Role of clay minerals in the heavy metals deposition on the Upper Vistula flood plains at the area of Krakow city (Poland)

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Introduction: Present study shows the discharge of heavy metals and their deposition on the flood plains of the upper Vistula River in the Krakow city during flood disaster in 2010. Additional threat was caused when the Vistula river dam break (length ca. 30m).

Methods: Total of 45 flood sediment samples were taken along (ca. 7 km) the Vistula river, close to the Krakow city center. The bulk samples and their < 20 µm size fraction were studied (conc. HNO_3, digestion in microwave oven). The mineralogy of 5 samples was determined by X-ray diffraction (PXRD).

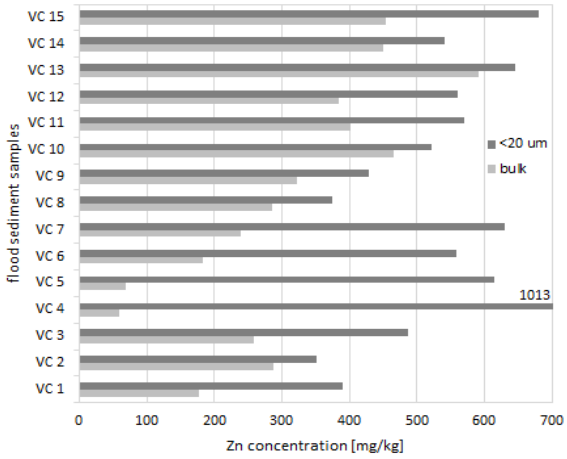

Fig. 1: Zn content in the Vistula river flood sediment (bulk and <20µm) samples of cross section.

The metal speciation's in the selected flood sediment samples was study using BCR sequential chemical extraction method [2].

Results: No differences in the mineralogical composition i.e. quartz, smectite, kaolinite, illite and calcite in the flood sediment samples were detected.

The maximum concentration of heavy metals in the Vistula river flood sediment samples from the cross section (VC samples 1-15) were considerable higher in the <20µm size fraction than in bulk samples ($mgkg^{-1}$): Zn 1013 (Fig. 1) and 591, Pb 227 and 137, Cd 17 and 23, Mn 979 and 469 respectively. The maximum content of Cu, Ni and Cr was lower than the regional geochemical background values [3]. High correlation was found for concentration of Fe, Mn, Zn, Pb and Cu versus the <20 µm size fraction content in the flood sediment samples from the cross section. The River Wilga – tributary of the Vistula River showed higher content of <20µm fraction than the Vistula sediments, but maximum concentration ($mgkg^{-1}$): 352 of Zn, 227 of Pb, 115 of Cu, 32 of Ni, 8.7 of Cd in the <20µm size fraction of sediments, was lower than in the Vistula river flood sediments.

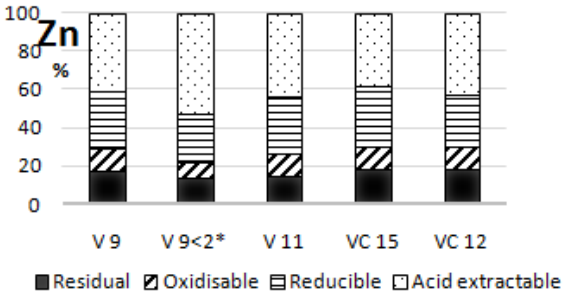

Fig. 2: Zn speciation's in flood sediments (<20µm).

In flood sediment samples (<20µm – 4, and <2*µm 1 samples), the relative amounts of exchanged and carbonate (step I) metal ions varied in wide ranges Zn 38-52% (Fig. 2), Cd 51-77%, Pb 8-54% and Cu 10-20%; in the case of Zn and Cu the maximal portion was found in the clay fraction of VC 7 sample. The highest amount up to71% of Pb, and up to 31% of Zn were associated in reducible fraction.

Discussion:

The results of present study showed that the fine grained size fraction <20 µm as well as suspended matter revealed high metal concentration. However, high water flow caused a diluting effect on the river system. After re-deposition of the Vistula river sediments being in reducing form, flood sediments due to an oxidation released portion of metal ions, since they moved into mobile forms; this portion of Zn and Cd reached 50 and 70%, respectively. Our findings corresponds well with a reported conclusion [4]; effective discharge mainly apply for metal bound to the fine silt and clay fractions deposited in the central parts of the flood plain section.

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References: [1] E.H. Rybicka, Strzebonska (1999) *Acta Hydrochim. Hydrobiol*. **27**: 331-337. [2] Quevauviller et al. (1997) The Science of the Total Environment, **205**: 223-234. [3] Helios-Rybicka (1986) *Geologia* **32**: 123. PL ISS 0138-0974. [4] Middelkoop et al. (2002) IAHS Publ., **276:** 151-159.