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Lead and Other Heavy Metals in Stream Sediments Draining the Mežica Mining District (Slovenia)

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Introduction

In the Meža valley around 19 million tons of lead-zinc ore were produced and processed during more than 300 years, which had a strong influence on the environment. Previous investigations of environmental media have shown increased concentrations of lead and some other metals. At the end of the 20th century, the Meža River was considered a stream with the highest concentrations of heavy metals in Slovenia. After the mine and processing plants had ceased to operate, the direct transfer of pollutants into the environment decreased sharply. However, the deposits of poor ore and wastes from ore processing have remained as an indirect source of heavy metal pollution. From those places heavy metals have been washed out into the nearby streams, and carried into the Meža River and further into the Drava River.

Previous investigations

Previous investigations of soil and river sediments, carried out by LAPAJNE and co-authors (1999), KUGONIČ & ZUPAN (1999), VREČA and co-authors (2001), BOLE and co-authors (2002) and ŠAJN (2002), ŠAJN & GOSAR (2004), GOSAR & ŠAJN (2005), ŠAJN (2006) have shown that, although more than 10 years have passed since the mine and ore processing plant in the upper Meža valley were closed and the production ceased, and although reclamation measures have been taken, the environment in the upper Meža valley is still highly polluted.

Sampling and analytical methods

In the upper stream of the Meža river, including significant tributaries (Topla, Helenski potok, Mušenik, Jazbinski potok, Junžarjev potok), the sampling points were placed approximately 1 km apart. From Mežica to the Drava River the sampling distance was increased to 10 km. Two samples of the Drava River sediments were also taken before and after its confluence with the Meža River (Fig. 1).

Two fractions (< 0.125 mm and < 0.063 mm) of air-dried and sieved sediments were analyzed at the ACME Analytical Laboratories Ltd. (Vancouver, Canada). The content of heavy metals in sediments was determined by sample digestion with 10 ml of the mixture of $HClO_4$, HCl, HNO_3 and HF at 200°C (ACME, 2003), followed by Inductively Coupled Plasma Emission Spectrometry (ICP).

For individual particle analysis, the <0.063 mm fraction sediment was sprinkled on a carbon tape, the excess removed by compressed air, sputter coated with gold and then analyzed using a scanning electron microscope JEOL-6490LV with an Oxford INCA energy dispersive spectrometer.

Heavy metals in stream sediments

Lead (Pb) and Zinc (Zn)

Lead content varies between 80 mg/kg and 14,200 mg/kg in fraction <0.063 mm and between 76 mg/kg and 19,300 mg/kg in fraction <0.125 mm. Zinc content ranges from 260 mg/kg to 22,500 mg/kg in fraction <0.063 mm and from 264 mg/kg to 37,900 mg/kg in fraction <0.125 mm. Lead and zinc contents in individual samples are shown in Fig. 2.

The highest contents of Pb and Zn were measured between Žerjav and Mežica (ME-11, ME-13, ME-15) and between Poljane and Prevalje (ME-18, ME-19). The increase in Pb content between Žerjav and Mežica was interpreted as a consequence of heavy metal pollution of soil near the smelter in Žerjav and of the contribution of heavy metal-polluted Helenski potok (ME-5) and mining waste dump in Mežica (ME-15). The elevated contents of Pb and Zn between Poljane and Prevalje (ME-18, ME-19) are most probably a consequence of mine water discharge through a 6 km long tunnel from Mežica mine to the Meža River, since no other source of heavy metal pollution has been found in the area.

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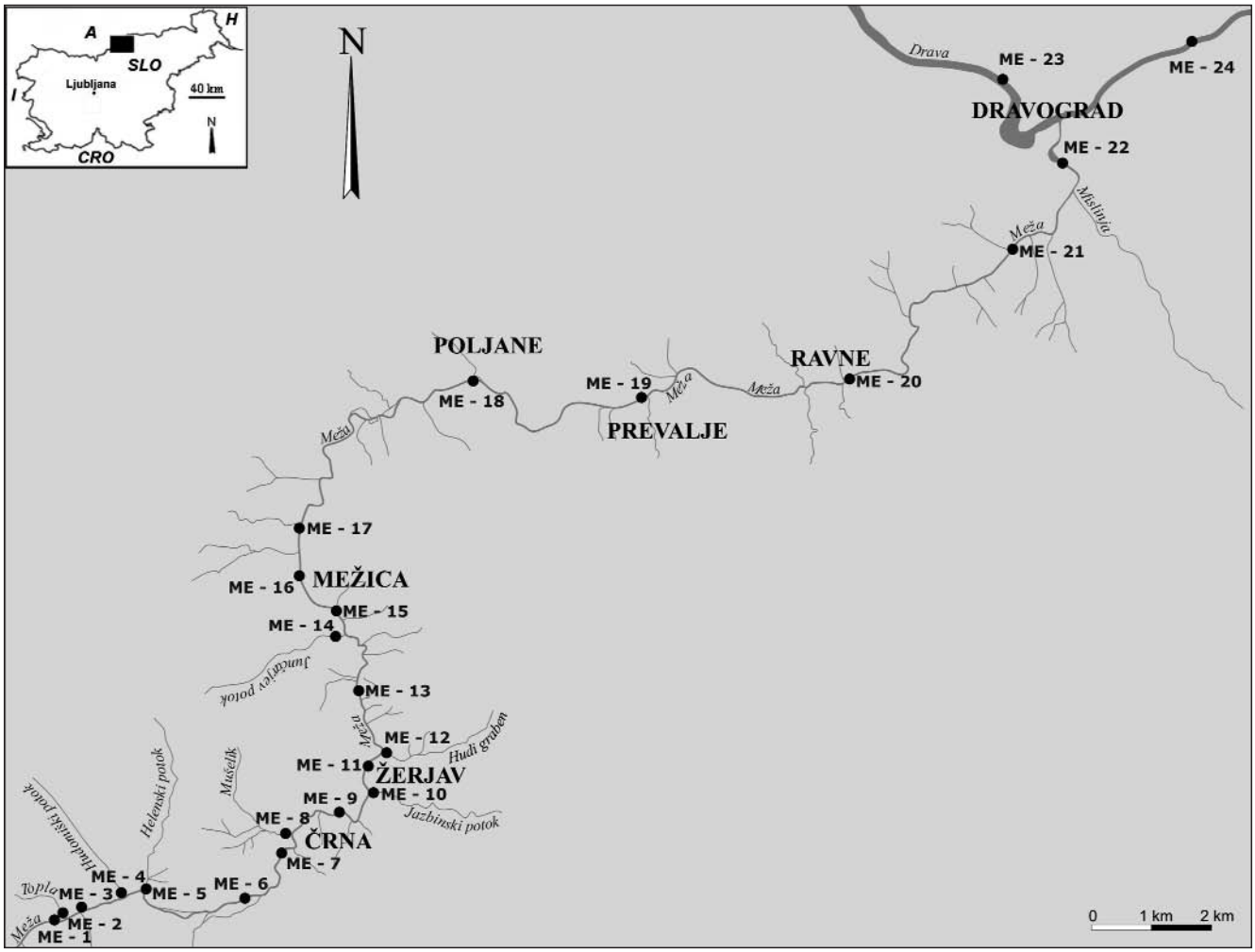

Fig. 1.
Location of study area with sampling locations.

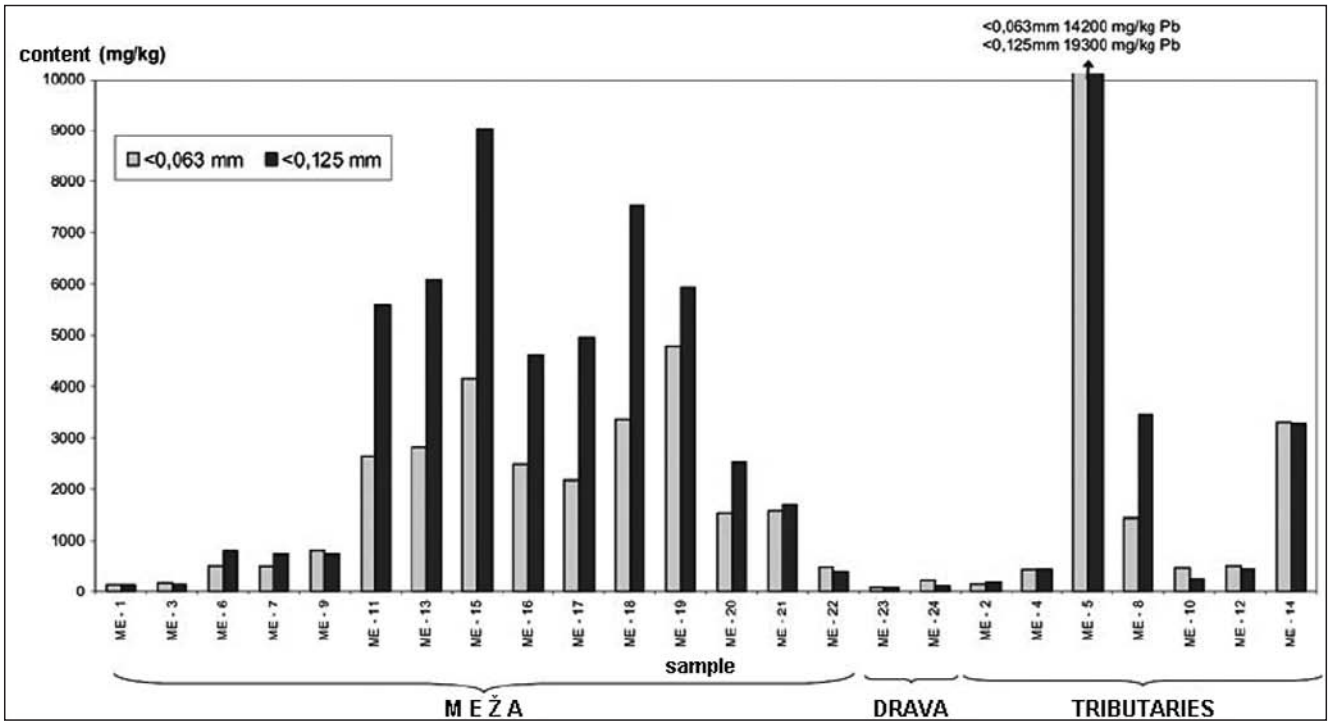

Fig. 2.
Lead (Pb) contents in sediments.

The highest contents of Pb and Zn in tributary sediments were measured in Helenski potok (ME-5) and Junžarjev potok (ME-14) and are a consequence of separation and mine tailings discharge.

Cadmium (Cd), Molybdenum (Mo) and Arsenic (As)

The trend of Cd, As and Mo contents is similar to that of Pb and Zn, because Cd, As and Mo usually occur together with Pb and Zn in ore minerals of Mežica mine (ŠTRUCL, 1984, FUX & GOSAR, 2007). The highest contents of Mo are reached in fraction <0.063 mm near the Ravne ironworks (ME-20) and are higher than the contents in fraction <0.125 mm. The highest contents of As in river sediments were identified in both Drava river samples (ME-23 and ME-24). The highest contents of Cd, As and Mo in tributary sediments were measured in Helenski potok (ME-5) and Junčarjev potok (ME-14).

Cobalt, Chrome, Copper and Nickel (Co, Cr, Cu and Ni)

Near Ravne (ME-20) the contents of Co, Cr, Cu and Ni are increased in fraction <0.063 mm compared to contents in fraction <0.125 mm, which is due to different methods of processing at Ravne ironworks.

Individual particle analysis

The individual particle analyses showed that lead and zinc appear in the form of carbonates (cerusite), oxides and sulfides (galena) (Fig. 3) bound to dolomite and calcite and could be geogenic or anthropogenic by source. Chromium, nickel and titanium are bound mostly to the iron-oxides (chromite, ilmenite, Ti-magnetite). Particle analysis of the Meža sediments near Ravne (ME-20) showed that most of the particles belong to iron, chromium and nickel bearing aerosols (Fig. 4) and to different ferroalloys containing chromium, molybdenum, vanadium and tungsten, which are used as a raw material in ironworks industry.

Conclusion

Chemical analysis of the Meža River and its tributaries has shown heavy pollution of the upper Meža River sediments with lead, zinc, molybdenum and cadmium, and partly with arsenic. In the lower Meža valley, contents of these are somewhat decreased. Contents of cobalt, chrome, copper and nickel are increased in the area around Ravne as a result of the ironworks industry. Mušenik and Junčarjev potok, both tributaries of the Meža River, contribute a high portion of heavy metal load to the Meža River. A specific case is Helenski potok, in which the contents of heavy metals strongly surpass the contents measured at all other locations. Results of the latest investigations of sediments showed even higher contents of heavy metals in sediments, compared to the results obtained by BOLE and co-authors (2002).

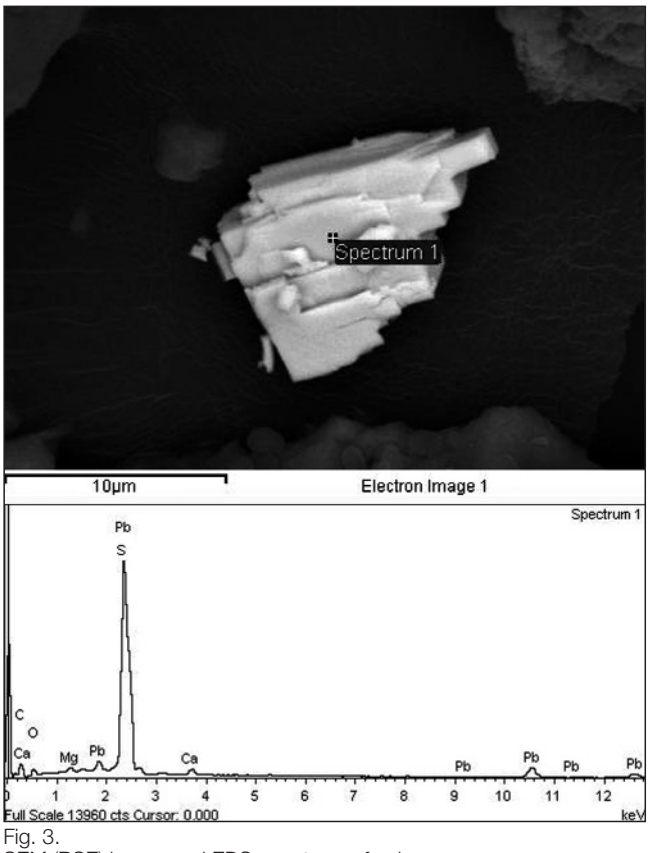

Fig. 3.
SEM (BSE) image and EDS spectrum of galena.
Sampling point ME-14.

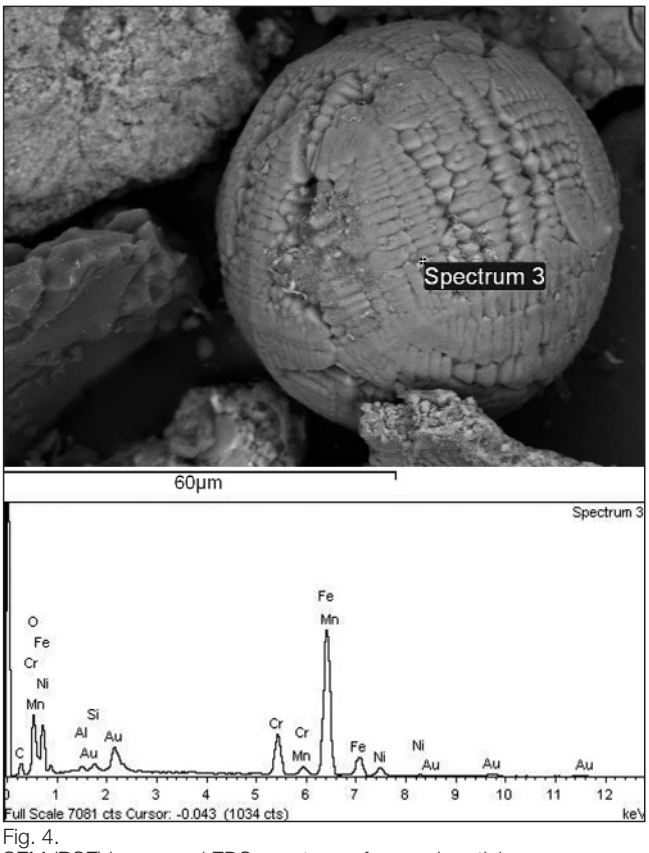

Fig. 4.
SEM (BSE) image and EDS spectrum of aerosol particle.
Sampling point ME-20.

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