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Spatial distribution and associated spatial uncertainty of potential toxic elements - the Lake Kalimanci case study (Republic of Macedonia)

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Abstract

Pollution from mining activities is a significant problem in various regions of the Republic of Macedonia. A geochemical survey of the surface deposits of Lake Kalimanci in the easterly region of the Republic of Macedonia was carried out before (2001) and later (2007) the dam failure and thus allowing the measurement of the tailings' material from Sasa Pb-Zn Mine-Osogovo Mountains (Eastern Macedonia). The concentrations of potentially toxic elements (PTE): Ag, Au, Cd, Co, Cu, Pb, Sb, Th, S, U and Zn were obtained by ICP Mass Spectrometry (ACME Laboratories in Vancouver, Canada). Data analysis, through Principal Component Analysis (PCA), was performed in order reduce the space of analyses by the construction of synthesis variables (Principal Factors). Geostatistical modeling was used, throughout conventional variography and the Sequential Gaussian Simulation algorithm (SGS), to model the new factors' spatial distribution. A hundred simulations, differing in their initial random-number seed, were performed and a Mean Image (MI) obtained. Spatial uncertainty evaluation (simulation's Standard Deviation) allowed the definition of future monitoring and sampling strategies as well as the measurement of remediation possibilities.

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Keywords: PTE distribution; Principal Componentes Analysys (PCA); Sequencial Gaussian Simulation (SGS); Spatial Uncertainty; Lake Kalimanc

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1. Introduction

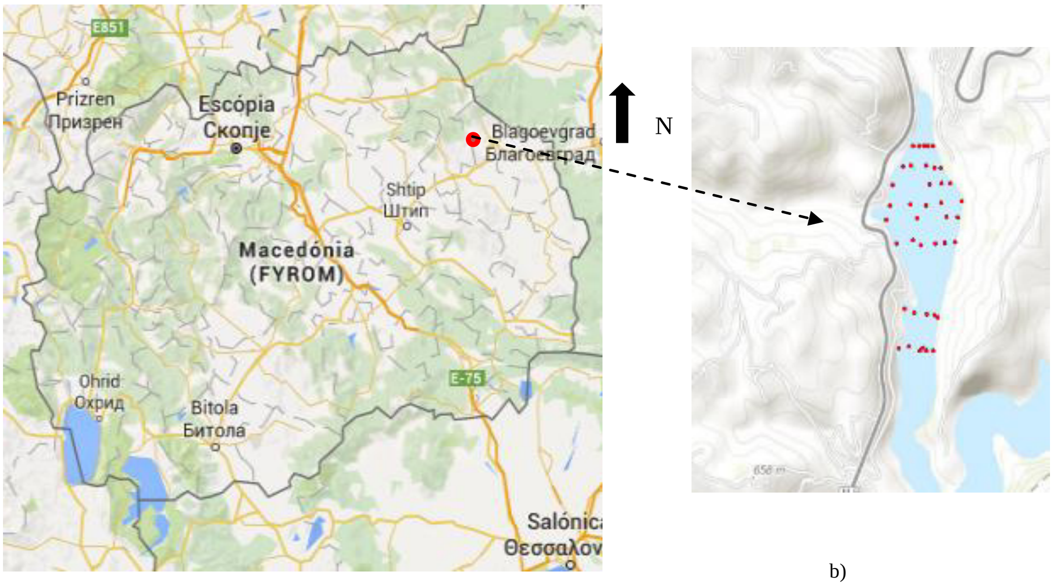
Lakes are important sedimentological environments. Input of heavy metals and metalloids has been increasing in last decades. Their occurrence in the environment results from different anthropogenic activities. Input of potential toxic elements (PTE) in fresh waters has been increasing in recent decades. Their occurrence in the environment results from different anthropogenic activities. In 2003, a major disaster occurred in the eastern Republic of Macedonia (Europe) and caused an intensive flow of tailing materials, from the Sasa Mine and through the Kamenica River Valley[1].

However, trace metals are natural constituents of lake waters and sediments, usually they occur in low concentrations. The huge expansion of human activities has acted as a trigger to environmental pollution with heavy metals, particularly mining activities. Several studies have evaluated PTE concentration in lake sediments as highly toxic and potentially dangerous for the surrounding ecosystem[2,3].

The main core of this study is to determine the spatial patterns in pollutants' concentration distribution and the associated spatial uncertainty, through a coupled multivariate statistics and stochastic simulation approach.

2. The Lake Kalimanci

Lake Kalimanci is located in the east of the Republic of Macedonia (Fig. 1 a) and b). It is an artificial lake, with its longest length 4 km and maximum width of 0.3 km and highest depth of 80 m (Fig. 1b). The surface area of the lake is about 4.23 km^2 with approximately 127 million m^3 of water[4]. The Pb–Zn Sasa mine is located approximately 12 km north. Since 1954, exploitation of the Pb–Zn Sasa Mine deposit has severely impacted the surrounding area, including Lake Kalimanci[5]. In 2003, part of the Sasa mine tailings dam collapsed and caused an intensive flow of tailings material and a consequent major impact in the surroundings of the Kalimanci Lake.



b)

a)

Fig. 1. a) Macedonia Map and Lake Kalimanci Location; b) Lake Kalimanci and sampling location.

3. Material and Methods

The samples were collected using 10 cm long plastic cores with 10 cm internal diameter and then, packed into plastic bags and stored in the laboratory at 4ºC. After dried at 50ºC for 48 h, were sieved through a 0.315 mm polyethylene sieve in order to eliminate plant debris. A mechanical agate grinder to a fine powder (<63 μm) was used for homogenization and subsequent geochemical analysis[5].

The geochemical dataset was firstly analyzed though PCA in order to reduce the space of analysis by a construction of synthesis variables (Pearson's rank correlation matrix) (Xlstat 2013.1.01 software). The purpose of PCA is to reduce data dimensionality while preserving at the same time the within variability structure (variance–covariance). The analysis begins with p random attributes X1, X2, …, Xp, where no assumption of multivariate normality is required. The axes of the constant ellipsoids correspond to the new synthesis variables, the principal components[6,7].

Geostatistical methodologies are based on the theory of regionalized variables[7] which states that attributes within an area exhibit both random and spatially structured properties[7-9]. Sample variograms should be first estimated and modeled to quantify the spatial variability of random variables as a function of their separation distance[7]. Sequential Gaussian simulation (100 runs) starts by defining the univariate distribution of values, performing a normal score transform of the original values to a standard normal distribution. Simulation of normal scores at grid node locations was done sequentially with simple kriging (SK) using the normal score variogram and a zero mean. Once all normal scores were simulated, they were back-transformed to original grade values (Space-Stat software V. 4.0.7). Standard deviation of the hundred simulations was calculated for spatial uncertainty computation.

4. Results and Conclusions

For the before dam failure characterization, was kept the second principal factor (F2) which allows to consider two major clusters: cluster 1 - Zn; Cu; Sb; Pb; Cd; Ag (F2 negative coordinates) and cluster 2 - Th; Au; Co; Sn; U (F2 positive coordinates). For the after failure dam characterization, were kept the two first principal factors, F1(positive coordinates) - cluster 1: Zn; Cu; Sb; Pb; Cd; Ag; Sn; U; and F2 (positive coordinates) - cluster 2: Th; Au; Co. It is worth notice that later on the dam's failure a cluster's reorganization can be detected. A stronger correlation between Th; Au and Co (cluster 2), with the approximation of Sn and U of the first cluster.

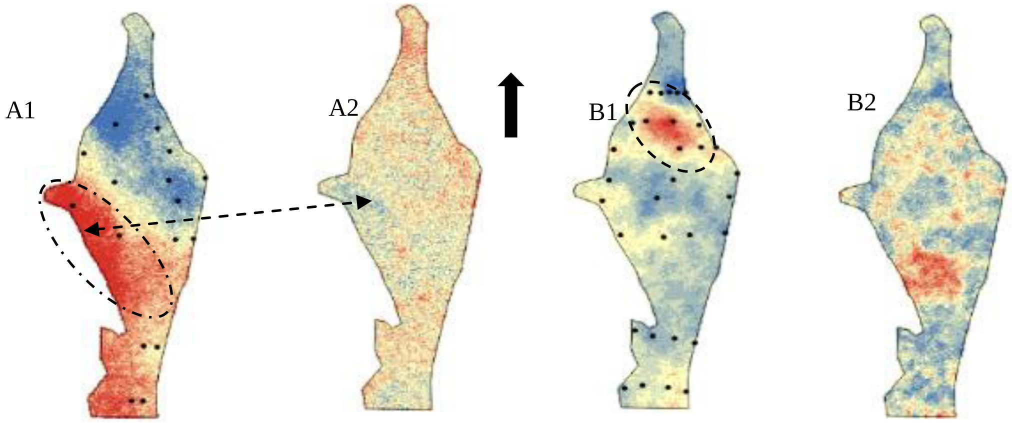
Sequential Gaussian simulation was used for conditional stochastic simulation of the Principal Factors[7-9]. F2 for the before dam failure characterization and F1 and F2 for the after dam failure characterization.

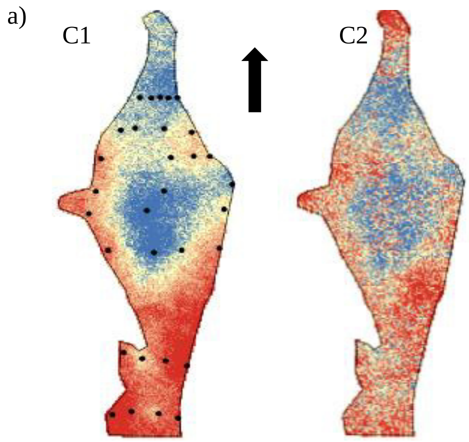
Selected results of factors' simulated realizations are shown in the hereunder fig. 2 a), b) and c). The Mean Images (MI) and associated spatial uncertainty, allows the identification of distribution spatial patterns and associated accuracy, before and after the dam failure.

Before failure, F2 pattern shows positive coordinates indicating a growing content in Th; Au; Co; Sn; U (cluster 2-red) and negative coordinates for growing content in Zn; Cu; Sb; Pb; Cd and Ag (cluster 1-blue) (Fig. 2a). The lower spatial uncertainty is overlapping the Th; Au; Co; Sn; U cluster, which leads us to conclude that a serious concentration on these elements is in need of regular monitoring.

After dam failure it is worth notice that patterns for F1 and F2 show a hot spot in Zn; Cu; Sb; Pb; Cd; Ag; Sn; U (cluster 1-red) in the northern area of the lake (Fig. 2b and c). There is a Th; Au; Co increasing content in the lake's southern part (Fig. 2c), associated with high levels of spatial uncertainty associated wish may lead to the conclusion that a new sampling campaign should be carried out with an improved sampling design.

Sn and U show a particular spatial distribution, increasing after the dam failure, in the northern area of the lake, which could be associated to a strong mobilization or other contributions that should be identified and analyzed in a future work.





c)

Fig.2. a) Before failure F2 – Positive coordinates (cluster 2-red) and negative coordinates (cluster 1-blue): A1) Mean Image; A2) Spatial Uncertainty Image (Standard Deviation – red higher uncertainty). b) After failure F1– Positive coordinates (cluster 1-red): B1) Mean Image; B2) Spatial Uncertainty Image (Standard Deviation – red higher uncertainty); c) After failure F2– Positive coordinates (cluster2-red): C1) Mean Image; C2) Spatial Uncertainty Image (Standard Deviation – red higher uncertainty).

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