Contaminated sediments as a potential source of heavy metals in the Upper Vistula River et historical mining and smelting area of South Poland

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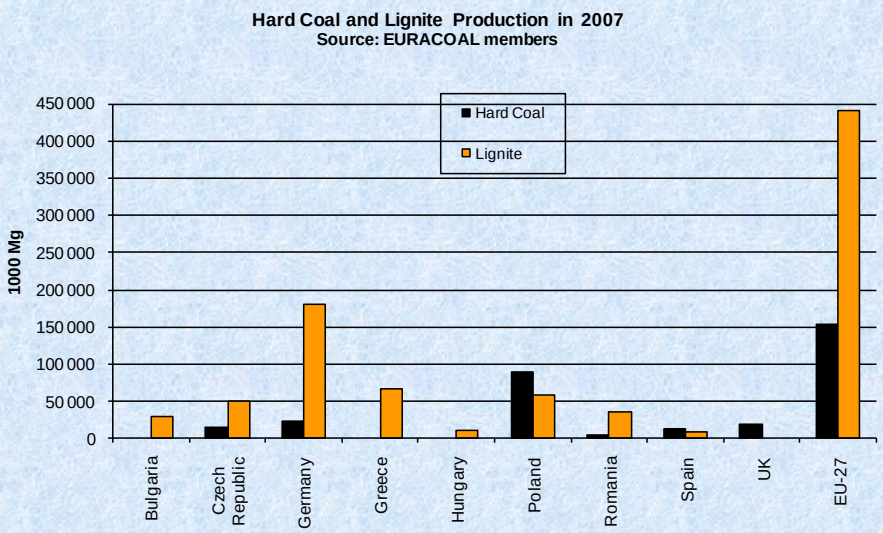
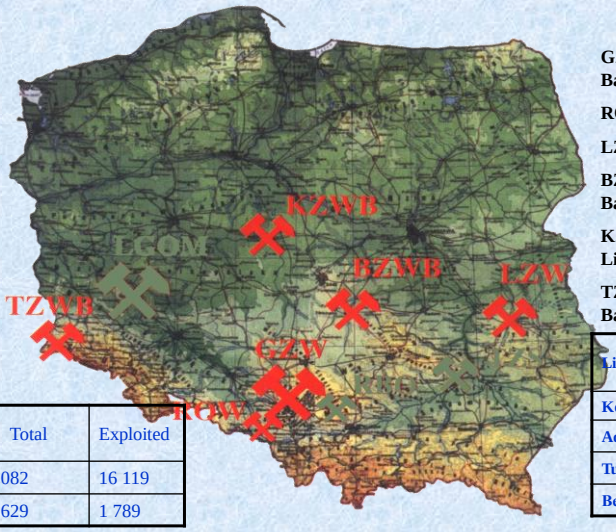
Coal mining in Europe



Hard coal and lignite basins in Poland



GZW – Upper Silesia Coal Basin

ROW – Rybnik Coal Region

LZW – Lublin Coal Basin

BZWB – Belchatów Lignite Basin

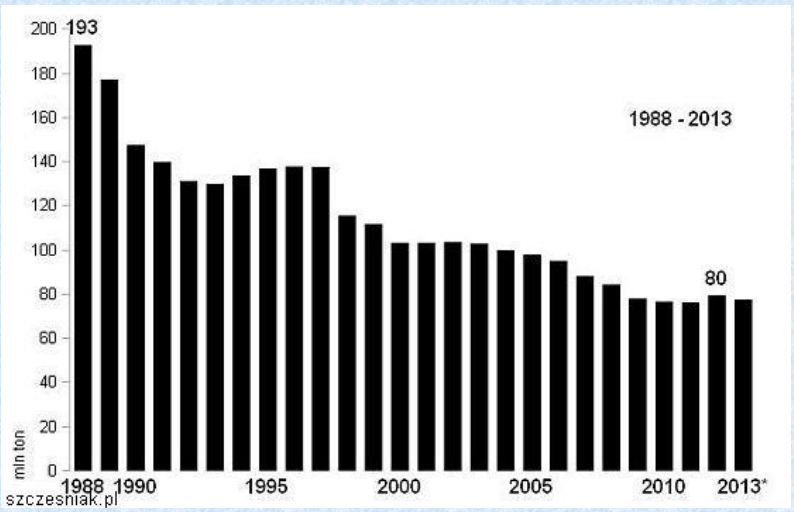
KZWB – Konin- Adamów Lignite Basin

TZWB – Turoszów Lignite Basin

Resources mln Mg	Total	Exploited
Hard coal	43 082	16 119
Lignite	13 629	1 789

Lignite Basin	Exploatation	
	From	To
Konin ZWB	1945	2035
Adamów ZWB	1963	2021
Turoszów ZWB	1770	2035
Belchatów ZWB	1980	2040

Hard coal production in Poland (1988-2014)



2014 Year
79.2 mln tons

Environmental impact of coal mining

Terrain deformation

Changes of landscape

Changes in hydrogeological system

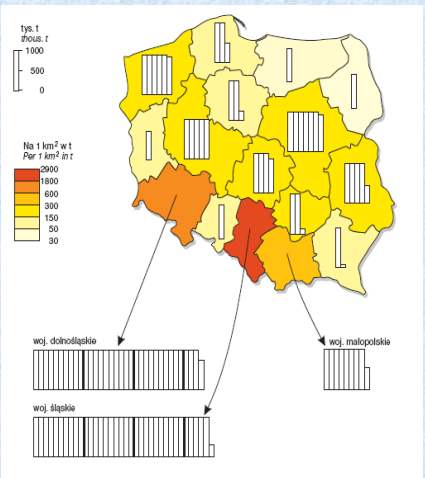
Hydrochemical transformations

Contamination of atmosphere

Contamination of surface water flows

Contamination of soils

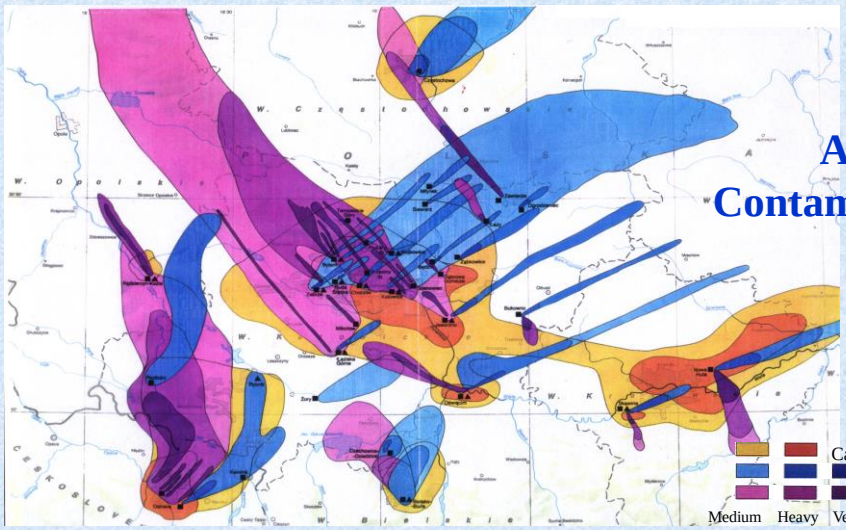
Wastes generated in Polish provinces in 2008



Source: CSO, Environment 2008

Spread of industrial smoke during periods of calm, SW winds and NW or SE winds (LANDSAT 1988)

(from: Jordan, Trafas, 1991)



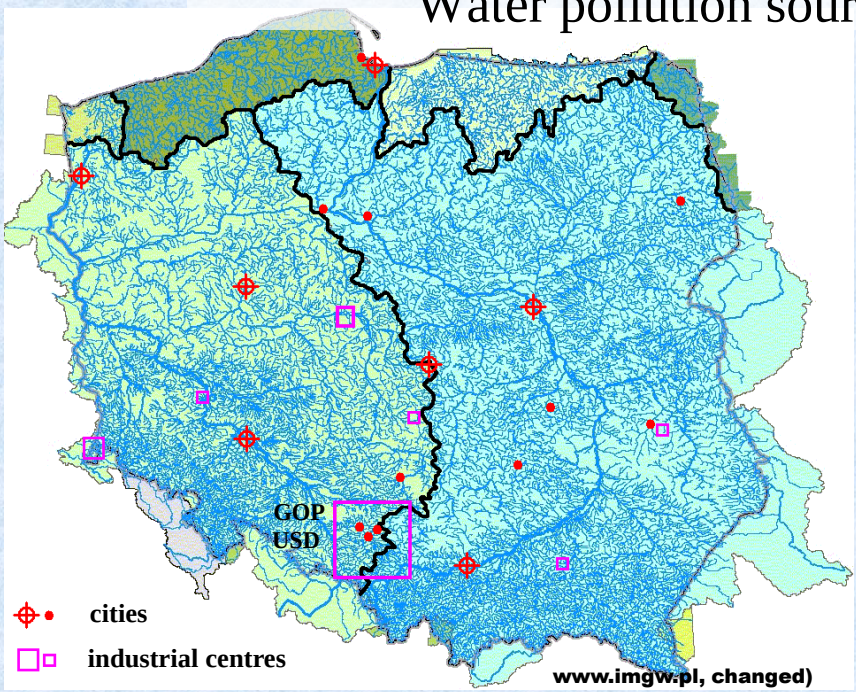
Air Contamination

Heavy metals emission (Mg/Y) in Poland in years **1980-2007** and **2012** (GUS, 1990-2009)

Emission decrease because of instalation of different dust collector e.g. electro-filters in years 1990th

Metal	Year						
	1980	1991	1995	1999	2003	2007	**2012**
As	129,7	79,8	73,4	58,8	49,8	44,9	43,72
Cr	280,9	133,5	118,3	89,8	54,8	49,3	45,67
Zn	5387,1	2780,9	2580,3	2377,1	1656,9	1517,6	1545,22
Cd	156,2	85	82,6	61,7	48,5	39,7	38,71
Cu	1971,7	530,4	464,9	420,9	397	367,4	347,82
Ni	571,7	354,8	312,3	295,8	260,8	177,9	148,07
Pb	2453,9	1335,6	936,6	745	596,1	573,4	553,55
Hg	38,8	32,7	32,3	27,1	20,2	15,9	10,24

Water pollution sources



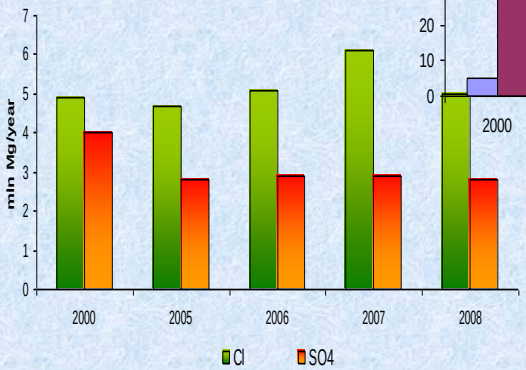
The outflow of heavy metals through the Odra and Vistula Rivers to the Baltic Sea

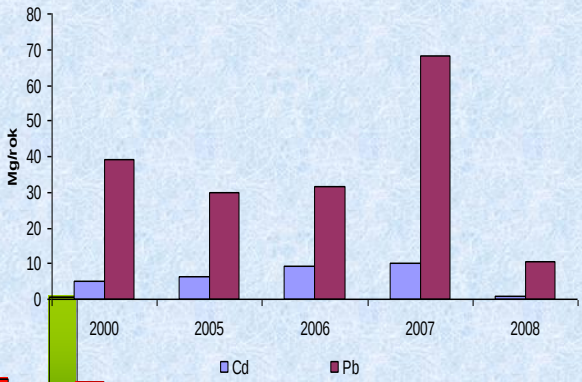
(from National Environmental Monitoring – Water Monitoring)

Metal Total Tons/Year	Year	Total	Vistula River	Odra River
Zn	2012	110.58	28.01	19.14
	2013	**189.15**	**43.50**	**82.72**
Cu	2012	136.36	70.04	56.14
	2013	**117.05**	**45.65**	**64.20**
Pb	2012	38.32	26.11	7.50
	2013	**53.83**	**38.21**	**11.78**
Ni	2012	56.75	25.16	26.47
	2013	**94.44**	**54.37**	**38.69**
Hg	2012	0.54	0.23	0.22
	2013	**0.71**	**0.38**	**0.26**
Cd	2012	1.63	0.85	0.38
	2013	**2.15**	**1.43**	**0.53**

Load of Cl, SO_4, Cd and Pb transported from the polish drainage basin to the Baltic Sea

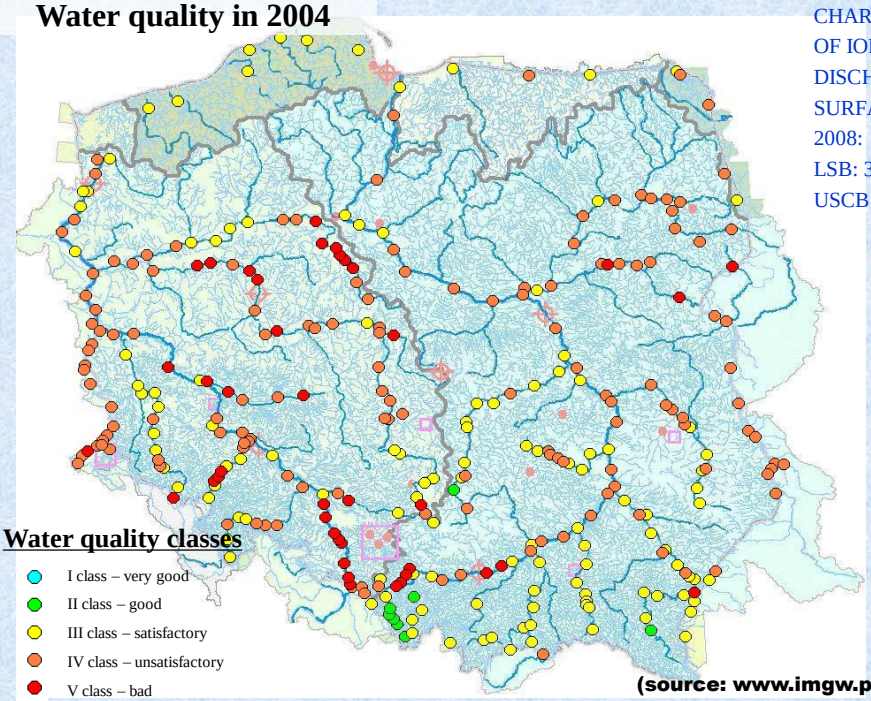
(from: CSO, Environment, 2008)





2008 data of Cd Pb load - not include the Vistula River.

Water quality in 2004



Water quality classes

- I class – very good
- II class – good
- III class – satisfactory
- IV class – unsatisfactory
- V class – bad

(source: www.imgw.pl, changed)

CHARGE OF SUM OF IONS Cl+SO4 DISCHARGED INTO SURFACE WATER IN 2008:
LSB: 313 273 Mg
USCB: 1 288 068 Mg

Contamination of surface waters in Poland - the most important environmental threat

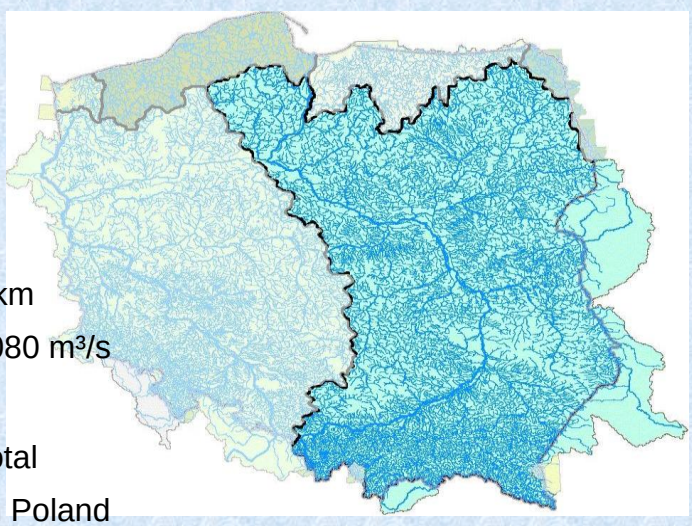
waters from coal mines dewatering and leaching processes of coal mining wastes have been polluted because of:

- **chlorides and sulfates,**
- **heavy metals and radioactive elements i.e. Ra^{226} and Ra^{228},**

  (radioactivity ranged from 0.1 to 20 kBq/$m^{3)}$;

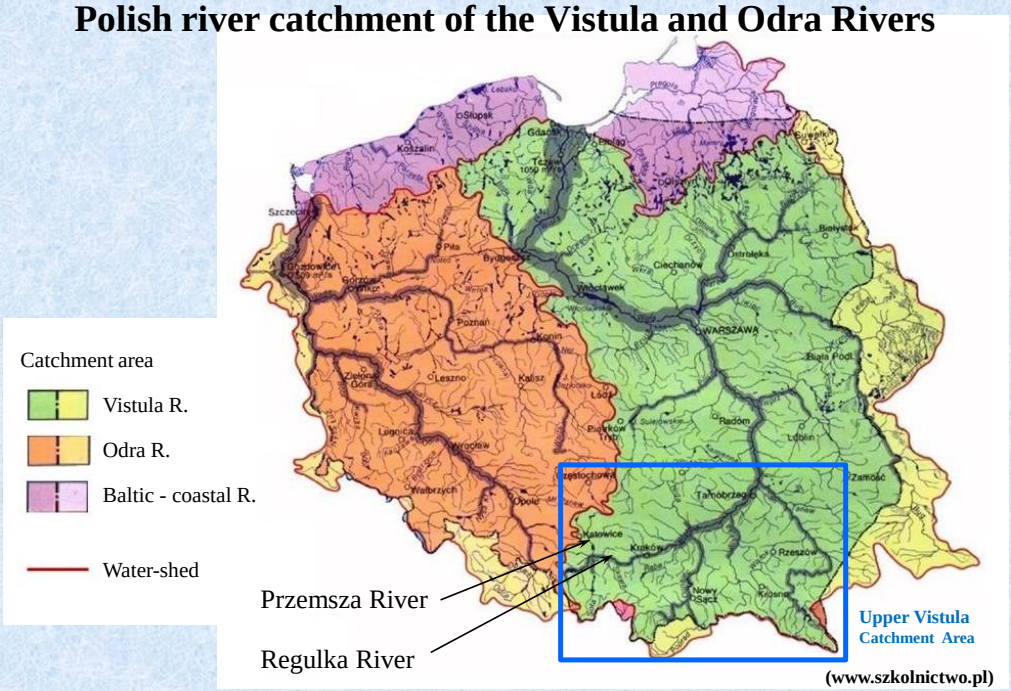
  (e.g. the upper Vistula and the Odra river sediments are strong and/or very strong polluted with Cd and Zn).

The Vistula river basin



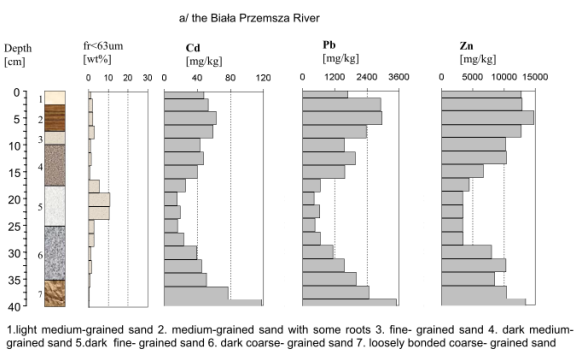
- Vistula river:
  - 16th in Europe
  - length – 1047 km
  - water flow – 1080 m^3/s
- Basin area:
  - 194 424 km^2 total
  - 168 700 km^2 in Poland
  - 52% surface of Poland

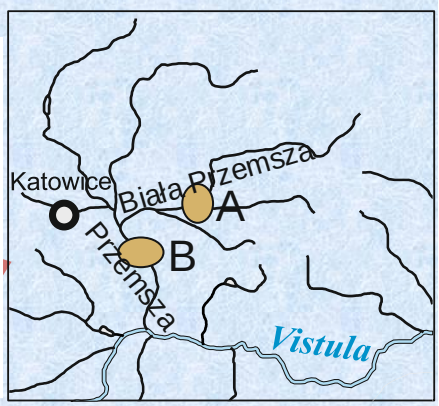
Polish river catchment of the Vistula and Odra Rivers



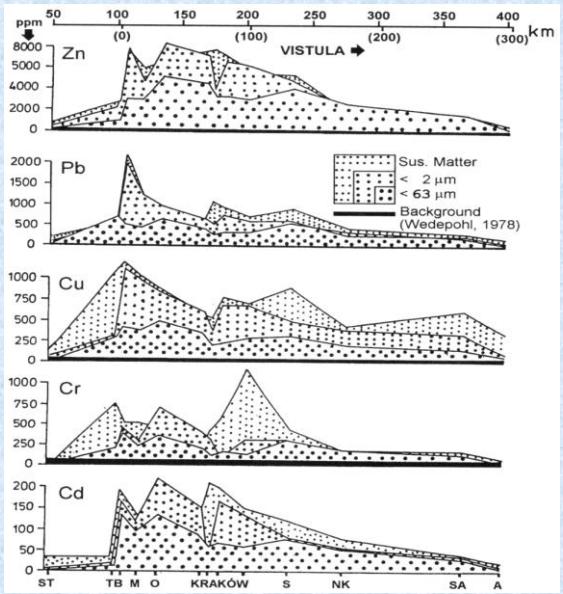
The Biała Przemsza River – sediment profile (fr. < 63um)

U. Aleksander-Kwaterczak, E. Helios-Rybicka, 1998



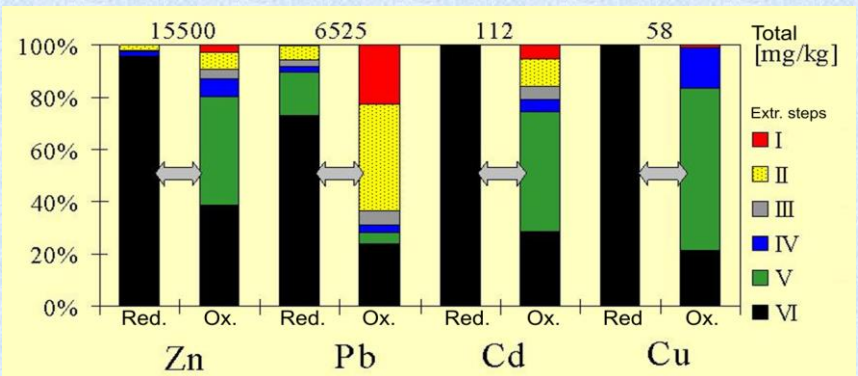


Heavy metals distribution among the suspended matter and the bottom sediment size fractions of the Upper Vistula River



(Helios-Rybicka et al. 2000)

Fractionation patterns of Zn, Pb, Cd, Cu of the Przemsza River sediment sumple close by Zn-Pb ore mining, procesing and smelting industry (reducing Red and oxidizing Ox conditions)

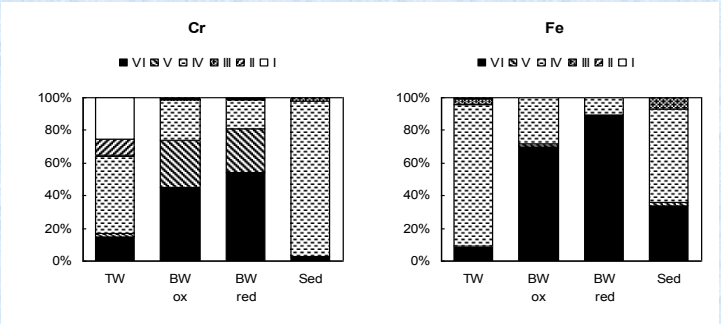


Extraction steps: I – Exchangeable, II – Carbonatic, III – Easily reducible, IV – moderately reducible, V – Sulfidic/organic, VI - Residual

Speciation of Cr i Fe in waste from **Alwernia chemical plant**

and in the fr. <2 μm of **Regulka River sediment** (red and ox conditions)

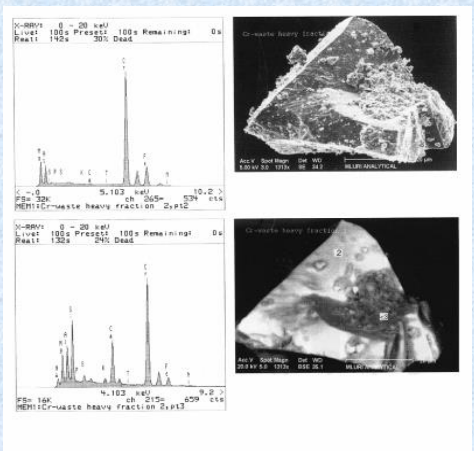
(fr. <2 μm of sedimnt contain: **Cr: 7.3 wt.%; Fe 4.1wt.%**)

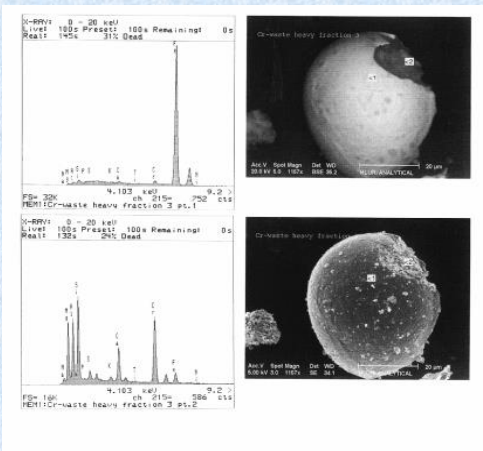


TW – top layer of waste
BW – bottom layer of waste
ox - oxic, and red – reduce condition
Sed – the Regulka River sediment size fraction < 2 μm

SEM and EDX of heavy fraction (HF>2.95)

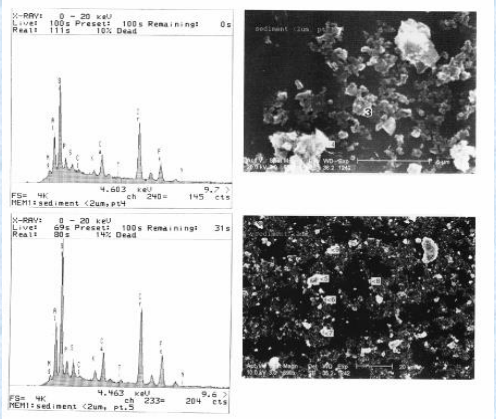
of bottom waste sample Chemical Plant Alwernia





XRD diffraction confirmed presence of Magnesiochromite – $MgCr_2O_4$ $(Mg,Fe)(Cr,Al)_2O_4$

SEM and EDX of the fr. <2μm of the Regulka River bottom sediment



The way of Cr transport in to Regulka River

- **Cr transport from waste dump into the R. River**
- **The highest content of Cr in the size fr.** <2μm (ca. 7 wt.%) mainly combined with Fe-oxides
- **It seems that in mineralized river neutral water disolved Cr (+6) converte into less soluble Cr(3+),**

$$CrO_4^{2-} \rightarrow Cr(H_2O)_4(OH)^{2+}$$

which are sorbed by Fe-oxides.

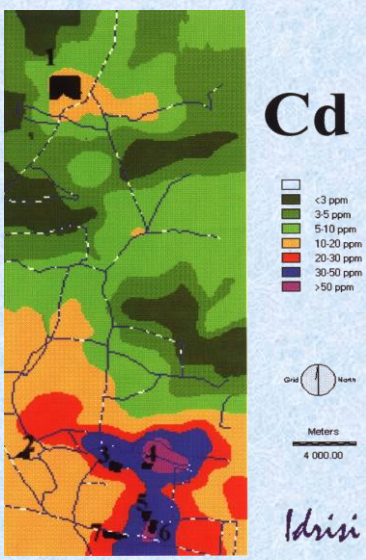
- **Formation of magnesiochromite in sediment is evident but also direct transport of this phase from waste to River ist possible.**

Line of Cr, Fe, Mg (magnesiochromite - $(Mg,Fe)\ (Cr,Al)_2\ O_4$), Si, Al i K (orthoclase and mica) and Ca i S (gypsum and calcite), and line of Zn (Zincite ZnO?)

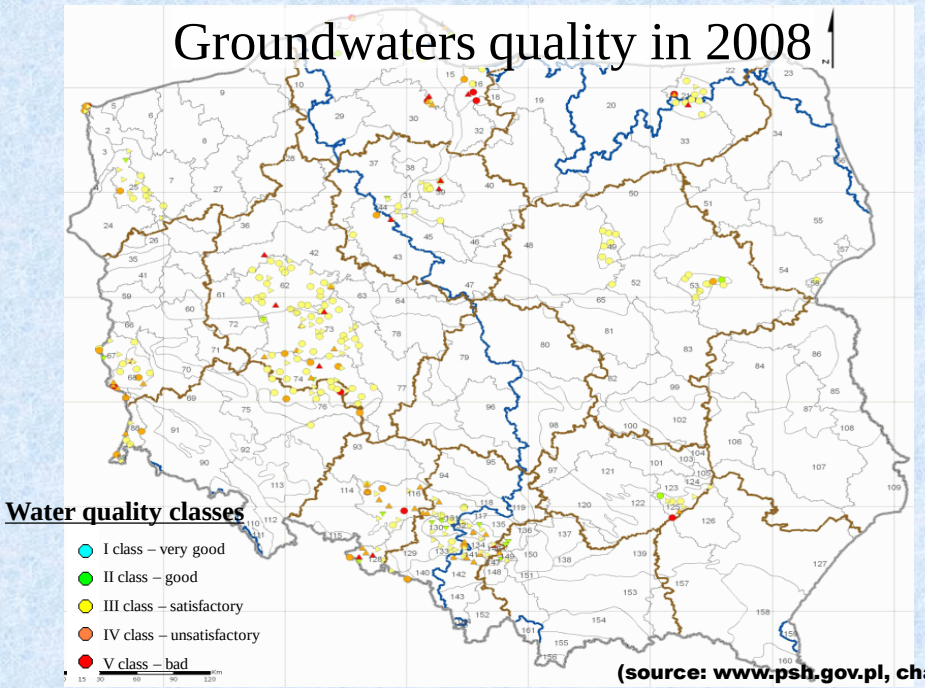
Coal mining and metallurgy cause the soils contamination

Example: Soil contamination with Cd at Upper Silesia

(Helios- Rybicka et al., 1998)



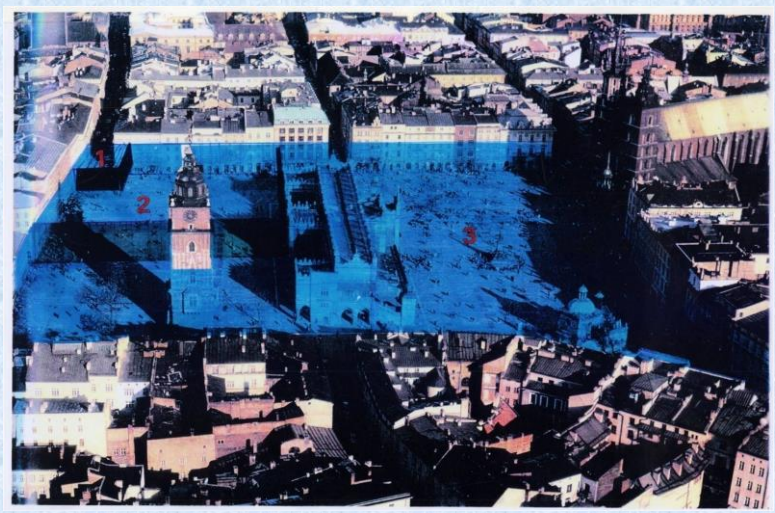
Groundwaters quality in 2008

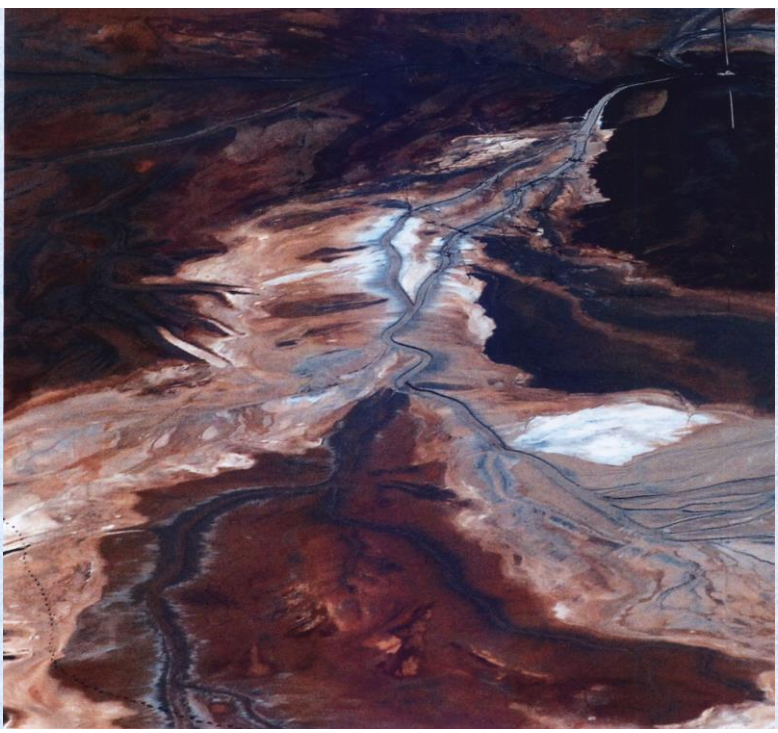


(source: www.psh.gov.pl, changed)

Krakow main square = Rynek Główny

1 groundwater, 2 consuption drinking water, 3 total used of water per day (ca. 800 000 residents)





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Upper Vistula River and its Carpathian tributaries: localization of the water dams in the river catchment