 1995).

## *4.2 Application of R-mode factor analysis*

With the aim of determining the main factors that control the chemistry of the stream waters, factor analysis was applied to the data (Table 2). Factor analysis characterizes different groups of chemical elements with approximately similar geological and geochemical patterns. The three factor model explaining 86% of the data variability was deemed appropriate for the obtained data. Iron and Ni were excluded from the application since a remarkable number of samples is characterized by concentrations below the detection limit of the analytical technique.

The most significant Factor, accounting for 51% of the total variance, reflects the signature of the massive sulfide carbonate replacement type mineralization of the area. This factor includes elements such as Ca and Mg that originate from the dissolution of the gangue minerals (calcite, dolomite), whereas $SO_4$ and metals derive from the sulfide minerals of the mineral deposits, and their oxidation products. Additionally, the participation of electrical conductivity with high factor loadings denotes that potentially toxic elements like Zn, Mn, Mo and Sb are primarily present as dissolved free ions. Surprisingly, Pb is not involved in this factor, despite its strong association with the sulfide deposits. Various authors have demonstrated that Pb is scavenged by iron oxide colloids and transported on their mineral surfaces in many water systems (e.g Hassellöv and Kammer 2008). These particles can be of such low diameter that they can be easily pass through conventional 0.45 μm membrane filters, mainly comprising ferrihydrite and schwertmannite at high and low pH conditions respectively. Thus, the low positive factor loadings of Pb in Factor 1, which consists of dissolved form of metals.

**Table 2.** Varimax component loadings of three factors, communality and percentage of variance explained for the analyzed parameters.

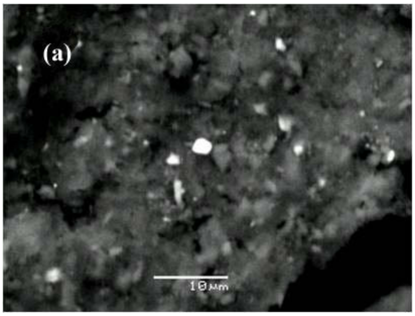
| Variable | Factor 1 | Factor 2 | Factor 3 | Communality |
|---|---|---|---|---|
| EC | 0.94 | -0.28 | -0.05 | 0.97 |
| K | 0.06 | -0.92 | -0.13 | 0.87 |
| Na | 0.76 | -0.20 | 0.15 | 0.64 |
| Ca | 0.95 | -0.22 | -0.04 | 0.95 |
| Mg | 0.88 | -0.32 | 0.02 | 0.87 |
| $SO_4$ | 0.94 | -0.22 | -0.18 | 0.96 |
| $HCO_3$ | -0.39 | 0.03 | 0.80 | 0.79 |
| Pb | 0.32 | -0.76 | 0.30 | 0.76 |
| Zn | 0.96 | -0.08 | 0.02 | 0.91 |
| Mn | 0.96 | -0.15 | -0.11 | 0.96 |
| Cu | 0.30 | -0.79 | 0.07 | 0.71 |
| As | 0.36 | 0.09 | 0.88 | 0.92 |
| Sb | 0.88 | 0.00 | 0.31 | 0.86 |
| Ba | 0.07 | -0.87 | -0.42 | 0.94 |
| Mo | 0.69 | -0.59 | -0.04 | 0.83 |
| % Variance | 50.6 | 23.3 | 12.4 | 86.4 |

The second factor, explaining 23% of the total variability, contains negative factor loadings for K, Cu, Ba, Pb and Mo, and indicates the influence of the porphyritic intrusions of Skouries and Fisoka areas on the chemistry of the examined streams. Intense potassic alteration halo, characteristic of the high-grade ore, and porphyry Cu mineralization are strongly associated to the Tertiary intrusive bodies, whereas the Skouries stock also exhibits unusual high Ba concentrations (Eliopoulos and Economou-Eliopoulos 1991). Galena representing the primary source of Pb, is found in the peripheral parts of the alteration haloes within the country rock basement, mainly in the propylitic zone. Molybdenum is a typical metalloid that accompanies many porphyry copper deposits around the world.

Finally, the third factor, accounting for 12% of the total variance, is controlled by $HCO_3$ and As, and signifies that the elevated concentrations of As in the studied water samples can be attributed to its desorption/release from the Fe(III)-hydroxides, due to the competitive behaviour of bicarbonate ions. Adsorption and desorption reactions between arsenic and ferric oxide mineral surfaces are considered the most important factors controlling the concentrations of dissolved As (Cheng et al. 2009). Bicarbonate ions adsorb onto hydrous ferric oxide particles, reducing in that way arsenic removal by adsorption phenomena onto the previously mentioned oxides.

## *4.3 Membrane filter SEM observations*

The examination of filters retained by the filtration of water samples H1,B and C revealed that particulate material is characterized by grains of Fe and S, enriched in Pb, As and Zn. It has been suggested that Pb can be removed in sulfidic environments by surface adsorption onto FeS particles and that sulfides compete with hydrous iron oxides to scavenge Pb (Taillefert et al. 2000). Additionally, filters from Kokkinolakkas stream are dominated by Pb oxidized particles (size< 3 μm), containing traces of Zn, Cu, As and Sb, and by sulfate oxidized phases of Pb and Zn (size 1-2 μm), comprising As and Sb. Fragments of probably pyrite and arsenopyrite (size> 10 μm) deriving from the mineral deposits, located upstream of the sampling locations, were routinely identified.



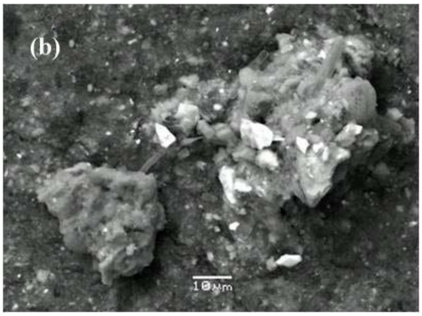




**Fig. 2.** Back-scattered microphotographs from the retained filters: a) Pb-Fe-S particle containing traces of Cu and Zn, Pb: 60%, S:10%, Fe:6%, Cu:2%, Zn:1% (sample H1), b) Grains of Fe and S, enriched in Pb and As, Fe: 38%, S: 42%, Pb:3%, As: 2% (sample B).

Figure 2 presents representative photographs from the retained filters, together the semi-quantitative chemical analyses of the corresponding spots. It should be mentioned that particles/phases with size smaller than 1.5 - 2 μm cannot be analysed and identified through SEM-EDS methods.

It becomes obvious that Pb is mainly transported in the particulate phase for Kokkinolakkas stream, a fact that is strengthened remarking the results of chemical analyses for filtered and unfiltered samples (Pb dissolved and Pb total respectively), provided by the Laboratory of Quality Control of Hellas Gold SA (Table 3).

**Table 3.** Dissolved and total concentrations of Pb in Kokkinolakkas water samples (April 2008).

| Sample | Pb Dissolved (μg/L) | Pb Total (μg/L) |
|---|---|---|
| H1 | 5 | 116 |
| H3 | 11 | 148 |
| G | 9 | 48 |
| B | 6 | 83 |

## 5 Conclusions

Results of this research clearly demonstrate that the chemistry of stream waters in the studied watershed is mainly governed by the regional geological and mineralogical characteristics. Geochemical processes also play an important role in controlling the environmental behavior of potentially toxic elements, such as Fe, Pb, Zn, Mn, As and Sb. Regarding Konninolakkas stream water, colloids and suspended matter represent a significant transportation pathway for Pb, and to a lesser extent for other metals like As, Cu, Zn and Sb. On the contrary, Mn, Mo, as well as Zn and Sb are mainly transported as free ions, presenting a high affinity for the electrical conductivity of the studied water samples.

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