# GRAIN-SIZE EFFECT ON HEAVY METALS CONTENT IN THE ODRA RIVER BOTTOM SEDIMENTS

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**Abstract**
Silty-sandy bottom sediments of the Odra River were studied (standard < 2 mm fraction, of diversified grain-size distribution). The heavy metals content was determined in various grain-size sub-fractions [mm]: < 0.2, < 0.1, < 0.06 and < 0.02. Samples contain variable amounts of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. Heavy metals concentrations increase with the decreasing grain size. In general, fractions < 0.02 mm contain from 7.7 (Co) to 19.0 (Cu) times more metals then the raw sediments, while in case of fractions < 0.2 mm metals content exceeds 5.7 (Co) to 14.5 (Cu) times content in the raw sediments. Finer fraction collects from 23% (Co) to 44% (Cu) of overall metal amount in the raw sediment whereas coarser one concentrates from 44% (Co) to 70% (Cu). The linear correlation between metal concentrations in the raw sediment and contents of the particular grain-size fractions has been found. Similarly, a linear correlation was also found between metal concentrations in the raw sediment and contributions of metals in each fraction to the raw sediments.

**Introduction**
Pollution of the bottom sediment, beside the water and suspended matter, is responsible for the condition of the water environment. Generally, it is treated as the factor describing the river pollution with the heavy metals. The researches have been performed on different grain-size fractions [mm]: < 0.2; < 0.18; < 0.125; < 0.1; < 0.063; < 0.04; < 0.02; < 0.016 and even < 0.006 and < 0.002 (1), (2), (3), (4), (5), (6). Polish monitoring researches of the sediment base on fraction < 0.2 mm, (7), (8), (9), (10), (11). Other fraction were studied, the following size of material < 1 mm (12), (13), < 0.1 mm (14), < 0.063 mm (12), (13), (15), (16), and < 0.02 mm (15), (16). A different distribution of the grain-size fractions in the sediments is significantly responsible for the sediment contamination (17).This study has shown the distribution of Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb concentration between different grain-size fractions of the bottom sediments from the Odra River (in the location from Chałupki to Połęcko) as well as which the grain–size fraction is the most responsible for sediments pollution.

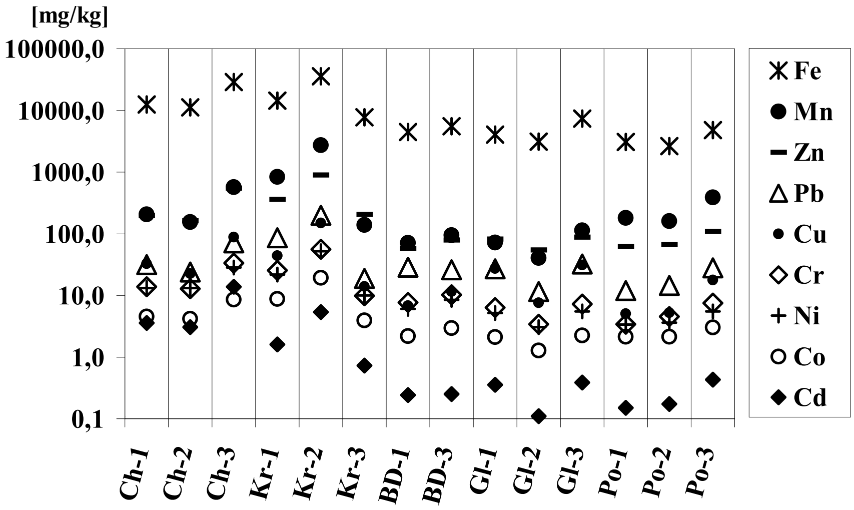
**Methods**
*Sampling strategy:* The samples of bottom sediments were taken from the Odra River in the region of the following towns: Chałupki (Ch), Krapkowice (Kr), Brzeg Dolny (BD), Głogów (Gl) i Połęcko (Po). Three superficial (0-10 cm) samples have been taken in every site (BD – only 2 samples), in the distance no more than 2 m from each other.
*Analytical methods:* the material < 2 mm was investigated, in this paper simply named as the sediment. It was subdivided into the following grain-size subfractions [mm]: < 0.2, < 0.1, < 0.06 and < 0.02.

The concentrations of Cd, Co, Cr, Cu, Fe, Mn, Ni i Pb in the extracts (HCl : $HNO_3$ = 3 : 1, microwave digestion (MDS 2000) was determined with ICP-MS application (Hewlett Packard 45000).

**Results and discussion**

The studied bottom sediments of the Odra River were silty-sandy samples of various grain-size distribution. They contain very different amounts of heavy metals [mg/kg]: Cd 0.11-5.36; Co 1.28-19.4; Ni 3.05-52.1; Cr 3.40-56.0; Cu 6.79-150; Pb 11.6-199; Zn 54.9-894; Mn 40.7-2740 and [wt.%]: Fe 0.31-3.57 (Fig. 1). The highest amounts of heavy metals were found in the sediment samples from Krapkowice and Chałupki, mentioned samples are the least sandy, as well.

Figure 1: Concentration of heavy metals in sediments



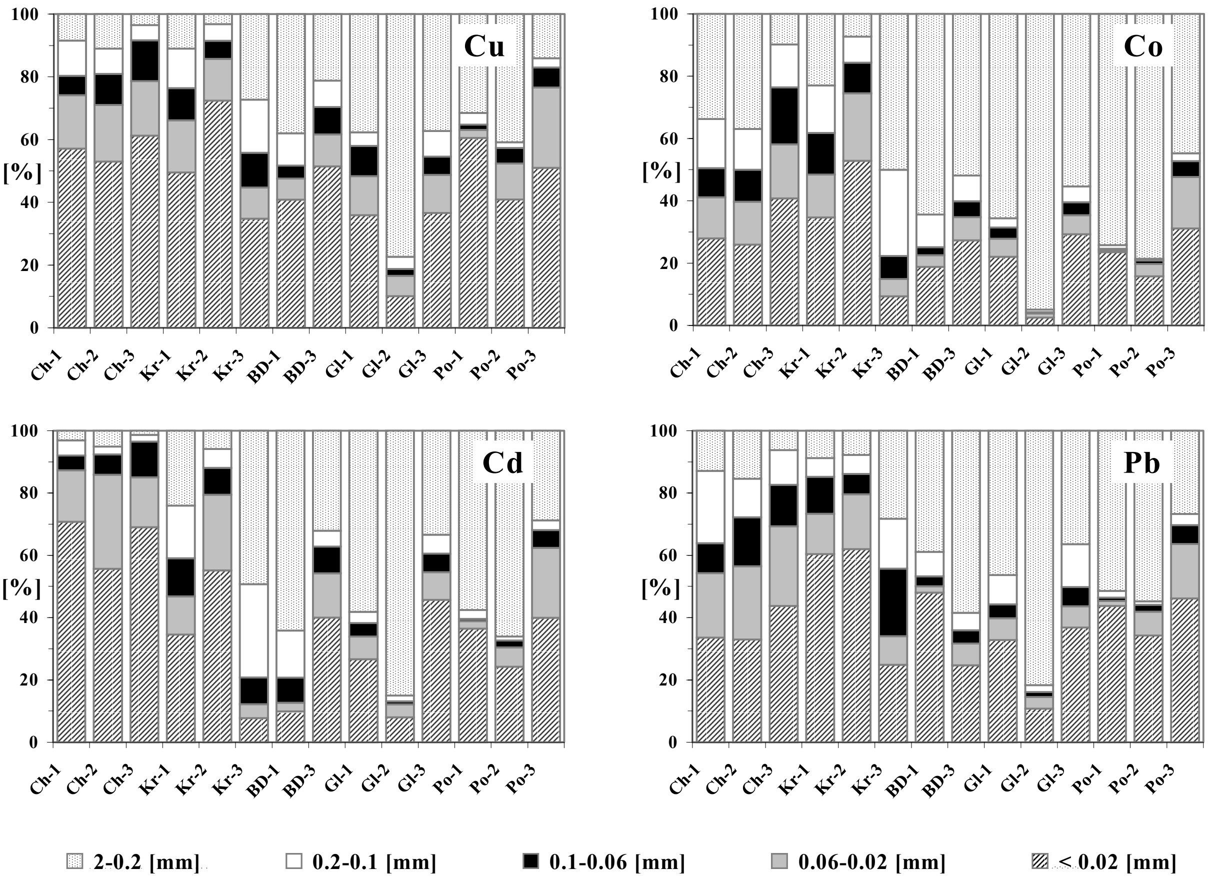

Heavy metals concentration increases with decreasing fractions grain-size; in the finest fraction their amount is, on average, from 7.7 (Co) to 19 (Cu) times higher than in the raw sediment, while for fractions < 0.2 mm metal content exceed 5.7 (Co) to 14.5 (Cu) times content in the raw sediments (Table 1).

Table 1: Average ratio of the metals concentrations in grain-size fraction and the raw sediment

| *Ratio* n = 14 | Cd | Co | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| [< 0.02] : [sediment] | 13.2 | 7.7 | 11.8 | 19.0 | 9.1 | 9.4 | 10.1 | 14.9 | 11.9 |
| [< 0.06] : [sediment] | 12.5 | 7.2 | 10.9 | 17.7 | 8.2 | 9.0 | 9.4 | 13.3 | 10.4 |
| [< 0.1] : [sediment] | 11.5 | 6.7 | 10.0 | 16.5 | 7.7 | 8.5 | 8.7 | 12.4 | 9.6 |
| [< 0.2] : [sediment] | 8.8 | 5.4 | 7.8 | 12.8 | 6.0 | 6.9 | 6.9 | 9.5 | 7.2 |

The distribution of the particular metals between the grain-size fractions was analyzed. Figure 2 shows Cu, Co, Cd and Pb amount distribution between grain size-fractions, as examples.
Metals contribution in fractions to their whole amount in sediment is the product of metal content in fraction and fraction portion in sediment.

Figure 2: Cu, Co, Cd and Pb amount distribution between grain size-fractions




In table 2, the statistical parameters of the average contribution of metals in different fractions to the raw sediments were compared. The finest fraction collects from 23% (Co) to 44% (Cu) of overall metals content in raw sediment whereas the coarsest one concentrates from 44% (Co) to 70% (Cu).

Table 2: Statistical parameters (average in %) of contribution of metals in differential fraction to the raw sediments

| ***Fraction* [mm]** | **n = 14** | **Cd** | **Co** | **Cr** | **Cu** | **Fe** | **Mn** | **Ni** | **Pb** | **Zn** |
|---|---|---|---|---|---|---|---|---|---|---|
| < 0.02 | *Arithmetic mean* | 36.1 | 47.4 | 31.5 | 44.9 | 26.9 | 29.0 | 27.0 | 36.4 | 31.6 |
| | *Standard deviation* | 21.0 | 27.5 | 13.1 | 13.9 | 13.2 | 13.3 | 10.6 | 12.5 | 13.3 |
| | *Median* | 36.5 | 46.8 | 34.6 | 49.5 | 27.6 | 30.1 | 29.3 | 34.2 | 31.3 |
| < 0.06 | *Arithmetic mean* | 47.4 | 32.2 | 41.0 | 57.7 | 35.3 | 39.4 | 36.0 | 47.5 | 40.1 |
| | *Standard deviation* | 27.5 | 15.2 | 17.3 | 17.1 | 18.0 | 18.1 | 15.1 | 16.2 | 17.5 |
| | *Median* | 46.8 | 34.8 | 42.0 | 61.6 | 36.2 | 39.8 | 38.7 | 45.3 | 44.9 |
| < 0.1 | *Arithmetic mean* | 53.6 | 38.4 | 46.9 | 64.9 | 42.1 | 47.5 | 42.8 | 55.3 | 46.3 |
| | *Standard deviation* | 28.7 | 19.7 | 20.5 | 18.9 | 21.8 | 22.3 | 19.2 | 19.3 | 21.3 |
| | *Median* | 59.0 | 39.5 | 47.9 | 64.8 | 42.2 | 45.7 | 43.6 | 53.3 | 49.1 |
| < 0.2 | *Arithmetic mean* | 60.9 | 47.5 | 54.6 | 72.4 | 51.7 | 58.6 | 52.2 | 64.1 | 55.0 |
| | *Standard deviation* | 26.7 | 23.5 | 22.2 | 19.8 | 25.6 | 24.1 | 23.0 | 22.4 | 24.6 |
| | *Median* | 66.6 | 48.2 | 52.9 | 72.7 | 52.9 | 63.9 | 53.2 | 63.6 | 51.2 |

In the study the existence of linear dependences was tested between:
1/ the total metal concentration in the raw sediment and fractions contribution to its metal content in the raw sediment,
2/ the total metal concentration in raw sediment and its concentration in fraction,
3/ the total metal concentration in raw sediment and the grain-size fraction content.
In tables 3, 4 and 5, the determination coefficients ($R^2$) of the linear dependences for 13 samples* were compared.

Table 3: The determination coefficient ($R^2$) of the linear dependences between the total metal concentration in raw sediment and fractions contribution to its metal content in the raw sediment

| n = 13 | Cd | Co | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| < 0.02 mm | 0.995 | 0.929 | 0.966 | 0.969 | 0.962 | 0.857 | 0.935 | 0.945 | 0.908 |
| < 0.06 mm | 0.996 | 0.939 | 0.972 | 0.973 | 0.972 | 0.895 | 0.953 | 0.978 | 0.915 |
| < 0.1 mm | 0.998 | 0.949 | 0.977 | 0.975 | 0.984 | 0.915 | 0.965 | 0.976 | 0.930 |
| < 0.2 mm | 0.789 | 0.983 | 0.992 | 0.981 | 0.996 | 0.974 | 0.988 | 0.976 | 0.975 |

Table 4: The determination coefficient ($R^2$) of the linear dependences between the total metal concentration in raw sediment and its concentration in fraction

| n = 13 | Cd | Co | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| < 0.02 mm | 0.699 | 0.118 | 0.138 | 0.052 | 0.009 | 0.052 | 0.544 | 0.058 | 0.005 |
| < 0.06 mm | 0.653 | 0.184 | 0.433 | 0.016 | 0.001 | 0.019 | 0.553 | 0.153 | 0.128 |
| < 0.1 mm | 0.709 | 0.173 | 0.354 | 0.016 | 0.010 | 0.020 | 0.440 | 0.184 | 0.141 |
| < 0.2 mm | 0.789 | 0.082 | 0.149 | 0.007 | 0.000 | 0.032 | 0.121 | 0.150 | 0.043 |

Table 5: The determination coefficient ($R^2$) of the linear dependences between the total metal concentration in raw sediment and the grain-size fraction content

| n = 13 | Cd | Co | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| < 0.02 mm | 0.843 | 0.824 | 0.949 | 0.897 | 0.950 | 0.564 | 0.918 | 0.720 | 0.909 |
| < 0.06 mm | 0.849 | 0.836 | 0.954 | 0.889 | 0.958 | 0.563 | 0.931 | 0.708 | 0.921 |
| < 0.1 mm | 0.827 | 0.874 | 0.972 | 0.875 | 0.964 | 0.579 | 0.959 | 0.722 | 0.947 |
| < 0.2 mm | 0.656 | 0.919 | 0.937 | 0.730 | 0.884 | 0.560 | 0.962 | 0.697 | 0.944 |

The linear correlation ($R^2 \geq 0,80$) between metal concentrations in raw sediment and contributions of metals in each fraction to the raw sediments has been found. Similarly, a linear correlation ($R^2 \geq 0,70$) has also been found for metal concentrations in raw sediment and contents of particular grain-size fractions (except of Mn).

## Conclusions

Investigation of the silty-sandy bottom sediments of the Odra River shows:

1. Samples contain variable amounts of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The highest amounts of heavy metals were found in the sediment from Krapkowice and Chałupki, which are the least sandy.
2. Heavy metals concentrations increase with the decreasing grain size. On average, fractions < 0.02 mm contain from 7.7 (Co) to 19.0 (Cu) times more metals then the raw sediments, while for fractions < 0.2 mm metal contents exceed 5.7 (Co) to 14.5 (Cu) times those detected in the raw sediments.
3. The finest fraction collects from 23% (Co) to 44% (Cu) of overall metals content in raw sediment whereas the coarsest one concentrates from 44% (Co) to 70% (Cu).

* In the calculation the sediment sample from Krapkowice (Kr-2) has not been taken into account due to relatively high amount of heavy metals (fig. 1).

4. The linear correlation has been found between metal concentrations in the raw sediment and contributions of metals in each fraction to the raw sediments. Similarly, a linear correlation was found also for the metal concentrations in the raw sediment (except of Mn) and the contents of particular grain-size fractions.

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