Mercury in sediments of Sava River and its tributaries

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Abstract: Sava River has been a subject of heavy pollution by heavy metals in the past Hg concentration in sediments of Sava River and some of its tributaries was monitored since 1998. Sediment samples were taken at 30 locations in Sava river and its most important inflows. There are two important anthropopgenic sources of Hg due to past mercury mininga in the upstream area and the operation of a Chlor-alkali plant in Hrastnik.. (TKI Hrastnik). Elevated concentrations of Hg in sediments have been observed only immediately after Hrastnik, while the influence of former mercury mining has no influence any longer.

Key words: total mercury, Sava River, sediment

INTRODUCTION

The largest and longest Slovenian river, the Sava River collects water from area, which is larger than one half of Slovenia (10,838 km^2). Water quality in the Sava River is influenced by several industrial and municipal releases and also by inflow waters that contribute naturally enriched sediments. In its upper flow it passes through typical alpine valley with clastic (clay stones, sandstones, conglomerates etc.) and carbonate (i.e. limestone and dolomite) rocks. The main source of pollution in this area is Acroni Jesenice steelworks, which smelted iron ore and deposited byproducts on landfill near HPP (Hydroelectric Power Plant) Moste water reservoir in the past.

Figure 1. Sampling locations on Sava River and its tributaries.

Few kilometers downstream Tržiška Bistrica River joins Sava River in which catchments area small abandoned Hg mine in Podljubelj is located. Mine was active from 16th to beginning of 20th century. Further downstream is town Kranj (population: 73,000) with strong industry. Nearby Ljubljana (population: 330,000) the Sava River receives two tributaries, the Ljubljanica River and the Kamniška Bistrica River, which are both heavily polluted with industrial and municipal releases that originate from Ljubljana, Domžale and Kamnik industry. Most industrial and municipal wastewater from Ljubljana is cleaned in wastewater treatment plant. The water from the plant is released to the Ljubljanica River few hundred meters upstream before it reaches the Sava River. Downstream the Sava River reaches Zasavje region with strong chemical industry (Hrastnik), coal mining (Trbovlje, Hrastnik) and thermal power plant Trbovlje. Further in Zidani Most, the Savinja River joins the Sava River with industrial and municipal releases from Velenje (coal mining), Šoštanj (thermal power plant), Celje (very strong chemical industry) and Štore (steelworks).

EXPERIMENTAL

Samples were taken during four sampling campaigns between 1998 and 2003. First sampling location was just few hundred meters downstream from Acroni Jesenice steelworks, few kilometers before Kranj, between Kranj and Ljubljana, downstream from Ljubljana, before Zidani most, in accumulation basin of Vrhovo HPP and downstream from Vrhovo at several locations where new HPP are planned. The sediment samples were also collected on main Sava's effluents such as the Kokra River, the Kamniška Bistrica River, the Ljubljanica River, the Sopota River and the Savinja River. The sampling locations are shown in Figure 1.

Hg in sediments was determined after liophylisation, acid digestion, $SnCl_2$ reduction followed by gold amalgamation and detection on an LCD Milton Roy instrument by cold vapor atomic absorption spectrometry (CV AAS) (HORVAT ET AL., 1991; HORVAT, 1996). Data quality was checked with the Certified Reference Material, CRM 320, Trace Elements in River Sediment.

RESULTS AND DISCUSSION

In the Sava River upper flow Hg levels shows natural background concentrations (Figure 2 and 3). There is no industry that could effects Hg levels in sediment. At the Moste HPP reservoir sediments were taken at two depths in order to compare current and past influence from Jesenice steelworks (Acroni Jesenice). Generally concentrations in all samples were relatively low (0,02 – 0,15 mg/kg). First location was few hundred meters upstream from steelwork waste water outflow. Other two locations in Moste reservoir shows higher levels of Hg in depth of 20 cm is most probably related to past operation of jesenice steelworks.

Downstream from Moste HPP reservoir Hg levels were constantly increasing (Figure 2). It was expected that after Tržiška Bistrica River inflow mercury would be increased due the past mercury mine in Podljubel. The results did not confirm this hypothesis. Slight increase of Hg can be noticed after

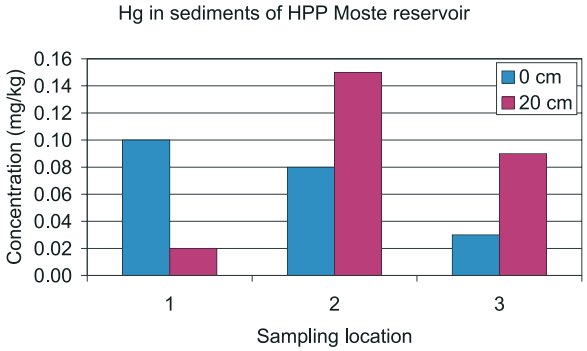

Figure 2. Hg in sediments of HPP Moste reservoir at two different depths (in mg/kg).

Ljubljanica River inflow as a consequence of Ljublana wastewater purifying plant discharge – location 10b (Figure 4). Hg concentration reaches the highest value immediately after Hrastnik (location 14) and in Vrhovo HPP reservoir (up to 1.51 mg/kg). Increase of Hg content in sediment was affected by discharges from chlor-alkaly industry in Hrasnik (TKI Hrastnik), which continuously operated since the end of 19th century. In 1997 Hg as a catalyst was removed from production processes. Unfortunately Hg emissions to Sava River from TKI Hrastnik in the past are not known. Downstream from HPP Vrhovo reservoir Hg levels decreased. In lower flow of Sava River Hg concentrations remains more or less constant. Lower flow is not much influenced by bigger cities or industry that could have significant influence on Hg concentrations in river water or sediment.

The concentrations of Hg were measured in sediments in outflows of main Sava River tributaries in order to establish the input of Hg into the river from different catchment areas. Among Sava River tributaries the highest levels of Hg (0.5 mg/kg) was found in Ljubljanica River, downflow from water purifying plant (Figure 4). This indicates in-

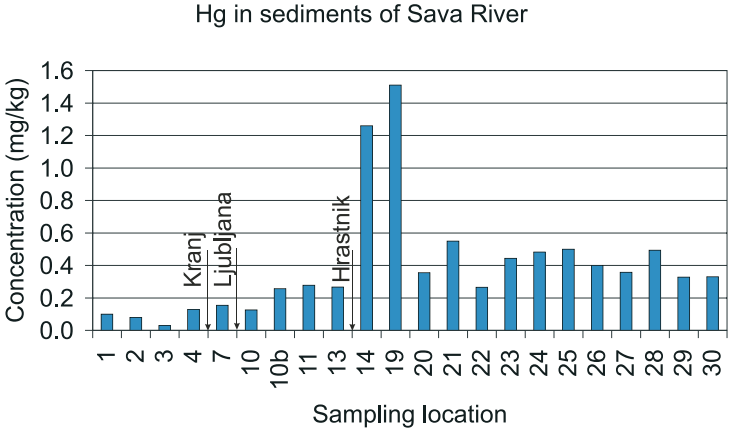

Figure 3. Hg in sediments of Sava River (in mg/kg).

fluence of industrial and municipal discharges from Ljubljana city. In sediments of other tributaries the Hg concentrations were lower.

Kamniška Bistrica River sediment that is heavily polluted by other heavy metals do not show significant increase of Hg concentrations (0.24 mg/kg).

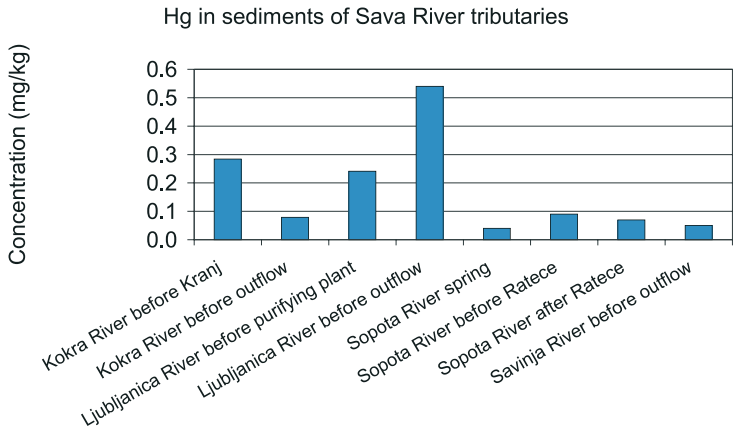

Figure 4. Hg in sediments of main Sava River tributaries (in mg/kg).

Relatively low concentrations of mercury were also obserwed in Savinja River, which is affected by strong chemical and steelwork industry in Celje and Štore. Sediment in Savinja River do not exceed 0.06 mg/kg Hg at outflow to Sava River. Same situation is with Sopota River with paper industry in its catchments area. It seems that both tributaries are not seriously affected by Hg pollution from municipal or industrial releases.

CONCLUSIONS

In comparison to Idrijca River which is heavily polluted by Hg, where Hg concentrations in sediments can exceed 100 or even 1000 mg/kg (GOSAR ET AL., 1996; HORVAT ET AL., 2002), Sava River sediment do not shows highly elevated levels. The exception is pollution of river sediment by Hg in the past by chlor – alkaly plant in Hrastnik. TKI Hrastnik stopped releasing Hg into the Sava River in 1997, when Hg as catalyst in production process was replaced with membrane technology. In the future more attention has to be focused on the biogeochemical cycling of mercury in artifical dams of the lower Sava River, as mercury accumulated in sediments may enter the aquitioc food web. In particular, fisheries become an important recreational activits in the area and it suggested to regulary control mercury levels in fish consumed by the local population.

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