On mercury dynamics in the aquatic environment of the Idrija mercury mine region, Slovenia

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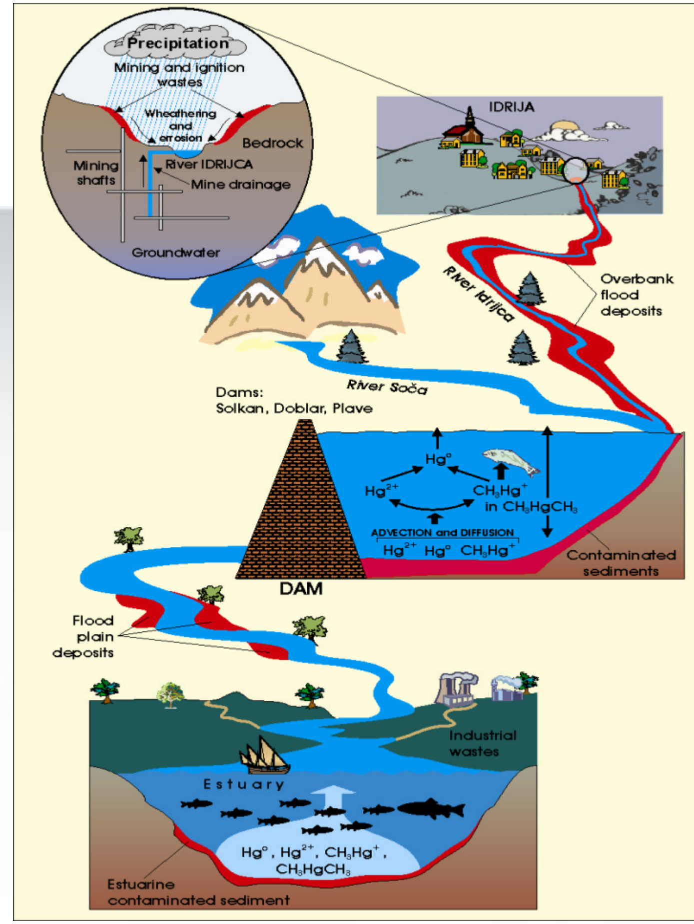
Objectives

- To synthesize the knowledge of environmental mercury behavior in the Idrijca River drainage system with an emphasis on the aquatic environment
- To gain an understanding of mercury’s chemical and transport processes in this specific mercury contaminated site
- To establish major sources and sinks, fate and distribution of mercury at the catchment scale (measurements of different Hg species in different environmental compartments)
- To develop a mass-balance model of mercury in the Idrijca River drainage system (simulation of future trends of Hg contamination → support for sound remediation planning)

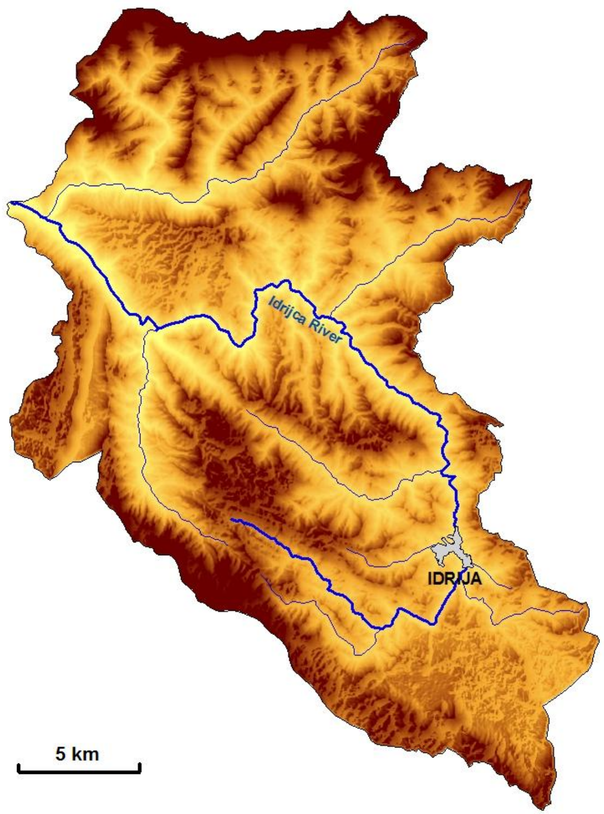
Study area – *Idrijca River drainage system*

IDRIJA MERCURY MINE

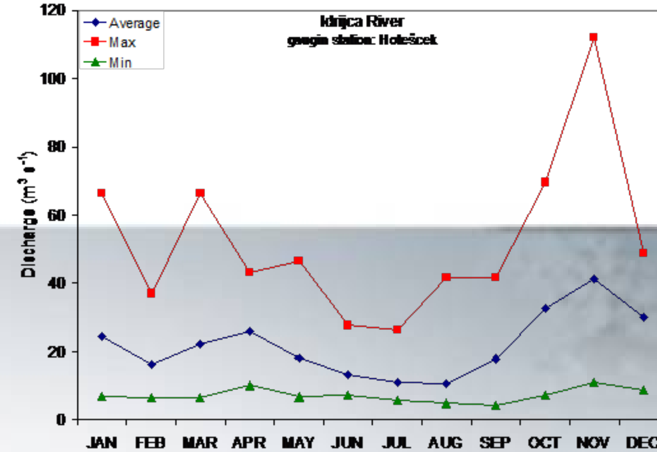
- 500 years of Hg mining (1490-1990)
- 127.000 tons of Hg extracted
- >37.000 tons lost into the environment



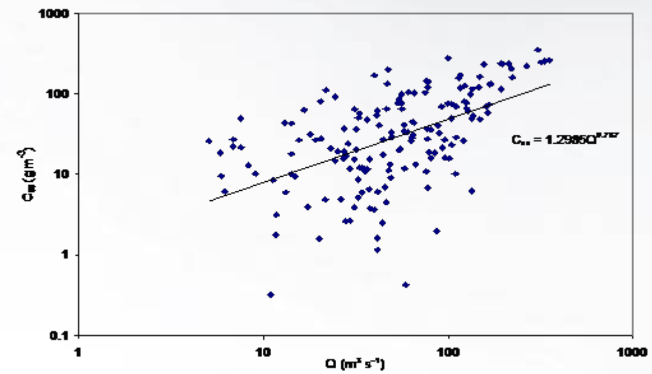
Study area - *characteristics*



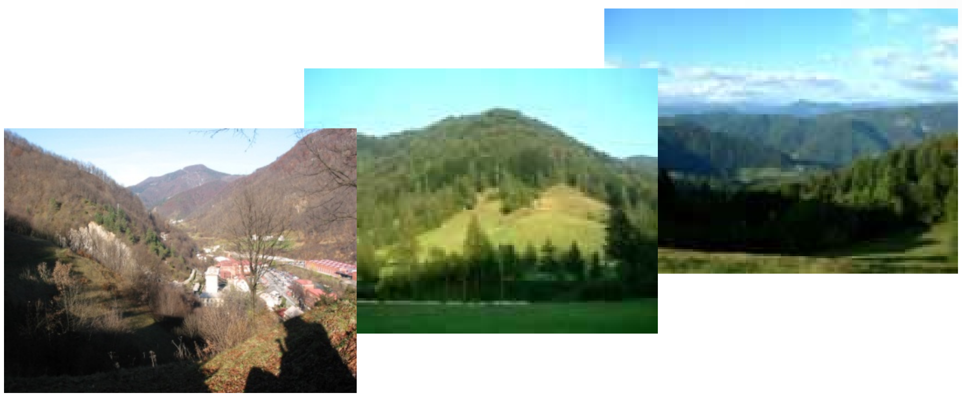
- River network density 1.51 km/km^2
- Geology: limestone and dolomite
- Land cover: forests >90%
- hilly area, steep slopes
- altitudes from 150 to 2000 m. a. s. l.
- Precipitation 2000 – 3000 mm year^{-1}



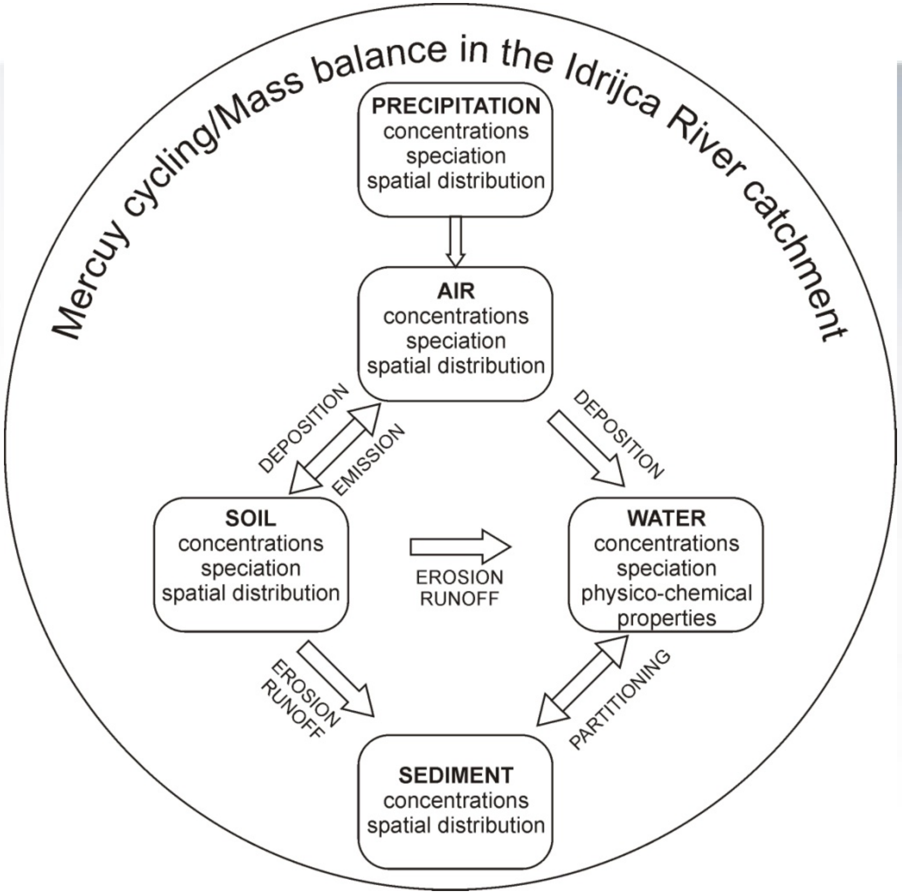
Maximum, average and minimum monthly discharges of the Idrijca River for the period (1991-2004)



Suspended sediment rating curve

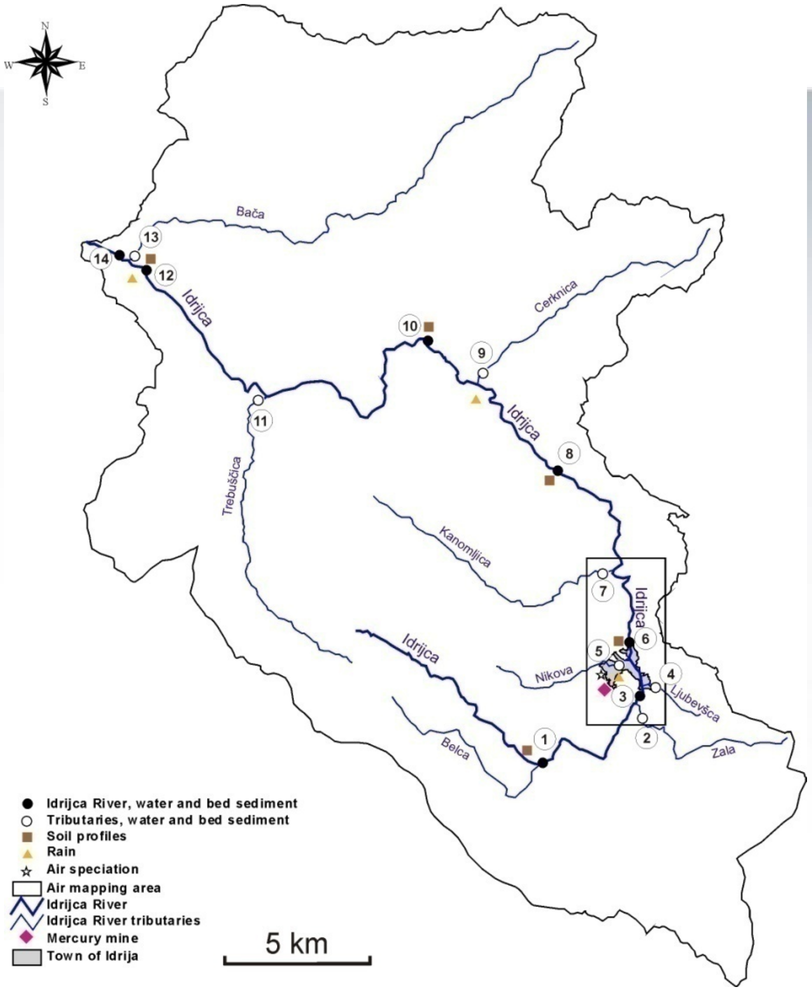


Outline of the study – *catchment scale approach*



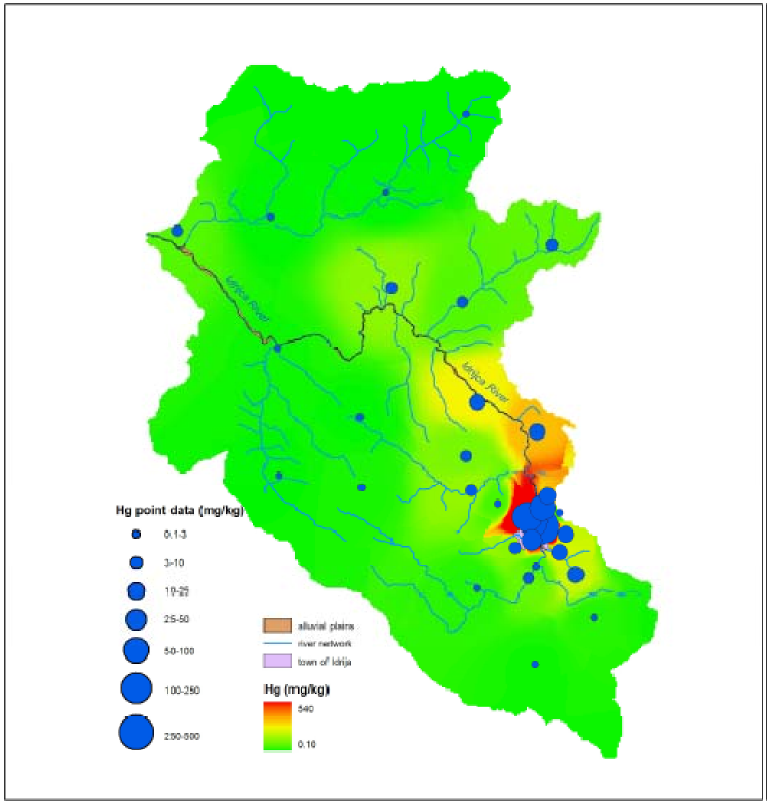
- Environmental compartments: water, river sediment, soil, atmosphere
- Processes: - Hg transformations within compartments
  - Hg transport/exchange between compartments

Experimental - *sampling locations*



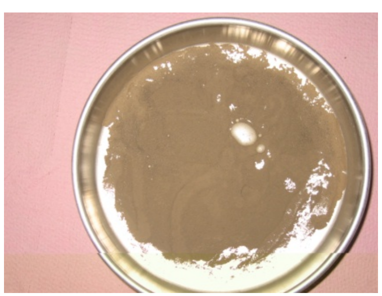
- Water: 7 loc. Idrijca River + 7 major tributaries, fall 2006 – spring 2007
- River bed sediment: 4 loc. Idrijca River + 6 major tributaries
- Soil: 4 loc. (different land cover: alluvial soil, forest, meadow)
- Air: *in situ* measurements (air mapping, speciation)
- Rain water, 17 events October 2006 - September 2007 (open air/throughfall)

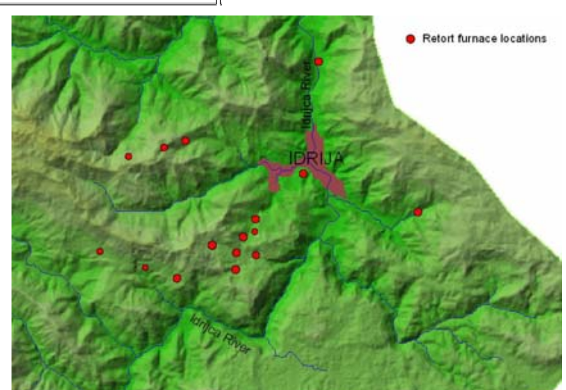
Hg distribution in soil – *terrestrial source of mercury*

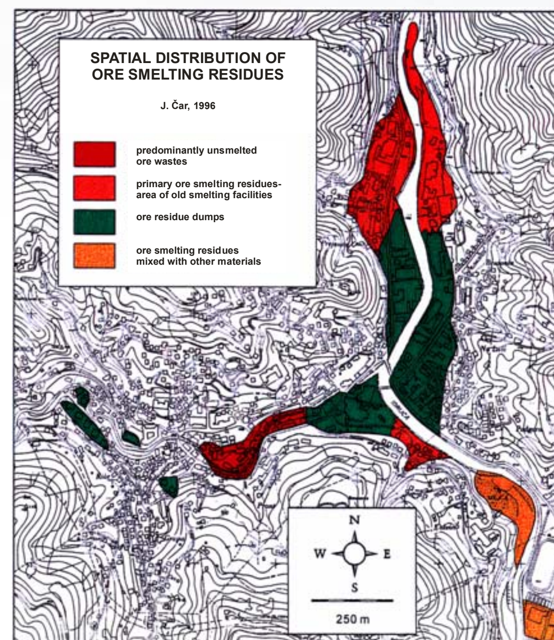


Most polluted sites: town of Idrija, alluvial soils along the Idrijca River, former smelting facilities, smelting residues – cinnabar fraction prevails

Sharp decrease with the distance from the sources – more mobile Hg fractions prevail

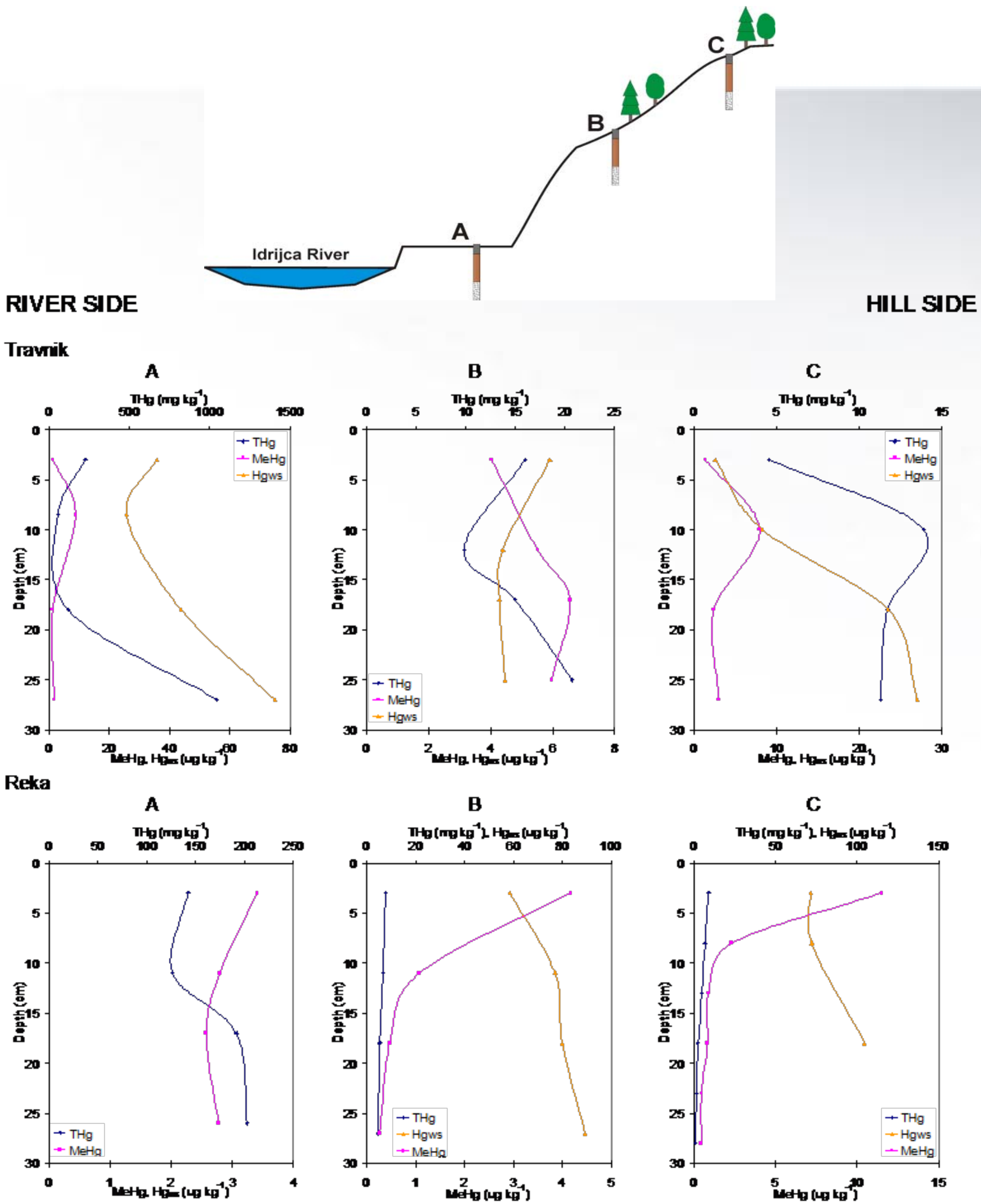






Hg in soil

Hg in soils – *spatial and vertical distribution*



(results of the JAP-SLO collaboration)

THg:

- Decrease with the distance from the mine
- > Hg in organic rich 5-15 cm topsoil
- B profiles enriched in Hg (denudation processes)
- Alluvial soils (heterogeneity → random deposition/erosion during flooding)

MeHg:

- < 1% of THg
- Concentrations of the same order of magnitude (demethylation enhanced in Hg reach soils, Hg-resistant bacteria)
- High THg (> cinnabar particles) → MeHg distributed heterogeneously (methylation inhibited when bioavailability of Hg^{2+} is low)

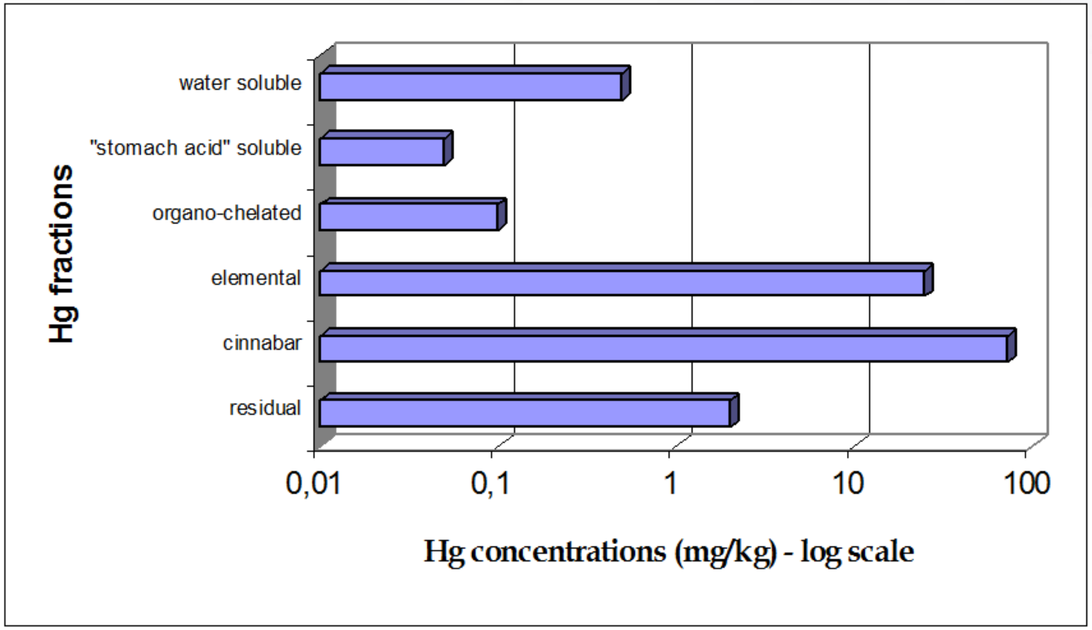
Hg_{ws}:

- Indicator of potential bioavailability ?
- No correlation between Hg_{ws} and MeHg → MeHg tightly bound to OM and not available for leaching

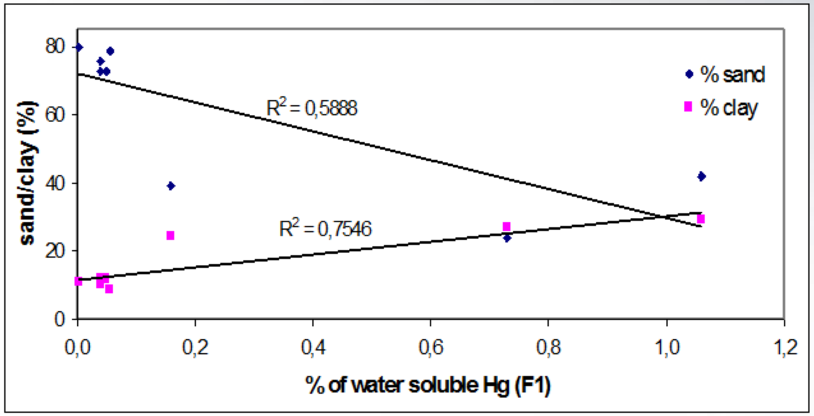
Hg in soils – *fractionation*

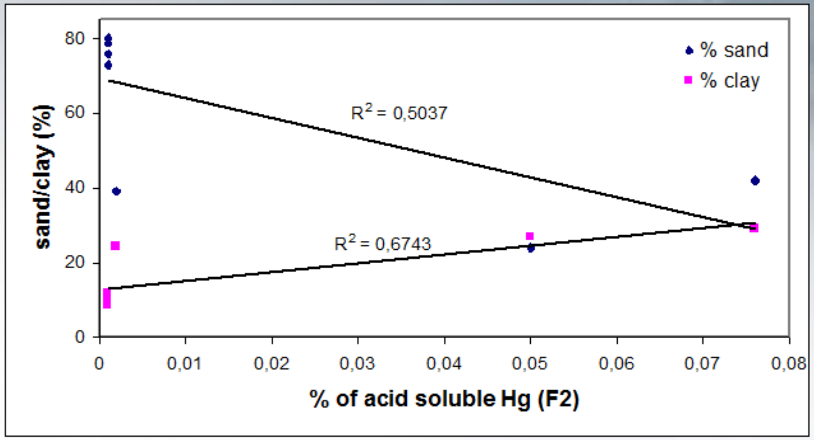
Fractionation – sequential extraction *(Bloom et al., 2003)*

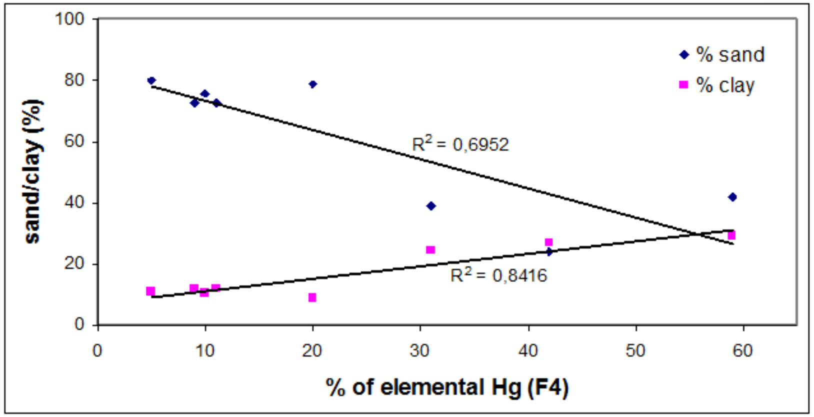
Step	Extractant	Fraction	Typical components
F1	Milli-Q water	Hg soluble in water	$HgCl_2$, $HgSO_4$
F2	pH 2 HCl/HOAc	Hg acid soluble pH 2	HgO
F3	1M KOH	Hg in organic complexes	Hg bound in humics, Hg_2Cl_2
F4	12 M HNO_3	Hg bound in mineral lattice	Lattice Hg, Hg_2Cl_2, Hg(0)
F5	Aqua regia	Cinnabar	HgS, m-HgS, HgSe, HgAu
Residual	HNO_3/HF/H_2SO_4	Hg bound in silicates	

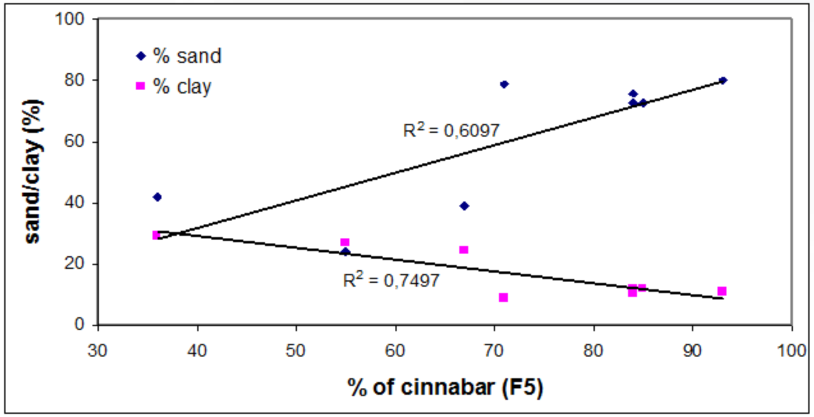


Hg in soils – *grain size effect on Hg fractionation*





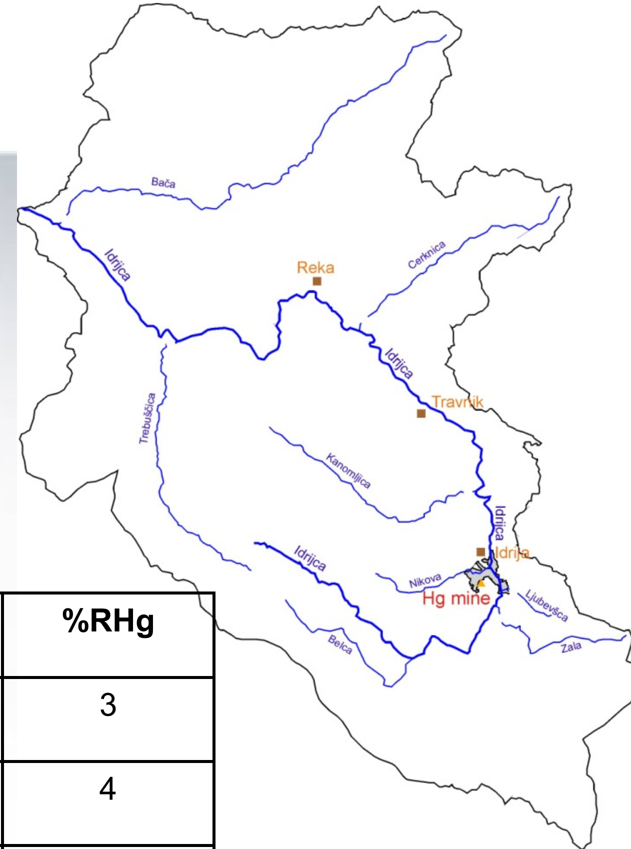




Potential bio-available Hg fractions are bound to fine grained soils which are more easily eroded and transported to aquatic environment.

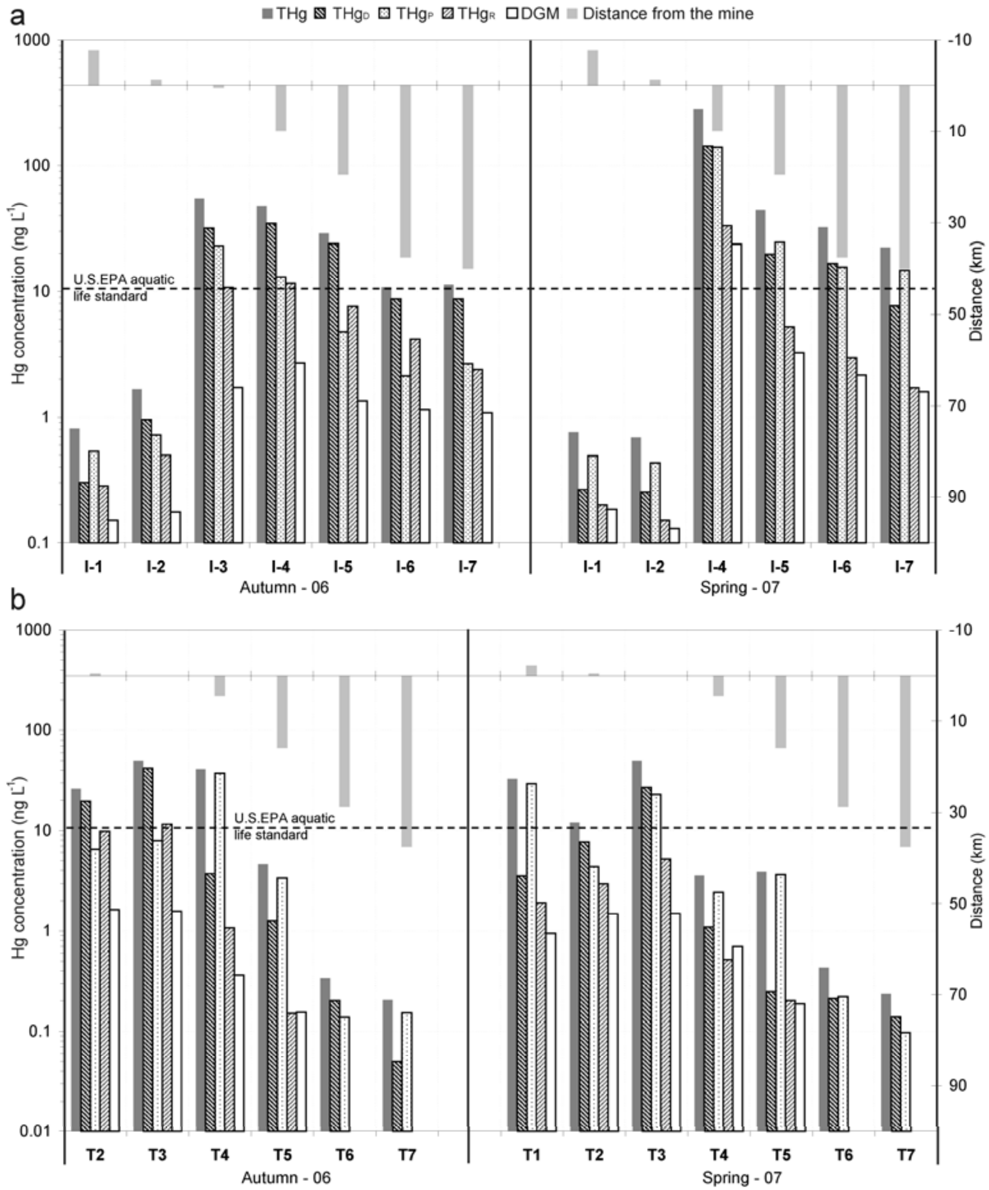
Hg in soils – *soil aqueous phase fractionation*

Leaching experiment:
- Soil weight/water volume ration 1:100
- Filtration through 45 µm pore size filter
- Measurements of Hg species (DHg, RHg, DGM)



Soil sample	THg (mg/kg)	DHg (ng/L)	RHg (ng/L)	DGM (ng/L)	%RHg
Idrija forest	251 ± 4.2	4927	147	6	3
Idrija meadow	100 ± 2.2	985	44	4	4
Travnik forest	19 ± 0.4	137	31	10	23
Travnik meadow	23 ± 0.7	260	67	4	26
Reka forest	9 ± 0.6	206	45	2	22
Reka meadow	4 ± 0.1	92	51	5	55

Inorganic mercury species in the Idrijca River system



a – Idrijca River, b - tributaries

Idrijca River:

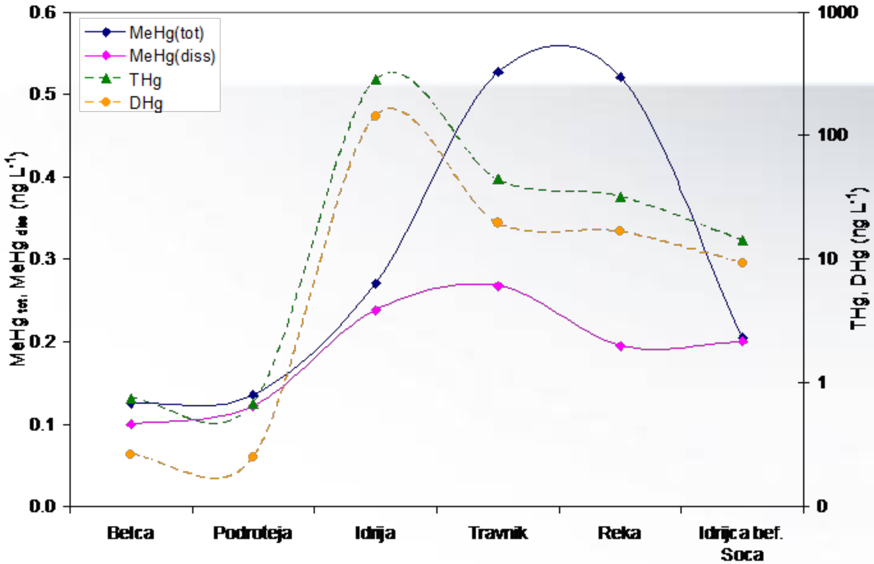
- THg range from < 1 to ~ 300 ng L^{-1}
- on average ~40 % bound to particulates
- corr. between DHg and RHg (R^2 = 0.82)
- >DGM → %RHg decreses => Hg^{2+} reduction

Tributaries:

- Hg mine area (erosion and leaching of contaminated soils, ore residuals)
- drainage of the native Hg-bearing rocks
- on average ~60 % bound to particulates
- sharp and clear decrease with the increasing distance from the Hg mine area

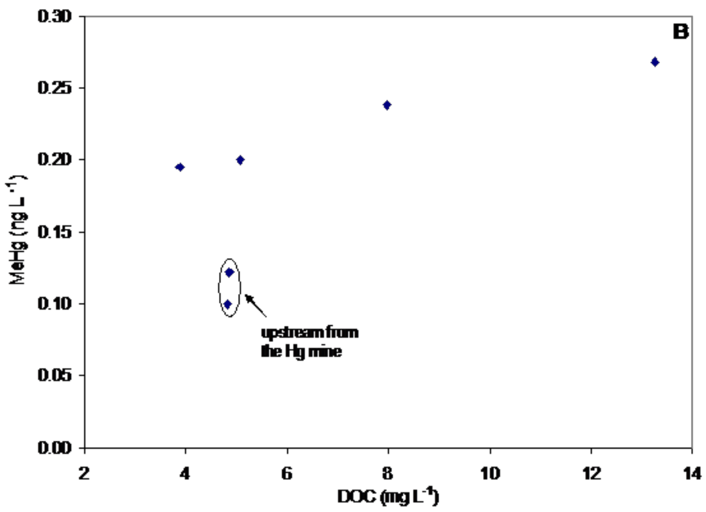
River water

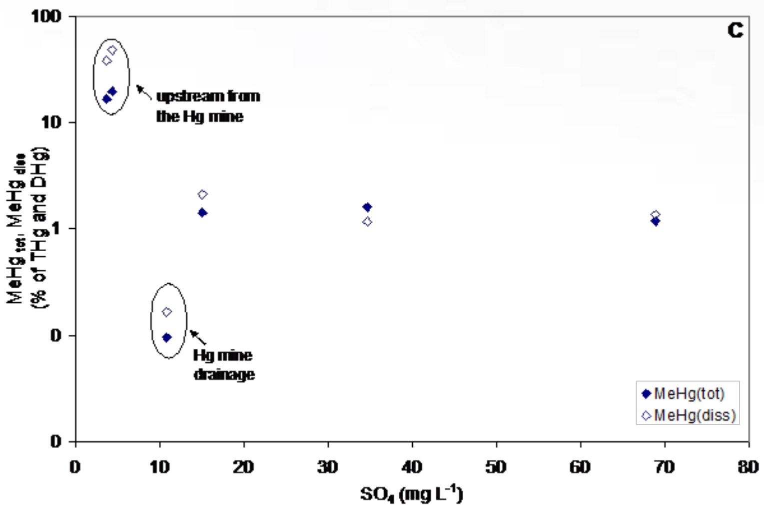
Methylmercury in the Idrijca River



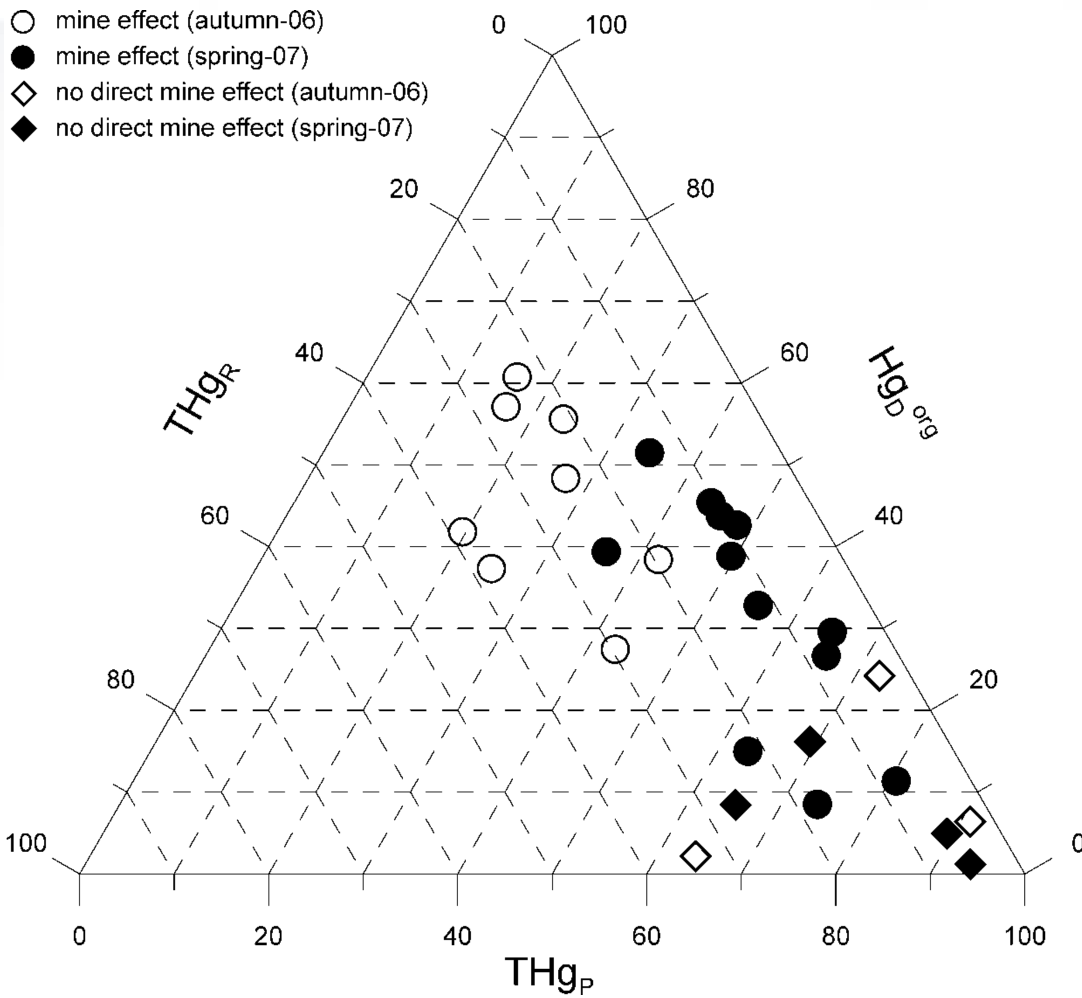
$MeHg_{tot}$ and $MeHg_{diss}$ concentrations and comparison with THg and DHg concentrations in the Idrijca River

- < 1.5 % of THg
- MeHg maximum cca. 10 km downstream from the mine (more sediment deposited, organic material → increased microbial activity)
- Methylation of Hg by SRB (Hines et al., 2000; Lapanje, 2005)



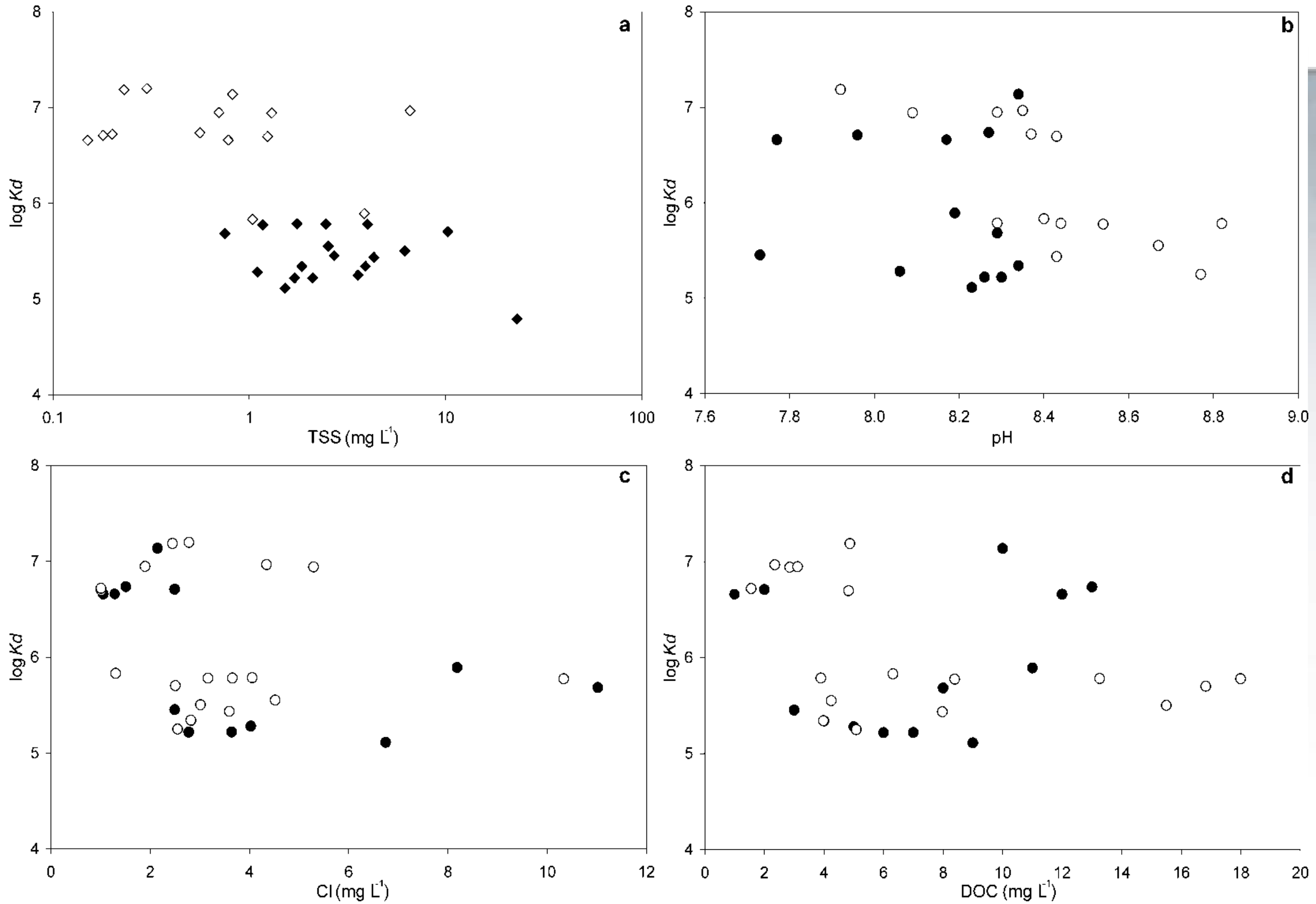


Dissolved and particulate Hg phases in river water



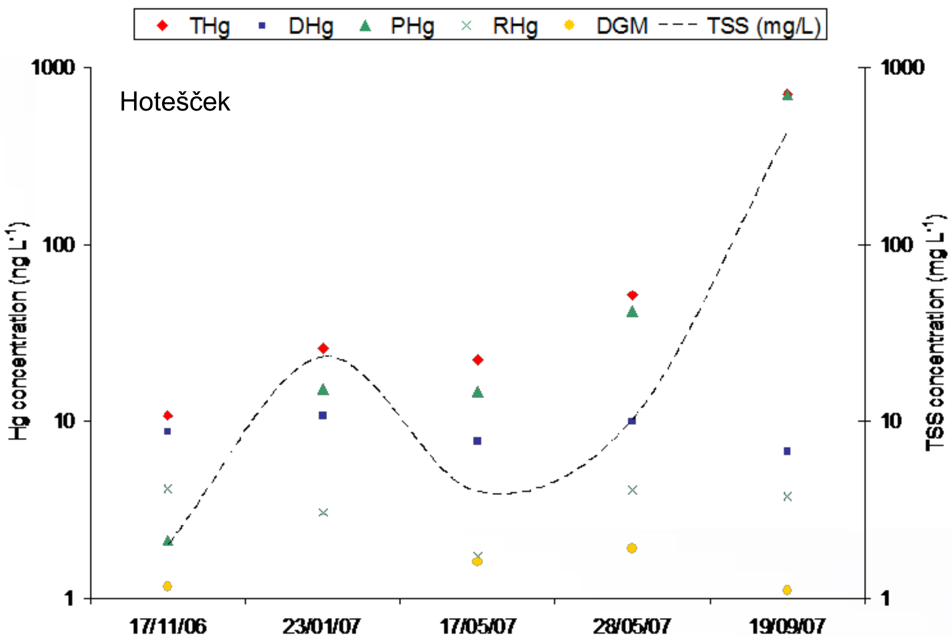
THg_P: total particulate mercury
THg_R: total reactive mercury
Hg_D^{org}: dissolved Hg associated with organic ligands

Hg partitioning between dissolved and particulate phases in river water



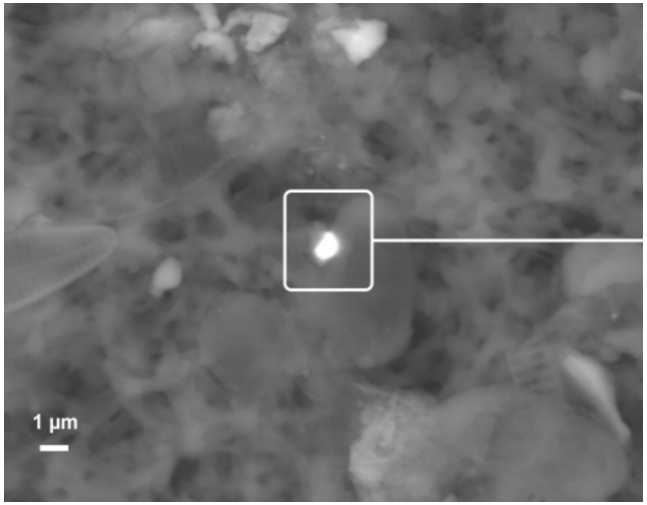
- Distribution coefficient (*Kd*) - ratio between Hg bound to TSS and dissolved Hg (L kg^{-1})
- Negative relationship between *Kd* and TSS
- pH >8 → increased complexation of dissolved Hg by organic and inorganic ligands
- At pH conditions and Cl concentration range, Cl is unlikely to compete with organic matter
- DOC seems to be the main ligand for Hg complexation

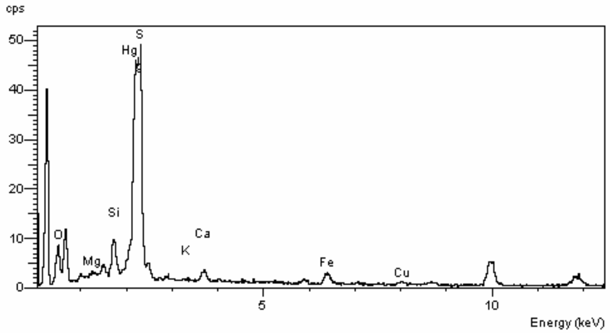
Hydrologic conditions and Hg speciation/partitioning in river water



Storm events:

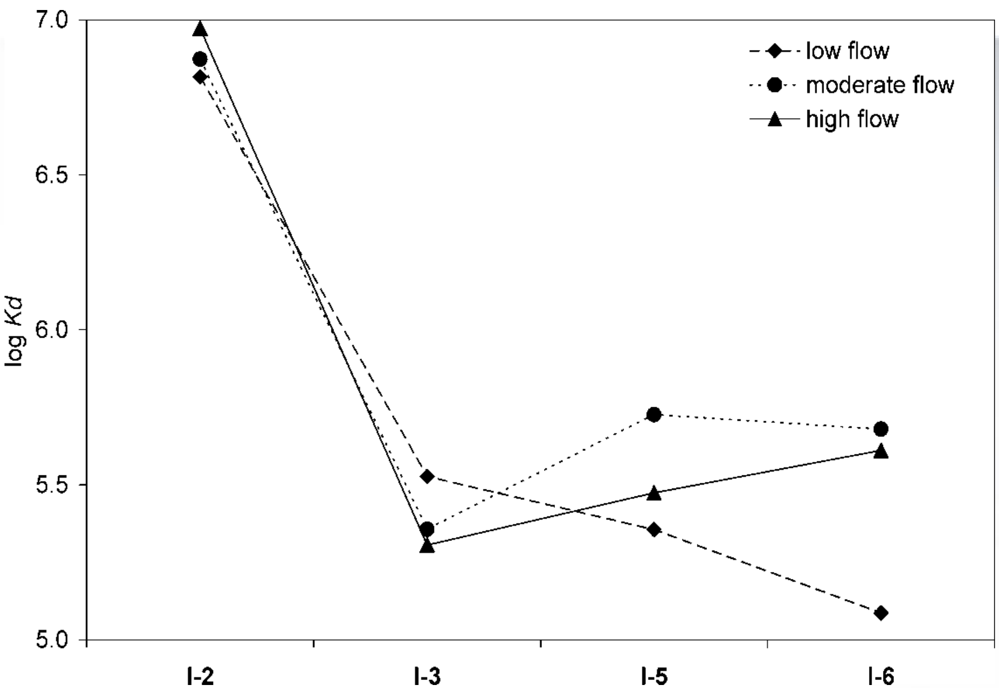
- THg concentrations up to 700 ng L^{-1}, > 99% bound to particulates
- Suspended sediment from 10 up to 3000 mg L^{-1}
- Riverbed erosion and transport of Hg enriched particles



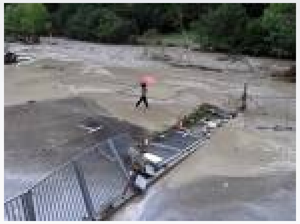


River water

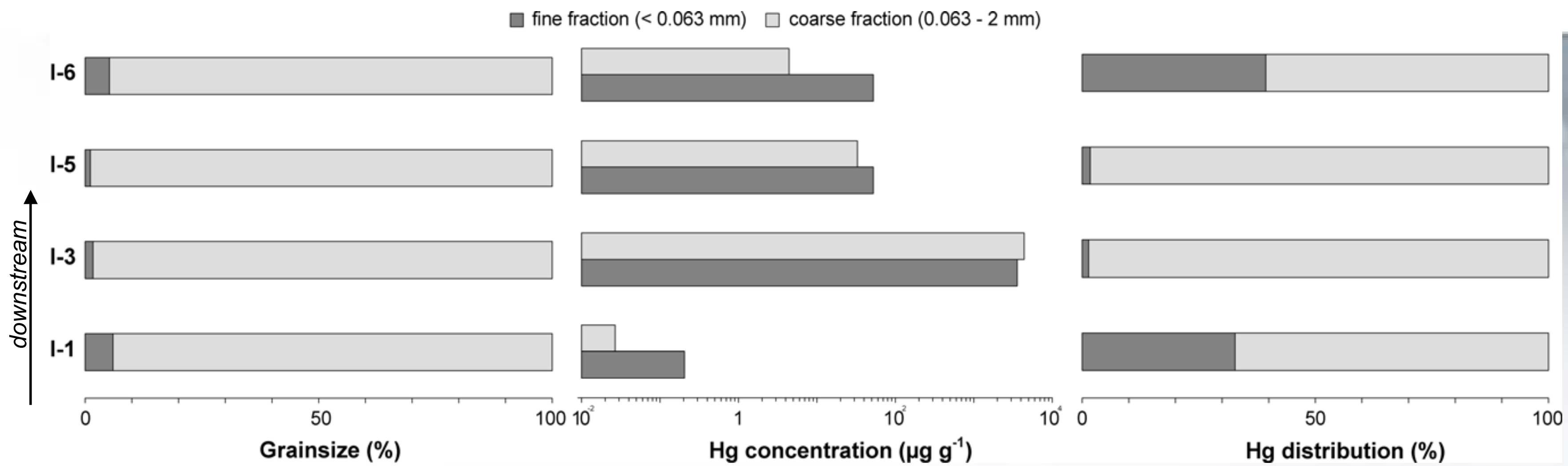
Hydrologic conditions and Hg partitioning



Spatial evolution of Hg distribution coefficient (log Kd) along the Idrijca River

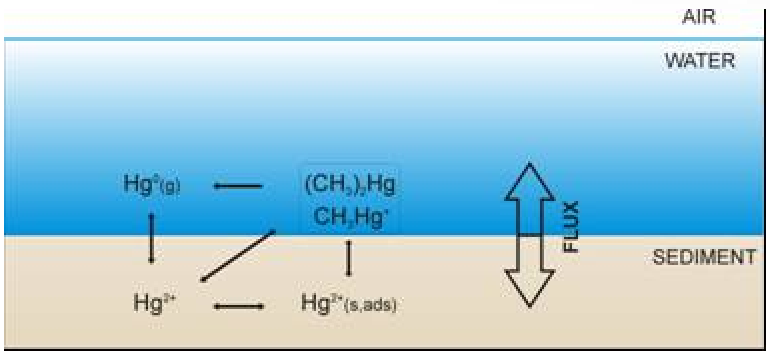


Mercury in the sediments of the Idrijca River

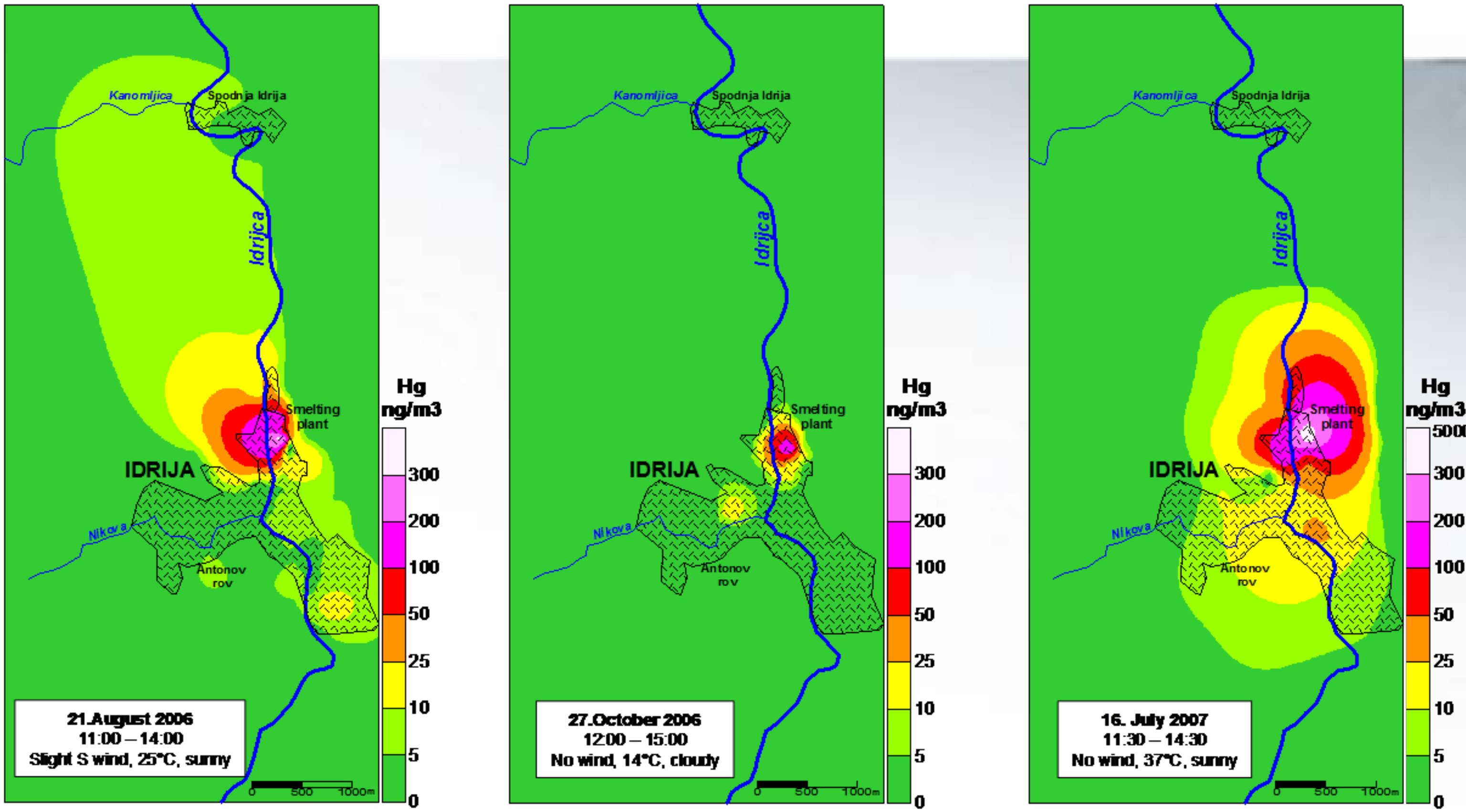


Grainsize, THg concentrations and mercury distribution in the sediments of the Idrijca River

- <0.1 up to > 4000 mg kg^{-1} near the Hg mine
- Fine particles (< 63 µm) up to 12 times more concentrated in Hg (! riverbed erosion and transport)
- ~ 75 % Hg bound to coarse grained particles (riverbed reservoir – methlymercury production)



Hg atmospheric distribution in the town of Idrija

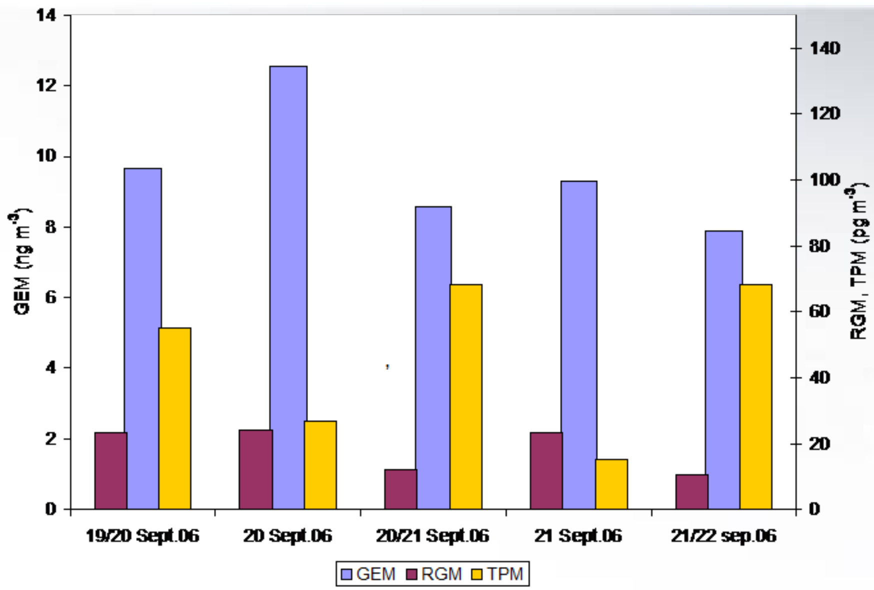


- former smelting plant (up to 5000 ng m^{-3}) and mine ventilation shafts are the main source of Hg in air over the Idrija Valley
- Hg^0 distribution: wind conditions, temperature

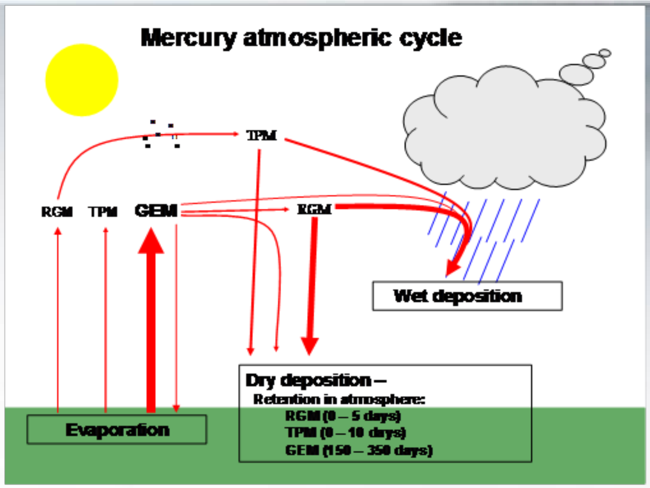
Portable Lumex RA 915⁺ + GPS

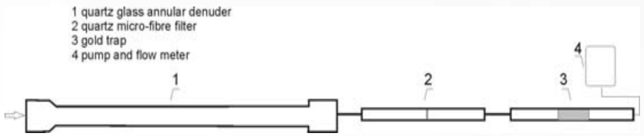
Mercury speciation in air over Idrija

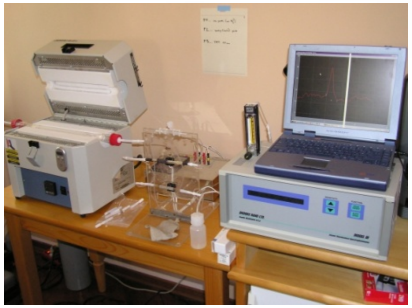
GEM – gaseous elemental Hg, RGM – reactive gaseous Hg, TPM – total particulate Hg



Hg speciation in the Idrija air, diurnal trends

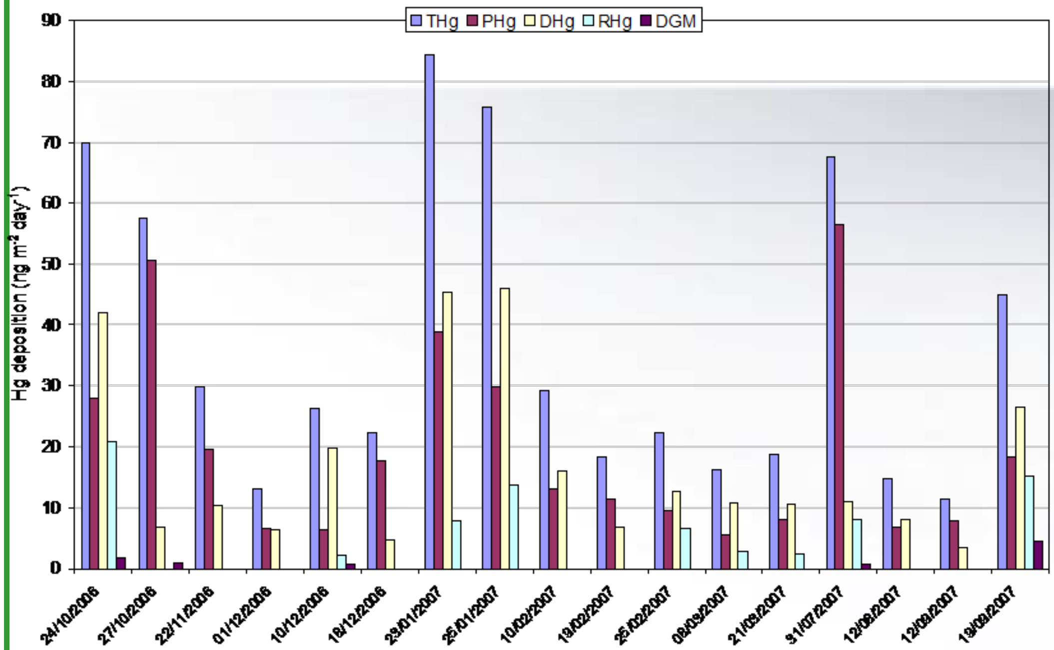






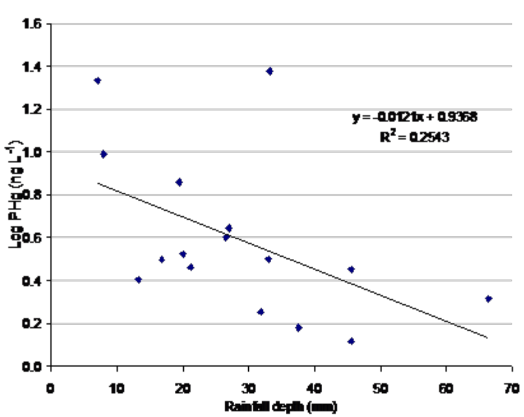
- All Hg species 2-3 fold higher compared to background sites
- GEM concentrations up to 1.5 times higher during the day (photoreduction of divalent mercury forms and increased Hg^0 evaporation from soils)
- higher RGM concentrations during the day (oxidation of Hg^0 to Hg^{2+} by reaction with O_3)
- higher TPM concentrations during the night hours (increased adorbtion of Hg^{2+} onto particles in the air water droplets)

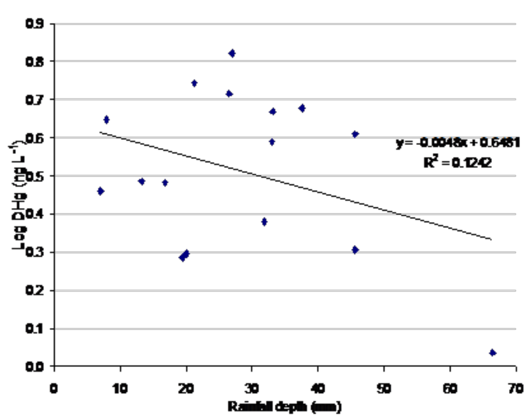
Mercury atmospheric deposition, town of Idrija (Oct.06 – Sept.07)

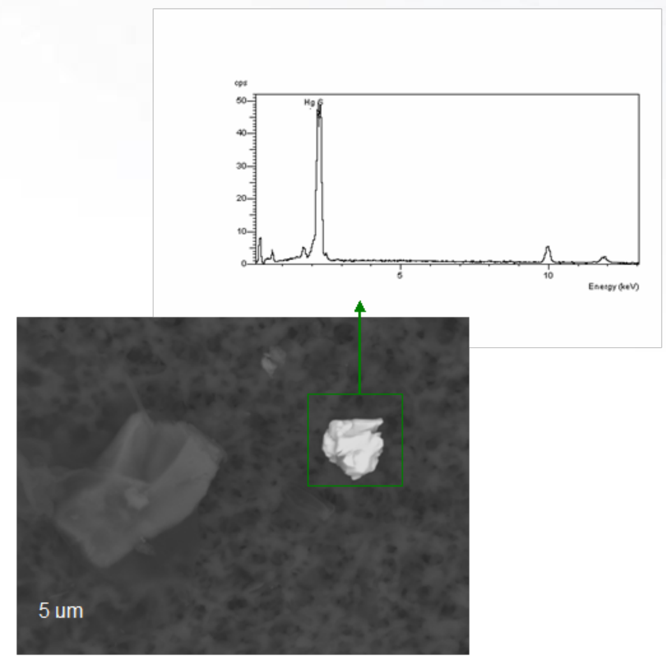


Deposition of different mercury species in precipitation in the town of Idrija

- Open sampling vessels (sum of dry and wet Hg deposition)
- Significant differences between precipitation events (duration, frequency, amount of precipitation)
- > 50% Hg in particulate phase
- no PHg vs. DHg correlation → particulate phase result of dry deposition
- cinnabar – eolian erosion

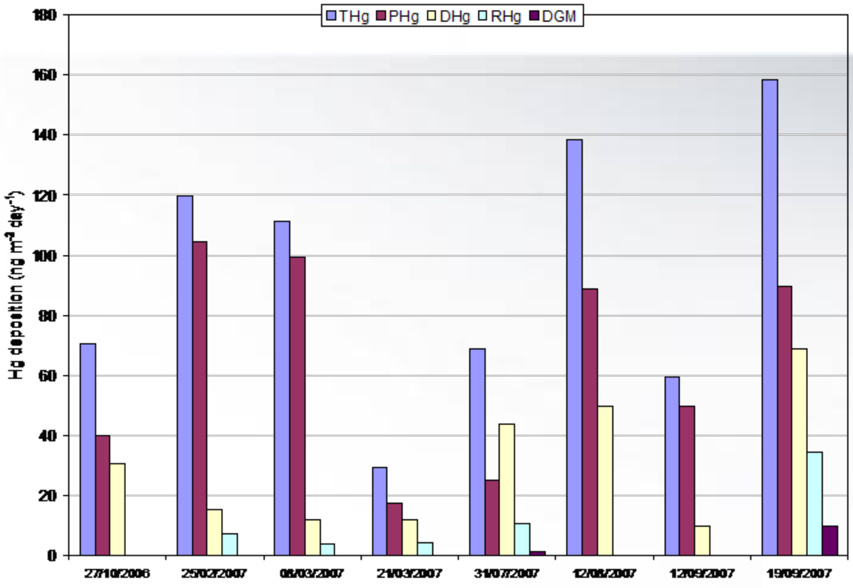




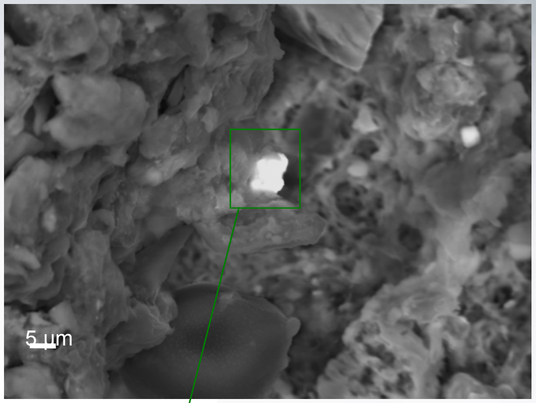


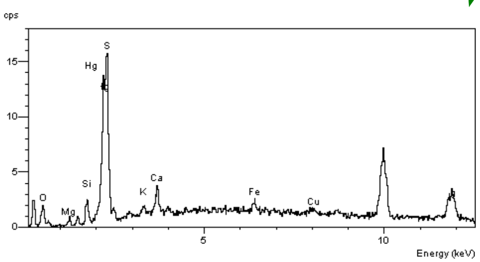
Precipitation

Mercury atmospheric deposition in throughfall, town of Idrija



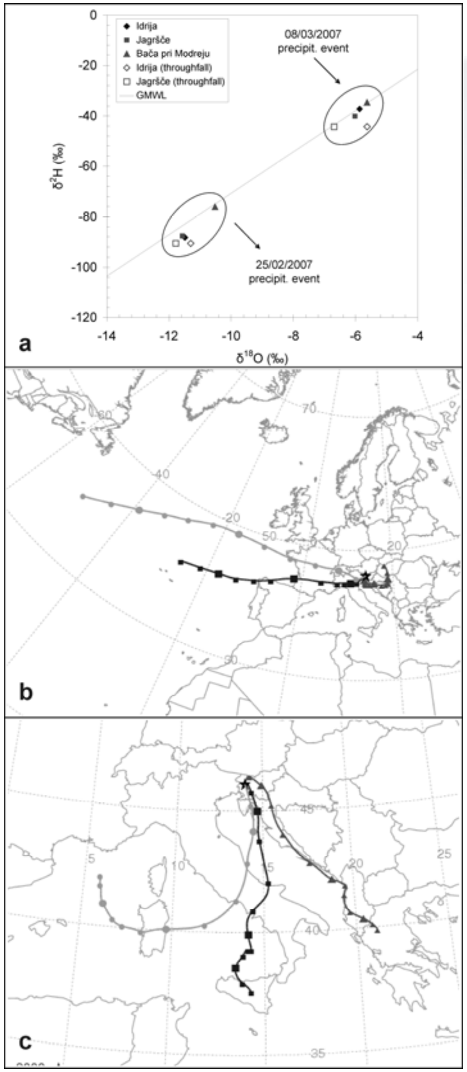
Deposition of different mercury species in the throughfall in the town of Idrija



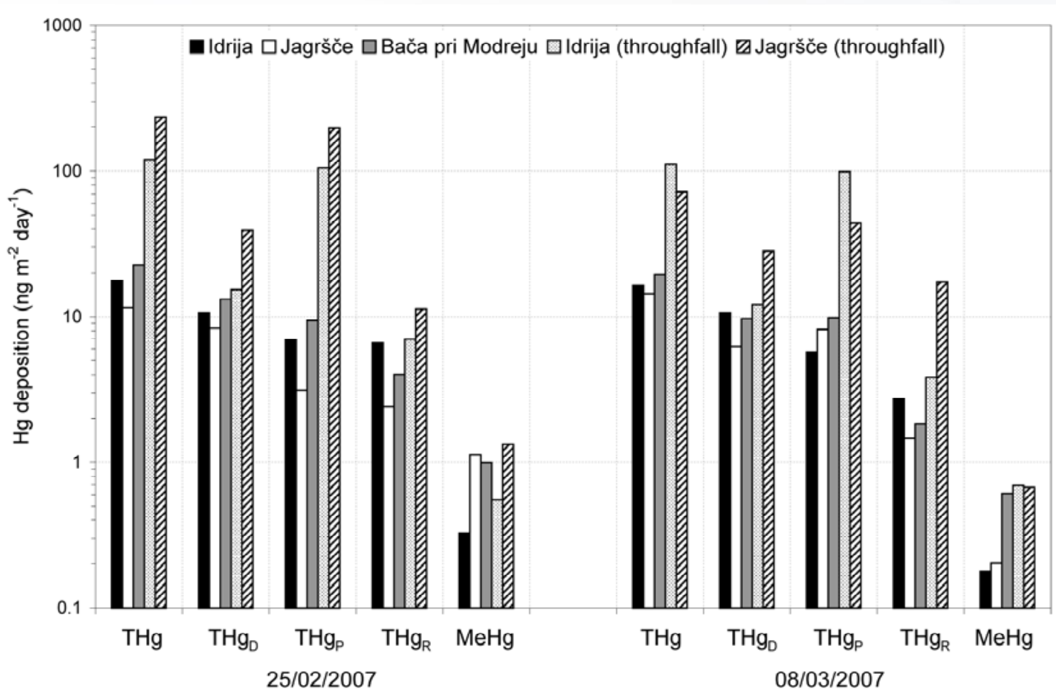


- Significantly higher (2-10 fold) Hg concentrations than in associated event precipitation
- Higher variations in throughfall deposition
- ~ 70% Hg particulate bound
- Throghfall influenced not only by the amount of rainfall but also duration of dry period, wind conditions, ground surface moisture (eolian erosion)

Results – *atmospheric deposition (spatial and meteorological variations)*

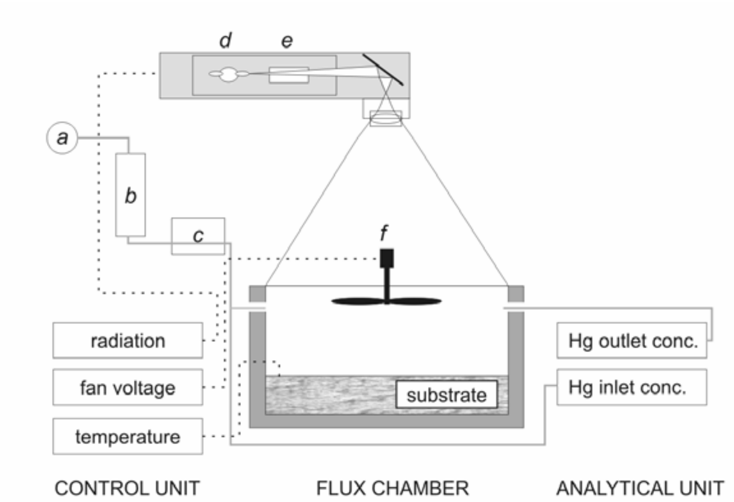


- Significant spatial variations in Hg deposition between sampling sites can not be explained by the distance from local sources
- → Hg deposition in Idrija region influenced by local meteorological conditions



Precipitation

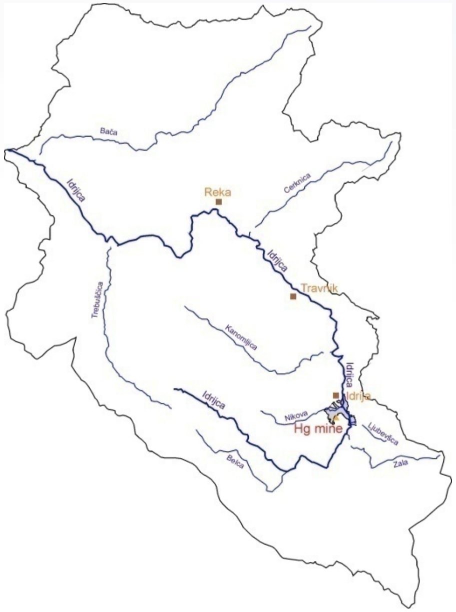
Mercury evaporation from soil - LFMS experiment



Experimental set up of the laboratory flux chamber system.
a: gas supply (ambient air), b: charcoal filter, c: mass flow controller,
d: XE-Arc light source, e: water filter, f: fan (Bahlmann et al., 2006)

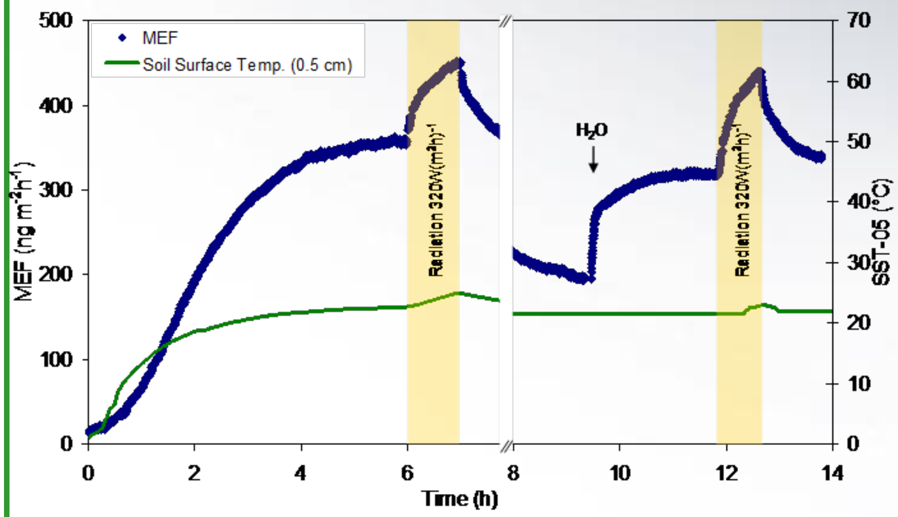
Parameters:

- Temperature
- Solar radiation
- Soil moisture



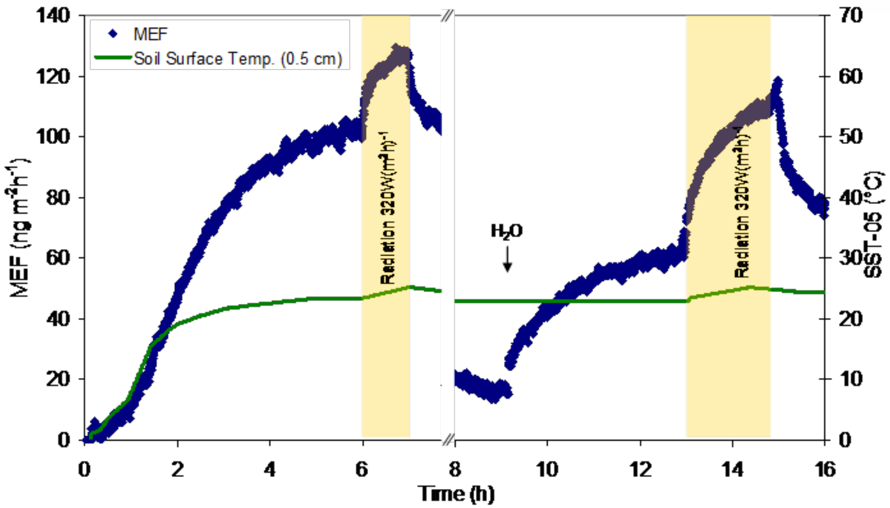
Sample	Type/Land Cover	Texture	OM (%)	THg (µg/g)
Idrija A	forest	clayey	16	251 ± 4.2
Idrija B	meadow	clayey	10	100 ± 2.2
Travnik A	forest	clayey	22	19 ± 0.4
Travnik B	meadow	clayey	18	23 ± 0.7
Travnik C	alluvial plain	loamy	8	417 ± 78
Reka A	forest	loamy	19	9 ± 0.6
Reka B	meadow	loamy	16	4 ± 0.1

Mercury evaporation from soil - LFMS experiment



Experimental design:

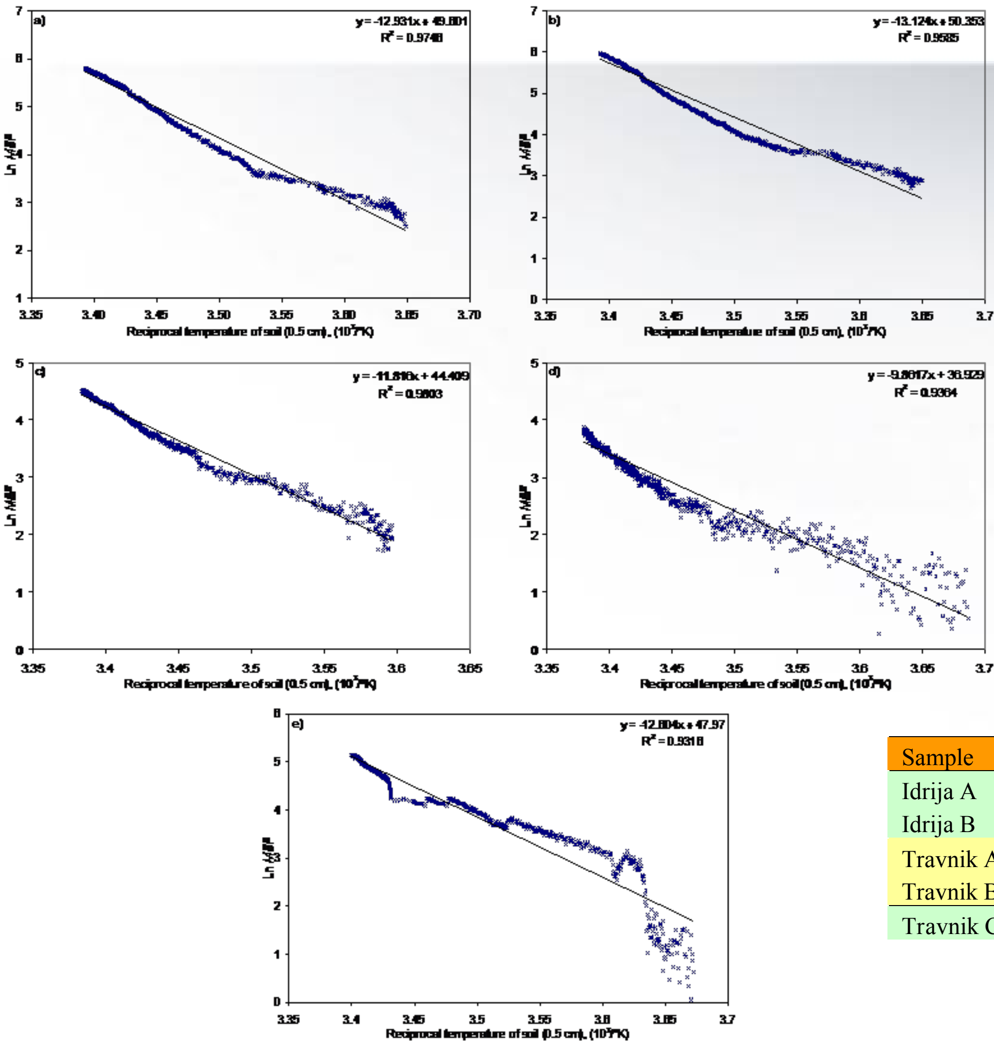
- Hg emission fluxes (MEF) measured 14-16 h
- Soil temperature 0-24 ° C
- UV radiation: 320 W $(m^2\ h)^{-1}$
- Precipitation simulation (300 mL milli-Q)



- MEF = f (Hg soil concentration >> temperature, moisture, solar radiation)

Evaporation from soil

Mercury evaporation from soil - soil temperature effect



Arrhenius equation:

$$Ln(MEF) = Ln(A) - \frac{E_a}{R \cdot T}$$

MEF … flux of Hg,

R … gas constant,

T … temperature (° K)

A … frequency factor

E_a … activation energy.

Sample	Type/Landcover	THg (mg kg^{-1})	Ea (kJ mol^{-1})
Idrija A	forest	251	108
Idrija B	meadow	100	109
Travnik A	forest	19	98
Travnik B	meadow	23	82
Travnik C	alluvial plain	417	105

- Higher E_a calculated for more Hg contaminated soils → Hg binding in soil influence the formation of volatile mercury species
- Higher E_a in soils where insoluble HgS is dominating

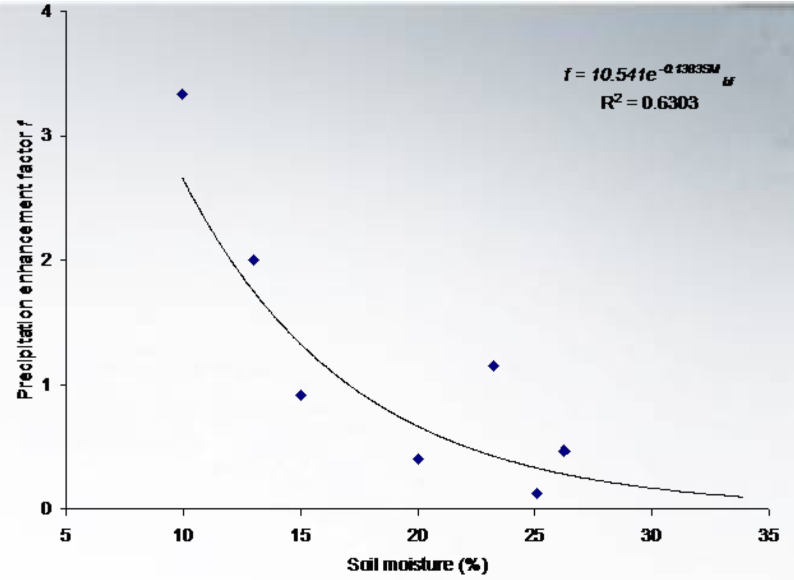
Mercury evaporation from soil - soil moisture effect

$$f = \frac{MEF_{aft} - MEF_{bf}}{MEF_{bf}}$$

f … precipitation enhancement factor

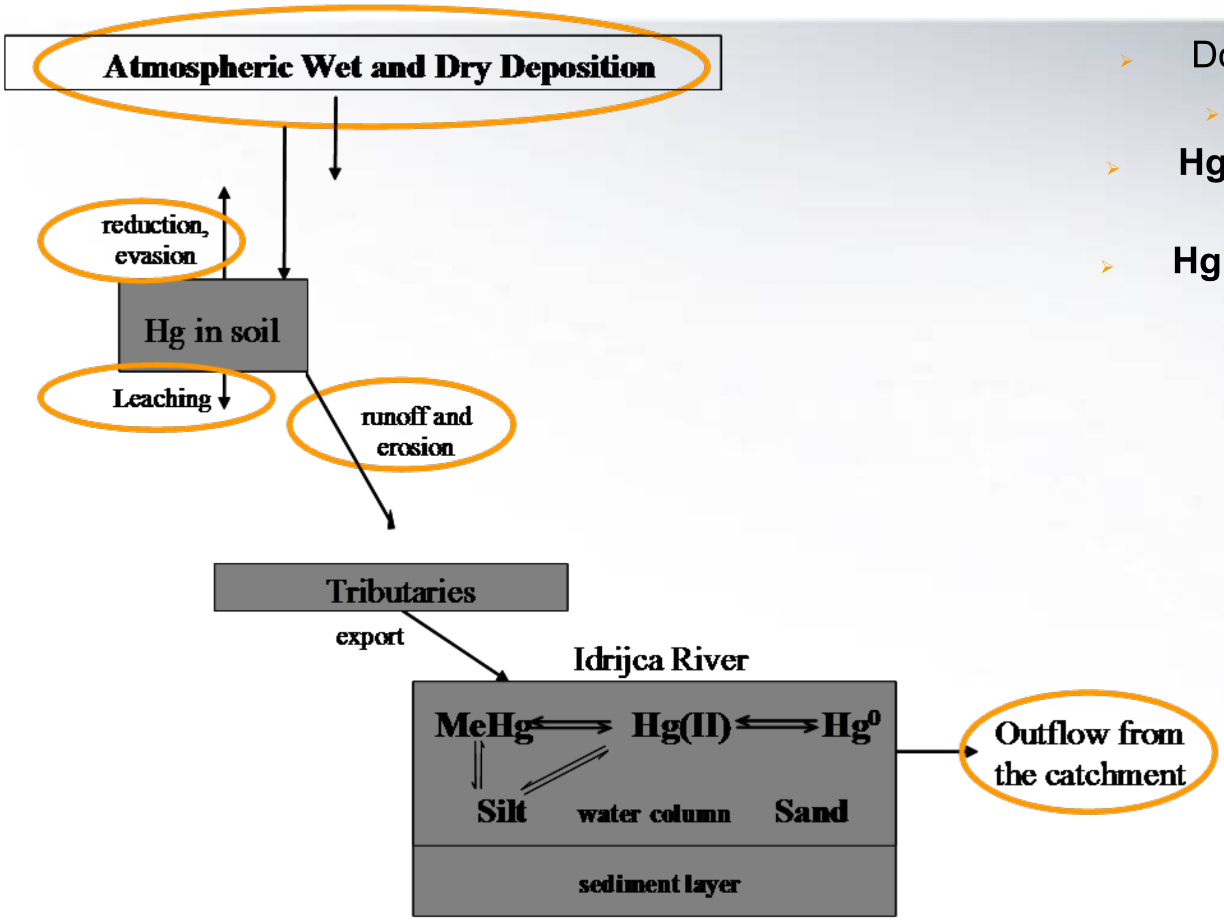
MEF_{bf} … Hg flux before precipitation

MEF_{aft} … Hg flux after precipitation



- Enhancement of the Hg flux after the simulated precipitation is significantly lower if the surface soil moisture is greater than ~ 15 %
- Enhancement of Hg^0 emissions from the soil related to the mercury in aqueous soil phase
- reduction of Hg^{2+} in soil (controlled by *OM* in soil and *DOM* in the aqueous soil phase)

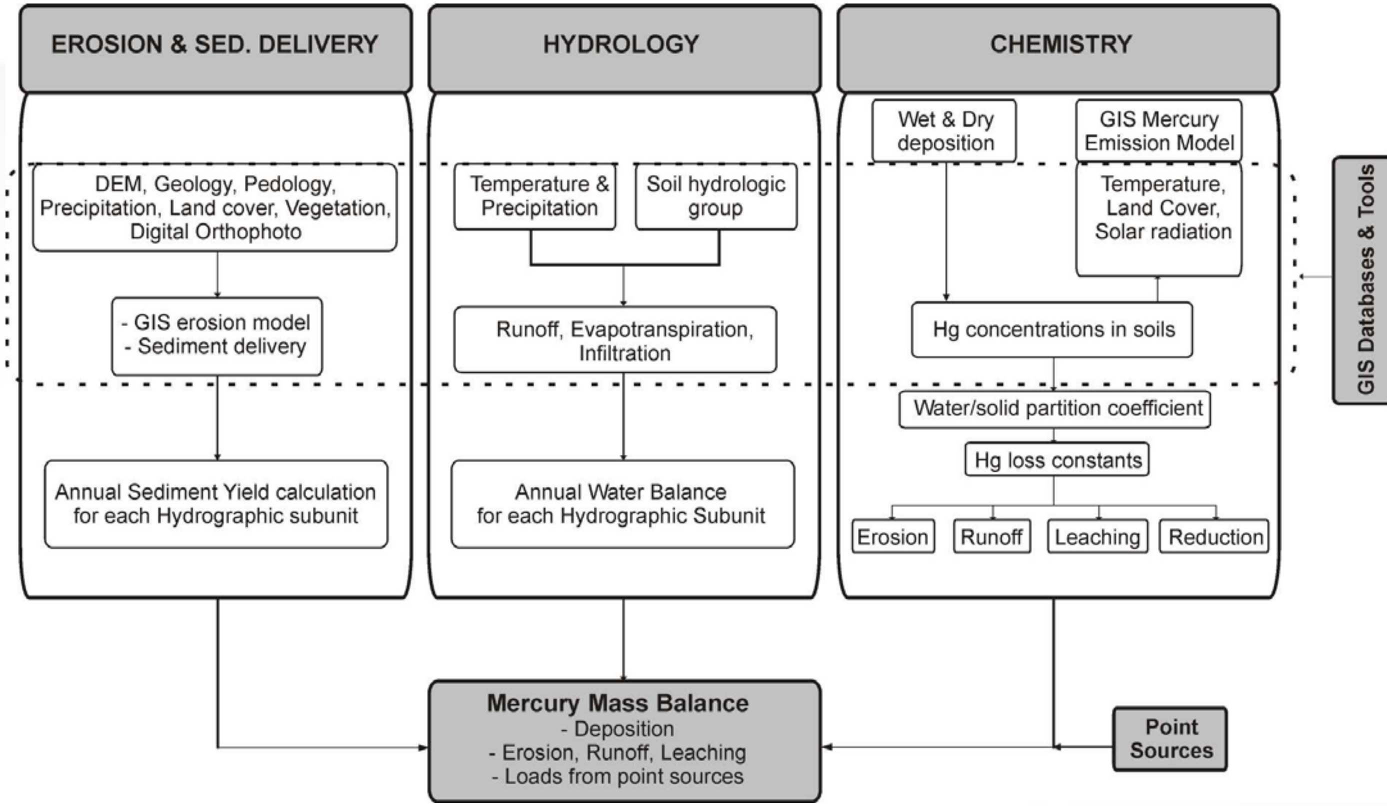
Mass balance model – *processes*



Mercury transport and transformation processes included in the model

- Domain: Idrijca River catchment
  - Annual mass balance
- **Hg input**: atmospheric deposition (wet, dry and throughfall)
- **Hg output**: gaseous flux from soil, leaching, surface runoff and erosion

Mass balance model – *modeling framework*



- *Terrestrial inputs to water system*: Watershed Characterization System—Mercury Loading Model (Dai & Manguerra, 2000) (GIS environment)
- *Soil erosion & Sed. delivery*: Erosion Potential Method (Gavrilović, 1972, 1976, 1988)
- *Hydrology*: long-term average annual water balance (GIS)
- *Hg emission*: calculated based on the flux chamber experiment

Mass balance model – *modeling assumptions*

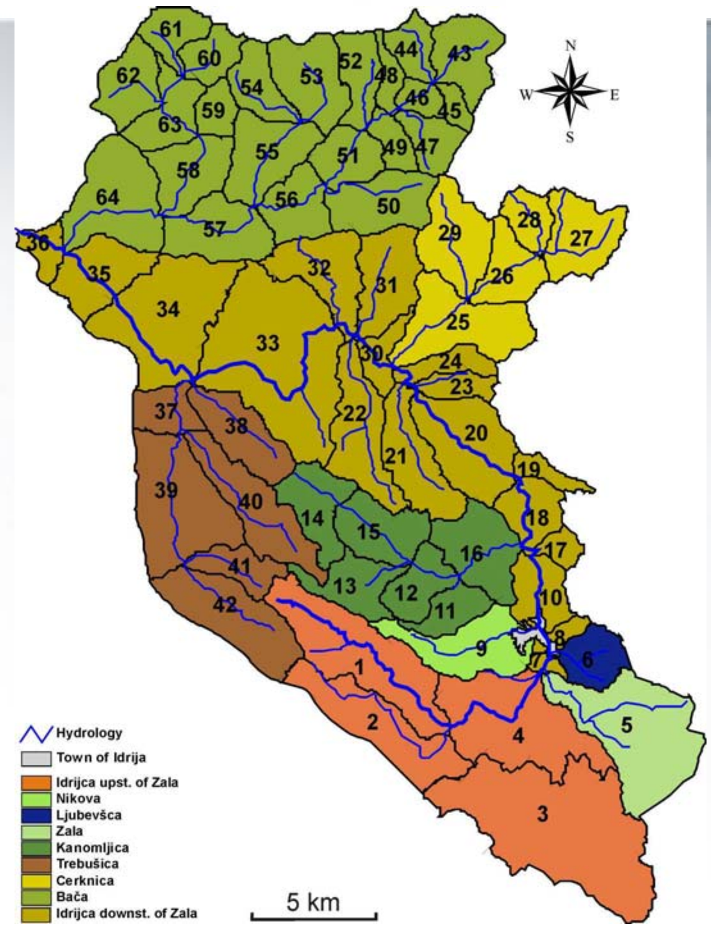
- Catchemnt can be subdivided into smaller subcatchments (hydrographic units -HU)
- Soil Hg concentrations within a HU is uniform
- Fraction of mercury in soil in dissolved and particulate phase is given as:

$$f_{ws} = \frac{\Theta_w}{\Theta_w + K_{ds} \cdot BD}$$

$$f_{ps} = \frac{K_{ds} \cdot BD}{\Theta_w + K_{ds} \cdot BD}$$

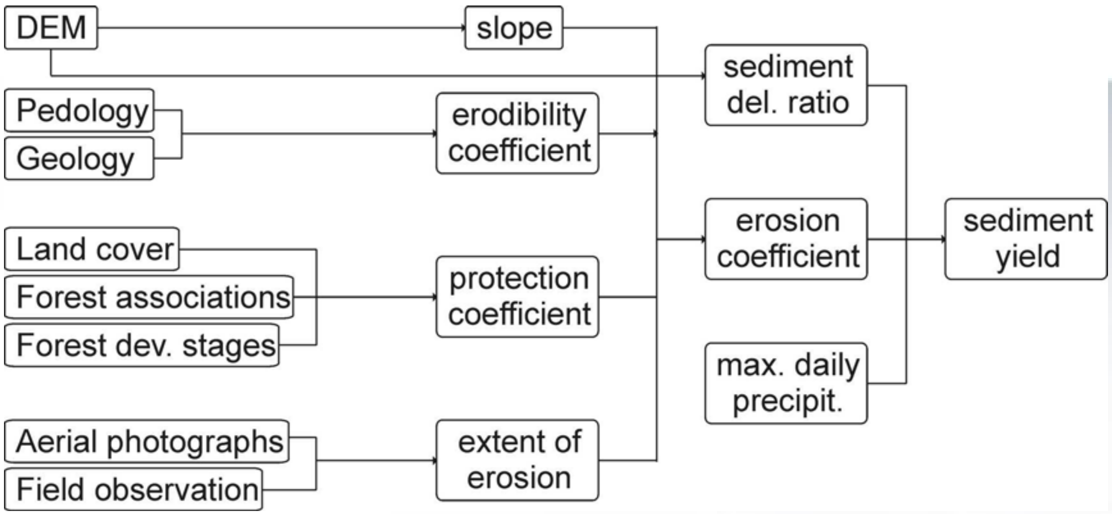
f_{ws} – soil mercury water fraction
f_{ps} – soil mercury solid fraction
θ_w – soil volumetric water content (ml cm^{-3})
K_{ds} – soil water partition coefficient (ml g^{-1})
BD – soil bulk density (g cm^{-3})

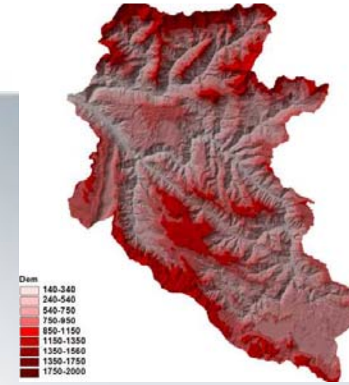
- Dissolved Hg is lost from the surficial soil layers through infiltration and runoff.
- Particulate Hg is lost through water runoff erosion.
- Hg outflow in runoff water and runoff erosion particles are delivered to the catchment tributary system.
- Hg(II) >> Hg(0), MeHg → soil mercury is treated as a single total mercury component.
- Atmospheric deposition (precipitation and throughfall measurements)

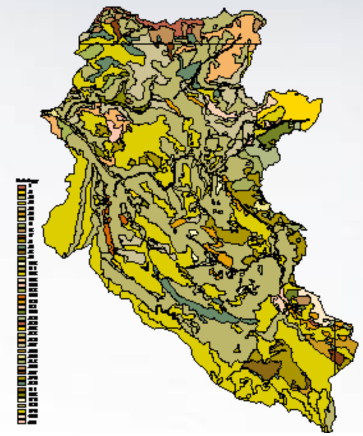


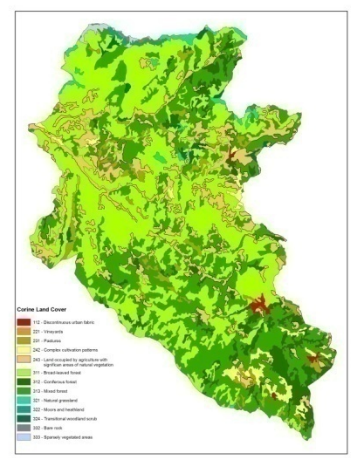
Hydrographic units and major hydrography of the Idrijca River catchment

Mass balance model – *Erosion Potential Method, GIS parameters extraction*









EROSION POTENTIAL METHOD (Gavrilović)

$$W_s = 20 * PM * K_z^{1.5} * F_w$$

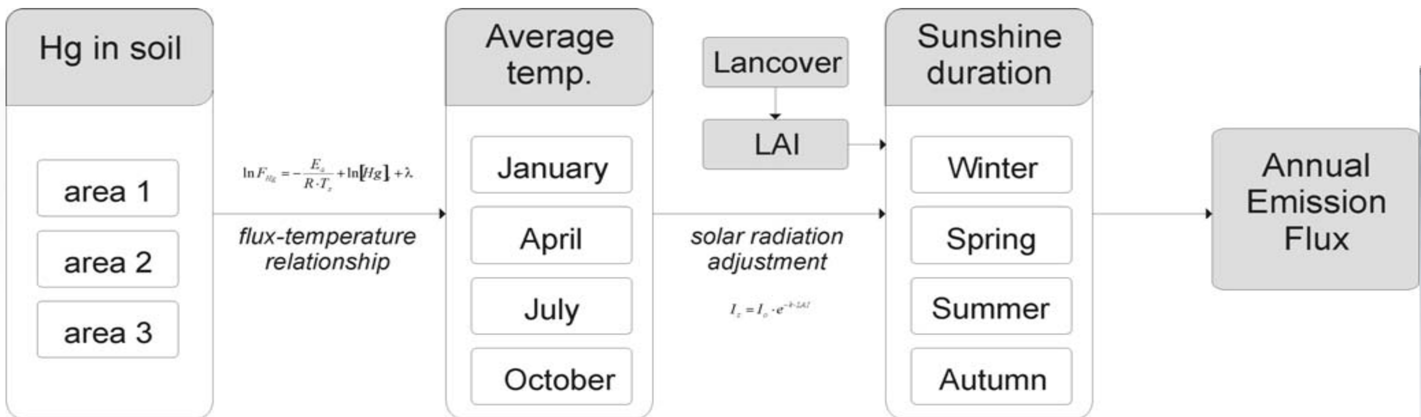
$$K_z = K_y * K_x * (K_o + F_{sl}^{0.5})$$

W_s… average annual sediment production (m^3/a)
PM… maximum daily precipitation (mm/d)
K_z… catchments erosion coefficient
F_w… catchments area (km^2)

K_z=f(geomaterial erodibility, slope, land cover)

K_y… soil erodibility coefficient
K_x… soil protection coefficient
K_o… erosion development coefficient
F_{sl}… average slope of the basin

Mass balance model – *GIS mercury emission model*



Flow chart of the mercury emission model

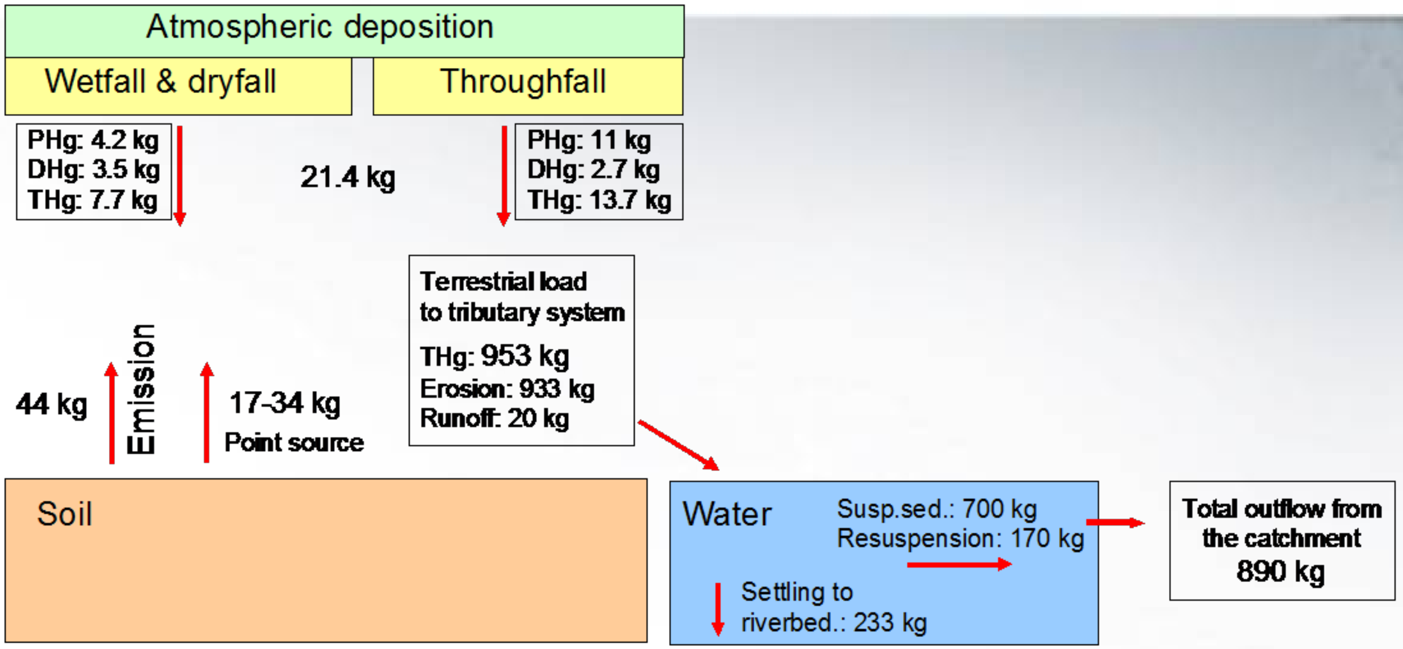
$$\ln F_{Hg} = -\frac{E_a}{R \cdot T_s} + \ln[Hg]_s + \lambda + 0.003 \cdot R_Z$$

$$R_z = R_o \cdot e^{-k \cdot LAI}$$

Generic steps:

- yearly emissions of mercury from soil calculated for each hydrographic subunit
- spatial distribution of mercury in soil, average monthly temperatures and intensity of solar radiation reaching the soil surface
- average monthly temperatures for the months of January, April, July and October
- adjustments for the influence of solar radiation (average monthly solar radiation energy)
- solar radiation reaching the forest surface (extinction coefficient, Leaf Area Index)
- annual emissions were estimated as three times of the four-month's sum.

Mass balance model – *evaluation*



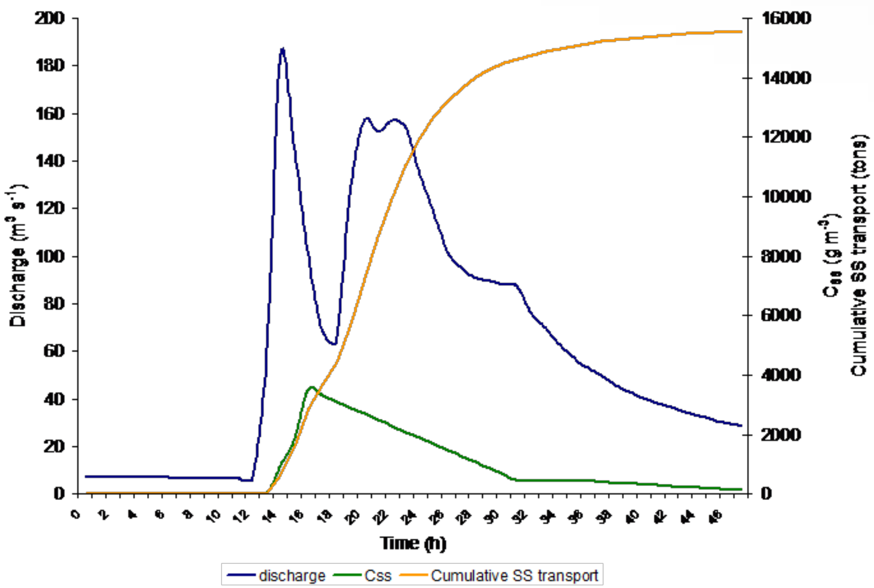
Annual mass balance of mercury in the Idrijca catchment

Annual terrestrial mercury input to the Idrijca River system:

- Total : **953 kg Hg**
- Erosion: 82 797 m^3 sediment yield → **934 kg Hg in particulate phase**
- Runoff: **19.3 kg Hg in dissolved phase**
- Of 934 kg Hg in particulate phase: **234 kg deposited as a bed sediment, 700 kg in suspended sediment phase**
- Q_2 flood wave → Resuspension of Hg enriched bed sediments: → **170 kg Hg/event**

Mass balance model – *evaluation*

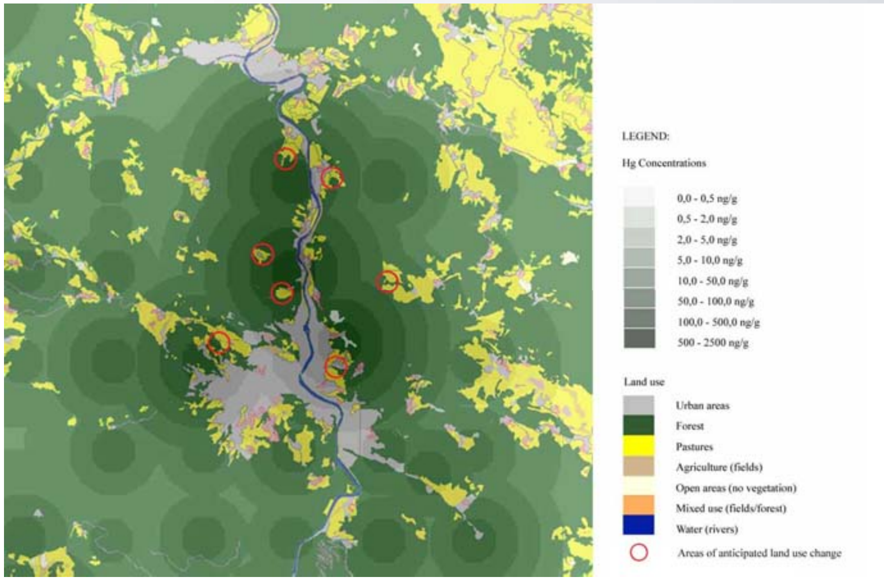
- *Soil erosion and surface runoff* – the major terrestrial source of mercury to the aquatic environment
- 98 % of Hg in particulate phase
- *Importance of the **hot spots**:* e.g. 25 % of total annual load from the area representing < 5%, 50 % of total emission to the atmosphere from the point sources
- *Extreme hydrological conditions:* contaminated riverbed sediment resuspension



Sediment transport by the 19/09/2007 flood wave – Hotešček measurement station

- Extreme event: TSS > 3.5 kg m^{-3}
- Total TSS outflow during the event: 15 500 t
- THg: 20-50 mg kg^{-1} → 300-800 kg Hg/event

Possible measures to reduce Hg from the “hot” spots - 1. Forestation



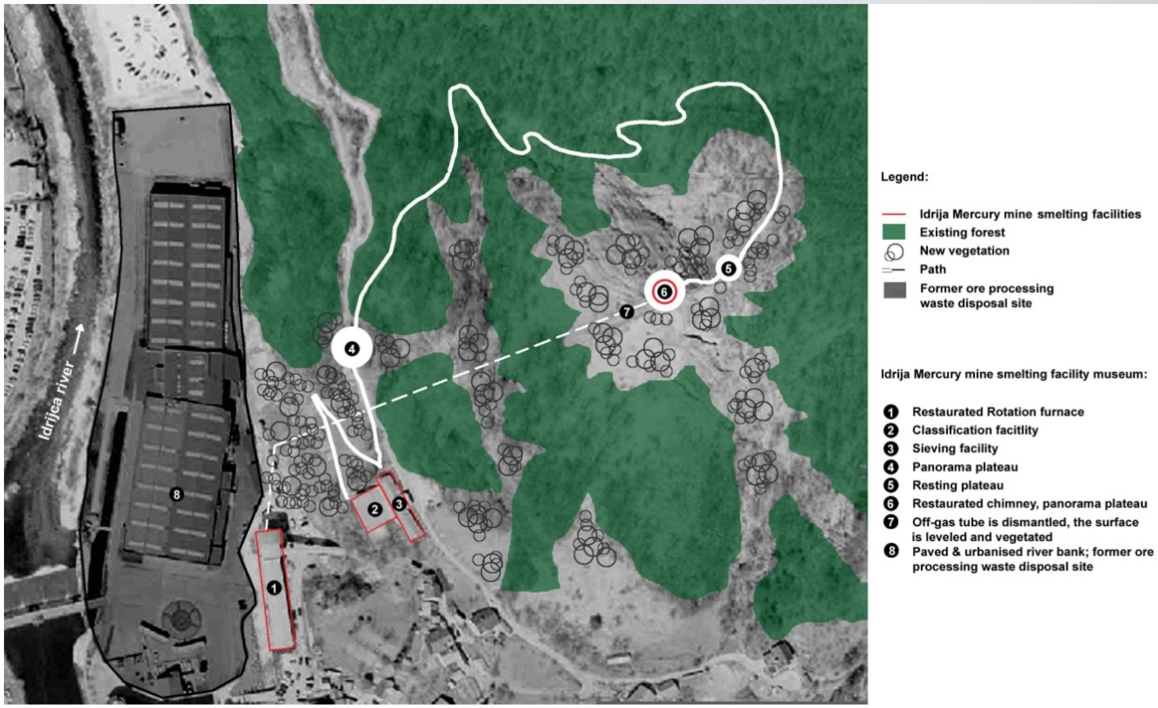
Areas predicted for forestation: cc. 40 ha

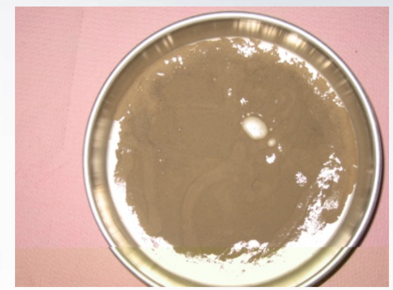
Changes in land use - replacement of agricultural or bare landscapes to forest (existing un-protective land cover to protective in terms of soil erosion)

Scenario: reduction of terrestrial load up to 30 %

Possible measures to reduce Hg from the “hot” spots –

2. Physical elimination





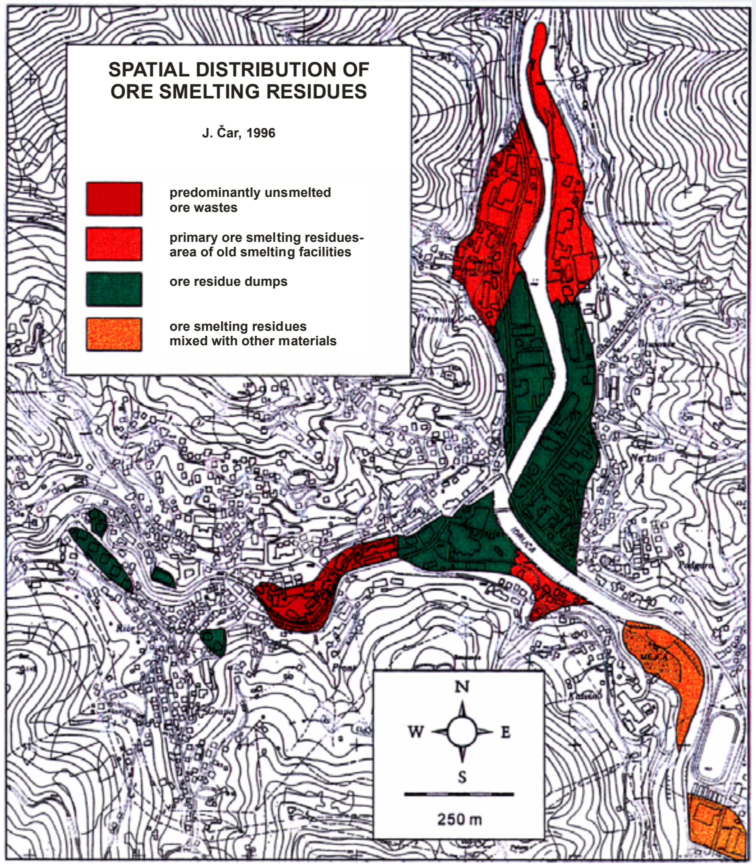
Approach:
- removal of the top soil layer
- surface leveling
- forestation

Scenario: reduction of Hg emission up to 50 %

Problem: Where to put Hg contaminated soil ?

Possible measures to reduce Hg from the “hot” spots -

3. Ore residuals along the Idrijca River



Approach:

-covering with a layer of uncontaminated material to prevent wash-off

- stabilizing the waste material in place by building retaining walls along the river bank

Conclusions

- More then 10 years after the end of the mining operations in this region, concentrations of Hg in all environmental compartments in the Idrijca River catchment remain elevated.
- Erosion and surface runoff are the main terrestrial inputs of mercury into the Idrijca River tributary system. Majority of mercury in soil is firmly bound in soils and is susceptible to leaching and runoff mostly by being attached in/to particles.
- Atmospheric input of mercury to soil exceeds the amount leached, and the amount of mercury partitioning to runoff is only a small fraction of the amount of mercury stored in soil.
- The quantity of mercury stored in the Idrijca River catchments soils and sediments significantly exceeds the annual quantity of mercury leaving the catchment.
- Taking the calculated inputs and outputs of mercury to/from the catchment into account, it can be concluded that without the suitable remediation actions a reduction of mercury pollution in the area can not be expected.
- Importance of the “hot spots” (major sources of mercury at the catchment scale) and extreme hydro-meteorological events.

On mercury dynamics in the aquatic environment of the Idrija mercury mine region, Slovenia

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Abandoned Hg mines are important sites which can represent strong source of mercury, even after active mining has been discontinued. Transport of mercury from such sources can result in its remobilization, making it available for methylation. Hence, secondary sources of toxic forms of Hg can be produced at great distances from the original source. In this context, mercury dynamics in the River Idrijca-Gulf of Trieste aquatic system impacted by former Hg mining activities in Idrija, Slovenia, is reported. The main objective was to identify recent sources of mercury, its fate and distribution, more than a decade after the end of mining operations. Accordingly, we describe the results of a comprehensive 4-year study on mercury speciation and partitioning in the River Idrijca drainage system. The effects of changing hydrological and physicochemical conditions on Hg distribution, including complexation with organic and inorganic ligands, the role of suspended particulate matter and river bed sediment remobilization, were also assessed. Based on the experimental results, a mass-balance model of sources, sinks and mercury transport process (including soil erosion, surface runoff, riverine transport, atmospheric deposition and Hg emissions from the surface) at the Idrijca River catchment scale was developed.

The distribution of Hg species in the Idrijca drainage system indicated contamination from mine tailings and contaminated soils in the town of Idrija. The partitioning between dissolved and particulate Hg phases in the aquatic system was found to be mostly controlled by the variable content of suspended solids resulting from changing hydrological conditions and complexation with various ligands present in river water, among which organic matter seems to be the most important. Hg is transported to downstream aquatic systems mainly as finely-suspended material including colloids. The riverine transport occurs mostly during short, but extreme hydro-meteorological conditions when remobilization of Hg from the river bed sediments occurs. During its transport, important Hg transformation mechanisms that increase the risk of mercury uptake by biota take place, evidenced by the increase in the relative contribution of reactive Hg (HgR), dissolved gaseous Hg (DGM) and monomethyl Hg (MeHg) downstream from the Idrija mine.