



ICMGP 2024
CAPE TOWN • SOUTH AFRICA • 21 - 26 JULY

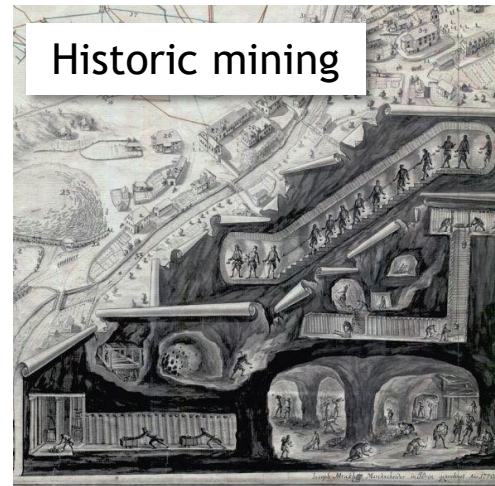
Dominik Božič, Igor Živković, Jože Kotnik, Gregor Puhar, Marta Jagodic Hudobivnik, Marko Štok, Nives Ogrinc, and Milena Horvat

Origin of mercury in soils in the vicinity of
emission sources using stable isotope approach

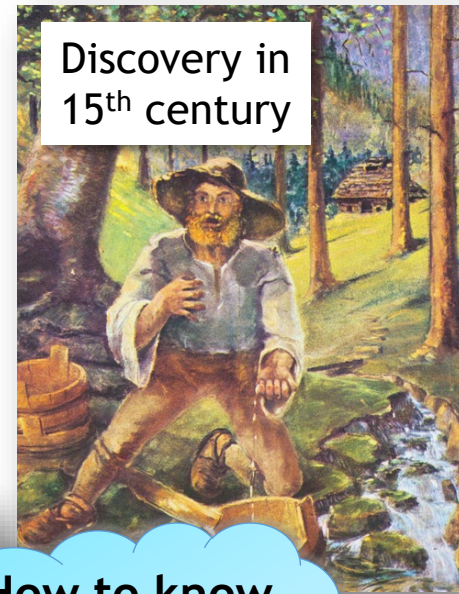


Mercury in Idrija

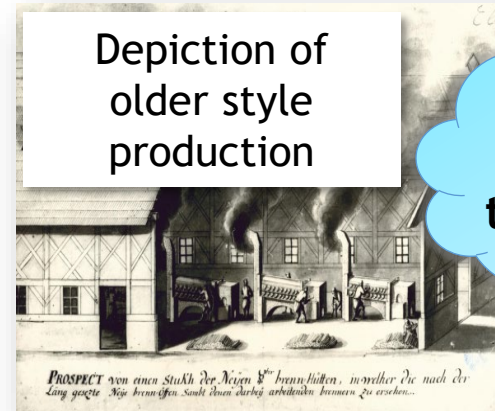
- Idrija (Slovenia)
 - Extensive mining and processing for 500 years
 - Hg released from waste piles, mine, and secondary reemission sources
- How to trace pollution spread in the wider region and how to attribute it to the mine?



Historic mining



Discovery in 15th century



Depiction of older style production



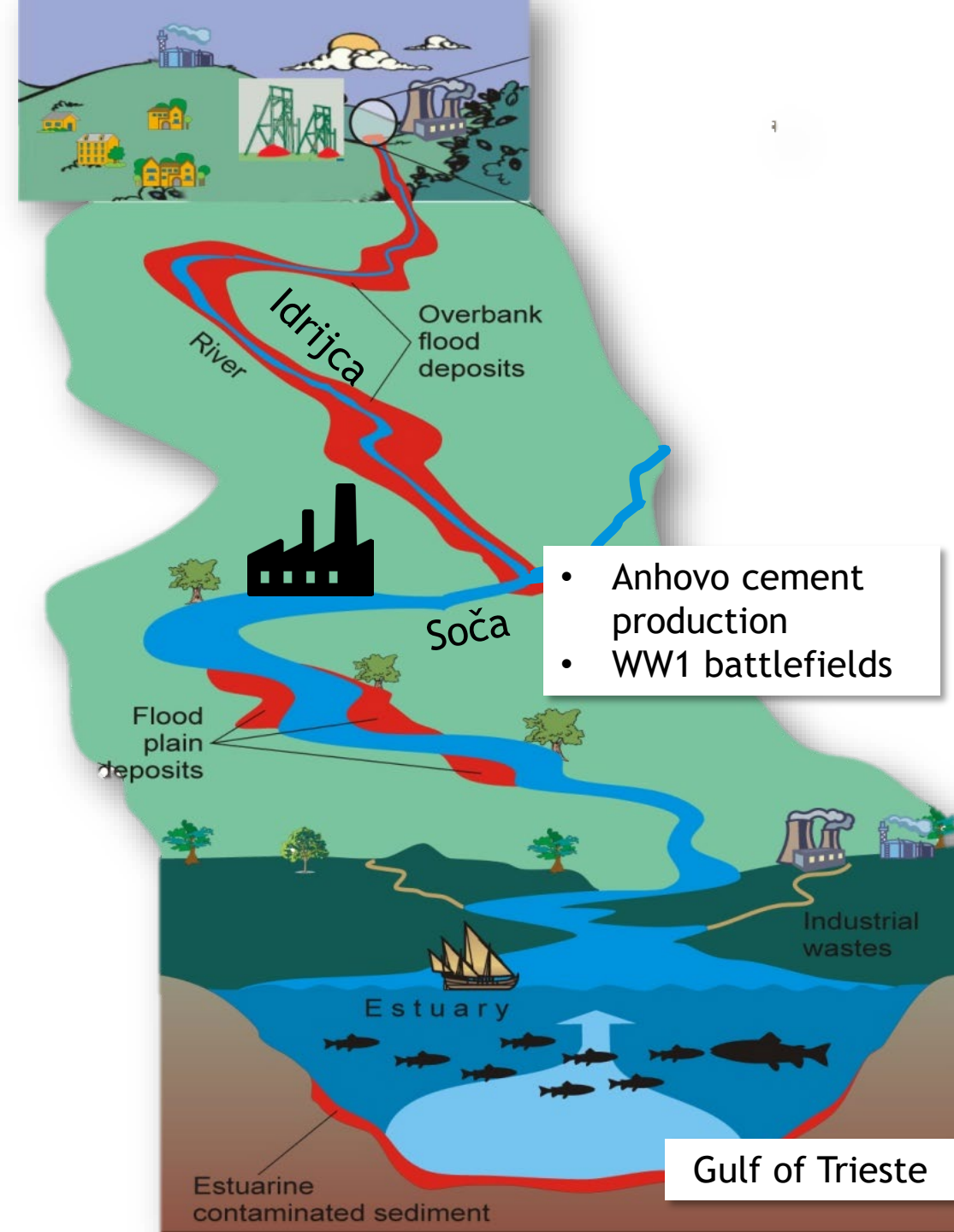
Waste piles

How to know where is all this Hg going?



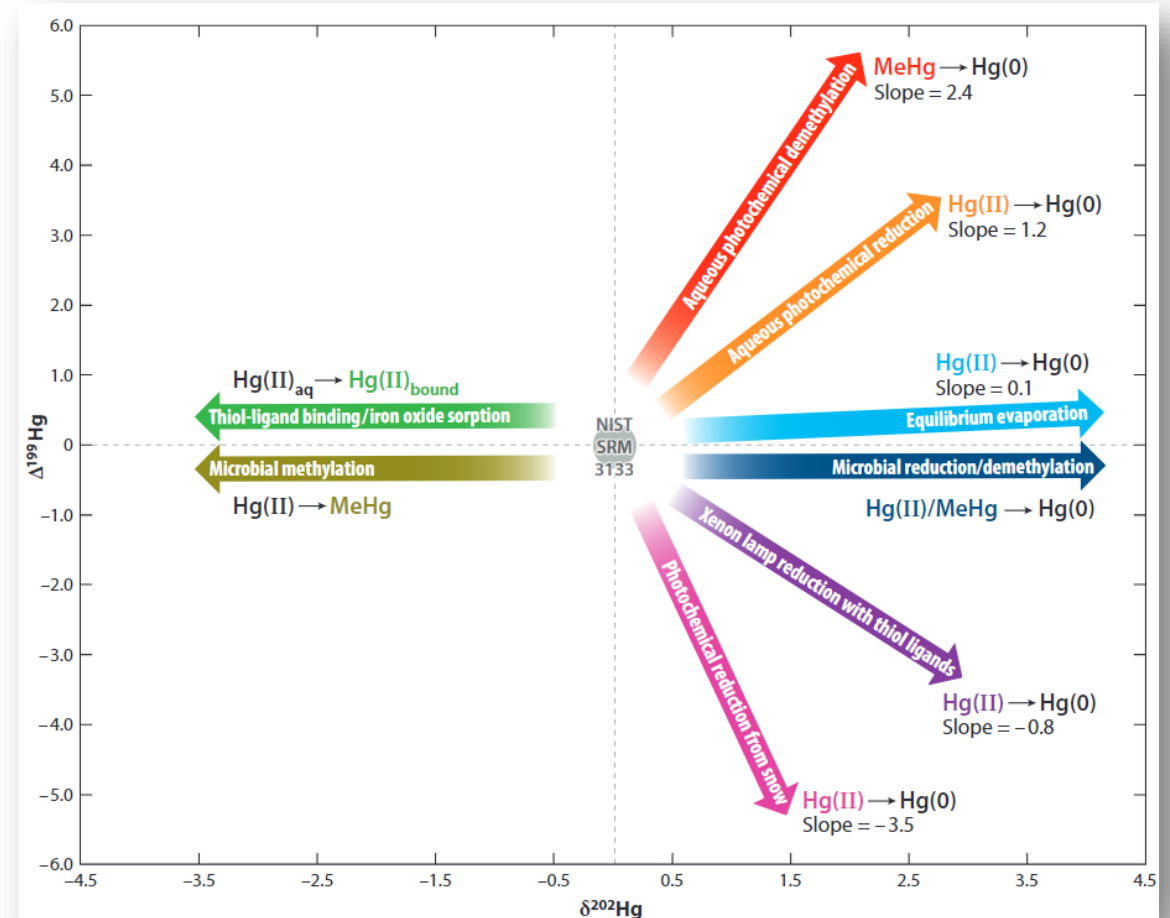
Where is Hg pollution observed?

- Pollution starts at the mine and waste ore deposits
- Transported via the Idrijca and later Soča river system
- Additional sources of Hg:
 - Anhovo cement production plant
 - Mercury fulminate - used as primer in WWI
- Deposited in the Gulf of Trieste



Mercury Isotopes

- Tracing processes and transport
- Mass dependent fractionation (MDF)
 - $\delta^{202}\text{Hg}$
- Mass independent fractionation (MIF)
 - $\Delta^{199}\text{Hg}$

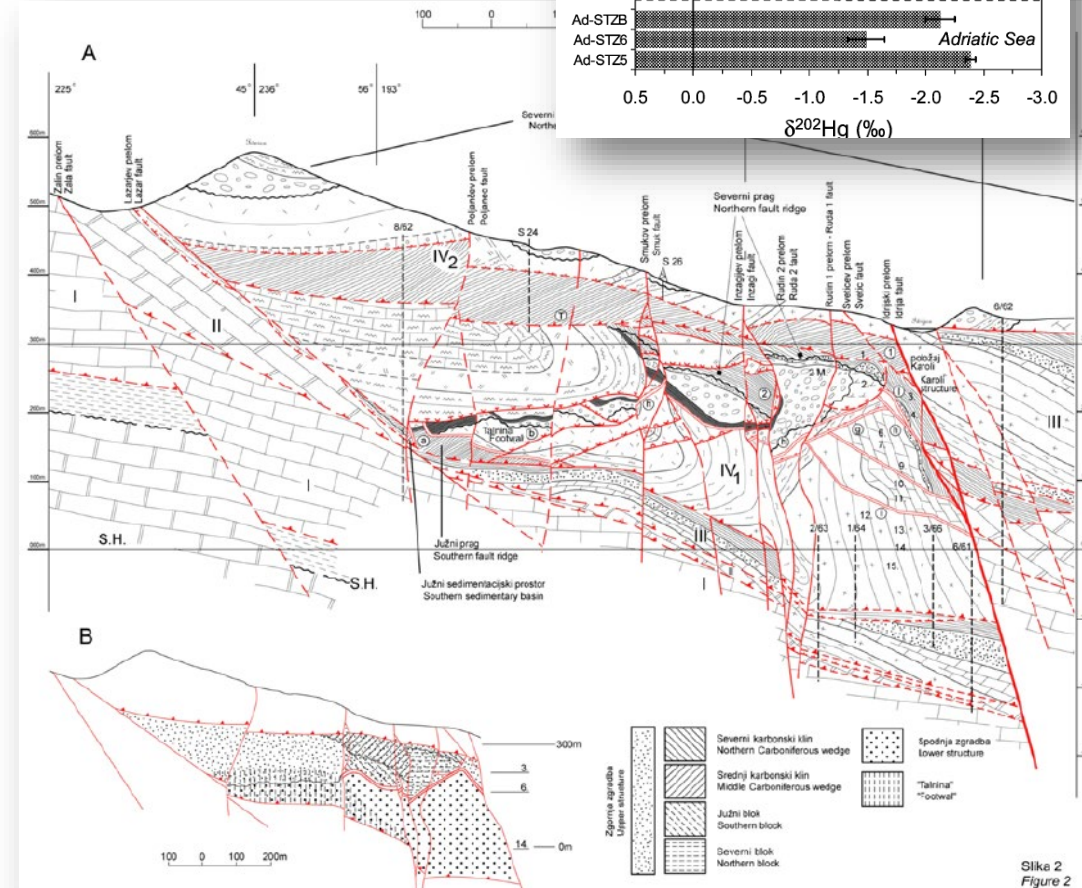
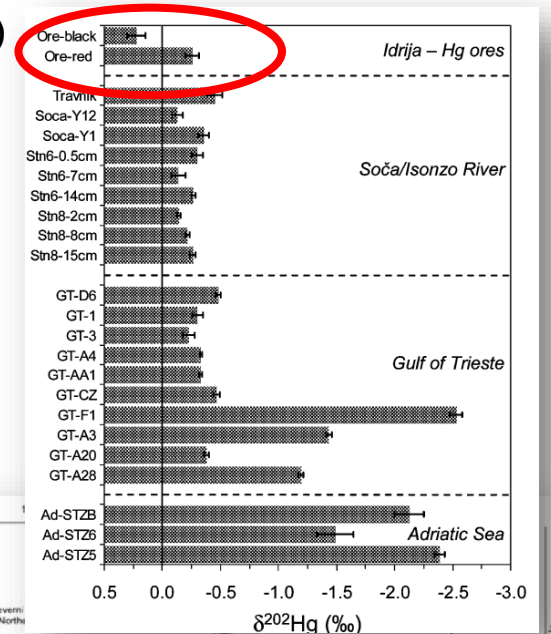


Previous research on Hg isotopes in Idrija

- Isotopic studies of mercury sediments raise new questions
- Only two ore samples measured
- Complex ore body in Idrija:
 - different excavation sites
 - various minerals and ore types (epi-, sin-genietic)
 - deposited in different geological periods
 - Hg leaching and mobilisation

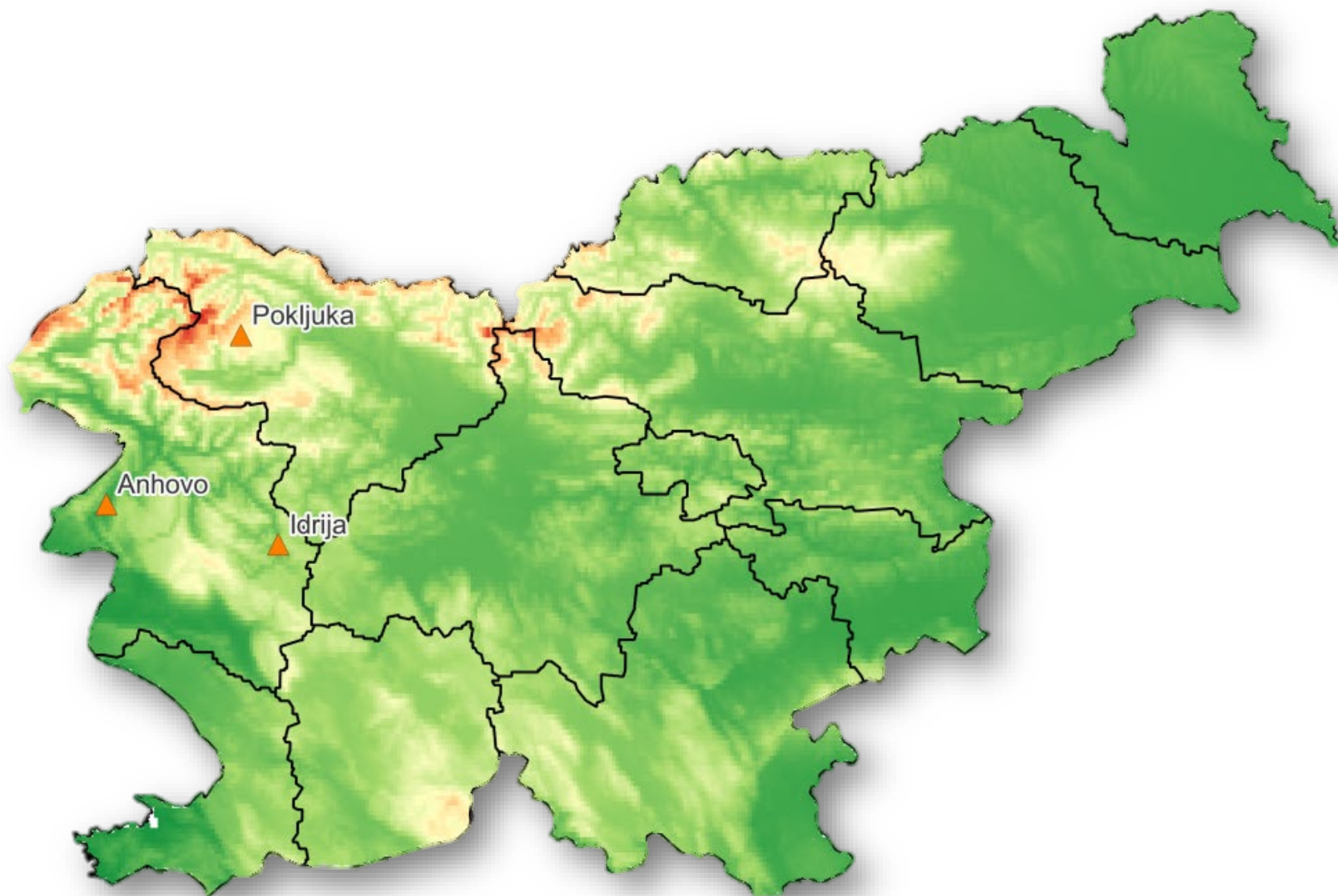
The complexity of the geological conditions becomes apparent in this figure: Position of richest beds in a present-day section of the Idrija ore deposit (Čar, 2013, *Geologija*).

(Foucher et al., 2009, EST)



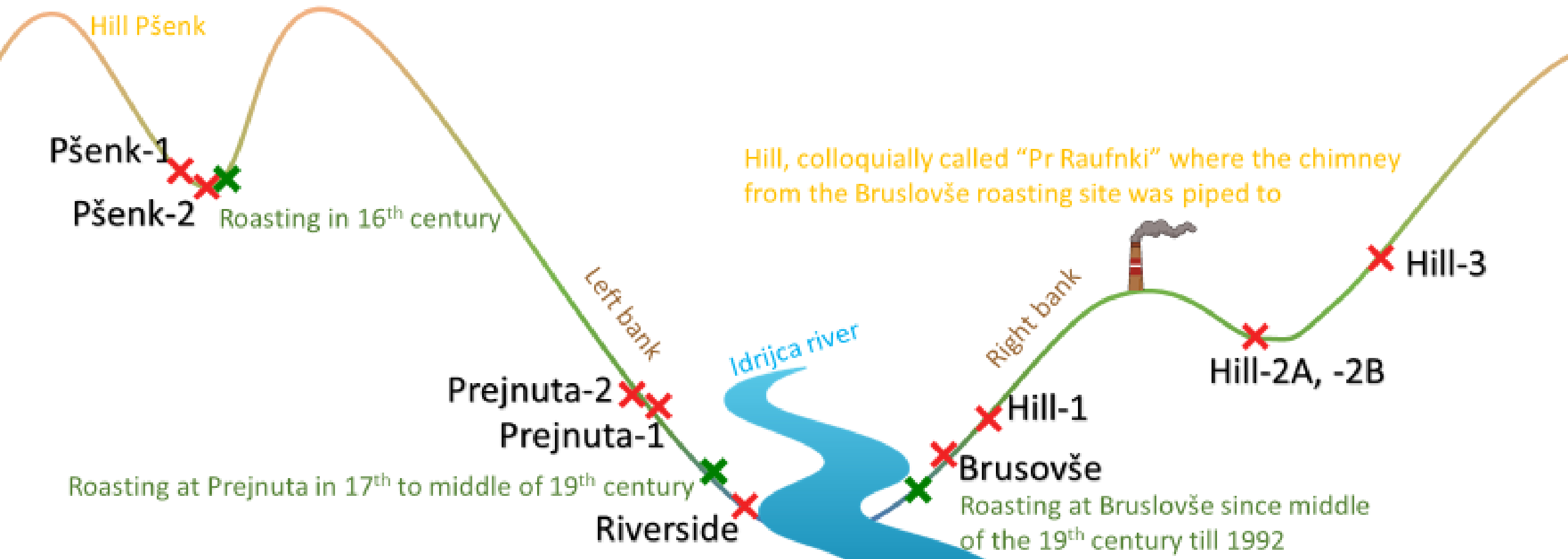
Slika 2
Figure 2

Sampling sites



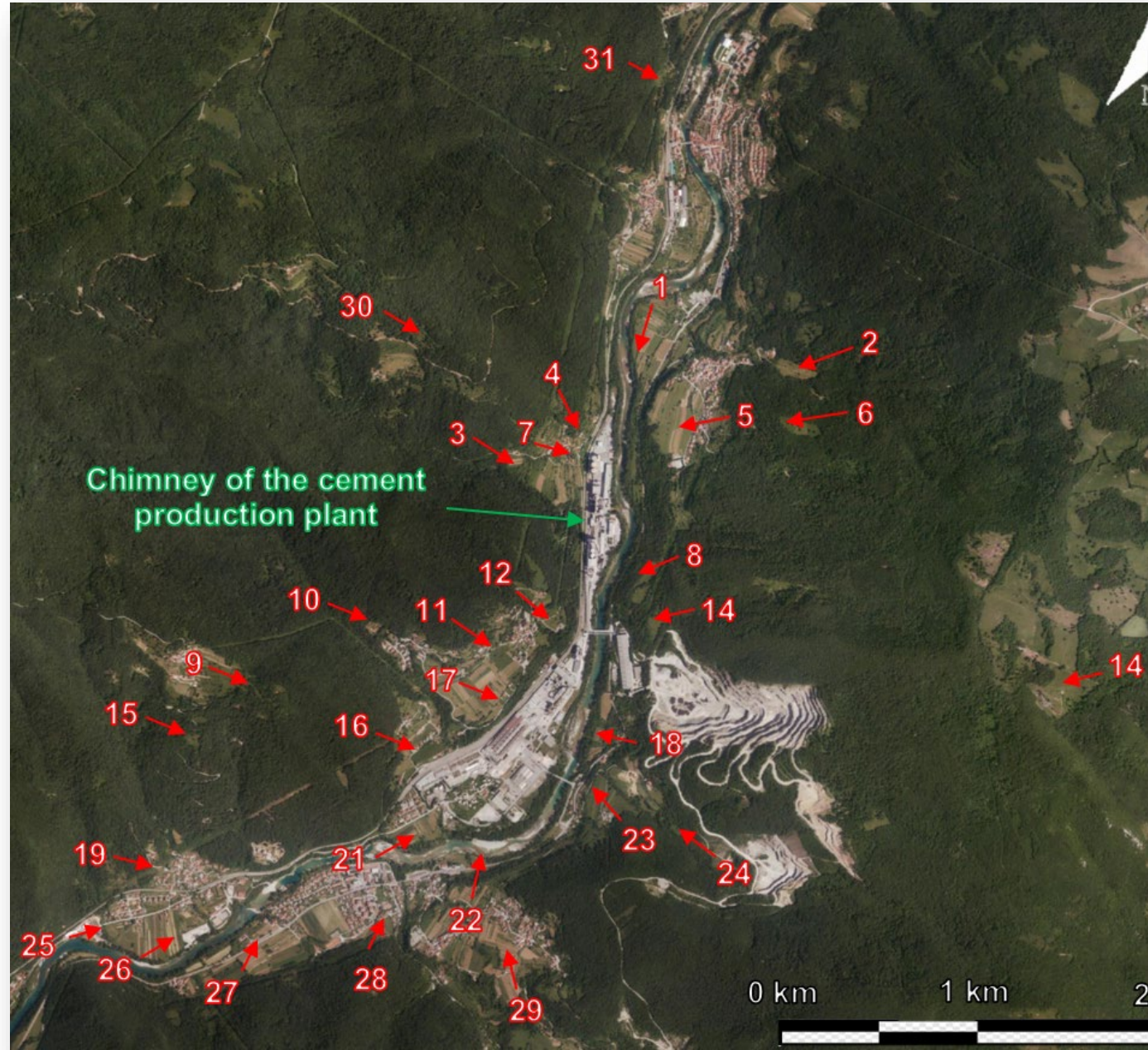
Sampling: Idrija

- Soil samples
 - From sampling by Tomiyasu et al., 2012 & 2017
 - Soil profiles
 - Close to the smelting sites



Sampling: Anhovo

- Multiple top soil sampling locations
 - Some distant from the plant
 - Some at higher elevations
 - Some closer to the Soča river



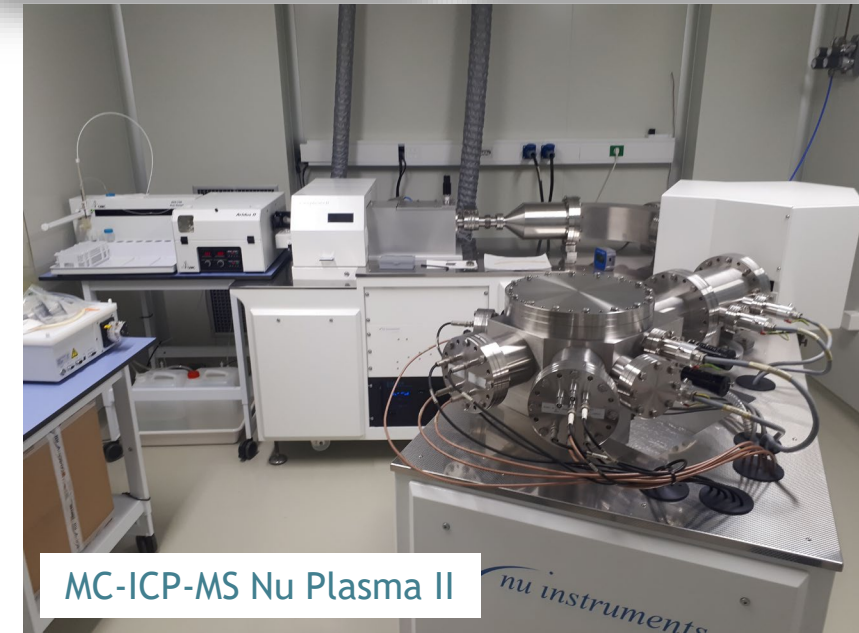
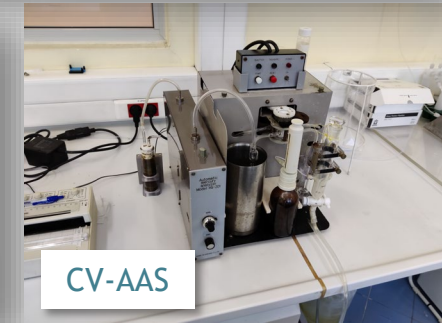
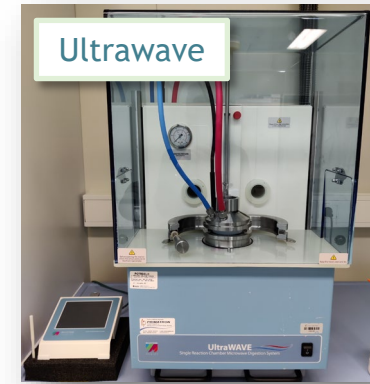
Sampling

- Mine samples
 - In the mine shafts and from the museum
 - Rocks needed to be ground down
 - Hg(l) diluted appropriately
- Soil
 - Cores (Idrija, Toomiyasu et al., 2017)
 - Topsoil (Anhovo, Biotechnical Faculty)



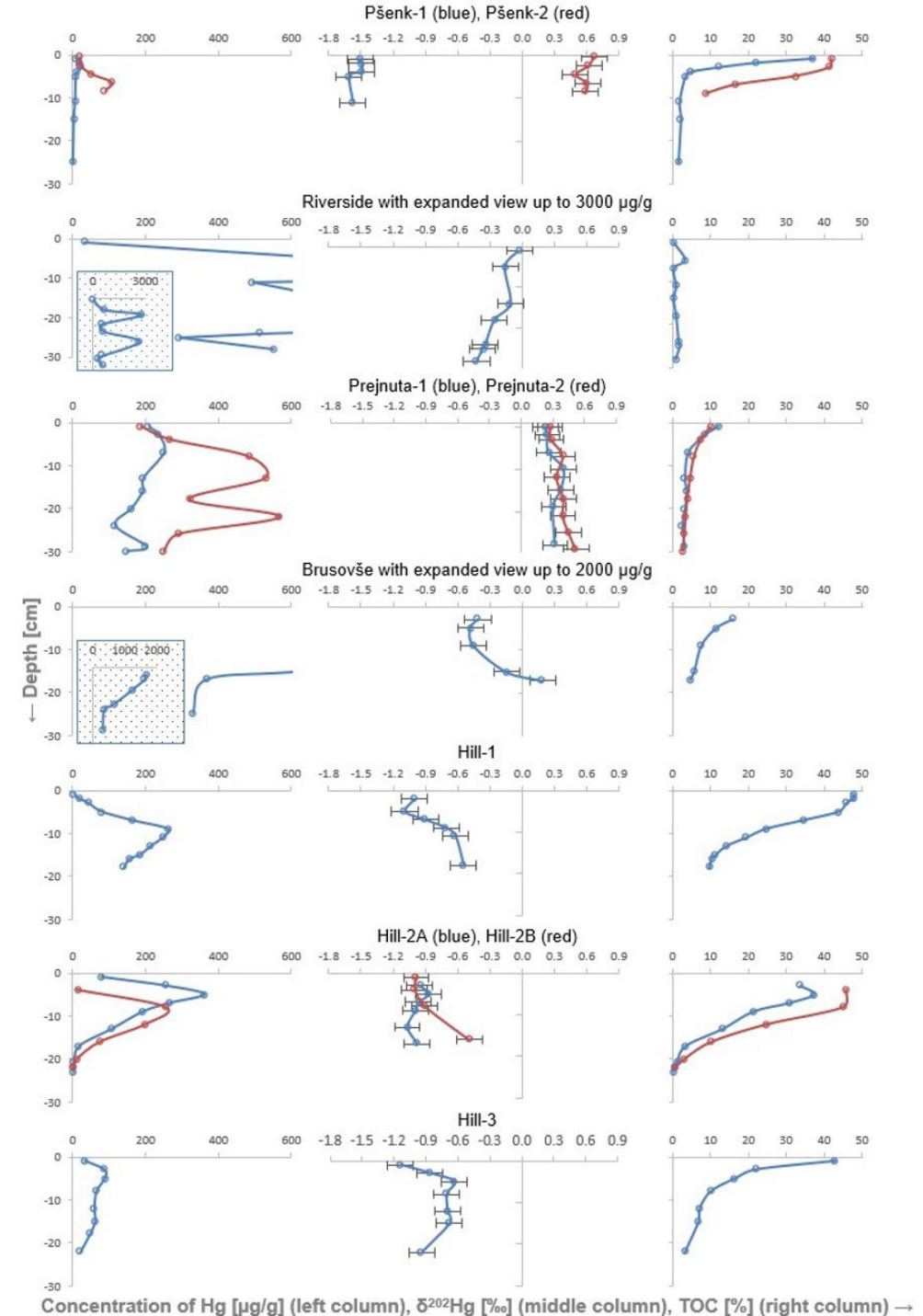
Sample preparation

- Digestion
 - HF, HNO₃, HCl, H₂O₂ mixture
 - Ethos and Ultrawave microwave digestion systems
- Hg measurement
 - CV-AAS
 - QQQ-ICP-MS
- Isotopes
 - MC-ICP-MS Nu Plasma II



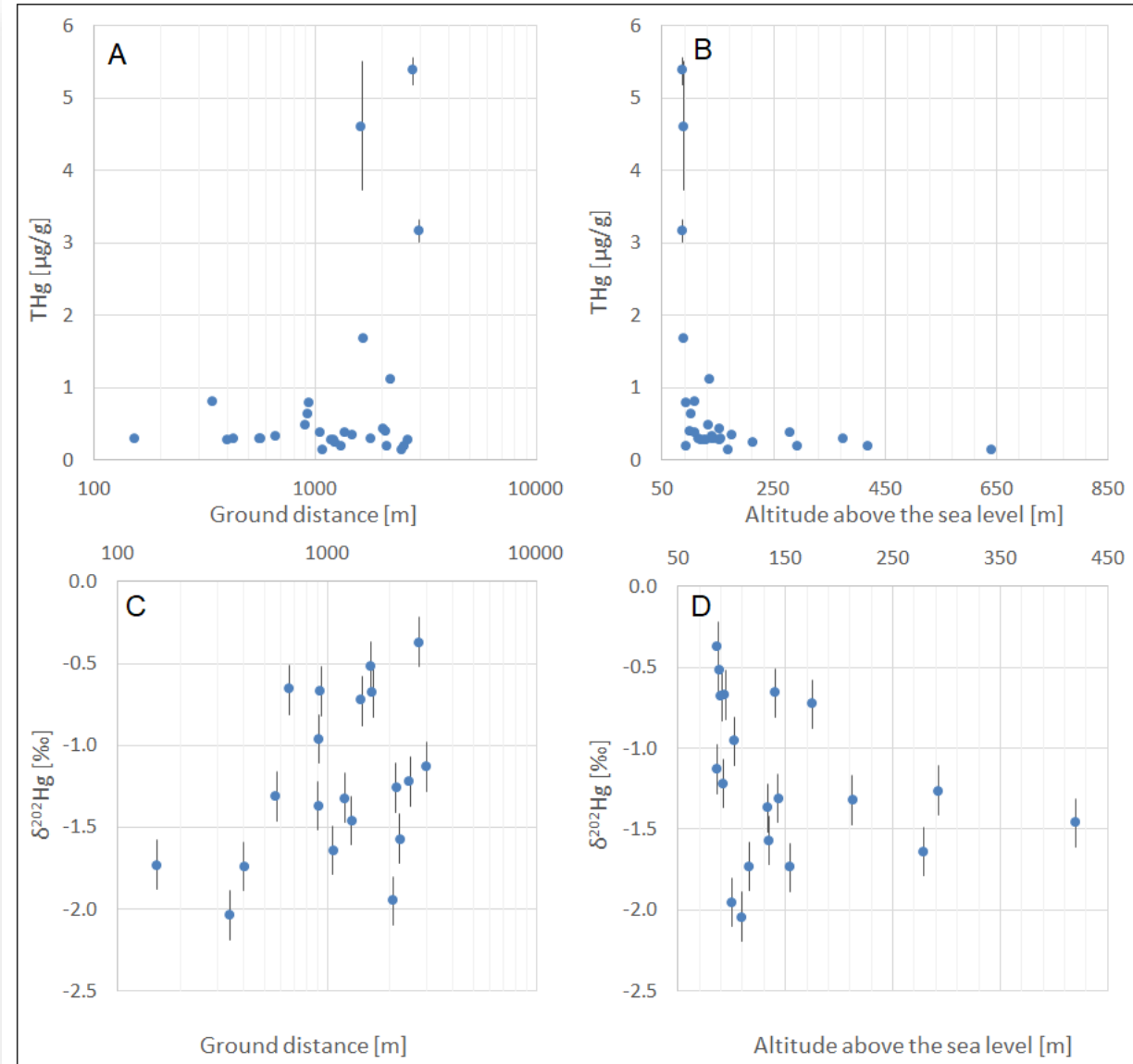
Mercury in the Idrija soil

- Higher THg and distinct isotopic compositions closer to historical roasting sites
 - heavier isotopic composition, likely from ore
- Background isotopic composition likely influenced by litterfall
 - lighter isotopic composition, likely from foliage
- Hg in topsoil reflects recent deposition history, correlating with vegetation recovery
 - transition from lighter to heavier with depth in correlation with lower concentrations of organic carbon



Mercury in the Anhovo soil

- Anhovo soils have significantly lower THg compared to Idrija
- Highest values are observed in soils near the Soča river
 - downstream transport of Hg from the Idrija mining area
- The isotopic range of Anhovo soils on floodplains is similar to that of Idrija sediments
 - supporting the theory of Hg transport from Idrija



Takeaway

- Mercury isotopes important for environmental research
- Few challenges:
 - **Heterogeneous distribution:** Mercury unevenly distributed, especially in polluted areas
- Overcoming the Challenges:
 - **Obtain adequate samples:** Gather representative samples to accurately represent environmental conditions (e.g., focus on areas near smelting sites)
 - **Mixing model development**