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# ACID MINE DRAINAGE SYSTEMS AND METAL POLLUTION AROUND THE ACTIVE POLYMETALLIC MINES IN THE EASTERN MACEDONIA

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A b s t r a c t: The study of acid mine waters and drainage systems of certain polymetallic and active mines in the Eastern Macedonia have shown that pH values are in the range 4.0÷7.8 in the Bučim porphyry Cu-deposit, 4.8÷5.1 in Pb-Zn mines Sasa and Toranica, and 3.4÷5.1 in the Zletovo Pb-Zn mine. Both the underground and open pit mines drainage systems on a vertical scale are of several hundreds of meters (from surface to depth) and are affecting the adjacent waters with heavy metals. Determined metal concentrations in the polluted mine waters from the Pb-Zn mines in Macedonia were in the range: 10÷1340 μg/l Pb, 40÷70070 μg/l Zn, 1÷240 μg/l Cd. Also, increased concentrations were determined for Ag, Fe, Al, Ca, Bi, Sb etc. In the copper mine waters were determined heavily increased concentrations of 4÷509838 μg/l Cu, 25÷300 μg/l Ag, 4÷4890 μg/l Co and increased concentrations of Fe, Ni, Cr, As, etc. In general, metal concentrations decreased downstream from the source due to dilution from other rivers and co-precipitation of metals on other mineral phases.

**Key words:** drainage system; metal pollution; mine waters; Macedonia

## INTRODUCTION

The modern metal mining activity in the Republic of Macedonia have started in 1939. The main activities were performed at the underground Pb-Zn mines (Zletovo, Sasa and Toranica). In 1979 has been started copper production from the open pit of the Cu-porphyry Bučim Mine. During the decades of intensive mining the impact of polluted mine waters on the environment has increased and the long term environmental concern in form of acid mine drainage have arised. Acid mine drainage as a process refers to waters that have leached through mine sites and have dangerously low pH values and high metal contents (Younger, 2002). The acid mine drainage has the most potential to affect water quality in the downstream agricultural areas of the Kamenica Valley, Zletovo Valley, Kriva Reka and Madenska Reka. The polluted mine waters from Pb-Zn mines are coming out from the main adits, usually at the lowest levels and direct conection with the surface. Polluted water from the open pit Cu-mine is a product of the tailing dam, waste dump and water pumped out from the pit.

## POLLUTION SOURCES

The most important Macedonian metal deposits are related to regional magmatic activity that occurred in the southern parts of the Carpatho-Balkanides during Eocene-Pliocene (Serafimovski and Alexandrov, 1995).

Water pollution is still a serious problem, since wastewater generated in ore processing and discharge seeping from tailings deposits receive no treatment at all (Alderton et al., 2005, Serafimovski, 2006).

In that context we have studied four separate mines and its adjacent areas (Fig. 1): Zletovo, Sasa, Toranica and Bučim.

*The Zletovo Mine* is located near the town of Probištip in NE-Macedonia. The mine production lasted from 1940 until 2003.

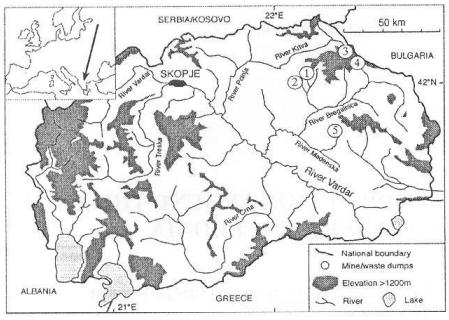


**Fig. 1.** Map of the R. Macedonia with major rivers and mining locations used in this study. 1 – Zletovo Mine, 2 – Zletovo (tailings dam), 3 – Toranica Mine, 4 – Sasa Mine, 5 – Bučim Cu-mine (*Alderton et al., 2005*)

The mineralization is related to Tertiary calc-alkaline magmatic rocks (dacites and andesites) and it is found in a dacitic volcano-sedimentary suite that has been altered to clays and micas. Ore bodies are located in sub-vertical veins. The main ore minerals are galena and sphalerite, but tetrahedrite, pyrrhotite, chalcopyrite and pyrite are also common. Annual production reached 300,000 t, with ore grades of 8.5 % Pb+Zn and significant concentrations of Ag, Bi, Cd and Cu. Ore was concentrated by flotation at Probištip and tailings were disposed of in two impoundments situated in adjacent valleys. The river of Kiselica drains the flotation plant at Probištip and the river of Reko drains the area containing the main workings of the Zletovo mine (locations 1 and 2 in Fig. 1).

*The Sasa Mine* is situated in NE-Macedonia near the city of Kamenica. The mine has been in production since 1962, yielding about 500,000 t of Pb–Zn ore annually. Mineralization is localized along the contacts between Miocene calc-alkaline igneous bodies (latites and dacites) and graphite-chlorite-sericite schists, gneisses, and limestones. The ore consists of pyrite, galena, and sphalerite, with additional magnetite and chalcopyrite. Ore grades are about 10% Pb+Zn with additional elevated concentrations of Ag, As, Cd, Mn, and Sb. Ore is concentrated at the mine by flotation and tailings are stored in a dam in a valley just below the mine. The Kamenica River is culverted beneath the tailings dam and flows 12 km until it meets the Kalimanci Lake near Kamenica.

*The Toranica Mine* is situated in NE-Macedonia, close to the Sasa deposit, but in a separate watershed. The Pb–Zn production from the mine occurred between 1987 and 2000, reaching total amount of ~$3 \times 10^6$ t excavated ore with an average contents of 6.5 % Pb+Zn. The deposit is geologically similar to Sasa. There are elevated concentrations of Cd, Cu, Mn, Ag, and Bi in the ore. Milling and flotation occurred at the mine and there is a tailings dam below the mine site with a culvert directing the Toranica River beneath the dam.

*The Buchim Cu-Mine* is situated in eastern parts of the Macedonia near the city of Radoviš. The Cu–Au production from this Cu-porphyry type of mineralization is active in the last 28 years and during that period were excavated ~ $70 \times 10^6$ t ore with average contents of 0.3 % Cu and 0.3 g/t Au. The deposit is located in the Precambrian gneisses around the Tertiary volcanic dykes. Ore reserves has been estimated to $120 \times 10^6$ t. Near the mine there is a tailling dam where has been deposited $70 \times 10^6$ t of material and waste dump with more than $100 \times 10^6$ t material. The milling and flotation discharge their drainage waters in the Madenska and Kriva Lakavica Rivers.

## MATERIALS AND METHODS

Sampling at Sasa, Zletovo and Bučim took place when the mines were operating and at Toranica the mine had ceased all activities. At each location, streams were sampled downstream as well as upstream of the mining sites to assess the contributions to the drainage from the mining activities. Collected water was passed through a 0.45 $\mu$m filter and transferred into polythene tubes and acidified with 0.4 ml of 50% nitric acid. Conductivity and pH were measured in the field for all water samples. Solutions were analyzed by ICP-AES or ICP-MS, depending on concentrations. A large number of analyses were determined but only those that are likely mining related and environmentally significant are discussed here. The concentrations were compared to reference standards to assess their significance (Mirsal, 2004).

## RESULTS AND INTERPRETATION

Several adits at the *Zletovo mine* contribute significantly to the Reko River. Water from the main adit is turbid with a pale brown colour, and flows directly into the Reko (Fig. 2). Concentrations

exceed water standards for most analytes and the pH of the discharge is low, at 3.4.

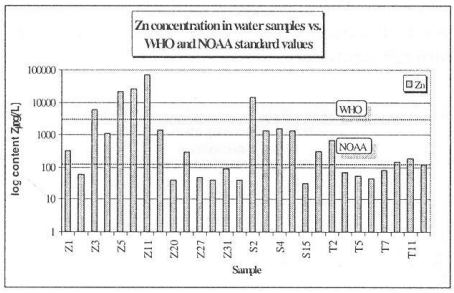


**Fig. 2.** Zn contents (µg/L) in waters samples from all Pb–Zn mines in Macedonia vs. WHO and NOAA standards. On *x*-axis: Z – Zletovo; S – Sasa and T – Toranica

Further downstream, concentrations of Al, Fe, Mn, Cd, Zn, and U are all grossly elevated above fresh and drinking water standards. For example, the Zn concentrations reach 70 mg/L. High values are maintained until approximately 3 km below the mine area, and then dilution reduces the concentrations markedly. Further downstream, the waters are diluted by non-contaminated waters in the river of Zletovska. Concentrations of metals are generally low and the water is alkaline all the way down to the confluence with the river Bregalnica, where the levels of some metals (e.g. Cu) increase.

Although in the *Sasa mine* there is some indication that the waters bellow the main mine workings have elevated levels for some metals, the water contaminant concentrations are not particularly elevated. The river waters are mostly near neutral, with the water discharging from only one of the main adits being slightly acid (pH = 5). This water is dark grey, due to transported sulfide particles, and has elevated concentrations of (µg/L): Al 9490, Cd 90 mg, Pb 1340, and Zn 14330. Most values decrease quite rapidly downstream, but concentrations of Mn and Zn remain high for at least 8 km downstream from the mine.

*Toranica* mining and processing facilities have had a major effect on the chemical composition of neighbour water flows. Waters from the Toranica area, in general, have a neutral pH and solute contents are fairly low. Elevated values for As, Bi, Pb, U, and Zn occur in the vicinity of the mining area but rarely exceed reference limits. High values for some elements (e.g. Co, Fe, Mn, Pb, Zn) in waters above the adit discharges suggest that more mineralization is present in bedrock upstream of the mine workings and that these values are thus representative of the regional geochemical background.

*Bučim* mining and processing facilities have had a major effect on the chemical composition of the neighbour river waters. Water concentrations of Cu, Al, Mo, Ni, Cd, Co, As and U are high in the stream that carries effluent from the mine and processing plant (Fig. 3).

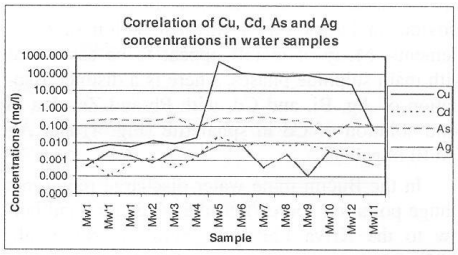


**Fig. 3.** Correlation of Cu, Cd, As and Ag concentrations in waters samples from the Bučim Cu-mine along the water flow

The pH ranged from acidic to slightly neutral. The deterioration of water quality downstream of the mine water input is massive. The pH of the water above the pollutant input is neutral and water concentrations of metals are within background values. Immediately downstream, the pH falls within the range 4.2÷5.3 and the concentration of Cu reaches upto 509,838 µg $l^{-1}$. Water quality does improve further downstream (Fig. 3), however copper concentrations are still well above fresh water averages and conductivity remains high.

## DISCUSSION

The composition of the mining associated waters is quite variable. However, and in spite of the dilution effects of melting snow on the river volumes, the effects of mining and mineralization can be detected in all the waters studied. In particular, waters from the active and recently-worked Pb-Zn and Cu mines have very high concentrations of dissolved metals, derived either from dissolution of 'ore' minerals or host rocks (Serafimovski et al., 2004; Turekian, 1977).

The waters at Zletovo have a low pH, no doubt due to the dissolution of pyrite. Sulphate, Mn, Zn, and Fe are all very elevated. The host lithology is dominated by silicate minerals and so there is little chemical buffering to counteract the acidity.

The mines at Toranica and Sasa have exploited similar Pb- and Zn-rich minerals to those at Zletovo, and associated river sediments are contaminated. However, the water contamination at these two localities is small compared to that at Zletevo. There appears to be a moderate but restricted acid mine drainage problem at Sasa, where the lower pH has mobilized some ore-related elements. This problem is most severe near the adit, but concentrations fall to background values downstream of Kalimanci Lake (Dolenec et al., 2007). Reduced drainage acidity and dissolved solids are probably due to the lower volumes of pyrite in the ore and buffering by the host limestones. Elevated element concentrations are clearly a consequence of mineral dissolution and strong element correlations provide an indication of the association of these elements. Many of metals appear to be associated with main sulphide phases. There is a distinct association of Ag, Bi, and Cd, with Pb and Zn, due to solid solution of Cd in sphalerite (Fig. 4) and Ag and Bi in galena.

In the Bučim mine water discharge represents a huge pollution source into the Madenska and bellow to the Kriva Lakavica (Serafimovski et al., 2005). River due to dillution and leaching of metals found in the mineral association and adjacent rocks (Cu, Co, Cd, Ag, etc.). Another problem with the open pit is the evaporation of ponded water in the pit, which significantly concentrate metal content and rendering it more harmful to downstream environments. The formation of soluble secondary salts due to the evaporation of pit waters is also a concern (Eichenberger, 1986).

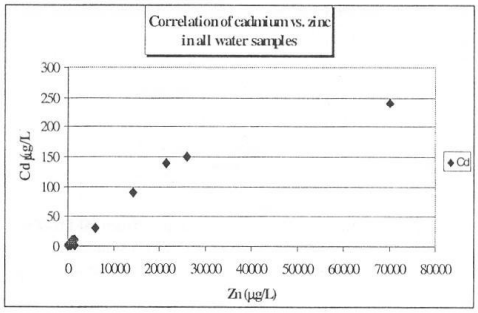


**Fig. 4.** Correlation of Cd vs. Zn (correlation factor 0.959) in all water samples from Pb-Zn mines

Decreases in concentration of elements downstream and further away from the mining regions can be explained by a combination of dilution from non-contaminated rivers and removal from solution due to co-precipitation and adsorption on various solid phases in the sediments. These phases are likely to include oxides/hydroxides of Al, Fe, and Mn. Predicted pH control on Fe, Al, Mn precipitation can be demonstrated to be in operation here.

## CONCLUSION

Contamination of water was high in the immediate vicinity of the mine sites but was reduced to near background levels at distances of 5–25 km from the mines. The tailings dams are a major potential source of water pollution; however, the use of culverts to direct water away from the tailings generally seems to be quite successful and largely prevents the ingress of polluted water to the streams.

Water contamination was often only moderate, such as at Sasa and Toranica, where the lack of pyrite and buffering by limestone keep metal concentrations low. In contrast, due to high presence of sulphides (pyrite) and its oxidation the waters associated with the Zletovo and Bučim deposits were acidic and highly contaminated with several metals.

The elevated concentrations of metals found in these waters can be related to the mineralogy of the individual deposits and metallic sulphides are the main primary source of the metals. Mine drainage commonly has a lower pH than background waters and the increased acidity has initiated metal dissolution. Mining and processing activities in Macedonia have therefore had an adverse impact on the environment.

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Резиме

## КИСЕЛИ РУДНИЧКИ ДРЕНАЖНИ СИСТЕМИ И ЗАГАДУВАЊЕ СО МЕТАЛИ ОКОЛУ АКТИВНИТЕ ПОЛИМЕТАЛИЧНИ РУДНИЦИ ВО ИСТОЧНА МАКЕДОНИЈА

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**Клучни зборови:** дренажен систем; загадување со метали; руднички води; Македонија

Проучувањето на киселите руднички води и дренажни системи на одредени полиметалични и активни рудници во источна Македонија покажа дека pH-вредностите се во опсег од 4.0 до 7.8 во порфирското Cu-наоѓалиште Бучим, 4.8÷5.1 во Pb-Zn-рудници Саса и Тораница и од 3.4 до 5.1 во Pb-Zn-рудникот Злетово. Дренажните системи и на подземните и на површинските рудници на вертикална скала се движат до неколку стотини метри (од површина до длабочина) и влијаат врз соседните води со тешките метали.

Одредените концентрации на метали во загадените руднички води од рудниците за олово и цинк во Македонија се во опсегот: од 10 до 1340 μg/l Pb, од 40 до 70070 μg/l Zn, од 1 до 240 μg/l Cd. Исто така, одредени се и зголемени концентрации на Ag, Fe, Al, Ca, Bi, Sb и др. Во рудникот за бакар во водите беа одредени силно зголемени концентрации на Cu од 4 до 509838 μg/l, од 25 до 300 μg/l Ag, од 4 до 4890 μg/l Co и зголемени концентрации на Fe, Ni, Cr, As и др. Концентрациите на металите се намалуваат надолу по течението на реките со оддалеченоста од изворите на загадување, како последица на разблажувањето од други реки и копреципитација на металите во други минерални фази.