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Assessment of past and present water quality in closed Mežica Pb-Zn Mine (Slovenia)

Avaliação da qualidade da água no passado e no presente na mina fechada de Mežica (Pb-Zn) na Eslovénia

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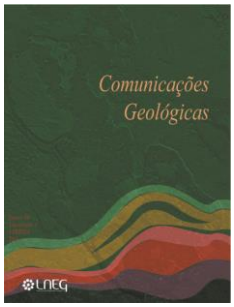

Artigo original
Original article

Abstract: Mežica lead and zinc closed mine, where mining lasted for more than 350 years, is located in Mežica valley with prevailing carbonate rocks. Waste material was deposited on more than 30 locations and treatment of the tailings was done together with flooding the mine with flotation silt in 90's. Concentration of Zn and Pb were the most problematic issue in water resources. The main objective of this study was to determine if water quality through time has changed. Complete chemical analyses were performed for major cations and anions and, in some samples, for trace metals of surface and groundwater. Results showed that water quality has improved. Concentration of Pb and Zn on measured sampling points in surface water lowered through time. Measured values of Electrical Conductivity and pH show stabilization after first years of mine flooding, and nowadays mine water can be used as drinking water from a trace metals point of view.

Keywords: Mežica mine, water quality, lead and zinc, saturation indices.

Resumo: A mina fechada de Mežica, onde a exploração de Pb e Zn durou mais de 350 anos, está localizada no vale Mežica onde predominam rochas carbonatadas. O material residual foi depositado em mais de 30 locais. Nos anos 90 a mina foi inundada com material siltoso resultante do processo de flotação. A elevada concentração de Zn e Pb registada nas águas superficiais e subterrâneas tem sido o aspeto mais problemático observado no local em estudo. O principal objetivo deste estudo é determinar se a qualidade da água sofreu alterações significativas ao longo do tempo. Os resultados das análises químicas de águas superficiais e subterrâneas (iões maiores e elementos traço) mostraram uma melhoria da qualidade da água. A concentração de Pb e Zn nas amostras de água analisadas é diminui ao longo do tempo. Os valores da Condutividade Elétrica e do pH mostram estabilização após os primeiros anos depois da inundação da mina. Com base nos dados analíticos obtidos verifica-se que atualmente a água é potável relativamente aos elementos traço.

Palavras-chave: Mina de Mežica, qualidade da água, Pb e Zn, índices de saturação.

1. Introduction

Impact of abandoned mines has great consequences on environment. Mežica lead and zinc closed mine is located in Mežica valley in northern part of Slovenia, through which flows Meža river. Mining in Mežica started in Roman times and lasted for more than 350 years (Uran *et al.*, 1965; Gosar & Miler, 2009). In 1994 the production was stopped and closing of mine with flooding of the lower shafts began (Fajmut Štrucl, 2005). Data from Prestor *et al.* (2003) and Dervarič *et al.* (2005) show that around 360000 m^3 of flotation silt was loaded in mine shafts, which were flooded and water level was risen from +268 m a.s.l. to +413 m a.s.l..

Mining activity left behind tailings and waste deposits in more than 30 locations (Miler and Gosar, 2011). Previous studies about sediments of Meža river shows high pollution with trace metals, because of leaching of flotation silt (Stopar, 2004). At the end of 20th century Meža river was known as one of the most polluted stream with heavy metals in Slovenia (Lapajne *et al.*, 1999). The highest values of Cd, Pb and Zn, were found in the sediment of Helena rivulet and on 2 locations on Meža river (Svete *et al.*, 2001). Druks *et al.* (2002) showed that concentration of heavy metals in surface water exceeded the allowed limit value in Helena stream and based on sediments results in river Meža and its tributaries, the influence of mining activity was still present in 2002. Later researches carried out by Fux (2007) put on evidence that sediments on Meža and its tributaries are still highly polluted with heavy metals, especially near the locations of former mining and smelting activity. Waste deposits along the stream, can be washed and cause leaching of toxic metals into stream, causing higher concentrations of trace metals in Meža river and its tributaries that directly drained these mine waste deposits (Gosar and Miler, 2011).

2. Study area

Mežica ore deposit is classified as a Mississippi Valey-type where the Pb and Zn are transported by hydrothermal fluids through major geological fractures (Gosar and Miler, 2011). This Pb and Zn bearing fluids circulated through geological fractures during the later phase of diagenesis and dolomitization process and then precipitated (Rečnik, 2010). The main ore minerals in Mežica mine are galena (PbS) and sphalerite (ZnS) and also secondary oxide and sulfide minerals, such as, limonite

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($FeO(OH)$), cerrusite ($PbCO_3$) and wulfenite ($PbMoO_4$) (Gosar and Miler, 2011).

Mežica valley, where Pb/Zn mine is located, lies between Uršlja Mountain and Peca, and covers the entire area from the source to the mouth of the river Meža to Drava, in the northern part of Slovenia. Valley has an Alpine character, with common temperature inversion and greater amount of precipitation in Spring and Autumn (Memić, 2006). Mean annual precipitation is 1178mm and was calculated based on data from local climatological stations between 1961/62 to 2013/14.

The main objectives of the present study were (a) to determine concentrations of heavy metals, pH and electrical conductivity (EC) in Meža river and its tributaries and also in mine groundwater (b) to identify temporal changes of EC, pH and heavy metals concentration and compare with previous studies, (c) to evaluate if water quality has improved through time and (d) to determine water saturation state in relation to mineral phases and predict conditions for mineral precipitation/dissolution.

3. Materials and methods

Water sampling points from Meža river and its tributaries (1V - 12V), together with sampling points from mine groundwater (1M - 4M) are presented in figure 1.

Chemical parameters (pH, EC and T) of surface water samples (2V, 5V and 12V) and also mine groundwater samples (1M - 4M) were measured on site with a portable multimeter WTW Multi 340i. Water samples were collected into 1L polyethylene bottles. Samples were filtered only in the moment of sample analyze for major ions in the Laboratory of Karst Research Institute. Samples 2V, 5V and 12V were also prepared for further analyses of major ions and trace elements. For cations and trace elements water samples were filtered in situ through a disposable disk filter of cellulose acetate membrane with a pore size of 0.40 µm. After filtration into polyethylene bottles, samples were immediately acidified at 2% HCl. These 3 samples were taken back to Portugal to the Laboratory of the LNEG in Porto and analyzed for Cl^-, NO_3^- and SO_4^{2-}, by ion chromatography, for bicarbonate by titration, and for major cations and trace elements by ICP-MS.

4. Results and discussion

4.1 Surface water

In 2002 analyses of surface water by Druks *et al.* (2002) on 12 sampling points (1V-12V on figure 1) were done. According to this study EC ranged from 98 µS/cm upstream the mine (1V) to 467 µS/cm at Helena stream (5V) and pH between 7.2 (6V) to

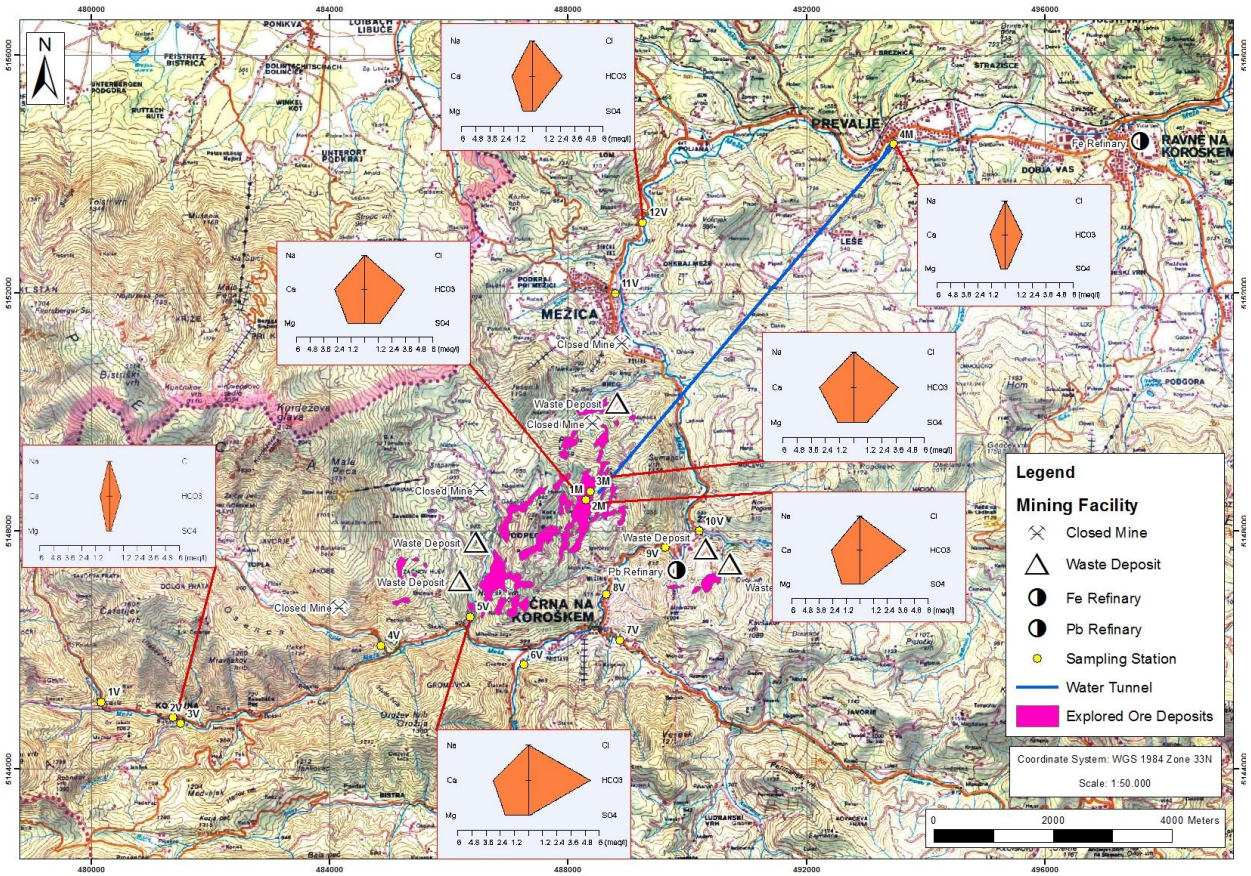

Fig. 1. Map showing the location of sampling points of Meža river and its tributaries (1V-12V) and of mine groundwater samples (1M-4M). Stiff diagrams from analyzed samples.

Fig. 1. Mapa com a localização dos pontos de amostragem no Rio Meza e tributários (1V-12V) e das amostras de águas subterrâneas da mina (1M-4M). Diagramas de Stiff das amostras analizadas.

8.3 (12V).

Three of these samples (2V, 5V and 12V) were analyzed again in 2015. Sample 2V represents Meža river before Janšek stream, background area. Around 5600 m downstream sample 5V is located (Helena stream) and around 14000 m further sampling point 12V (Meža after Šumc), which lies downstream after mine. Values of pH and EC through time are presented in table 1.

Table 1. EC and pH values through time.

Tabela 1. Valores da CE e do pH ao longo do tempo.

		Jan 93	Mar 02	May 02	June 02	July 02	Mar 15
2V	EC	/	112	124	139	130	119
	pH	/	8.0	7.7	7.5	7.4	7.7
5V	EC	435	298	340	391	345	467
	pH	7.7	7.7	7.4	7.3	7.8	8.3
12V	EC	/	308	317	360	358	272
	pH	/	8.3	7.9	7.7	7.6	8.1

According to the results, it's clear that pH values are alkaline throughout the whole time period and rising to values around 8. Background values of EC (on 2V) are about 100 µS/cm, and almost didn't change through time. Near Helena stream influence (5V) EC raised to about 400 µS/cm in recent years and is close to previous values of 1993, but downstream, after a period of smooth variation (300 to 350 µS/cm), now is lower than before (about 270 µS/cm).

Results plotted in Stiff diagrams (Fig. 1) point to Ca-(Mg)-HCO_3 facies, what is in agreement with water interaction with outcropping limestones and dolomites.

Figure 2 shows that the concentration of heavy metals in 2015, on 2V, 5V and 12V sampling points slightly fluctuate, but do not exceed any of the limit values in legislation (Pravilnik, 2004).

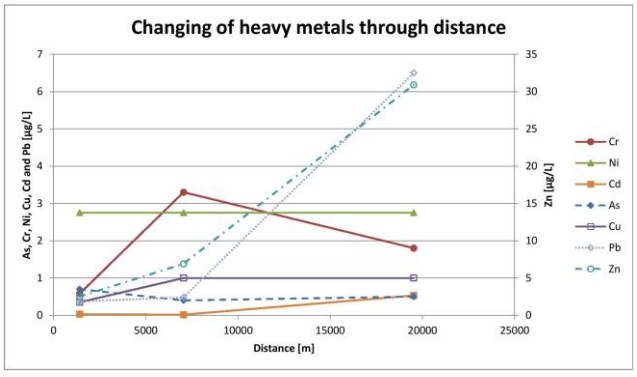

Fig. 2. Concentration of heavy metals in surface water with distance downstream mine, in 2015.

Fig. 2. Concentração de metais na água superficial a jusante da mina, em 2015.

Concentrations of Cr, Cu, Pb and Zn slightly increase on sampling point 5V (Helena stream) probably due to the presence of waste deposits. At 12V (downstream) the Cd, Pb and Zn concentrations slightly increase due to mining wastes, but most probably due to the presence of batteries factory and other metallurgic industry in this area.

Looking to the 2 main problematic trace metals in the area - Pb (Fig. 3), and Zn (Fig. 4) - it´s evident that background values of the region are quite low (2V). After a period of high concentration (reaching more than 200 µg/L of Zn in 2002, and about 90 µg/L of Pb, at Helena stream, 5V) at present time concentration of Zn and Pb are close to background values.

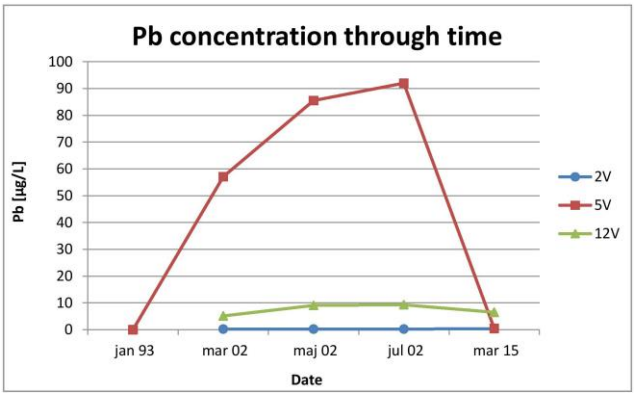

Fig. 3. Pb concentration in surface water samples.

Fig. 3. Concentração de Pb nas amostras de água superficial.

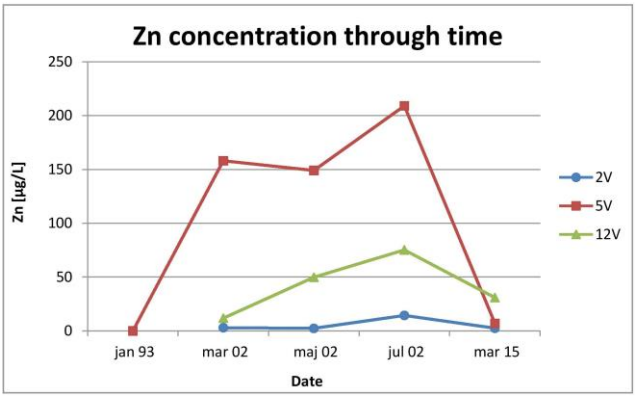

Fig. 4. Zn concentration in surface water samples.

Fig. 4. Concentração de Zn nas amostras de água superficial.

4.2 Groundwater

Before flooding, the mine sources of drinking water were captured and isolated in Union (1M) and Moring (2M) on +300m level, and on Union on 13th horizon on +417m (3M) (Uršič, 2005). After mine was flooded, in 1994, monitoring about water quality was done. Values of pH and EC for 3M groundwater sample, between 1995-2015 (Fig.5), show that in the first years after flooding, values started to decrease and stabilized. The decrease in pH for 2005/06 can be related with the decrease in recharge of the region, since it was a dry year, and with a higher contribution of the acid mine water.

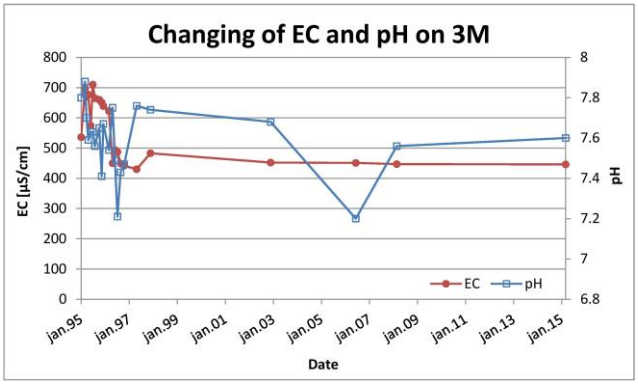

Fig. 5. Changing of EC and pH values through time in groundwater from Union on 13th horizon +417 m (3M).

Fig. 5. Variação da EC e do pH, ao longo do tempo, na água subterrânea de Union no 13º horizonte +417 m (3M).

Heavy metal concentrations, in first years after flooding, were high and with time they started to lower (Prestor *et al*., 2003); from 1995 to 1997 concentration of Pb (Fig. 6) still exceeded the limit value for drinking water (10 µg/L); after 1997 to 2008 concentrations were below the established limit. In first half of 1995 Zn values (Fig. 7) exceeded 1000 µg/L, but in second half the values were below 700 µg/L. From 1996 until 2008 Zn values were around 300 µg/L, or less. Zinc is an essential trace element and limit value for drinking water is not determined with legislation, however according to WHO (2011) Zn concentrations above 3000 µg/L may not be acceptable.

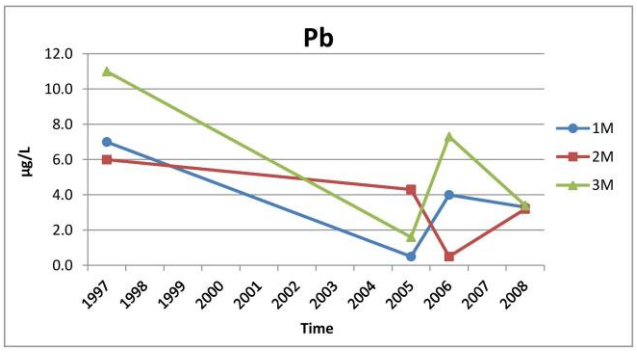

Fig. 6. Changing of Pb concentration with time in groundwater from Union (1M), Moring (2M), and Union on 13th horizon (3M).

Fig. 6. Variação da concentração em Pb, ao longo do tempo, na água subterrânea de Union (1M), Moring (2M) e Union no 13º horizonte (3M).

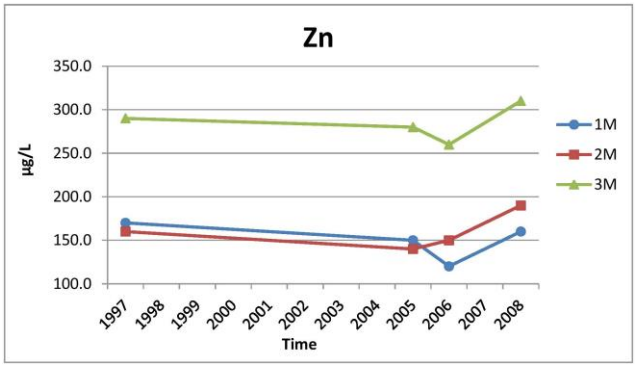

Fig. 7. Changing of Zn concentration with time in groundwater from Union (1M), Moring (2M), and Union on 13th horizon (3M).

Fig. 7. Variação da concentração em Zn, ao longo do tempo, na água subterrânea de Union (1M), Moring (2M) e Union no 13º horizonte (3M).

The EC and pH values registered in 1993 and 2015, in water from tunnel Prevalje (4M), ranges between 250 to 190 µS/cm and 7.4 to 7.8, respectively. This slight fluctuation is expected, because this water results from the mixing of water from Union (1M), Moring (2M) and Union on 13th horizon (3M).

4.3 Saturation indices

Saturation index is a measure of stability of a mineral in a thermodynamic system (Arocena *et al*., 2000). The PHREEQC code (version 2.0; Parkhurst and Apello, 1999) was used for calculating the activity and chemical speciation of dissolved species and the saturation index of minerals [SI = log (IAP / Ksp)], where SI is the saturation index, IAP is the ion activity product, and Ksp is the solid solubility product. If SI < 0, the solution is undersaturated with the mineral and if SI > 0, the solution is oversaturated and given mineral can precipitate. If SI = 0 the solution is in equilibrium to the given mineral (Younger *et al*., 2002).

Saturation indices for calcite and dolomite for sampling waters are presented in figure 8. Meža river before Janžek stream (2V) is undersaturated in relation to calcite and dolomite, so there are conditions to dissolution of limestones and dolomitic rocks present in the water pathway. Downstream, in Helena Stream (5V), more alkalinity is contributing to the water. Sample 5V is oversaturated in relation to calcite and dolomite, so precipitation of carbonate minerals can occur. In water sample 12V (Meža after Šumec) precipitation of calcite may occur, but not dolomite. Dolomite it's close to equilibrium but can keep dissolving until reaching it.

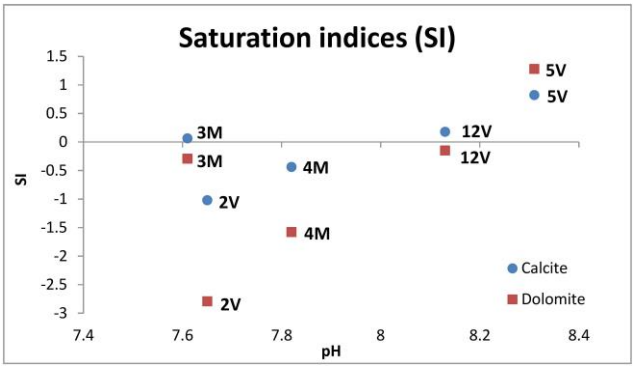

Fig. 8. Saturation Indices (SI) for calcite and dolomite for the 2015 samples.

Fig. 8. Indices de Saturação (SI) para a calcite e a dolomite, das amostras de 2015.

Groundwater sample 3M is in equilibrium with calcite and closer to equilibrium with dolomite. Water from the tunnel 4M is undersaturated in relation to calcite or dolomite and comparing to SI from 1993, values are now a little bit higher and the pH raised from 7.4 to 7.8 meaning that carbonate rocks are being dissolved.

Looking to SI for sample 5V, between years 1993 and 2015, bigger differences can be observed. In 1993 water was slightly oversaturated with both carbonate minerals and in 2015 is clearly oversaturated and pH increased from 7.7 to 8.3. Alkalinity is higher than 300 mg/L of HCO_3^- and conditions for precipitation of calcite and dolomite are met and can explain the low concentration on heavy metals that was attained nowadays in Helena stream that was one of the most polluted in the past.

5. Conclusions

In Mežica mine area quality of surface and groundwater improved through time. Nowadays Meža river is of good quality and groundwater chemical parameters are below limit values for drinking water. Concentration of Pb and Zn measured in 3 surface water locationss (2V, 5V and 12V) decreased from 1993/2002 to 2015. The biggest change occur in the case of Helena stream, where Pb and Zn concentrations were above limit value in 1993 and 2002, and in 2015 they are below the established limits.

Water tunnel (4M) and background sample (2V) are undersaturated with both carbonate minerals so, carbonates are being dissolved. Groundwater (3M) and surface water downstream the mine (12V) are slightly oversaturated with calcite and close to equilibrium with dolomite, with possible dissolution of mineral until reaching it. In Helena stream (5V) both calcite and dolomite can precipitate, what can promote trace metals adsorption or precipitation, and explain the lowering of heavy metals concentration in present times.

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