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Trace metal concentrations of water, paddy soil and rice of the Kočani field (Eastern Macedonia) due to base metal mining activities

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Heavy metal pollution from current and past mining is a significant problem in eastern Macedonia. The present study is aimed at measuring heavy metal concentrations of paddy soil, rice and waters of the Kočani Field impacted by heavy metals because of mining activities and acid mine drainage from the Zletovo-Kratovo

and Sasa-Toranica Pb-Zn ore district.

The analytical results obtained with the ICP-MS and ICP-AES methods revealed the heavy metal contamination of paddy soil from the western part of the Kočani Field due to the irrigation of acid mine drainage impacted riverine water from the river Zletovska. Repeated water sampling suggested marked chemical variations of Pb (10

 $24~\mu g/L), Zn~(101$ - $1250~\mu g/L), Cu~(6$ - $10~\mu g/L), As~(1.7$ - $2,5~\mu g/L)$ and Cd(0.5 - $5.0~\mu g/L)$ which can be explained by water-flow conditions and variable degrees of mine adits from Zletovo mine and the tailing dam leaching effluent inputs into the riverine water.

About 15% of paddy soil in the vicinity of the river Zletovska has highly elevated concentrations of Pb (994 mg/kg), Zn (1250 mg/kg), As (48 mg/kg) and Cd (6.8 mg/kg), which are far above the critical values for these metals reported by various environmental protection agencies. The paddy soil also exhibited elevated levels of Ba, Th,

U, V, W, Mo, Cu, Sb, Bi, Ag, Au, Hg and Tl, with concentrations above their median concentration values obtained during this study. Correlation matrix, R-mode factor analyses and XRD data revealed that these metals in the paddy soil were largely associated with Mn and Fe oxides/hydroxides. The rice contaminant concentrations of Pb, Zn and As are of lesser importance because their content in unpolished rice is usually lower than the limit level in food. The only exception is Cd, which attained, in about 10% of the rice samples, concentrations up to 0.21 mg/kg, which are higher than the limit level in food (0.1 mg/kg). The measured concentrations are, however, still below the range of the permissible levels reported for unpolished rice from most Asian governments (0.4 - 1.0 mg/kg). Taking into the account that very high concentrations of Pb, Zn, As and Cd in paddy soil and the elevated Cd level in rice could pose a problem for human health, a further study including monitoring the pollution of irrigating water and soil together with studies of the heavy metal mobility and bioavailability is needed.