# Geochemical signature of surface water and stream sediments of a mineralized drainage basin at NE Chalkidiki, Greece: A pre-mining survey

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## ABSTRACT

The geochemical characteristics of surface water and stream sediments in Asprolakkas drainage basin, an area of Tertiary mineralization within amphibolite, located at NE Chalkidiki peninsula, Greece, were investigated in order to establish the geochemical baseline conditions prior to any type of new mining activities. The area represents the only example of active mining and processing of base metal sulfide ore in Greece and also includes an unmined porphyry Cu–Au ore deposit at Skouries. In a wider context, this research represents a pre-mining baseline geochemical study that can be used as an analog for similar metallogenetic provinces in areas with a Mediterranean type climate.

Concentrations of dissolved major ions and trace metals displayed wide variability within the study area. Kokkinolakkas stream, draining the exploited Pb–Zn ($\pm$Ag) ore bodies, is strongly influenced by chemical weathering of sulfide minerals and presents elevated levels of $SO_4$ (429–857 mg l$^{-1}$), Pb (4–64 µg l$^{-1}$), Zn (290–1350 µg l$^{-1}$), Mn (1680–7899 µg l$^{-1}$), Ni (12–50 µg l$^{-1}$), Cd (2–8 µg l$^{-1}$), As (8–45 µg l$^{-1}$) and Sb (9–16 µg l$^{-1}$). Stream water of unmined areas demonstrated a different chemical composition with elevated values mainly for Pb (up to 45 µg l$^{-1}$) and As (up to 141 µg l$^{-1}$). Hydrological conditions highly influence the behavior of major elements and metals. Stream bed sediments from Kokkinolakkas and Tsarkia Lakkos, located at the head waters of Asprolakkas basin, have anomalous values in Pb (1165–3439 mg kg$^{-1}$), Zn (1368–4538 mg kg$^{-1}$), As (964–2714 mg kg$^{-1}$), Sb (30–70 mg kg$^{-1}$), Cd (3.8–21.6 mg kg$^{-1}$) and Mn (6811 up to >10,000 mg kg$^{-1}$). Mobility of selected trace metals was investigated through the application of a 5-step sequential extraction procedure. Results show that, despite the high total metal content, the majority of analyzed elements are mainly bound to relatively immobile operationally defined geochemical phases of amorphous to poorly crystalline Fe and Mn oxides and the residual fraction. Considering the planned mining developments in the area, the results of this study may assist mine planners to set realistic goals for monitoring and remediation programs.

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## 1. Introduction

The drainage basin, an area drained by a river or stream, is the fundamental unit for characterizing and understanding many of the environmental impacts of mineral deposits, mining and mineral processing (Plumlee and Logsdon, 1999). Detailed mapping of geochemical baseline conditions existing in a drainage basin that includes a proposed mine site is crucial, because any future environmental impacts will be assessed at the drainage basin level. Furthermore, these data will be of significant value for setting up realistic goals for monitoring and remediation programs (Runnels et al., 1998).

Undoubtedly, water represents the most significant transport pathway for metals and metalloids, derived from the chemical weathering of mineralized rocks. The ionic speciation (dissolved metals) is one of their most mobile and bioavailable forms. Together with

major ion content, they are routinely accomplished to the status of surface water quality. Stream sediments play a crucial role in controlling heavy metal concentration in aquatic environment as a sink for trace elements. A change of physico-chemical condition in the environment, however, may turn them into a secondary source, controlling water quality through storage and potential release of metals (Zoumis et al., 2001). Metals in sediments are present in variable solid phases, which control their mobility and bioavailability, offering information on the aquatic eco-system health. The phases are determined by sequential extraction procedures. The samples are treated with successive extraction to achieve specific operationally defined phases. There is a general agreement that the partitioning of metals obtained by such procedures is at large operationally defined, and they can be considered as relative rather than absolute chemical speciation phases (Li et al., 1995). Despite their limitations, sequential extractions are useful techniques for characterizing solid phase carrier of trace metals in sediments (Filgueiras et al., 2002; Hass and Fine, 2010).

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This study reports the present environmental status of surface water and stream sediments in the Asprolakkas water basin, located in the Kassandra metallogenic province of north-eastern Greece, including the wider mining area of Stratoni. The study area remained the only mining and processing operation of lead/zinc/silver sulfide ore in Greece, with current activities at the Mavres Petres deposit and a gold and copper mining project under development at Skouries. Publications covering the geology and mineralization in Kassandra mining district are numerous (e.g. Gilg and Frei, 1994; Kalogeropoulos et al., 1989; Kockel et al., 1975; Nebel et al., 1991). From an environmental point of view, Lazaridou-Dimitriadou et al. (2004) reported some general water and sediment quality characteristics, but their research focused mainly on the assessment of the applicability of European biotic indices in describing the water quality of streams. Also, a preliminary soil survey was undertaken by Kelepertsis et al. (2006) in order to assess the levels of soil contamination in the mining area of Stratoni. However, there is no published study that specifically focuses on a combined investigation of water and sediment samples of streams draining the Asprolakkas basin. In the light of planned mining developments, this research provides invaluable geochemical information that can be used in future comparisons. In a wider context, this research represents a pre-mining baseline geochemical study that can be utilized as an analog for similar metallogenetic provinces in areas with a Mediterranean type climate.

The specific objectives of the paper are: (a) to document the major ion and trace element concentrations in surface water and their variation throughout a hydrological year, (b) to determine the trace metal composition of stream sediments, prior to any type of new mining activities, and (c) to determine the chemical partitioning of selected trace metals in stream sediments in order to provide a geochemical model for predicting the ability to release elements to the aquatic environment and to discuss bioavailability implications.

## 2. Description of the study area

### 2.1. Geology and mineralization

The study area lies within the Greek part of the Serbo-macedonian Massif (SMM), a series of highly deformed and polymetamorphosed rocks that extend northward into Bulgaria and FYROM (Former Yugoslav Republic of Macedonia). The crystalline basement of the SMM comprises the upper Kerdylia and lower Vertiskos geotectonic units, of Palaeozoic or older age (Kockel et al., 1977). The two units are separated by the Stratoni–Varvara normal fault, a major structural feature that dominates the area (Fig. 1). The Kerdylia formation is mainly composed of biotite gneiss interlayered with several marble horizons, hornblende gneiss and amphibolite. The Vertiskos sequence, outcropping in the studied area, includes biotite–muscovite gneiss, amphibolite and ultramafic bodies (Gilg and Frei, 1994). The topographically lower parts of the area are covered by alluvial and Pleistocene deposits.

During Tertiary, the SMM was intruded by various post-orogenic granitoids. The earliest intrusion is represented by the Stratoni granodiorite (29 Ma) (Kalogeropoulos and Economou, 1987), followed by porphyritic stocks and dykes of granodioritic to quartz dioritic composition, mainly in the area between Fisoka and Stratoni. The latest magmatic phase is attributed to the Skouries shoshonitic porphyry intrusion (Kroll et al., 2002), which was emplaced into the metamorphic basement of SMM at 19 Ma (Frei, 1995).

Various ore deposits in the area are chronologically and spatially related to Tertiary intrusive bodies. The Madem Lakkos and Mavres Petres deposits are classified as Pb–Zn (Ag–Au) carbonate hosted replacement type, and are structurally controlled by the Stratoni–Varvara fault. They have a relatively simple sulfide mineral assemblage, comprising pyrite, sphalerite, galena, arsenopyrite, chalcopyrite, with subordinate tennantite, bournonite, pyrrhotite, marcasite, boulangerite, cubanite,

chalcosite, covellite, magnetite and native gold (Kalogeropoulos et al., 1989). Gangue minerals are represented by calcite, quartz and rhodochrosite. Manganese-oxide and mixed sulfide (Pb–Zn) deposits also occur in Piavitsa area along the Stratoni–Varvara fault, following the same marble horizon with Madem Lakkos and Mavres Petres deposits. In addition, the porphyry Cu–Au at Skouries and Fisoka areas are another ore type occurring in this metallogenic province (Kockel et al., 1975). Mineralization in Skouries mainly includes chalcopyrite, pyrite, bornite, chalcosite and magnetite in forms of veins, stockwork and disseminations (Eliopoulos and Economou-Eliopoulos, 1991). Native gold is present as small inclusions in chalcopyrite.

### 2.2. Physiography and hydrology

The study area is characterized by mountainous relief with approximately 92% of the surface covered by deciduous forest, and by a well developed dendritic style drainage network. Streams within the Asprolakkas drainage basin have their source in the foothills of Stratonikon Mountain, located northward of Stratoni–Varvara fault, and follow a general north–south direction. The three main streams that are studied are Piavitsa, Kerasia and Kokkinolakkas (Fig. 1). They all discharge their water in Asprolakkas, which has a west–east direction, flowing toward the Gulf of Ierissos. Maximum elevations (up to 600 m) are found at the west part of the area, mainly in Skouries, and gradually decrease toward the sea. The climate is of Mediterranean type, with rainy winters and dry, warm summers. The average pluviometry in the catchment area is 650 mm, with almost 50% of the annual rainfall occurring between November and February. March and April too have abundant rain, while during the summer months, rainfall is practically nonexistent.

### 2.3. Mining activity

Mining activity dates back to prehistoric times and continues today. During the last century, several mining companies exploited the sulfide and manganese ore deposits of the wider area (Madem Lakkos, Mavres Petres and Piavitsa ore bodies) extracting million of tonnes of mixed sulfide, manganese oxide and pyrite. In April 2004, the whole Kassandra mines property was transferred by the Greek State to "Hellas Gold S.A.", a subsidiary of "European Goldfields", including the mineral rights in an area of 26.5 ha, i.e. the Stratoni Operation (Pb/Zn/Ag) and two projects for development, the Olympias carbonate-hosted (Pb/Zn/Au/Ag), located some 8 km northward of Stratoni village, and the Skouries porphyry (Cu/Au).

Currently, in the Stratoni Operation, only the Mavres Petres deposit is mined, producing sphalerite and galena concentrates at the Stratoni flotation plant, by overhead drift and fill method using cemented tailings for backfill. The Madem Lakkos ore deposit has been exhausted. Acid mine water, deriving from both Mavres Petres and Madem Lakkos mines, is directed to the water treatment plant, located next to the Stratoni flotation plant where treatment is carried out in agitated reactors with hydrated lime $(Ca(OH)_2)$ for neutralization. Mine waste and fine grained tailings, produced by the flotation procedure, are disposed off at the controlled Chevalier site, next to Stratoni village. Coarse grained tailings mixed with cement and water are commonly used for backfilling the mining shafts and adits.

Ongoing mining activity includes the exploitation of Skouries ore deposit. According to the plans of the owner company, the project will benefit from a metallurgical process route and will produce clean Cu–Au concentrates via flotation as well as doré from the gravity circuit (http://www.egoldfields.com). The porphyry outcrop is located on a high plateau with no habitation in the immediate vicinity.
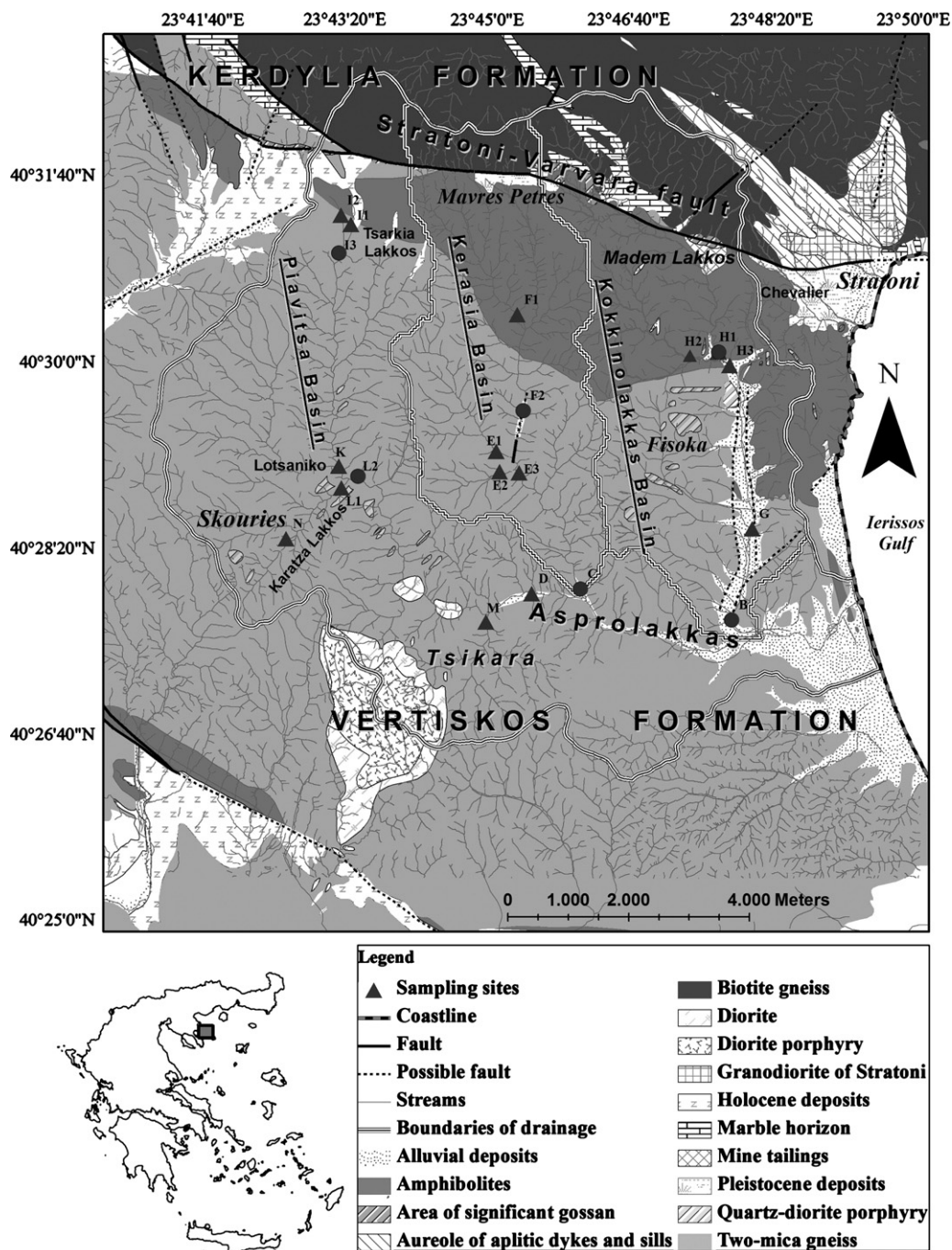
**Fig. 1.** Geological map of the studied area showing drainage basins and sampling sites. Stream sediment samples subjected to the sequential extraction procedure are marked as circles.
After Kockel et al., 1977.

## 3. Materials and methods

### 3.1. Field sampling and sample preparation

Sampling locations cover the three sub-basins that discharge their water in Asprolakkas, contributing to its water and sediment chemistry. Samples were collected along the main stream of each catchment basin and from tributaries. Regarding surface water sampling, fieldwork was performed during 4 periods: April 2008, July 2008, November 2008 and February 2009, covering all seasons of a hydrological year. Twenty samples were collected during each sampling period, making a total number of 76 samples. Sampling sites are shown in Fig. 1. Samples G and B from Kokkinolakkas stream

were only collected in April 2008 and February 2009, because of lack of water during the dry period. Sample N represents water discharged by the old exploration adit of Skouries deposit. Samples for the determination of major cations and metals were filtered in the field through 0.45 μm membrane filters using 60 ml-syringes, acidified down to pH<2 with concentrated $HNO_3$ (Suprapur 65%) and stored in 50 ml polyethylene bottles. A second sample set was collected using 1 l polyethylene bottles for alkalinity and $SO_4$ determinations, filtered but not acidified. All water samples were refrigerated until their analysis.

Active stream sediment samples were collected during April 2008 by using a hand trowel at the same points as the stream water samples. About 5 kg of the upper layer of stream sediment was collected

from 19 sub-sites to make a composite sample over a stream stretch of about 100 m at each sampling location, and the samples were placed in clean pre-numbered polyethylene bags. At the laboratory, stream sediment samples were oven dried at a constant temperature of 45 °C, sieved to <2 mm fraction and pulverized in an agate mortar to <0.075 mm. The sample preparation was the same with a previous study concerning the heavy metal content in soils samples from the wider area of Stratoni, in order for the results to be comparable.

### 3.2. Analytical procedures

#### 3.2.1. Surface water

Field measurements such as pH, electrical conductivity (EC) and redox potential (Eh) were measured in-situ using a Multi 350i instrument by WTW. The pH electrode was calibrated every 10 measurements, using standard solutions of pH 7 and 8. Alkalinity was measured at the end of each sampling day by using the digital titration method described by Hach Instruments (bromocresol green-methyl red indicator using $H_2SO_4$) for total alkalinity, whereas $SO_4$ was gravimetrically measured as $BaSO_4$. Potassium, Na, Ca and Mg concentrations were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) at the Laboratory of Quality Control of "Hellas Gold SA" at Stratoni. Concentrations of dissolved Fe, Pb, Cu, Ni, Cr and Cd were measured by graphite furnace Atomic Absorption Spectroscopy (AAS), while Zn and Mn were measured by graphite furnace and by flame (AAS), when necessary (University of Athens, Department of Geology and Geoenvironment). In addition, As and Sb concentrations were determined for November and February sampling periods by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) at the Acme Analytical Laboratories Ltd of Canada. Multielement standard solutions prepared from single certified standards were used for calibration of analytical instruments. Detection limits were calculated as 3 times the standard deviation of 5 measurements on blank solutions. Detection limits for graphite furnace AAS were: 5 μg l$^{-1}$ Fe, 1 μg l$^{-1}$ Pb, 5 μg l$^{-1}$ Zn, 1 μg l$^{-1}$ Mn, 0.5 μg l$^{-1}$ Cu, 1 μg l$^{-1}$ Ni, 0.5 μg l$^{-1}$ Cr and 0.5 μg l$^{-1}$ Cd, whereas the detection limit for flame (AAS) was 0.01 mg l$^{-1}$ for both Zn and Mn. Detection limits for As and Sb by ICP-MS were 0.5 and 0.05 μg l$^{-1}$, respectively. Certified reference materials for low and high levels of metals in groundwater (BCR 609 and BCR 610) were also analyzed in order to check the accuracy of analytical data and agreement with certified values.

#### 3.2.2. Stream sediments

Dissolution of stream sediment samples was performed using a modified aqua regia extraction method at the Acme Analytical Laboratories Ltd of Canada. A 0.5 g aliquot of each pulverized sample was digested by hot (95 °C) aqua regia (HCl–HNO$_3$–H$_2$O) for 1 h. After dilution to 10 ml with deionized water, solutions were analyzed for 33 elements by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). In this study, emphasis was given to the following chemical elements: Cu, Pb, Zn, Mn, Ni, Cr, Cd, As, Sb and Fe.

Analytical precision estimated by duplicate analysis of 3 random samples was lower than 10% for all analyzed elements (in most cases lower than 5%), while prepared blanks were always below instrumental detection limits. Accuracy was assessed using 3 soil certified reference materials: SRM 2709 San Joaquin Soil, SRM 2710 Montana Soil and SRM 2711 Montana Soil, covering low, high and moderate concentrations of heavy metals, respectively. The estimated analytical bias was commonly lower than 10%, indicating good accuracy of the analytical results.

#### 3.2.3. Partitioning of metals in stream sediments

The sequential extraction method developed by Tessier et al. (1979) was applied in this study for investigating the chemical partitioning of Pb, Zn, Mn, Cu, Ni, Cr and Cd. Six stream sediment samples,

two from each studied catchment basin were selected to provide an insight into the possible geochemical forms that the metals are bound to: i.e., samples I3 and L2 from Piavitsa, F2 and C from Kerasia, and H1 and B from Kokkinolakkas. The procedure was carried out progressively on an initial weight of 1.0 g of stream sediment material (<100 μm) in duplicate and their averages are discussed below. The extraction solutions were analyzed by flame AAS (Department of Chemistry, University of Athens).

The operationally defined fractions were as follows:

(a) Fraction I (exchangeable): extracted with 8 ml of 0.5 M $MgCl_2$ at pH 7.0 for 1 h at room temperature, with continuous agitation. The extract was separated from the solid phase by centrifugation at 4000 rpm for 15 min and the supernatant solution was decanted into a polyethylene tube. The residue was washed with 8 ml of deionized water, agitated for 5 min, and then centrifuged for 10 min. The supernatant solution was decanted slowly so that the solid residue was left behind, which was subjected to step II.

(b) Fraction II (bound to carbonates and specifically adsorbed): the residue from step I was leached for 5 h with 8 ml of 1 M NaOAc (adjusted to pH 5.0 with HOAc) at room temperature. Continuous stirring was maintained during the extraction. The extract was separated as in Fraction I.

(c) Fraction III (bound to Fe–Mn oxides; reducible fraction): the residue obtained from step II was extracted with 20 ml of 0.04 M $NH_2.OH.HCl$ in 25% (v/v) HOAc. The extraction was performed at 96 °C with occasional agitation for 6 h. After extraction, the solutions were diluted to 20 ml with deionized water and subjected to continuous stirring for 10 min. The extract was separated as in Fraction I.

(d) Fraction IV (bound to organic matter and sulfide; oxidizable fraction): 3 ml of 0.02 M $HNO_3$ and 5 ml of 30% $H_2O_2$ (adjusted to pH 2.0 with $HNO_3$) were added to residue from step III. The mixture was heated progressively to 85 °C, and maintained at this temperature for 2 h with occasional stirring. After cooling, 5 ml of 3.2 M $NH_4OAc$ in 20% (v/v) $HNO_3$ was added, followed by dilution to a final volume of 20 ml with deionized water and continuous agitation for 30 min. The extract was separated as in Fraction I.

(e) Fraction V (residual phase): the residue from step IV was digested by 4 ml concentrated $HNO_3$, 3 ml $HClO_4$ and 15 ml HF, and evaporated to near dryness. The residue was then dissolved in 6 ml weak $HNO_3$ at 70 °C for 30 min, and diluted to 50 ml with deionized water.

Analytical precision, determined by analyzing the selected sediments in duplicate, was found to be in most cases less than 20% for all steps, and can be considered as satisfactory for this particular study. In order to monitor the accuracy of the sequential extraction procedure, the sum of metal concentrations in the 5 phases was compared with the values obtained by aqua regia digestion. The overall recovery rates commonly ranged from 80% to 120%, which are of the same order as those reported by other researchers (e.g. Bird et al., 2003; Favas et al., 2011; Jung et al., 2005; Li et al., 1995). Regarding Ni and Cr, the summed concentrations in the 5 phases are significantly higher than the concentrations determined by aqua regia digestion. This can be explained by the fact that aqua regia extraction is insufficient in releasing the portions of Ni and Cr that are incorporated in the crystal structure of resistant minerals. For example, numerous studies have reported low Cr recoveries by aqua regia due to the presence of insoluble Cr-carrier minerals (Chen and Ma, 2001). Chromite and crystalline Fe oxides with Cr levels up to 10%, identified by scanning electron microscopy, were found to be present in Kokkinolakkas stream sediments (Kelepertzis, 2011).

# 4. Results and discussion

## 4.1. Surface water

### 4.1.1. Chemical characterization of surface water

Results of physico-chemical analyses of collected water samples are shown in Table 1. Surface waters are predominantly near neutral to mildly alkaline and Eh data indicate moderate reducing conditions. Electrical conductivity (EC) varied widely from 328 to 1669 μS cm$^{-1}$, indicating significant differences between the stream water ion content.

Stream water presents a wide range of values between sampling locations for most of the analyzed parameters, e.g. K, SO$_4$, HCO$_3$, Ca, Mg, Zn and Mn. Iron, Pb, Ni, Cd, As and Sb also display great variability among the examined samples (Table 2), reflecting the great diversity of geological and geochemical conditions in the drainage system (Kelepertzis et al., 2011). Chromium levels are either very low or close to the detection limit of the analytical technique, and consequently they have been omitted in Table 2. Concentrations of Na are mainly uniform throughout the basin, deriving from the dissolution of albite, abundant in the metamorphic rocks occurring in the studied area.

Plots of major ions on Piper diagrams showed that stream water from Piavitsa and Kerasia basins belongs to the Ca–HCO$_3$ type, reflecting the lower SO$_4$ concentrations with respect to bicarbonate content (Kelepertzis et al., 2010a). The only exception is sample M that drains the geological formations comprising diorite and diorite porphyries southward of Asprolakkas stream, displaying a Ca–SO$_4$ water type. On the contrary, maximum concentrations of Ca, Mg and SO$_4$ ions are found in Kokkinolakkas stream (Ca–SO$_4$ water type), draining the carbonate hosted polymetallic sulfide deposits of Madem Lakkos and Mavres Petres areas.

Fig. 2 shows the different metal composition of each catchment basin, according to the Ficklin diagram (Ficklin et al., 1992). The Ficklin diagram classifies water samples with respect to their pH and the sum of base metals Zn, Cu, Pb, Cd, Co and Ni. Stream water of Kokkinolakkas is characterized by near neutral to alkaline pH values and low to high dissolved metal concentrations, reflecting the fact that pH levels need not necessarily be low for significant high metal load to occur (Akabzaa et al., 2009). The cluster of points falls within the field typically associated with pyrite–sphalerite–galena ores with carbonate-rich host rocks (Seal et al., 2002). Regarding the metal content from the other basins, water samples from Piavitsa are slightly enriched in base metals in comparison with

Kerasia, due to the presence of different types of mineralization that occur upstream and downstream in this basin (see Section 2.1).

### 4.1.2. Origin and geochemical behavior of principal elements

*4.1.2.1. Piavitsa and Kerasia basins.* With respect to Piavitsa stream water samples, the most significant metal contents are those of Pb (2–45 μg l$^{-1}$), Mn (5–106 μg l$^{-1}$) and As (4–141 μg l$^{-1}$). In most cases, concentrations of these elements exceed the drinking-water quality standards (10 μg l$^{-1}$ for Pb, 50 μg l$^{-1}$ for Mn, 10 μg l$^{-1}$ for As) set by the European Union Council Directive 98/83/EC concerning the quality of water intended for human consumption. It is noted however that comparison with such standards is not very relevant as far as a mineralized area is considered. All the water samples demonstrate high Pb content, while Mn is enriched in water samples N, M and in Tsarkia Lakkos stream water, as result of dispersed metalliferous occurrences throughout this catchment basin. The highest concentrations of As (up to 141 μg l$^{-1}$) are found at the upstream sampling sites I1, I2 and I3 (Tsarkia Lakkos location), probably deriving from the weathering of arsenopyrite that accompanies the polymetallic sulfide deposits of Piavitsa. Antimony, a metalloid with similar geochemical behavior to As, forming oxyanions in water is also present at high levels at Tsarkia Lakkos. Potassium is the only major element with a high value at sampling location L1 (Karatza Lakkos stream). The drainage from the old exploration adit of Skouries deposit also has elevated K levels, reaching 12 mg l$^{-1}$ during the November 2008 sampling period. These elevated concentrations are attributed to the dissolution of orthoclase and biotite, which are characteristic minerals of the intense potassic alteration of the Skouries porphyry intrusion (Kroll et al., 2002). The chemical composition of water samples from Kerasia includes high concentrations of Pb (up to 33 μg l$^{-1}$) and As (up to 37 μg l$^{-1}$), and elevated levels of Sb (up to 4 μg l$^{-1}$).

High As concentrations were found in surface water of Piavitsa and Kerasia basins. Application of R-mode factor analysis on surface water data revealed that the high As levels could be attributed to the desorption of As oxyanions under the effect of competitive sorption of HCO$_3$ (Kelepertzis et al., 2011). Adsorption and desorption reactions between As 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 this way arsenic removal by adsorption phenomena onto the previously mentioned oxides (Cheng et al.,

**Table 1**
Minimum and maximum field measurements and concentrations of major ions in surface water samples of the four sampling periods.

| | Sample | pH | EC (μS/cm) | Eh (mV) | K (mg/l) | Na (mg/l) | Ca (mg/l) | Mg (mg/l) | HCO$_3$ (mg/l) | SO$_4$ (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|
| Piavitsa | I1 | 7.8–8.2 | 400–520 | (−75)–(−58) | 1 | 8–13 | 58–82 | 11–16 | 161–230 | 65–75 |
| | I2 | 7.9–8.2 | 520–685 | (−75)–(−63) | 1–2 | 9–13 | 73–96 | 20–27 | 195–265 | 72–138 |
| | I3 | 7.8–8.1 | 430–567 | (−74)–(−57) | 1–2 | 8–12 | 63–86 | 13–19 | 173–261 | 73–94 |
| | K | 8.0–8.2 | 328–514 | (−77)–(−67) | 3–8 | 7–10 | 40–71 | 12–19 | 137–208 | 28–88 |
| | L1 | 8.2–8.4 | 502–568 | (−88)–(−78) | 7–13 | 11–15 | 58–67 | 22–25 | 201–228 | 38–101 |
| | L2 | 8.1–8.4 | 440–551 | (−89)–(−74) | 3–8 | 8–14 | 55–74 | 16–23 | 166–222 | 64–95 |
| | N | 7.5–7.7 | 557–570 | (−46)–(−42) | 8–12 | 14–16 | 60–68 | 22–24 | 204–210 | 99–106 |
| | M | 8.1–8.3 | 477–583 | (−81)–(−72) | 2–6 | 11–17 | 65–85 | 11–14 | 79–155 | 121–151 |
| | D | 8.1–8.4 | 469–510 | (−94)–(−70) | 4–10 | 11–16 | 64–83 | 18–24 | 152–188 | 90–138 |
| Kerasia | F1 | 8.1–8.4 | 390–479 | (−86)–(−79) | 1–2 | 12–15 | 53–61 | 15–18 | 190–230 | 31–38 |
| | F2 | 8.0–8.3 | 400–498 | (−84)–(−72) | 2–3 | 14–18 | 53–60 | 16–19 | 196–237 | 36–40 |
| | E1 | 7.7–8.1 | 376–510 | (−67)–(−51) | 3–5 | 10–14 | 51–67 | 13–17 | 155–260 | 43–58 |
| | E2 | 7.8–8.3 | 420–536 | (−82)–(−55) | 2–4 | 9–12 | 63–75 | 17–21 | 206–252 | 43–50 |
| | E3 | 8.1–8.3 | 400–499 | (−86)–(−74) | 2–4 | 14–18 | 56–65 | 16–19 | 190–223 | 39–45 |
| | C | 8.2–8.5 | 420–496 | (−96)–(−79) | 3–9 | 14–17 | 56–68 | 16–19 | 199–224 | 45–61 |
| Kokkinolakkas | H1 | 8.0–8.2 | 1416–1669 | (−79)–(−56) | 4–5 | 19–23 | 191–231 | 68–94 | 130–188 | 705–857 |
| | H2 | 7.3–8.0 | 510–602 | (−62)–(−26) | 1–3 | 16–17 | 52–57 | 26–32 | 177–222 | 107–126 |
| | H3 | 7.7–7.9 | 1220–1502 | (−64)–(−47) | 3–5 | 17–21 | 167–196 | 57–82 | 143–185 | 464–631 |
| | G | 8.2 | 1008–1030 | (−84)–(−76) | 3 | 16–23 | 134–147 | 45–48 | 122–123 | 434–441 |
| | B | 7.9–8.2 | 986–1050 | (−82)–(−59) | 3 | 15–17 | 130–145 | 43–49 | 123–129 | 429–459 |

**Table 2**
Minimum and maximum concentrations ($\mu g\ l^{-1}$) of dissolved metals and metalloids in surface water samples of the four sampling periods.

| | Sample | Fe | Pb | Zn | Mn | Ni | Cu | Cd | As | Sb |
|---|---|---|---|---|---|---|---|---|---|---|
| Piavitsa | I1 | bdl–62 | 8–41 | 18–70 | 22–49 | bdl–2 | 1–6 | bdl | 37–41 | 3 |
| | I2 | 14–78 | 7–29 | 16–40 | 23–84 | bdl–2 | 1–4 | bdl | 130–141 | 6–9 |
| | I3 | bdl–34 | 6–34 | 15–50 | 16–55 | bdl | 1–5 | bdl | 58–74 | 4–5 |
| | K | bdl–36 | 5–43 | 6–30 | 5–12 | bdl–2 | 1–5 | bdl | 4–6 | 0,5 |
| | L1 | bdl–26 | 2–16 | 9–40 | 5–10 | 1–3 | 3–5 | bdl | 15–23 | 1 |
| | L2 | 19–67 | 6–23 | 12–14 | 6–24 | bdl–2 | 2–8 | bdl | 24–31 | 2–3 |
| | N | bdl–489 | 7–45 | 8–30 | 81–104 | 3–7 | 2–70 | bdl | 31–42 | 1 |
| | M | 17–170 | 7–29 | 5–13 | 43–106 | bdl–5 | 2–11 | bdl | 4–9 | 1 |
| | D | bdl–28 | 2–19 | 10–30 | 10–29 | bdl–3 | 2–7 | bdl | 16–24 | 2–3 |
| Kerasia | F1 | bdl–64 | 2–18 | 5–18 | 3–16 | bdl–2 | 2–11 | bdl | 12–16 | 2 |
| | F2 | bdl–242 | 11–21 | 13–16 | 8–26 | bdl–1 | 2–6 | bdl | 29–42 | 3–4 |
| | E1 | 15–32 | 4–33 | 4–15 | 6–11 | bdl–1 | 2–6 | bdl | 8–10 | 1 |
| | E2 | bdl–13 | 5–10 | 4–19 | 4–19 | bdl–2 | 1–11 | bdl | 7 | 0,5 |
| | E3 | bdl–20 | 4–18 | 9–16 | 6–11 | bdl–2 | 2–6 | bdl | 28–37 | 3–4 |
| | C | 29–78 | 5–10 | 8–50 | 7–16 | bdl–3 | 2–8 | bdl | 30–34 | 3–4 |
| Kokkinolakkas | H1 | 26–681 | 4–64 | 410–1350 | 5810–7899 | 23–50 | 2–5 | 3–8 | 8–45 | 14–16 |
| | H2 | bdl–120 | 2–5 | 10–22 | 91–220 | bdl–2 | 1–4 | bdl | 11–15 | 1 |
| | H3 | bdl–209 | 4–49 | 310–960 | 3675–6971 | 12–43 | 2–4 | 2–6 | 18–21 | 9–13 |
| | G | bdl–92 | 9–28 | 290–734 | 1860–4124 | 13–22 | 3–8 | 3–5 | 15 | 10 |
| | B | bdl–24 | 8–9 | 380–984 | 1680–3442 | 14–21 | 2–9 | 3–5 | 18 | 10 |

(bdl = below detection limit).

2009). Furthermore, the substantial dissolved concentrations of As and Sb could also be derived from dissolution of metals from the stream sediment (see Section 4.2.1) in near-neutral pH waters (Ashley et al., 2003), as those found in Piavitsa and Kerasia. The main mechanism is probably As desorption from Fe(III) hydroxides, occurring as coatings on mineral surfaces or as fine discrete particles in sediments (Casiot et al., 2005). Arsenic is also well known for its higher mobility compared to metals under near neutral to slightly alkaline pH conditions (Smedley and Kinniburgh, 2002) that prevail in these stream waters.

*4.1.2.2. Kokkinolakkas stream.* Water samples from Kokkinolakkas stream show a completely different chemical composition, characterized by elevated $SO_4$ (up to 857 mg $l^{-1}$), Mn (up to 7899 μg/l), Ni (up to 50 μg/l), Cd (up to 8 μg/l), As (up to 45 μg/l), Sb (up to 16 μg/l) and Pb (up to 64 μg/l) values. Such concentrations are, in most cases, considerably higher than the concentrations determined in the adjoining Piavitsa and Kerasia stream waters. The high sulfate and metal content is attributed to the chemical weathering of the sulfide minerals of Madem Lakkos and Mavres Petres ore deposits.

In general, the crystal structures of sulfide minerals can be broken up easily through two different paths, dissolution or oxidation, during the weathering processes. As the aqueous solubility of the sulfides is very low, redox reactions are usually regarded as the main way for $SO_4$ and metals to be liberated. In the study area, stream water reacts with the surrounding minerals comprising manganiferous calcite, dolomite and rhodochrosite liberating also ions, such as of Ca, Mg and Mn. Galena can be considered as the major source for Pb. Anglesite, a typical secondary mineral, formed by galena oxidation at surficial conditions, was detected by scanning electron microscopy in the sediments from Kokkinolakkas (Kelepertzis, 2011). Mobility of Pb is low due to the low solubility of anglesite ($PbSO_4$), and as a result Pb released by galena oxidation is relatively immobile and has low dissolved concentrations (Olias et al., 2004). Moreover, Pb is known for preferential adsorption onto suspended and colloidal particles of hydrous ferric oxides, resulting to relatively low dissolved Pb levels. Sphalerite can be regarded as the major source for Cd, since Cd has been reported to substitute zinc in sphalerite of the ore deposits of the area (Kalogeropoulos and Economou, 1987).

High solubility of minerals containing Mn and Ni is attributed to high concentration of these elements in water, even under slightly alkaline conditions (Plumlee et al., 1999). Despite the abundance of arsenopyrite in the sulfide mineral assemblage of the ore deposits, concentrations of As are relatively low, due to the strong tendency of this metalloid to adsorb on mineral surfaces of Fe (III) oxides (Smedley and Kinniburgh, 2002). It is noted that Godelitsas et al. (2009) reported the presence of schwertmannite nanoparticles in the drainage from the active mines of the studied area, transporting metals on their mineral surfaces. Schwertmannite is a poorly crystalline iron colloidal precipitate that acts as sorbent for trace metal removal at pH values between 2.5 and 4.5 (Bigham et al., 1990), especially for the less soluble elements like As and Pb. According to Kelepertzis et al. (2011), Mn, Zn, Ni and Sb in water samples from Kokkinolakkas are mainly present as dissolved ions. On the other
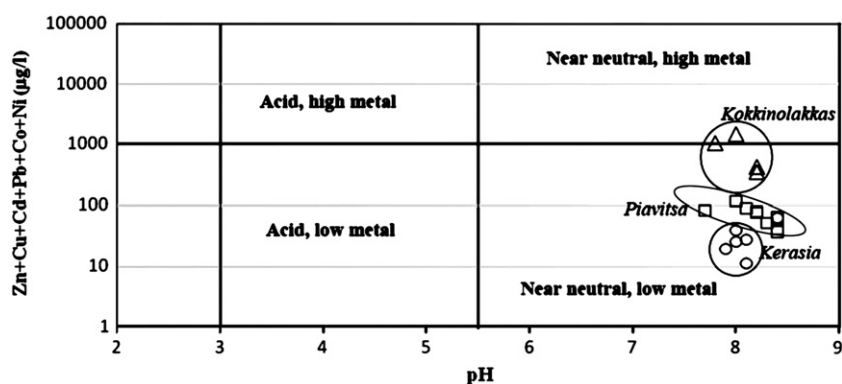


**Fig. 2.** Ficklin diagram of water samples showing the sum of dissolved base metal concentrations as a function of pH (data from April sampling period).

hand, elements, like Pb and As are associated with colloids through adsorption phenomena.

### 4.1.3. Seasonal variation of major ion and metal content

The collection of water samples at different periods during the hydrological year revealed that hydrochemical characteristics undergo significant seasonal changes. Fig. 3 shows the seasonal variation of Ca upstream to downstream for each studied basin. November 2008 is included in the dry period since no rainfall was recorded until then, whereas April 2009 is included in the wet period. The Ca content decreases in the wet period (April and February), because of dilution by the heavy rainfall during these months. The remaining major ions, such as K, Na, Mg, $SO_4$, and $HCO_3$ exhibit a similar pattern. The dilution effect of meteoric waters is observed for all collected water samples from the three catchment basins.

Hydrological conditions seem to highly influence the metal load transported by Kokkinolakkas stream water. Fig. 3 shows the seasonal variation of Pb, Zn and Ni regarding Kokkinolakkas stream. In particular, Fe, Pb, Zn, Mn, Ni, Cd, As and Sb concentrations reach maximum concentrations during the wet period. This behavior could be attributed to either the enhanced dissolution of sulfide minerals associated with the primary mineralization, or the additional transport of colloids that had been temporally stored in the stream bed over the preceding months of low flow. Colloids are particles with a size range of 1–1000 nanometers (nm), and are well known to have a significant impact on the transport of metals and metalloids through sorption mechanisms (Kretzschmar and Schäfer, 2005; Wigginton et al., 2007). In Fe-rich systems, it is unavoidable that the conventional 0.45 μm filter membrane may allow Fe colloids to pass through and be analyzed as part of the aquatic dissolved phase, mainly comprising ferrihydrite and schwertmannite at high and low pH conditions, respectively. Ferrihydrite is considered to be the most important Fe oxide phase that binds and transports ions in most aquatic systems (Hasellöv and Kammer, 2008). Under high flow conditions, the downstream dispersion of metals is favored by adsorption processes onto colloids and suspended matter, resulting to a flush of contamination. Such fluctuations in metal concentrations, when the stream flow increases in mine drainages, have been also reported by Cidu et al. (2011).

Regarding the metal concentrations in water samples from the other two basins, the seasonal pattern is unclear and no safe conclusions can be reached. An enrichment of Pb and Zn (Fig. 3) in Piavitsa
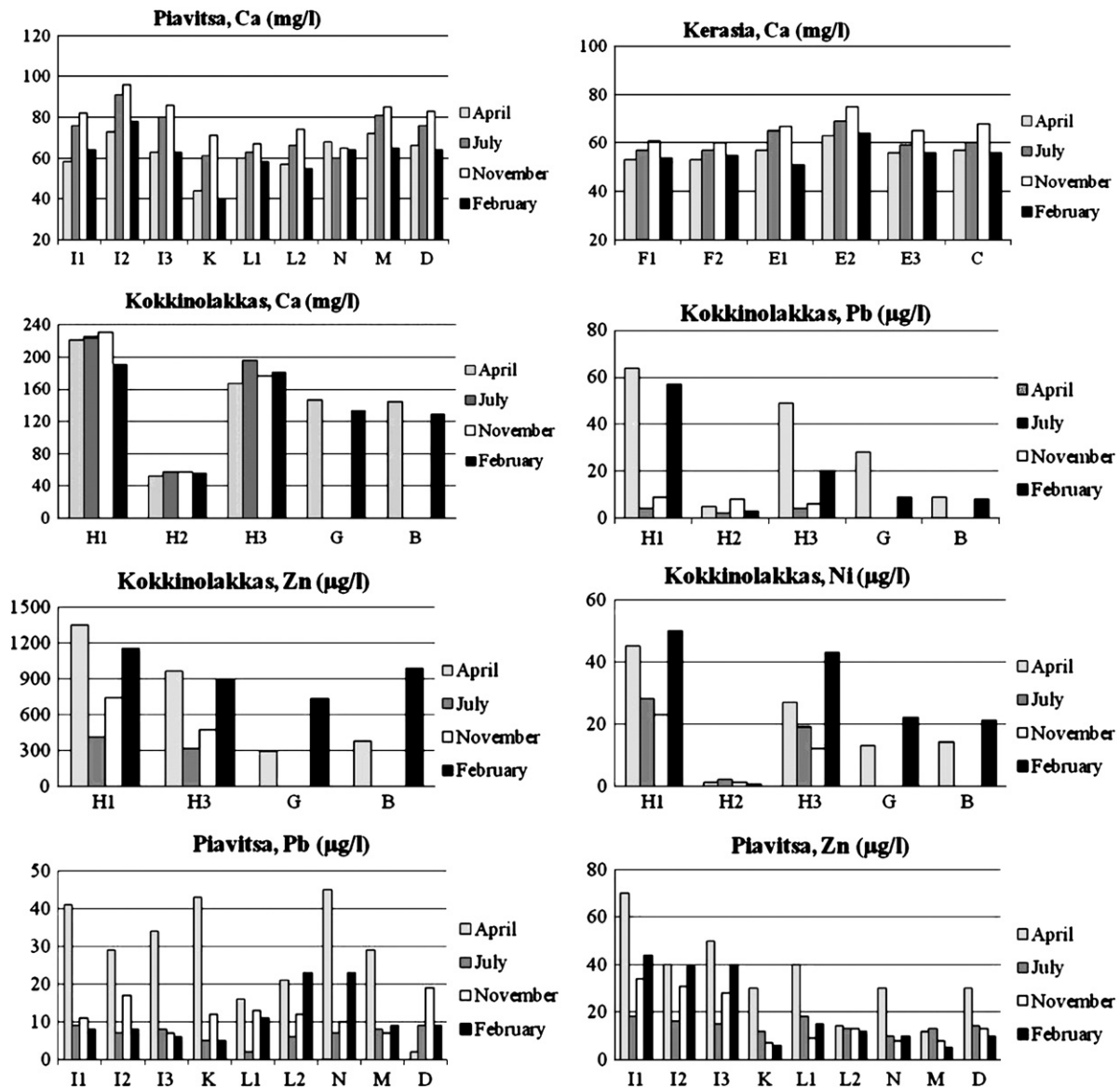


Fig. 3. Seasonal evolution of representative chemical constituents of the water samples.

stream water during the April 2008 sampling period could be as-cribed to increased metal levels during spring flood episodes (Gundersen and Steinnes, 2001).

### 4.2. Stream sediments

#### 4.2.1. Aqua regia extractable metal concentrations

Concentrations of metals extracted by aqua regia from the stream sediment samples are tabulated in Table 3. For comparison purposes, the same table shows the median values for stream sediments collect-ed throughout Europe (Salminen et al., 2005), as well as the median values for soils of the wider area of Stratoni reported in the study by Kelepertsis et al. (2006).

In general, the digestion by aqua regia is considered not complete-ly total, as it extracts metals bound as water-soluble salts, in cation exchange sites, statically bound to clay particles, in organic chelates, in amorphous oxides and hydroxides of Fe and Mn, in carbonates, in sulfides and some sulfates. It also partially solubilizes metals in sili-cates and some crystalline oxides of Fe, Ti and Cr. However potential toxic elements are efficiently dissolved, thus assisting in the assess-ment of toxicity (Mlayah et al., 2009).

All studied elements are present in stream sediment samples at concentrations well above the published median values for stream sediments from Europe (Table 3), reflecting the elevated geochemical background of the area. When compared to the median values for soils of the wider area of Stratoni, it becomes obvious that most Cu, Ni and Cr concentrations are similar to the corresponding medians. Sample L1 (Karatzas Lakkos stream) has a notable high Cu concentra-tion (349 mg kg$^{-1}$), probably being influenced by the porphyry cop-per mineralization occurring at nearby Skouries. The same sample has also elevated Ni (242 mg kg$^{-1}$) and Cr (319 mg kg$^{-1}$) values, due to the presence of serpentinite and peridotite within the Vertsikos geo-tectonic unit (Kockel et al., 1977). The Tsarkia Lakkos site, located at the headwaters of Piavitsa stream (Fig. 1), and Kokkinolakkas stream are characterized by high Pb, Zn, Cd, Mn, As and Sb concentrations. Kokkinolakkas stream is also characterized by increased Fe levels.

The elevated levels of Pb, Zn, Cd, Mn, As, and Sb determined in stream sediment samples from Tsarkia Lakkos and Kokkinolakkas sig-nify the fact that sediments can be considered as a favorable sink for

elements, which are introduced to the aquatic environment of the drainage system following chemical weathering of the sulfide min-erals of Piavitsa, Madem Lakkos and Mavres Petres ore deposits. The remaining samples are characterized by significantly lower element concentrations, but within the elevated geochemical background of the area for Pb, Zn, Mn, As and Sb (Kelepertzis et al., 2010b).

#### 4.2.2. Geochemical forms of metals

The concentrations of Pb, Zn, Mn, Cd, Cu, Ni and Cr within the op-erationally defined phases of the sequential extraction procedure are given in Table 4. The partitioning patterns (%) of elements are pre-sented in Fig. 4.

Large amounts of Pb are mainly associated with the reducible frac-tion, ranging from 35% for sample I3 to 65% for sample F2 of the total concentration. Accumulation of Pb in the Fe–Mn oxide phase is in ac-cordance with numerous studies, which showed that Fe and Mn ox-ides are important scavengers of Pb and play a significant role in controlling its mobility in the environment (e.g. Evans and Davies, 1994; Galán et al., 2003; Jain, 2004). The residual fraction is also sig-nificant, reflecting the potential presence of PbS, not totally dissolved during the 4th extraction step (Kheboian and Bauer, 1987), and/or the Pb held in silicate minerals and slag particles in which discrete amounts of Pb may be occluded. Slag was detected by scanning elec-tron microscopy (Kelepertzis, 2011) and macroscopically confirmed at Skouries and Kokkinolakkas areas. The percentage of Pb associated with the exchangeable fraction is negligible, while the proportions of Pb in the carbonate phase range from 1% (sample I3) to 7% (sample B) of the total concentration. The concentrations of NaOAc-extractable Pb in stream sediments samples H1 and B from Kokkinolakkas are 79 mg kg$^{-1}$ and 170 mg kg$^{-1}$, respectively. This signifies that a por-tion of Pb is bound to carbonates, such as calcite, and/or has precipi-tated as a mineral, such as cerussite (PbCO$_3$). With the exception of stream sediment samples from Kokkinolakkas, where the oxidizable form is of minor importance, the organic/sulfide fraction accounts for 4–17% of the total Pb in sediment samples.

Zinc partitioning is dominated by the hydroxylammonium chloride soluble phase (51 to 70%), bound to Fe–Mn oxides, a feature found by other authors (Baruah et al., 1996; Covelo et al., 2004). The proportion of Zn bound to the residual phase is also high, accounting

**Table 3**
Concentrations of aqua regia extractable elements in stream sediment samples, together with the median values for stream sediments from Europe and the median values for soils from the Stratoni area (values in mg kg$^{-1}$, except Fe in %).

| | Sampling site | Cu | Pb | Zn | Ni | Mn | Fe | As | Cd | Sb | Cr |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Piavitsa | I1 | 89 | 1812 | 2090 | 59 | >10,000 | 2.5 | 964 | 8 | 40 | 38 |
| | I2 | 52 | 1165 | 1368 | 160 | >10,000 | 3 | 1098 | 4 | 39 | 98 |
| | I3 | 70 | 1716 | 1621 | 121 | >10,000 | 2.8 | 1136 | 7 | 51 | 63 |
| | K | 30 | 68 | 137 | 110 | 1079 | 2.8 | 43 | <0.5 | <3 | 134 |
| | L1 | 349 | 208 | 390 | 242 | 679 | 2.9 | 70 | 1 | <3 | 319 |
| | L2 | 47 | 271 | 476 | 92 | 7252 | 2.9 | 220 | 1 | 8 | 107 |
| | M | 111 | 39 | 73 | 57 | 861 | 3.8 | 63 | 0.6 | <3 | 50 |
| | D | 86 | 245 | 405 | 134 | 7400 | 3.0 | 195 | 1 | 10 | 144 |
| Kerasia | F1 | 52 | 153 | 223 | 67 | 1215 | 2.9 | 70 | 0.7 | 4 | 98 |
| | F2 | 46 | 243 | 273 | 72 | 1849 | 3.0 | 130 | 0.9 | 6 | 101 |
| | E1 | 45 | 76 | 101 | 84 | 1086 | 3.4 | 117 | <0.5 | <3 | 94 |
| | E2 | 38 | 97 | 107 | 160 | 1509 | 3.4 | 153 | <0.5 | 4 | 163 |
| | E3 | 40 | 313 | 370 | 71 | 1547 | 2.8 | 143 | 0.8 | 8 | 91 |
| | C | 46 | 320 | 330 | 78 | 1986 | 2.9 | 185 | 1 | 9 | 93 |
| Kokkinolakkas | H1 | 119 | 2492 | 4538 | 61 | >10,000 | 6.6 | 2714 | 22 | 70 | 78 |
| | H2 | 67 | 76 | 139 | 47 | 1375 | 4.0 | 42 | 0.8 | <3 | 89 |
| | H3 | 84 | 1412 | 2929 | 59 | 7290 | 5.1 | 1435 | 13 | 48 | 89 |
| | G | 157 | 2074 | 4115 | 79 | 7464 | 5.8 | 1428 | 13 | 30 | 94 |
| | B | 175 | 3439 | 3749 | 68 | 6811 | 6.4 | 2657 | 15 | 50 | 92 |
| Stream sediments, Europe[a] | | 15 | 14 | 59.5 | 17 | 453 | 1.97 | 6 | 0.29 | 0.64 | 22 |
| Soils from Stratoni[b] | | 104 | 325 | 240 | 69 | 1501 | 5.95 | 119 | 1.3 | * | 178 |

*not available.
[a] Salminen et al., 2005.
[b] Kelepertsis et al., 2006.

**Table 4**
Heavy metal concentrations ($mg\ kg^{-1}$) in stream sediment samples subjected to a 5 step sequential extraction procedure.

| Step | I | II | III | IV | V | I | II | III | IV | V |
|---|---|---|---|---|---|---|---|---|---|---|
| | Pb | | | | | Zn | | | | |
| I3 | 3 | 9 | 501 | 60 | 847 | 21 | 73 | 1228 | 60 | 373 |
| L2 | 2 | 6 | 188 | 24 | 52 | 6 | 14 | 306 | 42 | 106 |
| F2 | 2 | 5 | 187 | 19 | 38 | 4 | 5 | 155 | 30 | 99 |
| C | 2 | 6 | 218 | 59 | 67 | 3 | 5 | 208 | 51 | 75 |
| H1 | 6 | 79 | 1284 | 4 | 749 | 23 | 222 | 1832 | 658 | 872 |
| B | 4 | 170 | 1590 | 2 | 791 | 24 | 221 | 1976 | 658 | 400 |
| | Mn | | | | | Cd | | | | |
| I3 | 30 | 82 | 48,796 | 5447 | 15,043 | 1 | 1 | 4 | nd | 2 |
| L2 | 12 | 28 | 6888 | 831 | 452 | 1 | 1 | nd | nd | 1 |
| F2 | 10 | 24 | 1536 | 184 | 536 | 1 | 1 | nd | nd | nd |
| C | 11 | 24 | 1876 | 219 | 404 | 1 | 1 | nd | nd | nd |
| H1 | 14 | 183 | 9928 | 302 | 302 | 2 | 2 | 9 | 3 | 5 |
| B | 29 | 290 | 6010 | 421 | 364 | 3 | 2 | 7 | 2 | 3 |
| | Cu | | | | | Ni | | | | |
| I3 | 2 | 2 | 33 | 3 | 29 | 3 | 4 | 72 | 6 | 56 |
| L2 | 2 | 2 | 19 | 3 | 28 | 4 | 3 | 39 | 8 | 75 |
| F2 | 2 | 2 | 12 | 2 | 28 | 3 | 3 | 26 | 5 | 68 |
| C | 2 | 2 | 12 | 3 | 21 | 3 | 3 | 28 | 5 | 53 |
| H1 | 2 | 4 | 14 | 26 | 39 | 4 | 5 | 29 | 8 | 39 |
| B | 2 | 7 | 18 | 60 | 51 | 3 | 3 | 35 | 7 | 49 |
| | Cr | | | | | | | | | |
| I3 | 2 | <nd | 18 | 1 | 126 | | | | | |
| L2 | 2 | 1 | 29 | 5 | 284 | | | | | |
| F2 | 3 | 1 | 31 | 4 | 263 | | | | | |
| C | 2 | nd | 26 | 5 | 164 | | | | | |
| H1 | 3 | 1 | 22 | 11 | 192 | | | | | |
| B | 2 | 1 | 33 | 11 | 240 | | | | | |

Note: Piavitsa samples: I3, L2; Kerasia samples: F2, C; Kokkinolakkas samples: H1, B.

for 12–35% of the total Zn. As expected, Zn in sediments from Kokkinolakkas exhibits a stronger association with the $H_2O_2$ soluble phase (Fraction IV), probably reflecting Zn held in sphalerite. As in the case of Pb, it should be stated that primary sulfides cannot be totally dissolved in this step, so Zn in the oxidizable fraction should be regarded as Zn related to the partial dissolution of sphalerite. The carbonate phase accounts only for 2–7% of total Zn concentration. The relative partition of Zn in the exchangeable fraction is very low (Table 4, Fig. 4).

Most Mn is related to the Fe–Mn oxide fraction (Fraction III), ranging from 67% (sample F2) to 93% (sample H1) of total concentration. This result indicates that most of Mn is in the form of relatively soluble oxides and that Mn could have an important role in scavenging trace metals in these sediments. A considerable proportion of Mn appears to be accumulated in the residual (up to 23% of total) and the oxidizable phase (up to 10% of total) for Piavitsa and Kerasia sediment samples. In Kokkinolakkas (sediments H1 and B), a small amount of Mn (2–4% of total) is found in the NaOAc soluble form, corresponding to 183 $mg\ kg^{-1}$ and 290 $mg\ kg^{-1}$, respectively. The exchangeable phase for Mn is of minor importance for all the studied sediment samples. The sequential extraction procedure revealed the extremely high Mn concentrations of Tsarkia Lakkos sediment samples. Such high concentrations may be attributed to the old Mn mining wastes, deposited in the wider area of Piavitsa.

Sediment samples from Tsarkia Lakkos and Kokkinolakkas are characterized by elevated concentrations of Cd. This metal is mostly present in the reducible fraction (between 40 and 50% of total) and the residual fraction (from 18 up to 24% of total). However, substantial proportions of Cd occur in the exchangeable (up to 17% of total) and the carbonate (up to 12% of total) fractions. High percentages of total Cd have also been found to be associated with more labile fractions by other researchers (Morillo et al., 2002; Song et al., 1999). A significant contribution from the $H_2O_2$ soluble phase for Kokkinolakkas sediments is found, as a result of the dissolution of sphalerite. The Cd

concentrations of samples L2, F2 and C are too low to assess their relative distribution in each fraction.

Large amounts of Cu are bound to the residual phase, accounting for 37% (sample B) and up to 61% (sample F2) of total Cu concentrations. In Piavitsa and Kerasia sediment samples, the second most abundant fraction for Cu is the Fe–Mn oxide phase (26–48% of total). The higher percentage of Cu in the oxidizable fraction for Kokkinolakkas sediment samples (31 and 43% of total) can be explained by the presence of chalcopyrite, a mineral occurring in the Madem Lakkos and Mavres Petres deposits. The strong Cu-sulfidic binding could be related to the extremely low solubility of CuS — solubility product $Ksp = 10^{-36}$ compared with around $10^{-26}$ for PbS and ZnS (Stumm and Morgan, 1996). The exchangeable and carbonate fractions do not account for much of the total Cu content (<5% of total).

Finally, Ni and Cr mainly partition into the residual fraction (up to 65% and 88% of total, respectively), indicating incorporation into the crystalline structures of silicate mineral particles. Especially for Ni, a significant amount is also bound to the hydroxylammonium chloride soluble phase (up to 51% of total). In this case, it is probable that Ni is coprecipitated with the Fe–Mn oxy-hydroxide coatings on the particles.

### 4.2.3. Metal mobility and bioavailability

Trace element mobility from the solid fraction to surface water mostly depends on the solid phase stability. The investigation of partitioning of metals in the selected stream sediment samples allows better understanding of metal behavior by providing information on the mobility and bioavailability of metals. The different fractions determined in this study have different behavior with respect to remobilization of metals under changing environmental conditions. The principal variables that govern the mobilization of trace metals from sediments are pH and Eh.
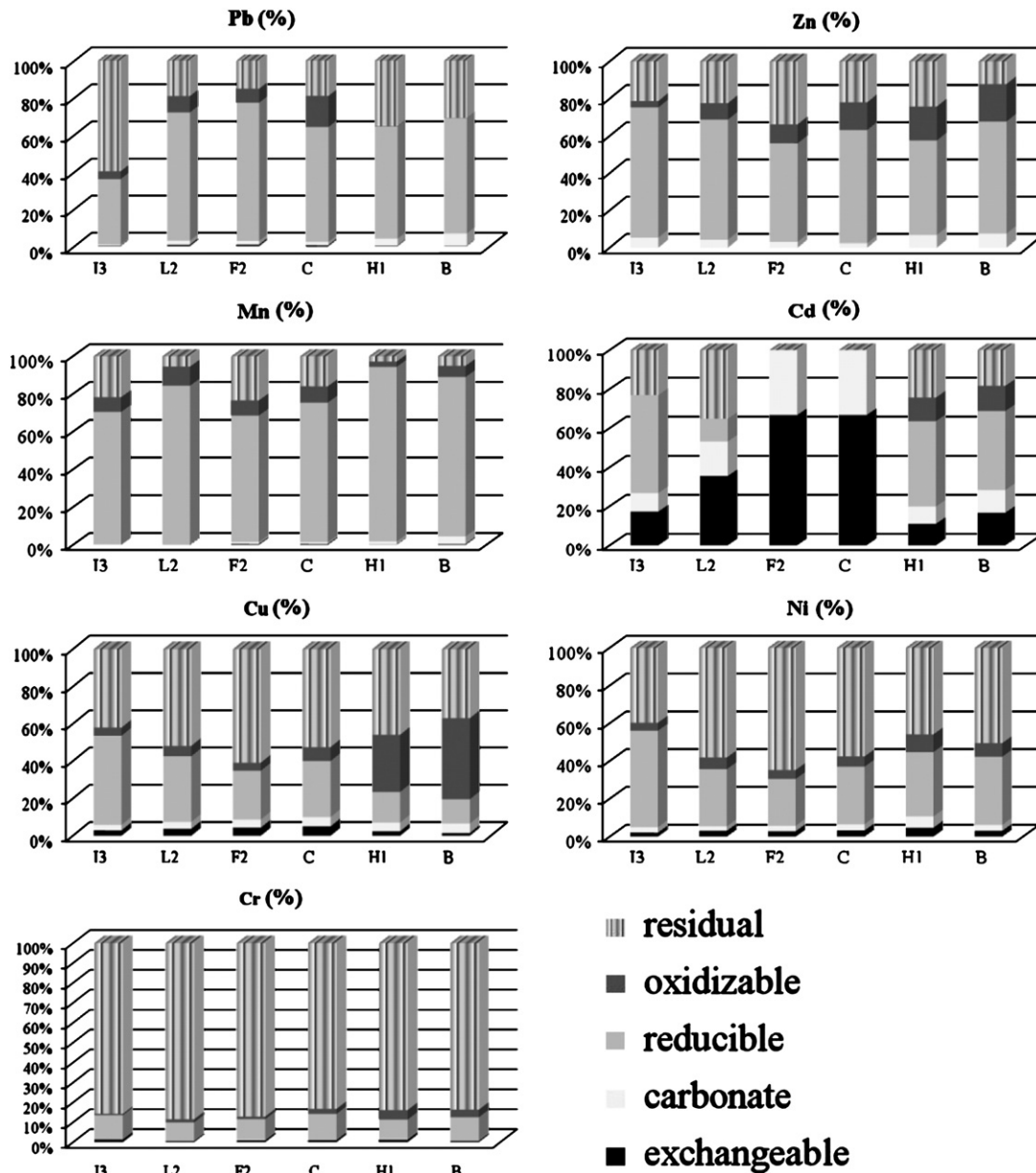
**Fig. 4.** Geochemical partitioning of metals in stream sediment samples of the study area.

The exchangeable fraction includes the proportion of metals considered to be ion-exchangeable and specifically adsorbed on the sediment surface (such as clay minerals and hydrous oxides). Metals recovered in this form are subject to sorption–desorption processes, according to the change of water properties, such as pH and ionic strength. The low percentage of partitioning in the exchangeable form indicates that the examined metals have a low potential to be easily mobilized and a low bioavailability for aquatic biota. The only exception is Cd, which is characterized by high mobility, facilitating its potential accumulation by organisms living in close proximity to sediments.

The carbonate fraction also displayed low proportions of metals, highlighting that trapping of metals by carbonates is not very effective. However, the elevated actual concentrations of Pb, Zn and to a lesser extent Mn, partitioned in the NaOAc soluble phase (Fraction III) for Kokkinolakkas stream sediment samples, suggest the potential release of these elements to the dissolved aquatic phase under acidic conditions. As Rodríguez et al. (2009) stated, even a low percentage

of labile metals in highly polluted sediment could involve a considerable environmental risk.

Results of the sequential extraction revealed that the majority of the analyzed elements are mainly bound to the operationally defined geochemical phase of amorphous to poorly crystalline Fe and Mn oxides. The incoming elements released by the chemical weathering of mineralized and/or mining parts of the study area might initially exist in unstable chemical forms. Continuous accumulation of elements leads to the formation of precipitates, especially as reducible forms. Both Fe and Mn oxides are important adsorbents of trace metals in aquatic systems, as already mentioned. However, they can also become a secondary source, releasing the adsorbed and coprecipitated metals to the water column after dissolution under reducing conditions (Filgueiras et al., 2002). Hence, they could have a significant impact on the drainage system quality and aquatic biota. The combined exchangeable, carbonate and Fe/Mn oxide phases are considered to be geochemical forms that are highly to moderately available to aquatic organisms as they can interact with organic tissue

more easily than sulfide/organic and residual bound metals. Furthermore, other researchers have stated that the most important geochemical components considered to influence the bioavailability of metal to sediment ingesting organisms are Fe oxides, Mn oxides and organic matter (Tessier and Cambell, 1987). Thus, metals associated with the Fe–Mn oxide phase may not be as mobile as the exchangeable and the carbonate phases are, but they could affect the accumulation of potentially toxic elements in the tissue of sediment related organisms.

Under oxidizing conditions (increase of redox potential), metals bound to organic matter and sulfides may be released from storage into solution and/or re-adsorbed onto the more labile binding fractions (easily exchangeable, carbonate and reducible phases) (Byrne et al., 2010; Kelderman and Osman, 2007). Additionally, the disturbance and subsequent oxidation of sediments could also release exchangeable and carbonate bound metals, due to the drop of sediment pH that accompanies oxidation (Byrne et al., 2010). Oxidizing conditions may occur during high stream flows (especially during flood events) and drying of the stream bed. Substantial proportions of the total Zn, Cu and Cd are found in the organic matter/sulfide fraction for Kokkinolakkas sediments.

Finally, the residual phase mainly contains primary and secondary minerals, which incorporate trace metals within their crystal structure. These metals are significantly less reactive and are not expected to be released in solution under the conditions normally encountered in nature.

## 5. Summary and conclusions

For the first time, the geochemical characteristics of surface waters and stream sediments in the Asprolakkas drainage basin were investigated. Chemical elements exhibit a wide spatial and seasonal variation and elevated concentrations occurring in water are primarily related to the mineralogy of individual deposits. Geochemical processes also appear to play an important role in controlling the concentrations of elements.

Kokkinolakkas stream water presents high levels of Ca, Mg and SO$_4$, trace metals and metalloids, such as Pb, Zn, Mn, Ni, Cd, As and Sb, as a result of the dissolution of gangue and sulfide minerals of the Madem Lakkos and Mavres Petres ore deposits, occurring upstream of the sampling points. Surface water samples from Piavitsa catchment basin have significantly lower element concentrations with specific water samples being characterized by elevated contents for K, Sb, Pb, Mn and As. Kerasia stream water has even lower concentrations of major ions in relation to Piavitsa basin, and only Pb and As show elevated values, which may be due to metal mineral occurrences that are not exposed.

Hydrological conditions are important in modeling the element concentrations. Major ion content decreases in the wet period as a result of dilution owing to the heavy winter rainfall. A contrasting behavior was observed for trace metal composition in Kokkinolakkas water samples, due to the enhanced base metal dissolution under high runoff conditions. It appears that downstream dispersion of metals is favored by transport via adsorption processes onto very fine particles (<0.45 μm).

A significant amount of trace metals and metalloids released by the chemical weathering of mineral deposits was found to be associated with stream sediment. Stream sediment samples from Kokkinolakkas and Tsarkia Lakkos have elevated concentrations in Pb, Zn, As, Sb, Cd and Mn, i.e. the elements that are abundant in the ore deposits of the area. Concentrations of these metals at other sampling locations are lower, but within the elevated geochemical background of the area.

Metal partitioning in stream sediment samples, using the scheme proposed by Tessier et al. (1979), was successfully applied and provided information on the mobility and bioavailability of sediment bound metals. This study revealed that weathering of the mineral deposits supports the occurrence of a prevalent Fe–Mn oxyhydroxide surface, which is considered to be capable of scavenging toxic metals. However, these precipitates could be a secondary source of trace metals for the water column upon dissolution of the oxides under reduced conditions. Cadmium is the only labile metal indicating the different chemical binding, and higher solubility of this element, compared to the other metals. High contents were also measured in the carbonate fraction of Kokkinolakkas stream sediment samples, highlighting that pH is the principal variable governing the potential release of these elements to the dissolved phase.

Bearing in mind the ongoing mining developments in the area, results of this comprehensive study are very significant, providing scientific data about the present environmental–geochemical baseline conditions of the Asprolakkas drainage basin and are available for any future comparison. These data can enable mine planners to better anticipate and plan for potential environmental impacts and are useful for setting up realistic goals in monitoring and remediation programs.

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