Field-portable X-Ray Spectrometry as Rapid Measurement Tool for Environmental Geochemical Investigations in Former Mining Areas: The Case of Kirki Mines (Greece)

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Field-portable X-Ray Spectrometry as Rapid Measurement Tool for Environmental Geochemical Investigations in Former Mining Areas: The Case of Kirki Mines (Greece)

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Introduction

Geochemical environmental monitoring, as a prerequisite for environmental risk assessment, is crucial in abandoned mining and mineral processing sites, where one of the most important environmental problems is associated with the disposal of extraction wastes, as well tailings, directly into streams or at their edge, the generation of acid mine drainage and the resulting environmental pollution of soil, stream and floodplain sediment, surface and ground water. However, in most cases, environmental monitoring is severely restricted, due to lack of funds and, consequently, environmental geochemists need of a cost-saving alternative method to classical laboratory analysis programmes, dealing efficiently with remote or harsh field conditions. Nowadays, portable X-ray fluorescence (pXRF) analysers are a key technique for investigating a wide range of fields (Lemiere, 2018). The technique introduces the acquisition of real–time measurements in the field, making possible the real-time geochemical mapping of areas by identifying elements of interest and gaining an understanding of the trends in elemental soil or sediment pollution.

This paper explores the potential for a wider use of Field Portable X-Ray Fluorescence Spectroscopy instruments (pXRFs) in geochemical environmental assessment by using as case study the abandoned Kirki mine area in north-eastern Greece. The results demonstrated that handheld XRF analyzer in the Kirki mine area is a rapid and practical tool for fast, real-time and cost-effective environmental surveys for potential hazardous element dispersal in a short period of time.

The former mining area of Kirki (Aghios Philippos) is located in the gently mountainous part of Thrace, in the north-eastern part of Greece, situated at 22 km to the NNW of Alexandroupolis (NE Greece, Fig.1). First mining works dated since 1880. More recently, the area has been intensively mined during two period: (a) from 1973 to 1982 by the private company 'Kirki Mines Inc.', with underground mining, and (b) from 1989 to 1998 with surface mining operation by 'Evros Mines Co', (Papassiopi *et al*., 2009; Liakopoulos *et al*., 2010). Ores were beneficiated by flotation in the plant located near the railway, 5 km south of the mine. Lead and zinc were the main commodities, along with copper and precious metals. A total of 250,000 tons of Pb-Zn ore were processed, whereas galena and sphalerite concentrates were exported to Balkan and Central European smelters (Arikas *et al*., 2007; Triantafylidis *et al*.; 2016). Mining and ore beneficiation for Cu, Zn and Pb ceased in 1998 and no remediation action was taken (Liakopoulos *et al*., 2010; Triadafylidis *et al*., 2016). Tailings and impoundments were exposed to atmospheric conditions and their chemical, mineralogical, physical and geotechnical characteristics were affected. Climate, which can be an important destabilizing factor, is harsh in the Kirki area, with hot and dry conditions during summer, and cold, rainy and windy days in the winter (temperate Mediterranean continental climate). Drainage from the Kirki mine is collected by the Kirkalon stream, joining a small river, Eirini, near the plant (Fig.1), which reaches the sea near Alexandroupolis through a cultivated plain overlying an aquifer used for water supply.

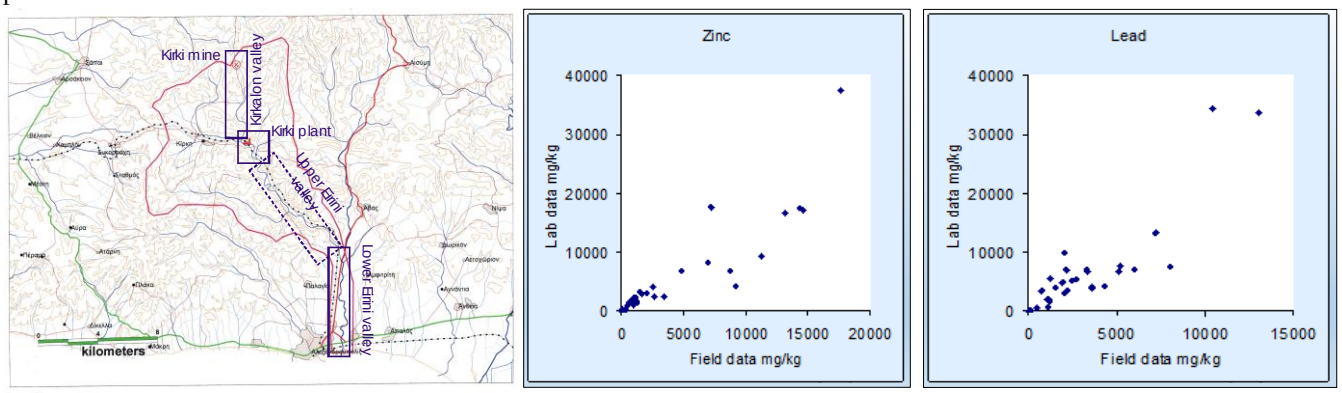
Method

The field portable X-Ray fluorescence (pXRF) unit used was a NITON TM XLt792WY equipped with an X-ray miniaturized tube (40 kV/50mA max.), multifilter configuration with the ability to determine 22 elements (Mn, Fe, Co, Ni, Cu, Zn, As, Se, Pb, Hg, Rb, Sr, Cd, Ag, Sn, Sb; Cr, V, Ti, Sc, Ca and K) in optimum matrix conditions (Lemiere *et al*., 2006). The spectrometer was factory calibrated for the analysis of bulk and/or of soil samples in field, as well as in laboratory conditions. The pXRF unit was used either (a) directly in contact with the soil, sediment or rock target, (b) on-site on a roughly homogenized soil or sediment sample, and/or (c) a near-site location where sample drying, sieving and milling was possible in order to allow sample preparation to be close as possible to laboratory conditions. Methods (a) and (b) were suitable for target identification and sample selection whereas method (c) provided quantitative results (US EPA, 1998). A total of 635 measurements were performed with the pXRF spectrometer during two field trips, including on-site measurements on a roughly homogenized sediment sample as well as analyses in laboratory-controlled conditions. For verification of field results, a total of 39 sediment samples, analyzed by pXRF laboratory conditions, were analyzed by ICP-MS at OMAC laboratory in Ireland.

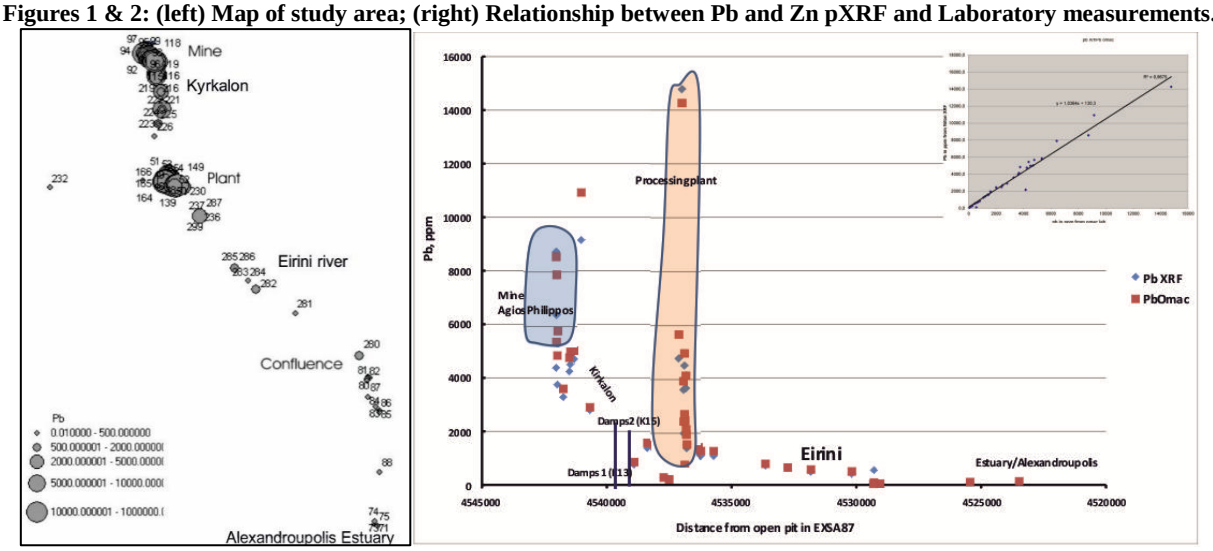
Results – Discussion

The relationship between field and laboratory XRF data, is good for Pb, Zn and Cu, and poor for As (Fig. 2). The latter is due to high Pb concentration in Kirki samples, resulting in strong Pb interference, as the As-Kα line is overlapped by the Pb-Lα line. For the geochemical conditions of Kirki, the pXRF field measurements are satisfactory for mapping reliably Zn, Pb and Cu contamination, whereas high As can be interpreted in terms of As contamination probability. Serious Pb, Cu and Zn pollution has been recorded in Kirkalon stream sediments as well as at the upper part of Eirini river (Fig. 3&4), whereas extremely high concentrations of Pb, Cu and Zn were found in stream sediments close to the

Aghios Philippos mine and also near the tailing dumps area. Downstream of the ore-beneficiation plant contamination levels decrease gradually and it is markedly lower when the river crosses the alluvial formations of the Alexandroupolis plain.



Figures 1 & 2: (left) Map of study area; (right) Relationship between Pb and Zn pXRF and Laboratory measurements.



Figures 3 & 4: (left) Cartographic distribution of pXRF Pb measurements along Kirkalon and Eirini rivers from Kirki to sea, which have been obtained by on-site measurements on a roughly homogenised sediment; (right) plot shows analyses performed under lab conditions on pre-treated samples and results are compared with data obtained by ICP-MS.

Conclusion

In the Kirki mine area case study, we took advantage of pXRF as a compositional analysis technique, used as part of environmental monitoring processes, since it was straightforward to use, did not require laborious sample preparation, it was cost-effective, providing higher sampling density data sets and real-time or near real-time decision support for operational decisions.

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