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Heavy Metals in Alluvial Sediments of the River Drava (Slovenia and Croatia)

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Introduction

Geochemical research of soil, stream and overbank sediments as well as rocks in Slovenia and Croatia has been carried out continually within the last two decades. Its objectives were to obtain geochemical data, especially content of heavy metals in topsoil and bottom soil horizons in the valley of the river Drava. Research works has been focused on the alluvial sediments (river terraces and floodplains) downstream from Austrian border to the confluence of rivers Mura and Drava.

The objectives of study have been specified as follows: assessment of geochemical background before industrial revolution and evaluation of anthropogenic influence on sediment and soil pollution in the Drava valley; determination of the spatial distribution of heavy metals in soils on alluvial deposits of the river Drava (river terraces and floodplains); determination of the vertical distribution of heavy metals in the sediment and soil profiles; and depth of anthropogenic influence.

Description of Study Area

The Drava watershed, with confluents, is important area of mining and smelting activities, have begun in antic period, developed in Middle century and have achieved the maximum in the middle of the last century. Numerous mines and smelters (Bleiberg-Kreuth in Austria, Cave del Predil in Italy and Mežica in Slovenia) have left great consequences on chemical composition of the Drava alluvial sediments.

The study area covers a flow of the river Drava from the Slovene/Austrian border up to confluence of the rivers Mura and Drava. The study area can be divided into two zones: Drava canyon from the Slovene/Austrian border up to the town Maribor where dominant alpine characteristics of landscape and zone from the Maribor until the confluence of Mura and Drava rivers, where the river valley is wide and has all characteristic of Pannonian basin. We are focused on the second zone, Pannonian part of the Drava valley.

The study area covers c. 130 km of the flow of the river. On this territory, extensive areas of alluvial sediments are developed: flooded area (today mainly behind bank systems) covers 58 km^2, historically flooded area (today protected by the bulks, where is intensive agriculture production) covers 205 km^2, and sediments of alluvial terraces on c. 941 km^2. Because of often floods, especially in autumn time, great average flow rate and great electricity requirements, on study area five hydroelectric power plants (Zlatoličje, Formin, Varaždin, Čakovec and Dubrava) are built, with flumes and accumulate lakes that make a new anthropogenized river. According to this, is not possible to talk about natural river-bed, which occupies only biological minimum, which is approximately 30 m^3/s (what is basically $^1/_{10}$ of the average flow of the river).

Materials and Methods

In order to define the pollution outspread of heavy metals in the alluvial sediments of the river Drava, 149 topsoil samples are collected in the period from 2004–2006 (25 samples on recent flooded area; 35 on historical flooded area, which is protected by bank as well as 89 on river terraces). In treatment of geochemical map making of study area, have been included 246 topsoil samples from experimental geochemical map of Croatia and Slovenia.

For determination of historical influence on pollution, the 6 profile lines were placed perpendicularly to the river flow. The profiles were set equally in both sides of Croatia- Slovenian border in order to get better information of depth distribution of heavy metals in the research area. Total of 272 samples, in 40 soil profiles in both countries, Slovenia and Croatia are collected.

Sampling in soil horizons have been made with hand operating borehole driller. Drilling was performed until first thikker a gravel layer. The samples are collected in each 20 cm of depth. Minimal drilling depth is 120 cm, in range from 60–240 cm.

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All samples are air-dried. For the chemical analyses, size fractions smaller than 0.125 mm, are prepared by sieving. Analysis of 41 was performed by inductively coupled plasma mass spectrometry (ICP-MS) after four-acid digestion.

Results and Discussion

Preliminary data processing has shown that primary pollution, which is the consequence of historical mining and smelting in Carinthia, has a huge influence on chemical composition of alluvial sediments of the river Drava.
On river terraces, the mean value is within the limits of local background. On the historical flooded area (today behind the bulks) the mean concentrations of Cd (1.7 mg/kg), Pb (150 mg/kg) and Zn (480 mg/kg) are 4 times higher. More critical situation is on territory of recent flooded lowland. Mean values of Cd (5.3 mg/kg), Pb (480 mg/kg) and Zn (1400 mg/kg) exceed the local background approximately 12 times.
According to concentrations of mentioned elements, significant changes with depth are not determined. The values on the deepest soil horizons vary little compare to the topsoil. On historical flooded plains, the concentrations of Cd, Pb and Zn in the deepest soil horizons represent about 30 % of surface concentration and on recent flooded areas about 50% of surface concentration.
There is found that 150 km^2 of recent and historical alluvial sediments, according to legislation of both countries exceed the critical concentrations. High content of heavy metals (Cd, Pb and Zn) is also significant before the confluence of Drava and Danube rivers, which is proven by geochemical sampling in the past.

In Progress and in Future

Sampling on short distances and geochemical analyses of recent alluvial sediments along the flow of the river Drava, from spring to the Danube mouth (Italy, Austria, Slovenia, Hungary and Croatia), a soil sampling in denser sampling grid for making the 3D models and calculating amount of heavy metals in soil and analyses of occurrence of a mineral phases are in progress. In future period we will start with sampling of sediments in accumulation lakes of the mentioned hydroelectric power plants