

## OCCURRENCE OF ARSENIC IN WATERS AND SEDIMENTS OF THE PALEA KAVALA RIVER, NE MACEDONIA, NORTHERN GREECE

Giouri K.<sup>1</sup>, Vavelidis M.<sup>1</sup> and Melfos V.<sup>1</sup>

<sup>1</sup> Department of Mineralogy-Petrology-Economic Geology, Faculty of Geology, Aristotle  
University of Thessaloniki, agiouri@geo.auth.gr

### Abstract

*Inorganic arsenic (As) is a naturally occurring metal, present in various ecosystems. However, it can also be added to an aquatic system by anthropogenic activities. The aim of the present study is to determine the total As content in the Palea Kavala river (NE Macedonia, Northern Greece). The correlation between As content and some chemical and physico-chemical parameters of the samples was also examined. Research demonstrated significant As concentrations in the water and the sediments of the river. No correlation was found between As and pH, Fe, Mn in the water samples. Concerning the sediment samples, positive correlation was revealed for As with Fe and Mn content, while negative correlation was revealed between As and pH. This is probably indicative of a higher arsenic mobility in the Palea Kavala river water than in sediments. Since no anthropogenic activities were observed in the river's catchment area, elevated As concentrations are probably due to the lithology of the broader area and especially the presence of extended ore mineralizations including As-bearing sulphide minerals. However, the research in the study area is in progress since a more detailed evaluation of the local sources of As and mechanisms of As release is required.*

**Key words:** Inorganic contamination, heavy metals, Northern Greece.

### Περίληψη

*Το αρσενικό (As) είναι χημικό στοιχείο που μπορεί να υπάρχει στα επιφανειακά υδάτινα οικοσυστήματα λόγω φυσικών αλλά και ανθρωπογενών δραστηριοτήτων. Ο σκοπός της παρούσας μελέτης είναι να προσδιοριστεί η περιεκτικότητα σε ολικό As τόσο των υδάτων αλλά και των ιζημάτων του ρέματος Παλαιάς Καβάλας, που βρίσκεται στην Ανατολική Μακεδονία (Β. Ελλάδα). Έγινε επίσης μία προσπάθεια να διερευνηθεί τυχόν συσχέτιση των συγκεντρώσεων του As με κάποιες χημικές και φυσικοχημικές παραμέτρους των δειγμάτων. Με βάση τα αποτελέσματα, δεν βρέθηκε κάποια συσχέτιση του As με τις περιεκτικότητες του Fe και Mn στα δείγματα ύδατος, καθώς ούτε και με το pH τους. Αντίθετα, προσδιορίστηκε ως θετική η συσχέτιση του As με τις συγκεντρώσεις Fe και Mn καθώς και με το pH των ιζημάτων. Οι υψηλές περιεκτικότητες As σε όλα τα δείγματα, πιθανόν να οφείλονται στην ύπαρξη μεταλλοφοριών στην ευρύτερη περιοχή έρευνας με μεικτά θειούχα ορυκτά που περιέχουν As, παρά σε ανθρωπογενείς δραστηριότητες. Παρόλα αυτά, είναι απαραίτητη περαιτέρω έρευνα, ώστε να προσδιοριστούν με μεγαλύτερη λεπτομέρεια οι πηγές του As στην περιοχή.*

**Λέξεις κλειδιά:** Ανόργανοι ρυπαντές, Βαρέα μέταλλα, Βόρεια Ελλάδα.

## 1. Introduction

Trace elements, especially heavy toxic metals, in surface waters are attributed to natural or anthropogenic sources. In elevated concentrations, toxic metals may lead to irreversible health diseases. For this reason, the pollution of the surface aquatic systems, especially rivers, with inorganic pollutants has been attracting the attention of public and scientific community over the last few decades (Kabata-Pendias and Pendias, 2001; Suthar et al., 2009). A naturally occurring element in ecosystems is inorganic arsenic (As). It occurs in a variety of environmental media, including minerals, rocks, sedimentary deposits, soil, water and plants and usually is incorporated in sulfide minerals. Nevertheless, arsenic can also originate from anthropogenic activities and transmitted in the environment as a contaminant through sewage discharge or use of fertilizers in agriculture (Nordstrom, 2002; Hoang et al., 2010).

Arsenic contamination in water has caused severe health problems around the world, since it causes serious natural hazards when exceeding the established standards. The association between arsenic and human health effects is well described by numerous related surveys globally. Furthermore, the chemical analysis of river sediments is very useful when studying inorganic contamination in an area (Förster and Salomons, 1991; Abernathy et al., 2003 and references therein).

The objective of the present study is to determine the presence of the total arsenic content in water and sediments of the Palea Kavala river and examine if there is any correlation with chemical and physico-chemical parameters of the samples. Palea Kavala river is located 6 km north of the Kavala city, in northeastern Greece (Figure 1). It emanates from the Lekani mountains and passing through the Palea Kavala village it flows towards the Philippoi plain. When entering the plain, due to the extensive karst formations, the river disappears into the sediments.

## 2. Geological Setting

Geologically the study area belongs to the lower Pangeon unit of the Rhodope massif, consisting mainly of gneisses overlain by marbles. In the Palea Kavala area the metamorphic rocks of the Rhodope massif, were intruded by the Kavala pluton of a Lower Miocene age (21-22 Ma). The latter has the characteristics of an I-type intrusion and is mainly composed of amphibole-biotite granodiorite. Alluvial deposits which consist of clays, sands and gravels overlie the crystalline rocks (Kronberg, 1970; Kronberg and Melidonis, 1970; Christofides, 1996; Vavelidis et al., 1997; Melfos et al., 2008) (Figure 1).

The Palea Kavala region contains ~150 minor hydrothermal–magmatic base- and precious-metal occurrences within the Kavala pluton and the surrounding metamorphic rocks of the Rhodope massif. These occurrences have variable metal assemblages that include Fe-Mn-(Pb±Zn±Ag), Fe-Mn-Au, Fe-As-Au, Fe-Cu-Au and Bi-Te, but most are weathered and oxidized. Primary metallic minerals consist of pyrite, arsenopyrite, chalcopyrite, pyrrhotite, galena, sphalerite, tetrahedrite-tennantite, petzite, bismuthinite, tetradymite, cosalite, bismuthinite, lillianite, proustite, pyrargyrite, argentite, jalpaite, stephanite and native gold. Arsenic is mainly related with arsenopyrite, proustite and tennantite (Vavelidis et al., 1996a,b; Melfos et al., 2008; Fornadel et al., 2011).

## 3. Materials and Methods

### 3.1. Sample Collection

Seven sites were sampled for water (PKW1 to PKW7) and thirteen sites for their sediments (PK1 to PK13) downstream the Palea Kavala river (Figure 1). Water and sediment sampling was carried out in November 2009, after the dry season, and in May 2010, after the rainy season, leading to fourteen in total water samples.

Water sampling was performed with plastic bottles of 300 ml capacity, rinsed with distilled water. Following that, the samples were delivered on the same day to the laboratory. Sediment samples were collected at the top of the riverbeds and their banks, avoiding the input of other materials. All sediment samples were collected with a plastic shovel and were put in plastic bags.

### 3.2. Laboratory Treatment of Samples

The water samples were filtered through 0.45 µm Whatman filter paper, acidified with HNO<sub>3</sub> (1:1) to pH 2, and stored at 4° C in polyethylene plastic bottles until they were sent for analysis.

At the laboratory, after the removal of organic material, sediment samples were dried in an oven at 60° C. They were gently ground with rolling pin to disaggregate the samples but not break down the grains themselves, sieved to collect less than 0.063 mm grain size and stored in polyethylene bags until they were sent for analysis. The <0.063 mm fraction was used due to the fact that the environmentally available trace elements mainly remain in this fraction, because of its larger specific area. Therefore, fine sediments have been used by many researchers in order to investigate river pollution (Kabata-Pendias and Pendias, 2001; Salomons, 1995).

### 3.3. Sample Analysis

The physico-chemical parameter pH of the water was measured in the field during sampling, using a portable combined instrument. The pH of sediments was measured at the laboratory using a digital pH-meter. The chemical analyses were performed at the Acme Analytical Laboratories (Vancouver, Canada). Metals in the sediments were extracted using the aqua regia digestion, while their concentrations were determined in all samples by ICP-MS.

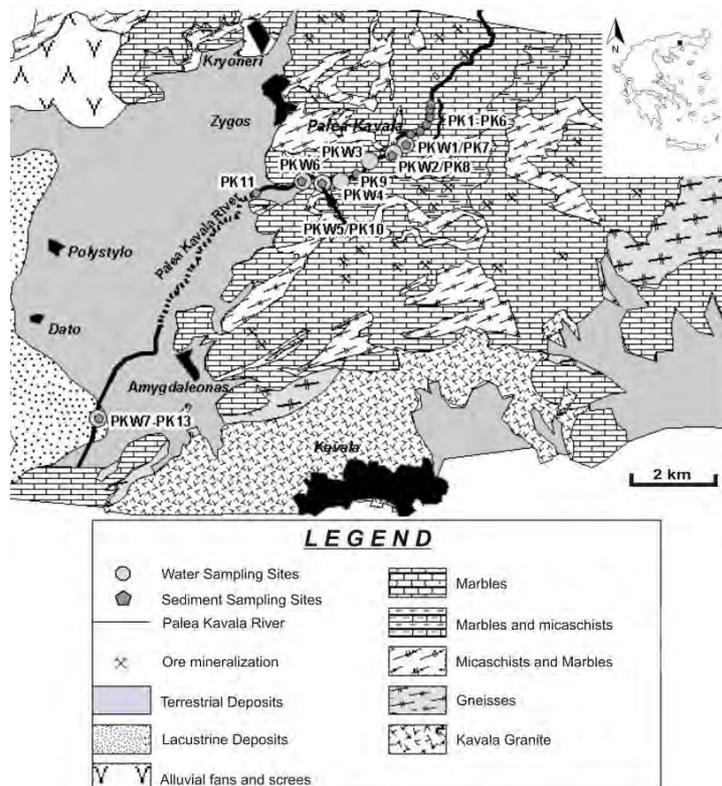


Figure 1 - Geological map of the studied area with the Palea Kavala river and sampling sites (according to Kronberg, 1970; Kronberg and Melidonis, 1970 with modifications).

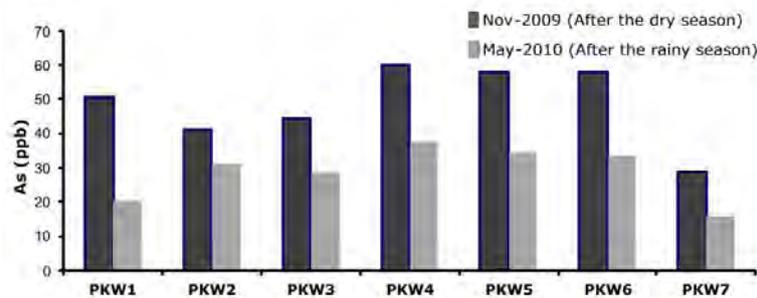
#### 4. Results and Discussion

The results of the physico-chemical analyses and of heavy metals content in water and sediment samples are shown in Table 1 and Table 2, respectively. The pH values were approximately neutral to slightly alkaline, with a range of 7.36 to 8.14. The range of concentration for As and Mn in the water samples was 15.9- 59.9 ppb and 0.5-152 ppb, respectively.

Arsenic content after the wet season ranges from 28.9 to 59.9 ppb, and after the dry season from 15.9 to 37.4 ppb. This demonstrates that arsenic levels after the dry season (November 2009) are higher than the respective ones which followed the wet season (May 2010). It is apparent, therefore, that arsenic contents were higher during the period of a low river flow (Figure 2). This has also been confirmed by previous studies (Giouri et al., 2012), according to which significant variations of As content were found in most of the sites. However, clear trends in these changes between wet and dry season were not determined, as it was also concluded by the coefficient of determination ( $R^2$ ). According to its value ( $R^2=0.60$ ) there was found a positive but moderate correlation between wet and dry season As concentrations.

**Table 1 - Results of the pH and the As, Mn concentrations in surface waters of the Palea Kavala river.**

Number of samples		pH	As (ppb)	Mn (ppb)
n=14 (PKW1a-PKW7a→Nov-2009) (PKW1b-PKW7b→May-2010)	min	7.36	15.9	0.5
	max	8.14	59.9	152.0
	median	7.63	35.9	2.8
	mean	7.71	38.7	22.7



**Figure 2 - Variation in the concentrations of As in the water samples collected downstream Palea Kavala river, for both sampling periods.**

**Table 2 - Results of the pH and the As, Mn, Fe concentrations in the sediments of the Palea Kavala river.**

Number of samples		pH	As (ppm)	Mn (ppm)	Fe (wt %)
n=13 (PK1 - PK13)	min	6.33	51.3	405	1.6
	max	8.18	705.5	5268	4.0
	median	7.58	170.1	822	3.6
	mean	7.37	231.0	1097	3.1

The pH values of the sediments range from 6.33 to 8.18, without any drastic differences among sampling sites. As and Mn concentrations are high in all samples, ranging from 51.3 to 705.5 ppm and from 405 to 5268 ppm, respectively. Fe was also relatively high varying from 1.6 to 4.0 wt% (Table 2 and Figure 3). From the diagram in Figure 3, it can be concluded in general that the variation in As concentrations, follow the variations of Mn and Fe.

The distribution of As in water and sediments of surface streams or rivers, is related with the pH, the deliberate pollution and the release of other compounds which can adsorb arsenic. In the case of rivers, the As content may be strongly affected by geological characteristics of the drainage area of the rivers and by anthropogenic inputs. The adsorption of As on precipitated hydrous Fe and Mn oxides that exist in the sediments of the rivers, is significant. It is apparent, therefore, that the correlation between the content of As, Mn and Fe in the collected water and sediment samples should be further studied (McLaren and Kim, 1995; Smedley, P.L. and Kinniburgh, D.G., 2002; Gault et al., 2003; Sanchez-Rodas et al., 2005; Nordstrom, 2011; Sarmiento et al., 2012).

According to the water analyses results in Palea Kavala river, the relationship between As content and pH is weak but negative (Figure 4) with a correlation coefficient factor  $R^2=0.18$ . Similarly the correlation of As with Mn is also very poor, with  $R^2=0.0051$  (Figure 4). Arsenic in water is also very poorly correlated with Fe. According to the present study, Fe in most of the samples was below detection limits, with the exception of 2 samples (data not shown). This means that there is not any relationship between As and Fe and therefore As in the water is not adsorbed because of the presence of Fe.

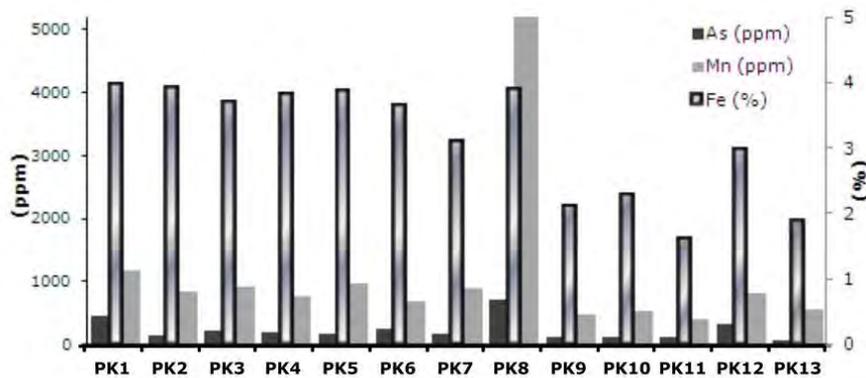


Figure 3 - Variation in the concentrations of As, Mn and Fe in the sediment samples collected downstream Palea Kavala river.

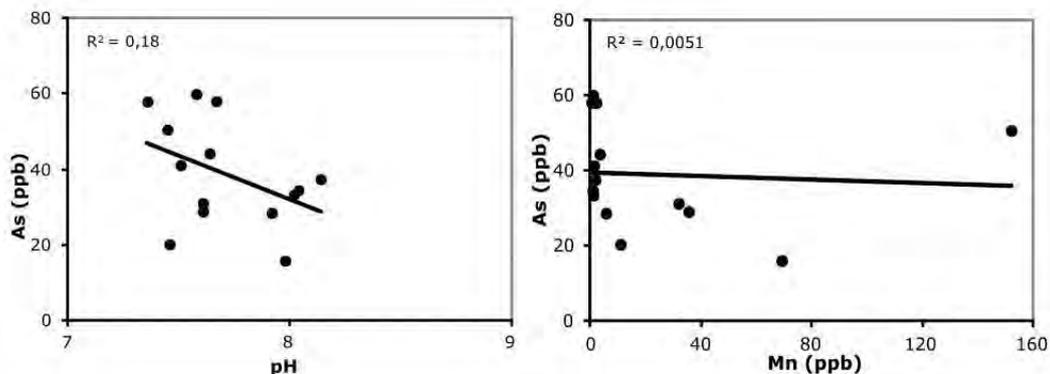


Figure 4 - Scatter plot of arsenic concentrations in the water sample in correlation with pH and Mn content.

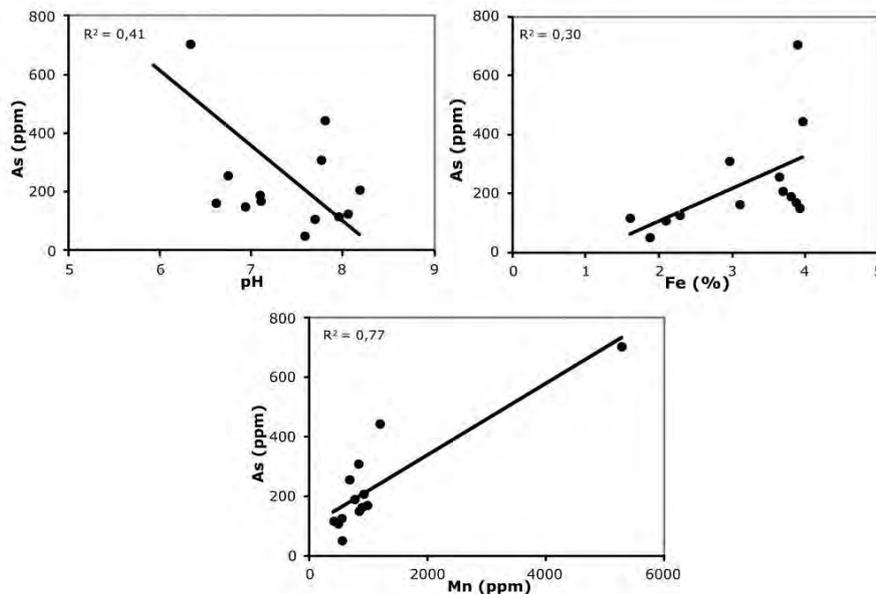
According to the results of sediment analyses (Figure 5), a moderate negative correlation was observed between arsenic and pH ( $R^2=0.41$ ). The correlation of As is stronger with Mn than with Fe. This is concluded since the value of correlation coefficient factor for As with Mn is  $R^2=0.77$ , while for As with Fe is  $R^2=0.30$ . It should be mentioned that the sample with the most elevated concentrations of As and Mn is not plotted close to the rest ones (Figure 5). However, by exempting that specific sample, the correlation between As and Mn is slightly weaker ( $R^2$  decreases from 0.77 to 0.54), remaining still positive and relatively good. As illustrated in Figures 4 and 5, arsenic shows a closer relationship with pH, Fe and Mn in the sediments than with the corresponding parameters in water.

Since in the catchment area of Palea Kavala river any anthropogenic activities were not observed, which as a consequence can increase metal concentrations in the sediment and water, it is assumed that high arsenic content can be attributed to the geological environment. After all, some of the primary minerals that comprise the metal assemblages occurring in the Palea Kavala region, mainly arsenopyrite, proustite and tennantite (Fornadel et al., 2011), are related with the elevated As concentrations. This is also demonstrated in Figure 6, since it is revealed that higher concentrations of As are observed mainly upstream Palea Kavala river, where the majority of As-bearing ore mineralizations occur.

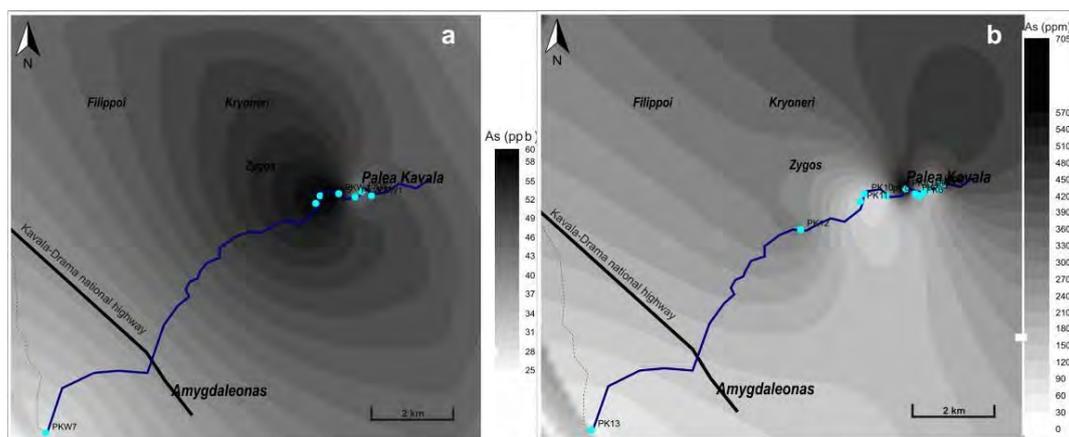
## 5. Conclusions

The purpose of the present study was to determine the total arsenic content in water and sediments of the Palea Kavala river (NE Macedonia, Northern Greece). Furthermore, it was examined if there is any correlation between As and some chemical and physico-chemical parameters in the samples.

Results of chemical analyses demonstrated considerable concentrations of As, both in water and sediments of the river. This is probably due to some geological factors such as the lithology of the broader area. Especially the presence of extended ore mineralizations which include arsenopyrite ( $\text{FeAsS}$ ), proustite ( $\text{Ag}_3\text{AsS}_3$ ) and tennantite ( $(\text{Cu,Ag,Fe,Zn})_{12}(\text{As, Sb})_4\text{S}_{13}$ ) in metal occurrences in Palea Kavala region, and so in the river water and sediments because of weathering and transportation, can be related with As content.



**Figure 5 - Scatter plot of arsenic concentrations in every sediment sample in correlation with pH, Fe and Mn content.**



**Figure 6 - Spatial distribution of  $As_{(tot)}$  in the water (a) and sediments (b) of Palea Kavala river.**

Physicochemical factors such as pH and the presence of Mn and Fe oxides, can contribute to the adsorption of As. However, no correlation was found between As content and pH, as well as Fe and Mn in the water samples. On the other hand, positive correlation was revealed for As with Fe and Mn and negative correlation was observed between As and pH in the sediments. It can probably be concluded that mobility of arsenic in Palea Kavala river is higher in water than in sediments. However, the research in the study area is in progress since a more detailed evaluation of the local sources of As and mechanisms of As release in surface water is required.

## 6. Acknowledgements

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