

Assessment of the relationship between the concentration of arsenic and the physicochemical parameters of groundwater in a river floodplain affected by metal ore mining

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Introduction

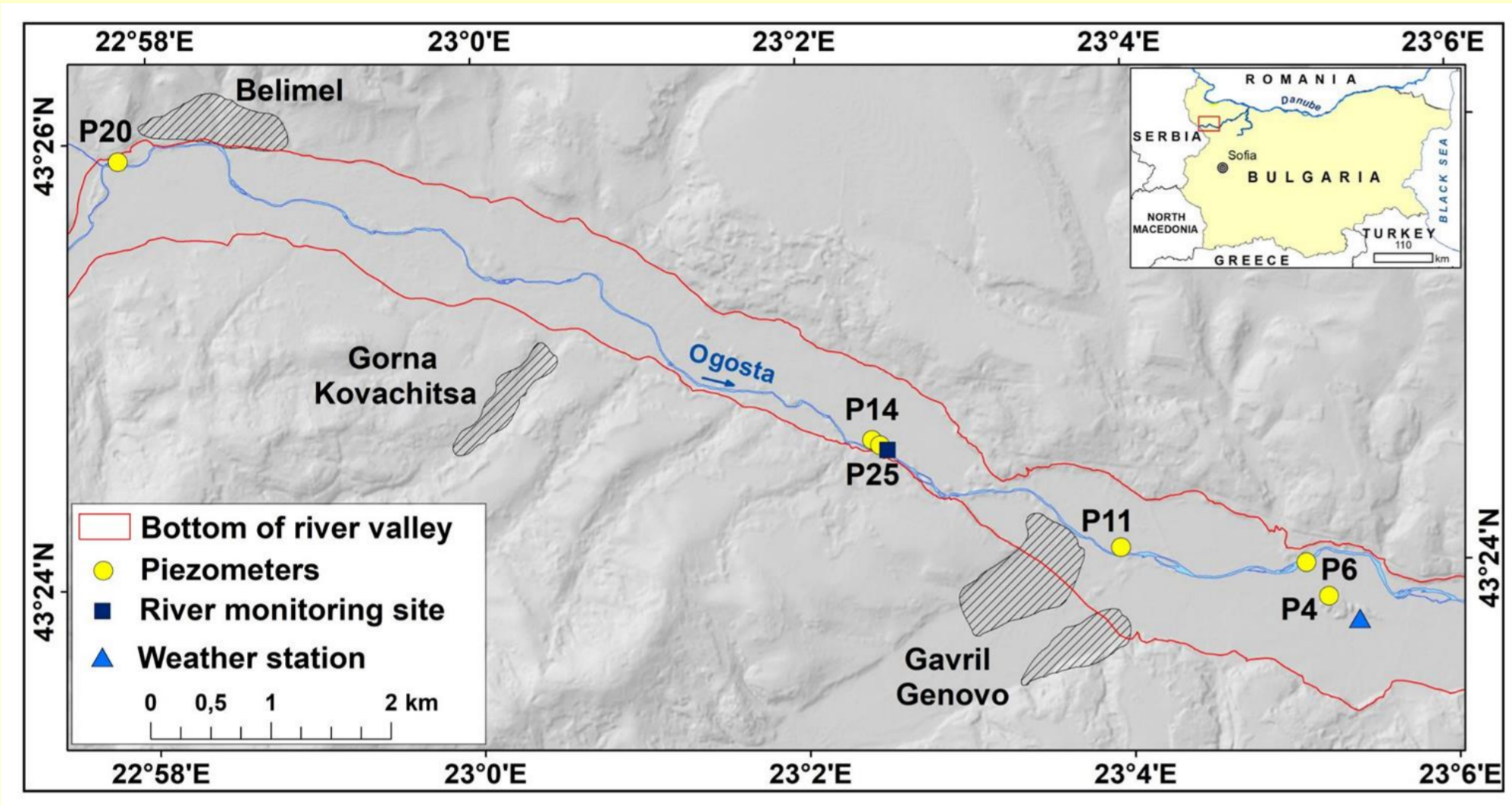
The riverine environment in mining areas is often subject to the accumulation of arsenic (As) in the soil due to the deposition of contaminated sediments during river floods. Shallow aquifers of the affected river floodplains are highly vulnerable to pollution where As concentration in groundwater may vary widely as a result of the interactions within the system soil-aquifer-river. We studied As dynamics in the groundwater in the Ogosta River valley which was severely contaminated by the historic ore-mining in the vicinity of the town of Chiprovtsi, NW Bulgaria. The research aimed at elaboration of a regression model of As concentration in the groundwater using data from field studies.

Methods

We collected 80 groundwater samples from 6 piezometers in the period 2016-2020. The piezometers are installed in the low floodplain which is 1-2 m above the bottom of the Ogosta River. The average distance between the groundwater monitoring sites and the riverbank is 13.4 m.

We used multimeter KLL-Q (Seba Hydrometrie) to determine the physicochemical characteristics of water. An automatic weather station measured the air temperature and rainfall in the Ogosta Valley next to the monitoring sites. Water samples were passed through 0,22-micrometer cellulose acetate membrane filters, and transported and stored at a temperature near 4 °C. The concentration of As in water was measured with ICP-MS.

We applied linear regression for logarithmic values of As concentrations [µg/l] with the following predictors: sample site (categorical parameter); river water level, groundwater level, water temperature, electric conductivity, pH, redox potential, dissolved oxygen, and monthly precipitation. The optimised model is obtained by forward and backward stepwise procedures using separately F-ratio and AIC criteria.



Results

Concentrations of As show distinct seasonal dynamics with peaks at the end of winter and during the autumn when the river stages are often at a high level. The minimum is usually in the summer and in January when the river water level is lower. Arsenic tends to increase in the groundwater right after high flow events and this causes higher variability of As concentrations in months like March and December. The measured parameters of river water and groundwater characterise the change of water inflow in the piezometers from the river and floodplain which carry different amounts of soluble arsenic.

The obtained regression model is in good agreement with the measured As concentration in water (R-square of 0.8993). The most important predictor is the sample site, which reflects the different level of soil contamination at the monitoring points. The river water level is the second important factor in the model and it can be considered the main driver of As dynamics in groundwater.

Table 1. Presumed relationship of the predictors with the concentration of arsenic in groundwater

Predictor	As increases when	Physical connection
Sample site		Reflects the spatial variability of soil contamination and environmental settings among the sample sites
River water level	the predictor is increasing	Raised river stages cause an uprise of the groundwater table
Groundwater level	the predictor is increasing	When groundwater table goes up it gets into contact with more contaminated soil layers
Electric conductivity (EC)	the predictor is increasing	Decrease of EC indicates infiltration in the aquifer of river water which has less As content than groundwater
Dissolved oxygen	the predictor is increasing	Still not clear
Redox potential (ORP)	the predictor is decreasing	Decrease of ORP favours reducing of As (V) species to the more soluble As (III) species
Water temperature	the predictor is increasing	Increased temperature intensifies the microbiological reduction of As species
Monthly rainfall	the predictor is decreasing	Rainfall facilitates the transport of As from contaminated soil to groundwater and raises the river water level

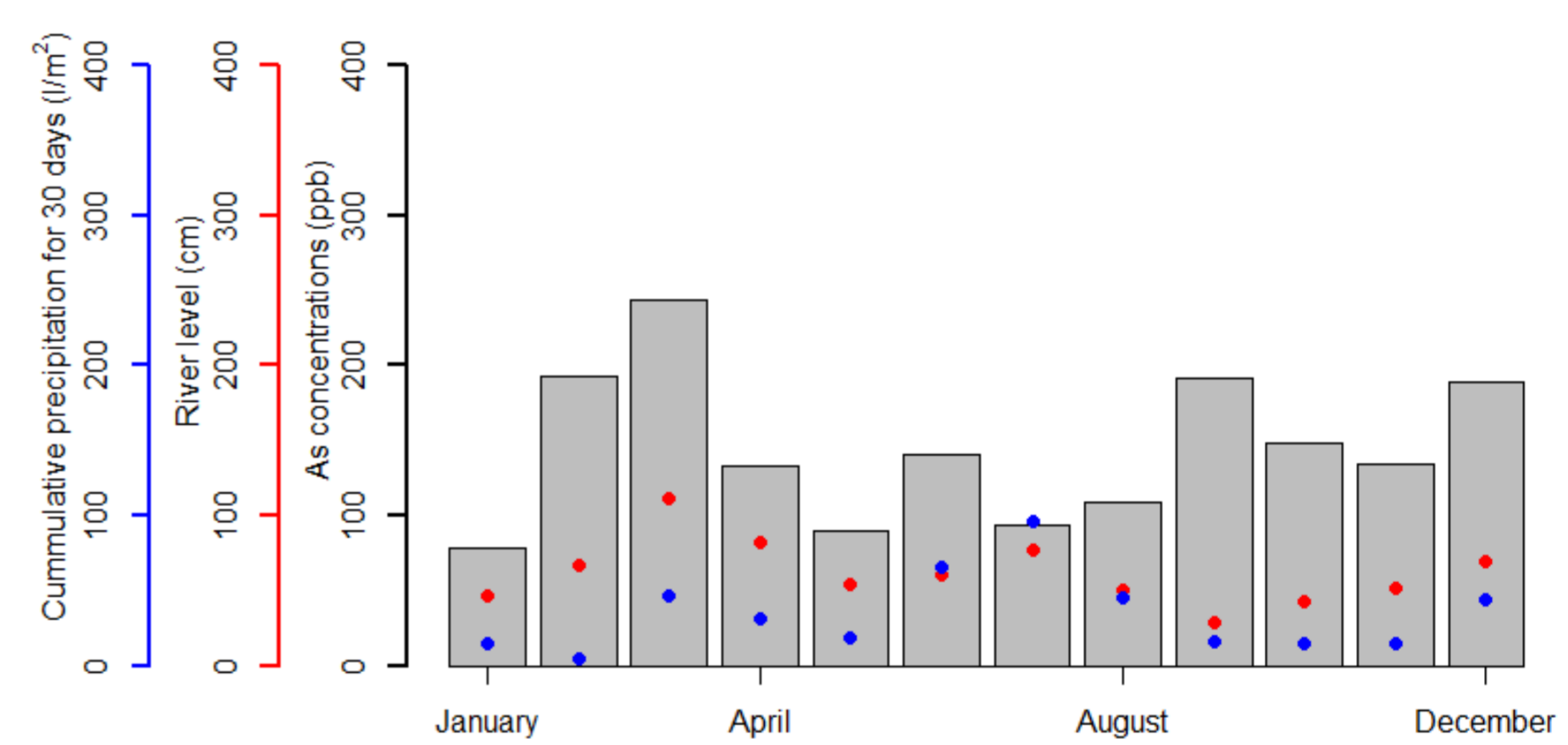


Fig.1. Seasonal distribution of soluble As in groundwater

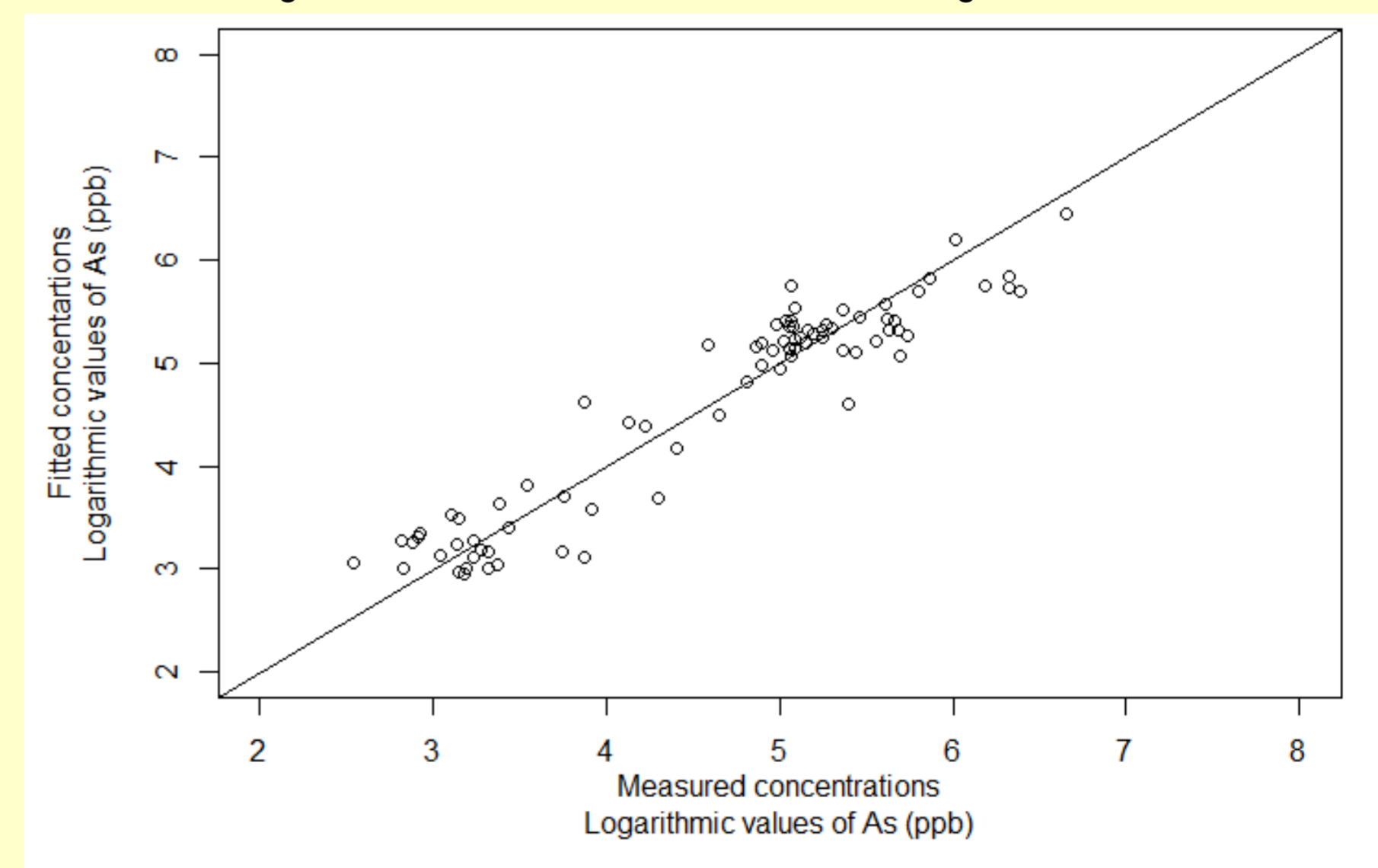


Fig.2. Correlation between measured and fitted concentrations of As in groundwater

Conclusion

The results show that physicochemical parameters which are common for water quality monitoring can be used for predicting the concentration of As in groundwater of metal-contaminated river floodplains. The river water level is found to be one of the most explanatory factors in the regression model. Special attention should be paid to river high flow events when peak concentrations of As are likely to be registered in the contaminated aquifers. Therefore, samplings of groundwater at high river stages need to be envisaged in the groundwater monitoring programmes executed in mining-affected river valleys.

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