Anthropogenic contamination in fluvial systems

“selected lessons“

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Sb Zn Pb Hg Cr Cd As Cr Ni

Toxic compounds in fluvial settings

- **Toxic compounds (toxic metals, persistent organic pollutants /POPs/, radioactive pollutants) are bound to:**
  - (mineral) particulate matter → **hydrodynamic energy**
  - organic matter; particulate, degraded *in situ* → **redox potential, hydrodynamics**
  - Diagenetic phases, remineralized organic matter → **redox, water table, geochemistry of host rock**
  - … all sensitive to environmental settings

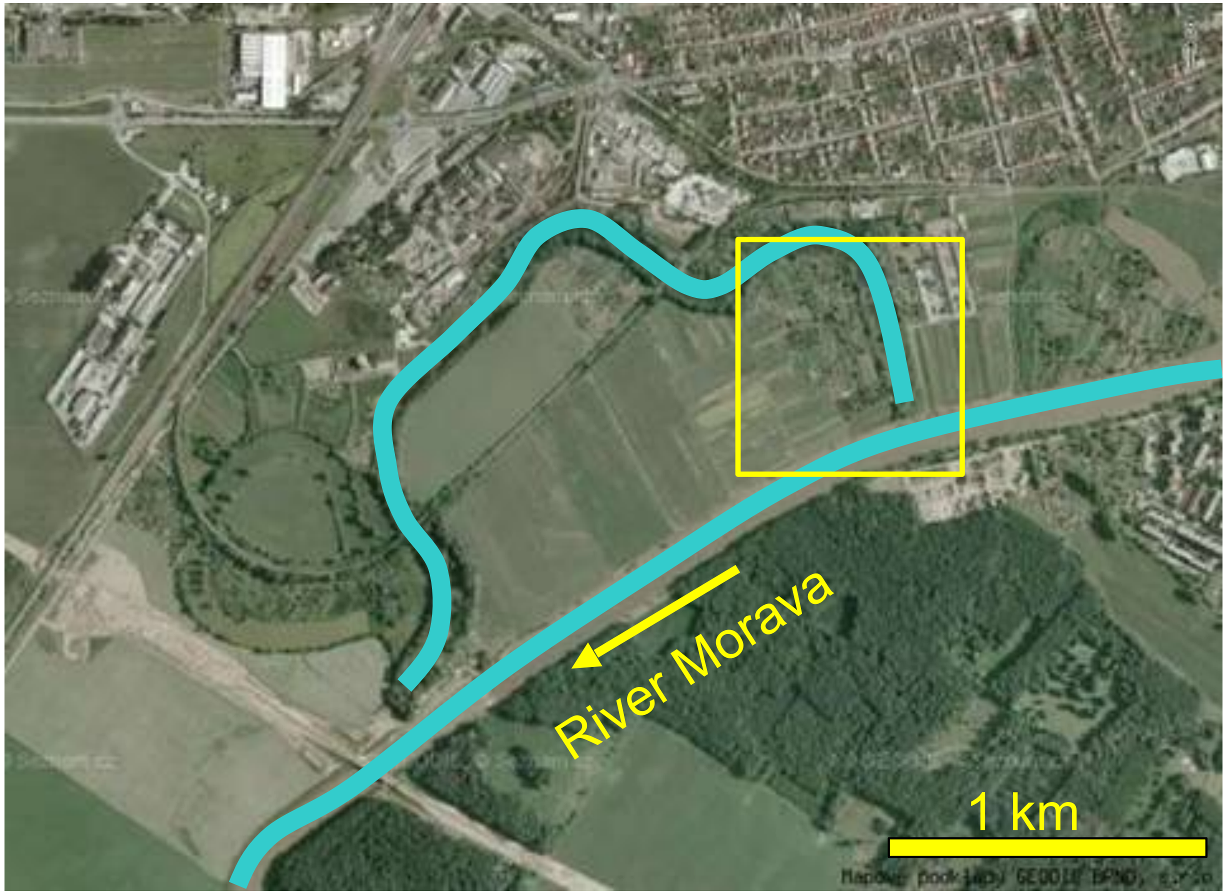
- **Fluvial depositional environments are everything but uniform and homogeneous, because:**
  - decreasing hydrodynamic energy along **river graded profile**
  - **non-uniform discharge (floods)** → rivers are "jerky conveyor belts"
  - **surface morphology** of natural fluvial depositional settings, and
  - complex **architecture of fluvial sediments**
  - **anthropogenic influence** (deforestation, embankment, stream streightening, dredging, dams)

Therefore, fluvial sedimentary archives of anthropogenic contamination are highly complex ….

… but too often they are the only ones at hand

- **Distribution of contaminants in space (and time)**
  - Identification of dangerous "STORED WASTE"
  - Tracing SOURCES of contamination
  - Risk of REMOBILIZATION
  - HISTORY of contamination and river proceses (human and natural history)
  - The AMOUNT of contaminants

Vertically aggrading lacustrine sediments “simple architecture“

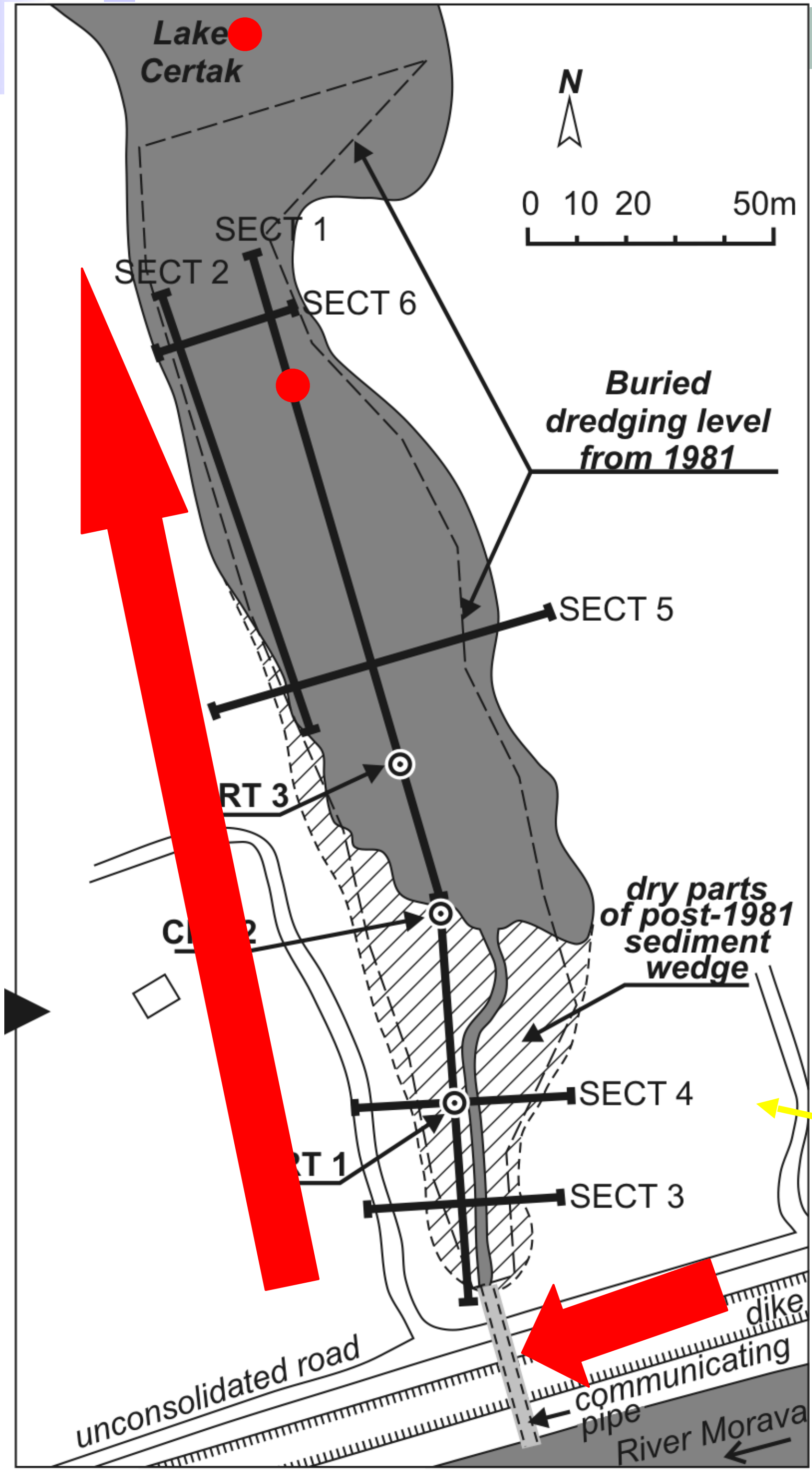


River Morava, Czech Republic
- tributary of Danube River
- Catchment area: 7891 km^2
- Average annual discharge: 55.4 $m^3.s^{-1}$

Industrial impact

Certak Meander – artificial abandoned meander
- Channel reloading in 1930s
- dredging in 1981

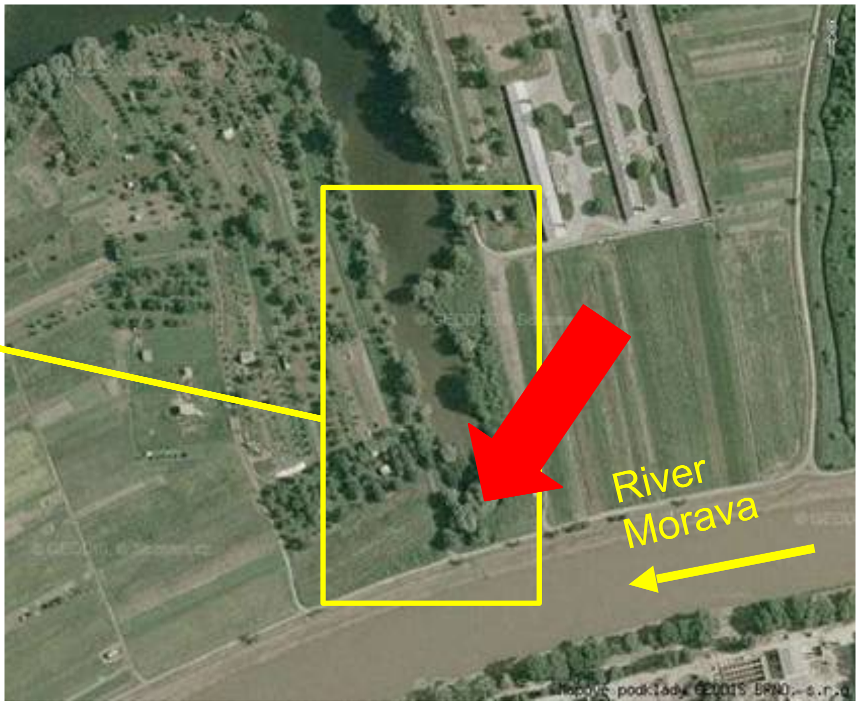
Certak meander



Permanent communication with active channel

“delta“ → sediment wedge

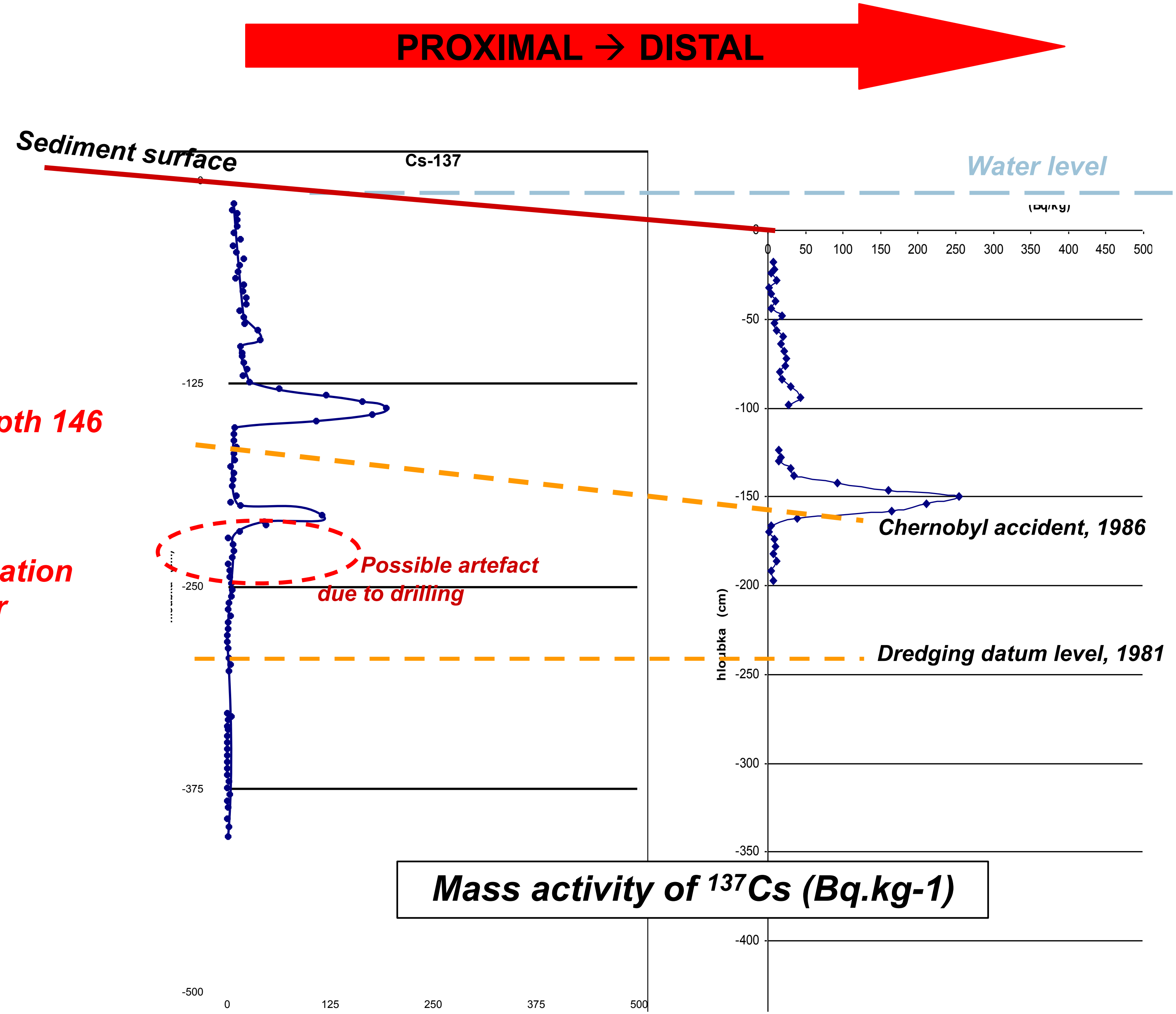
series of cores in proximal → distal transect



^{137}Cs dating

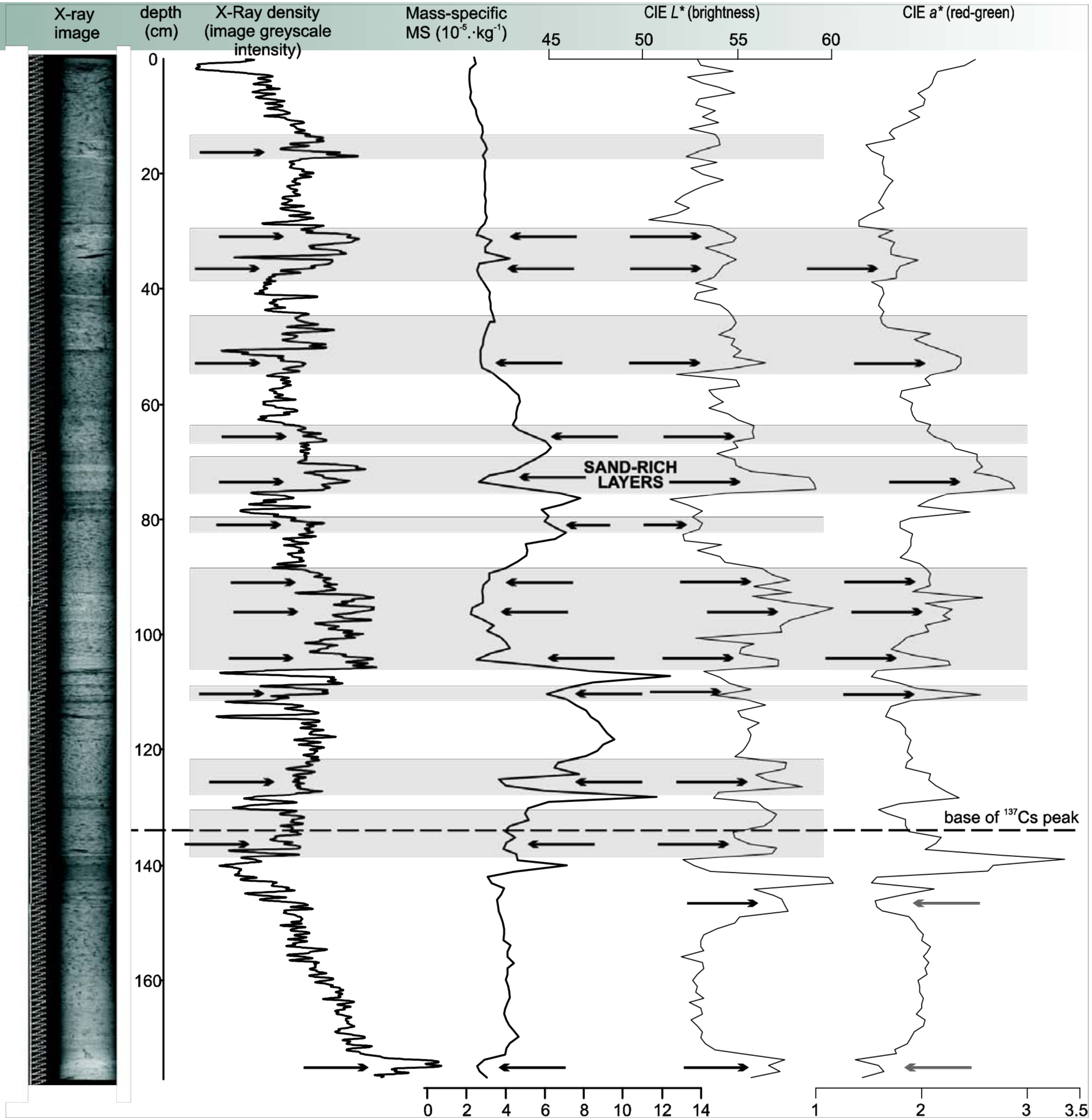
^{137}Cs anomaly – 1986 Chernobyl accident (depth 146 – 165 cm b.s.)

High sediment accumulation rates: ~6 - 7 cm per year

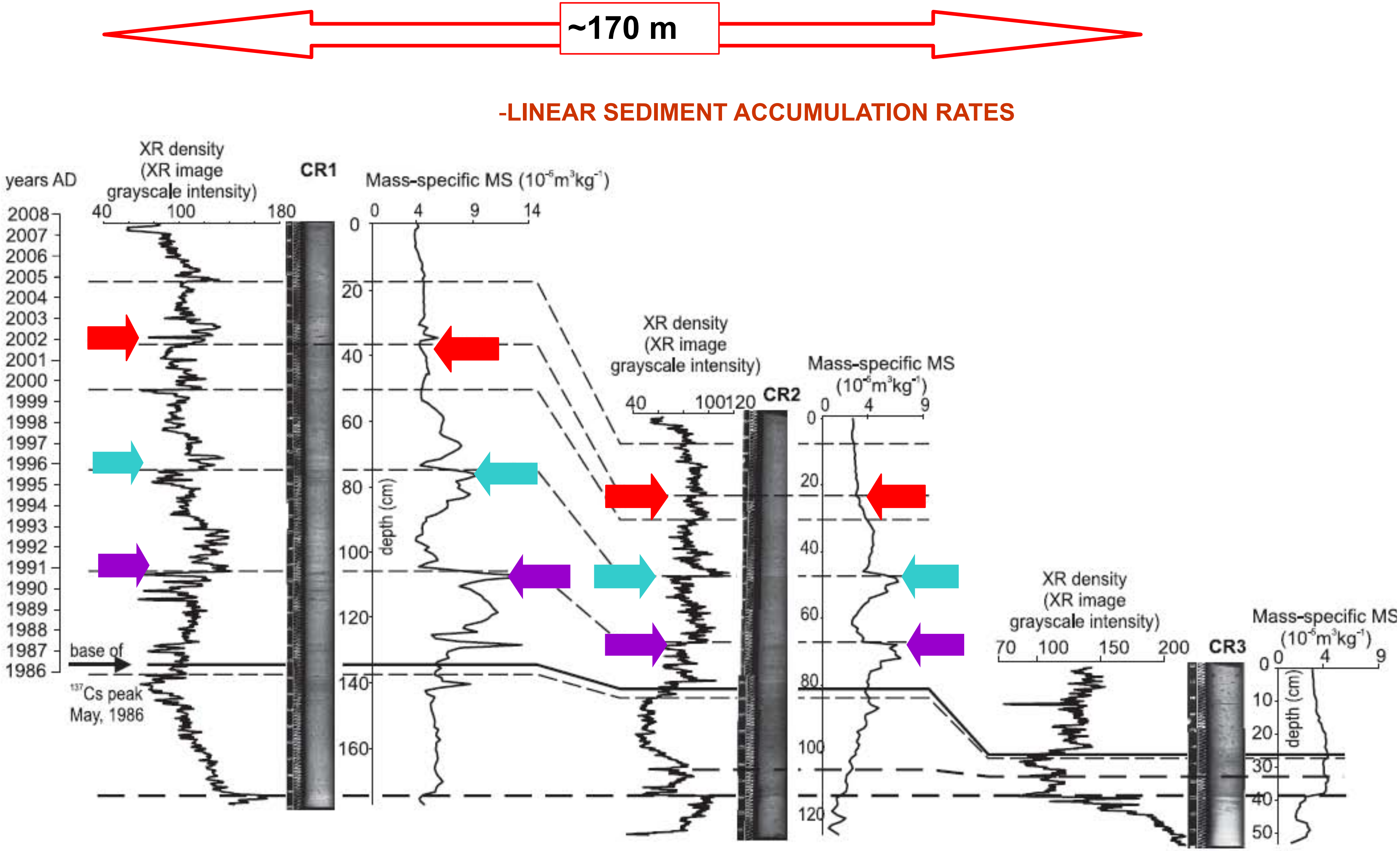


Event-like sedimentation

- RTG densitometry
- Magnetic susceptibility
- VIS spectral reflectance
- Coarse- and fine-grained laminae → **Flood layers**



Proximal - distal core correlation

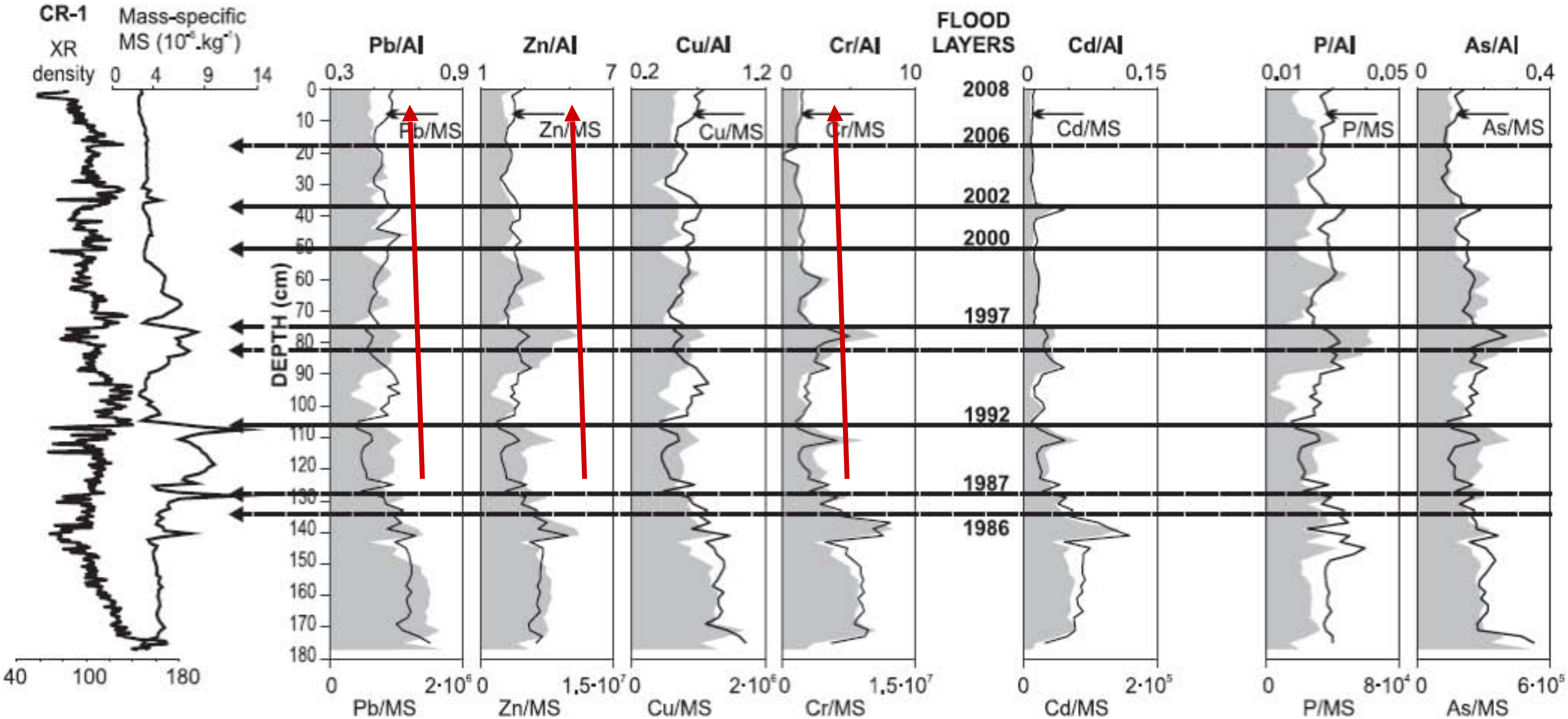


Simple layer-cake geometry; depth proportional to time

Al-normalized element concentrations

- Increased contrast of flood vs. background sedimentation →

something wrong with Al-normalization

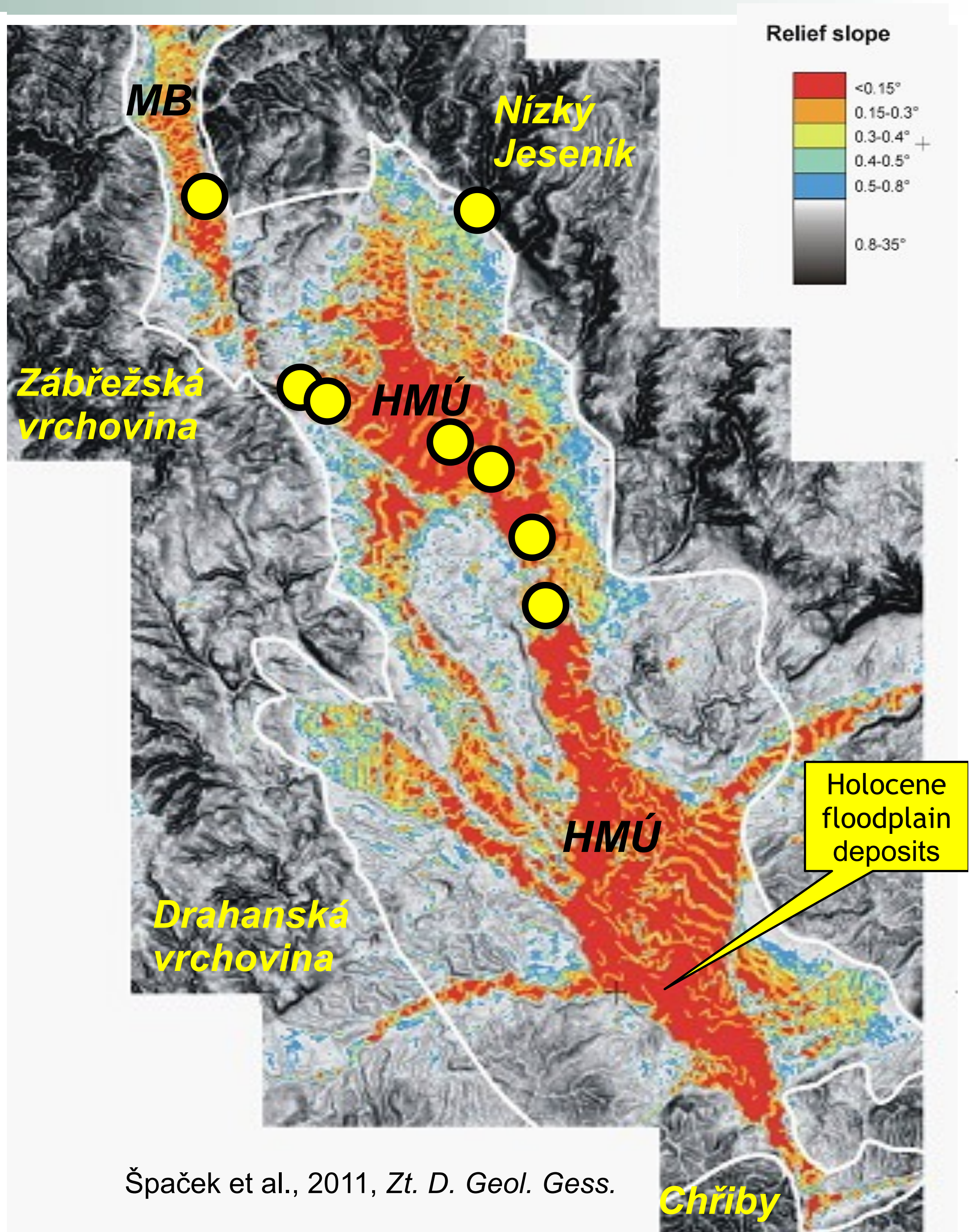


River conveyor belts are indeed jerky ! And so is the record !

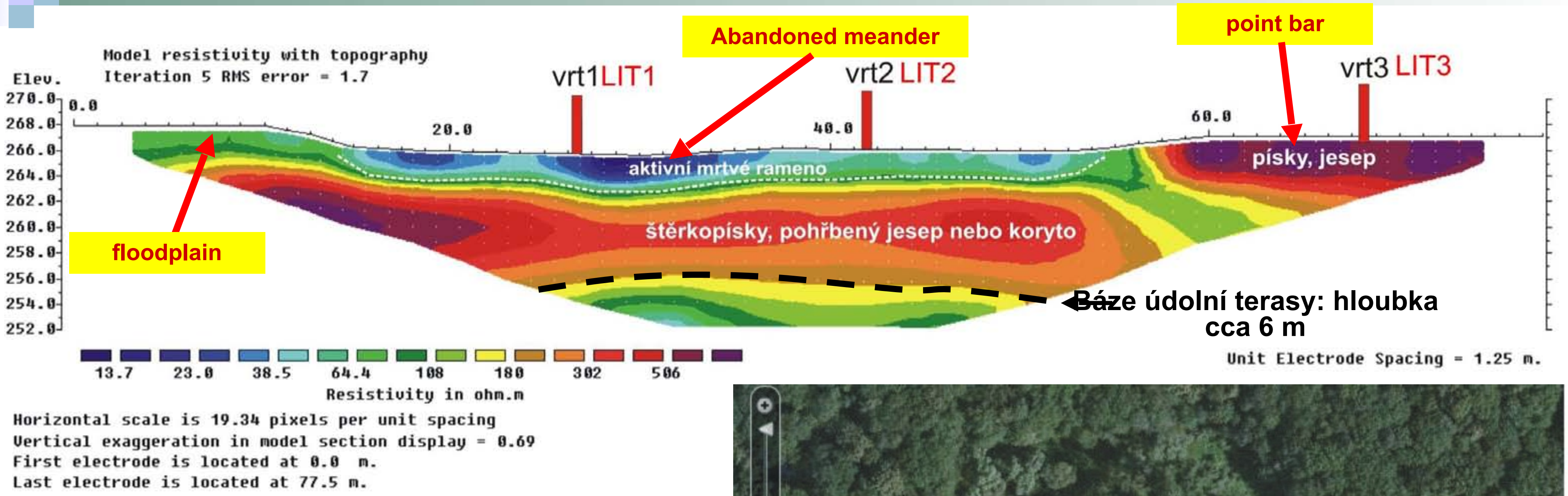
Laterally accreting fluvial sediments “complex architecture“

Geomorphology
- Morava River floodplain (in red), slope gradient map
- floodplain size: ~80 km (length) x ~13km (max. width)
- Very low slope gradient (< 0,15º)

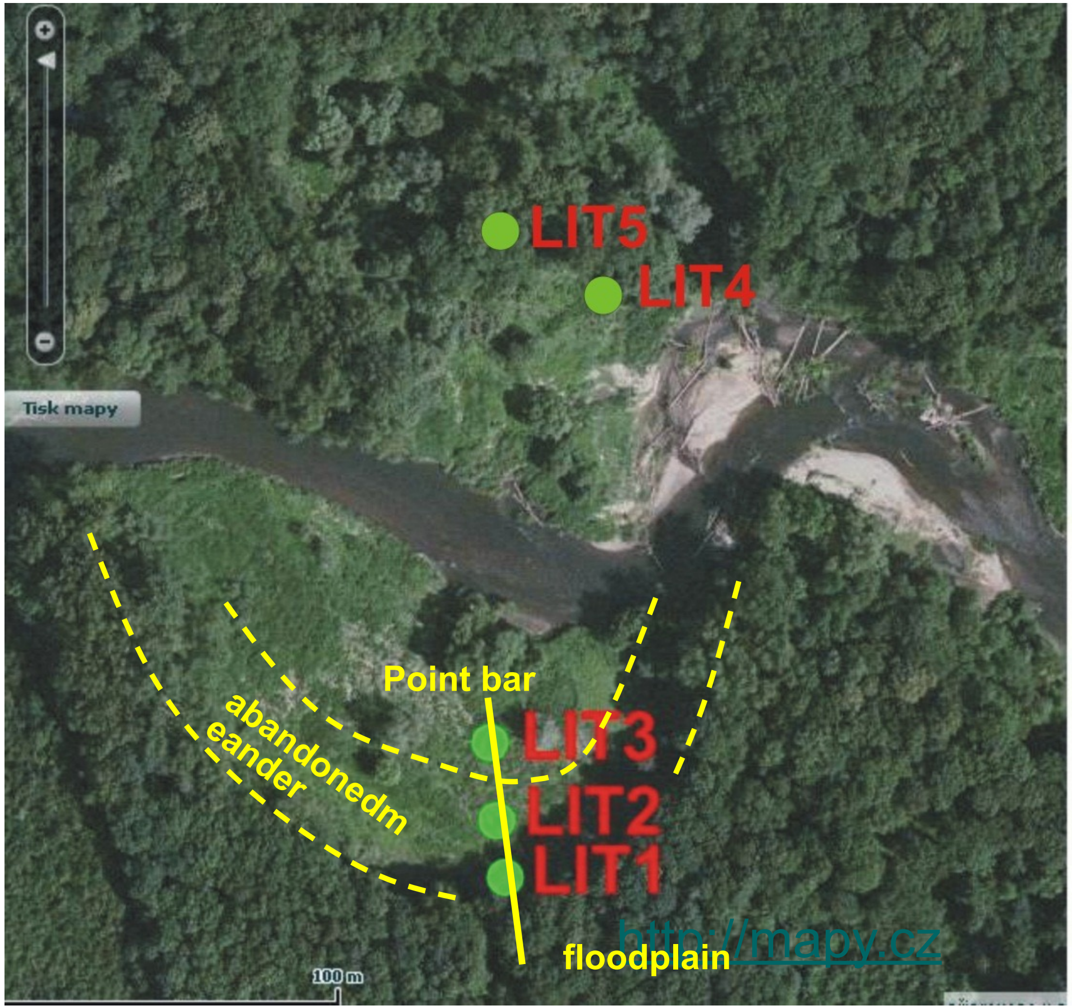
Methods
- Percussion drill-cores
- Shallow geophysics: Electrical resistivity tomography (ERT), dipole EM profiling (DEMP)
- Multiproxy analysis
- geochemistry



Špaček et al., 2011, *Zt. D. Geol. Gess.*



Natural meander, freshly abandoned

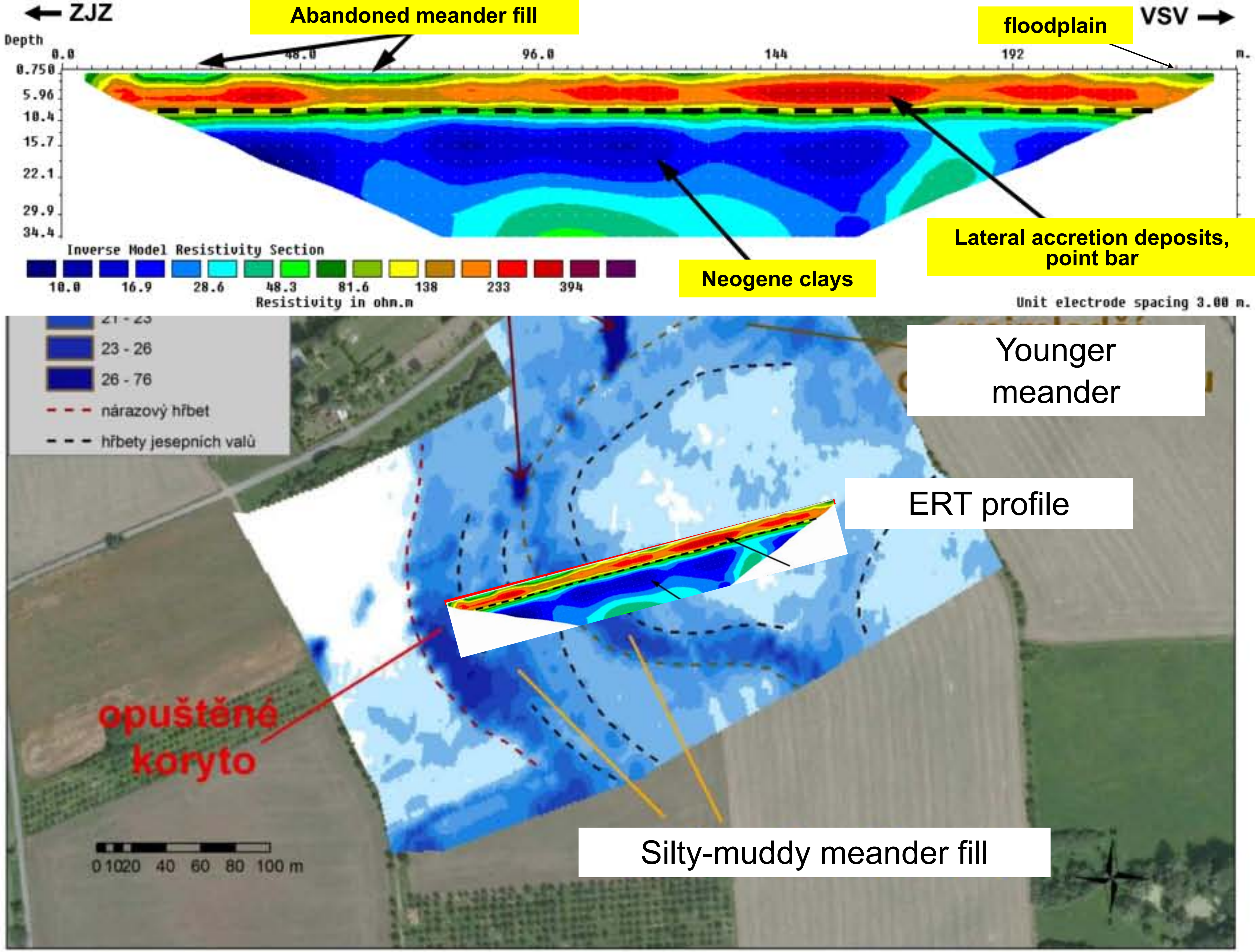


- ERT profile, core control
- Point bar: sand-gravel, resistivity 350 – 550 ohm.m
- Abandoned meander: silts, clays: resistivity 10 – 50 ohm.m
- Floodplain: silts, clays: resistivity 60 – 80 ohm.m

Filled-up meander

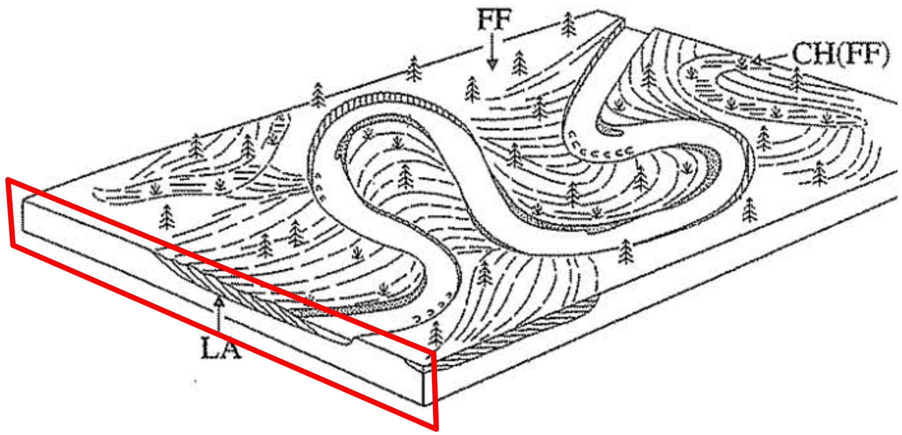
Olomouc – "Bázler sand pit"

- Abandoned meander, now completely filled
- Vegetation signs
- **Electrical conductivity map**
- **Resistivity profile**



← ZJZ
Abandoned meander fill
floodplain
VSV →
Depth
0.0
48.0
96.0
144
192
m.
0.750
5.96
10.4
15.7
22.1
29.9
34.4
Inverse Model Resistivity Section
10.0
16.9
28.6
48.3
81.6
138
233
394
Resistivity in ohm.m
Lateral accretion deposits, point bar
Neogene clays
Unit electrode spacing 3.00 m.
23 - 26
26 - 76
nárazový hřbet
hřbety jesepních valů
Younger meander
ERT profile
opuštěné koryto
0 10 20 40 60 80 100 m
Silty-muddy meander fill

Facies model, Morava River

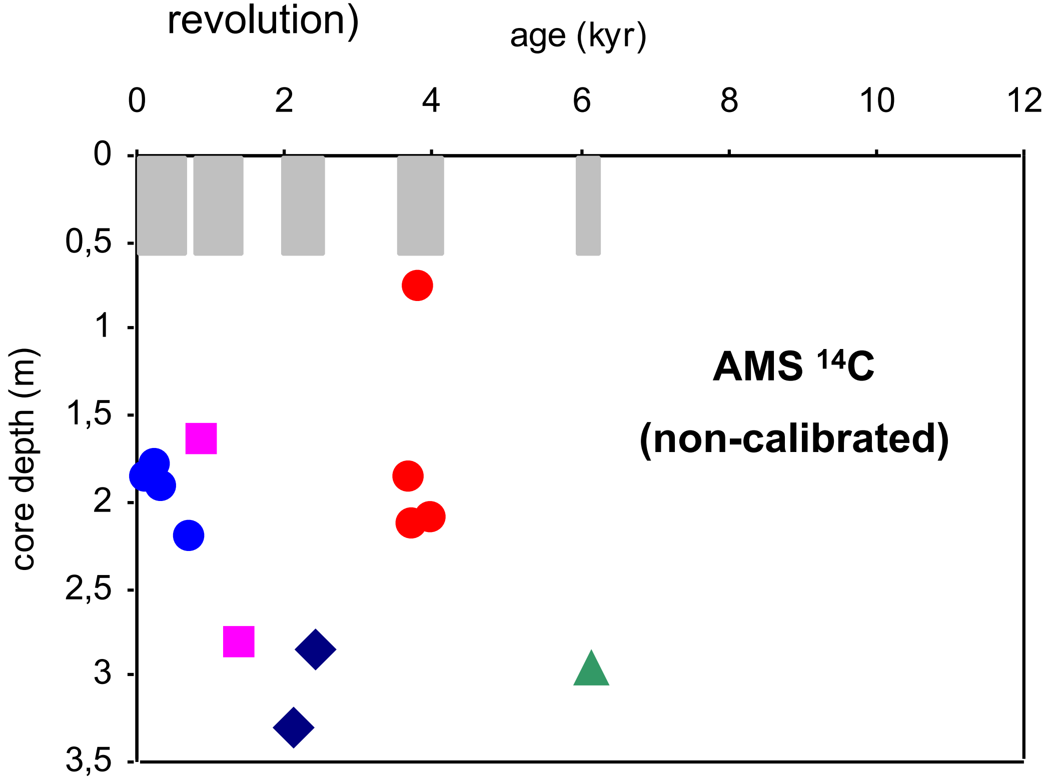


LA : lateral accretion deposits
CR : crevasse channels
CS : crevasse-splay sediments
FF : floodplain sediments
CH(FF) : abandoned meanders

Sandy meandering system

- Channel reloading and meandering
- AMS ^{14}C dates: 0.13 – 6.14 kyr BP
- Depth range: 0.76 – 3.3 m, lack of superposition

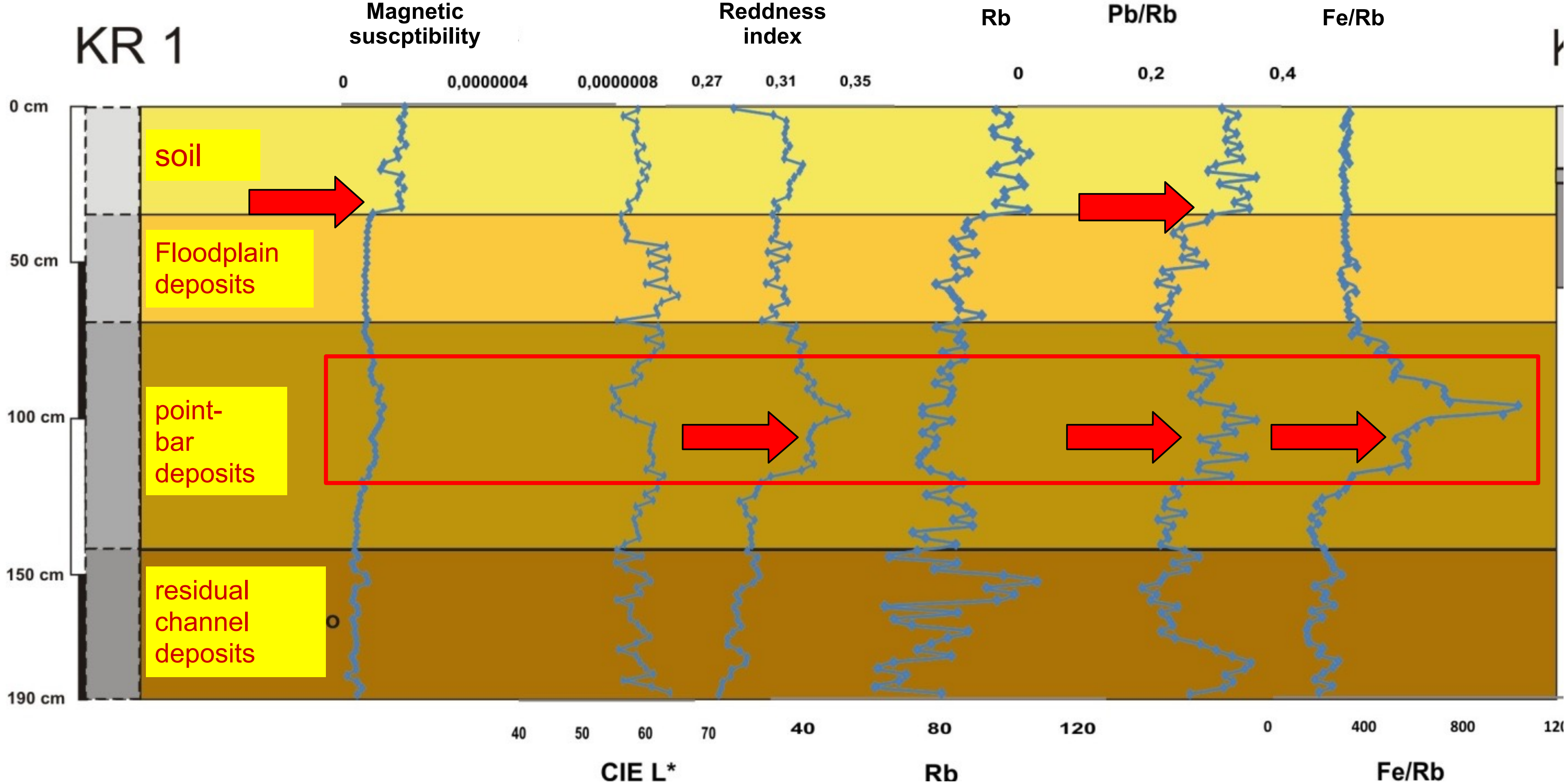
- Continuous recycling of floodplain deposits due to meandering (younger Atlantic – industrial revolution)



"Deeper is older" can be a misconception in floodplains

Floodplain core: Pb contaminated or not ?

- Increase of MS, Rb and Pb/Rb in soil (normalized to Rb) - contamination
- Zone of fluctuating water table, cca 80 – 120 cm (“reductiomorphic zone“)
- Increased MS, reddness index, Fe/Rb and Pb contamination – diagenetic precipitation of Fe- oxy-hydroxides



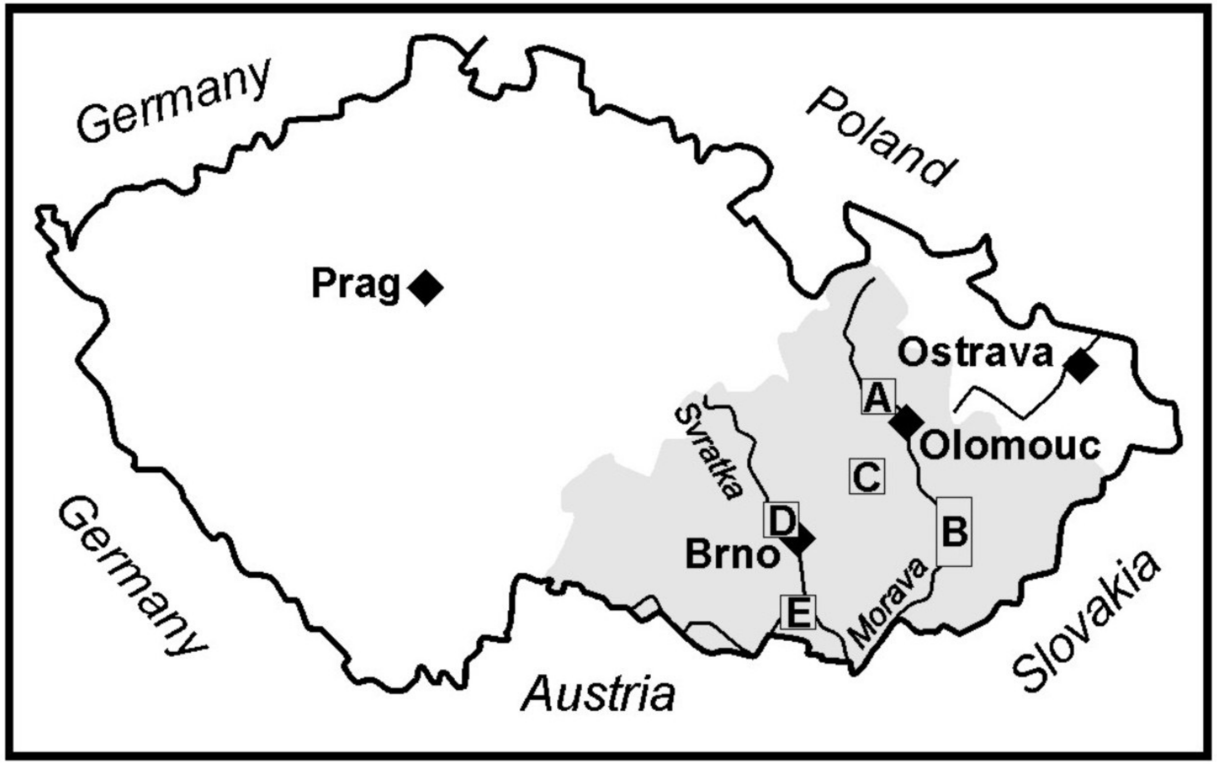
Even greater complexity due to post-sedimentary processes

Geochemical background and anthropogenic contamination:

What is polluted and what is not ?

- effect of depositional setting / grain size

Morava River case study: Effects of depositional environments on lithogenic background ?



Sampling in floodplain deposits

We test geochemical variability across four types of depositional environments :

- **River channels** (3 sites)
- **Floodplain** (5 sites)
- **Dammed reservoirs** (14 sites)
- **Oxbow lakes** (3 sites)

- **River Morava and tributaries (Svratka, Dyje, Hloučela)**

- Drill core at each site
- Total 576 samples
- EDXRF analysis (rapid and inexpensive)
- Known contamination from previous studies

- ***Local vs regional background and contamination***

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Sampling in abandoned meander deposits

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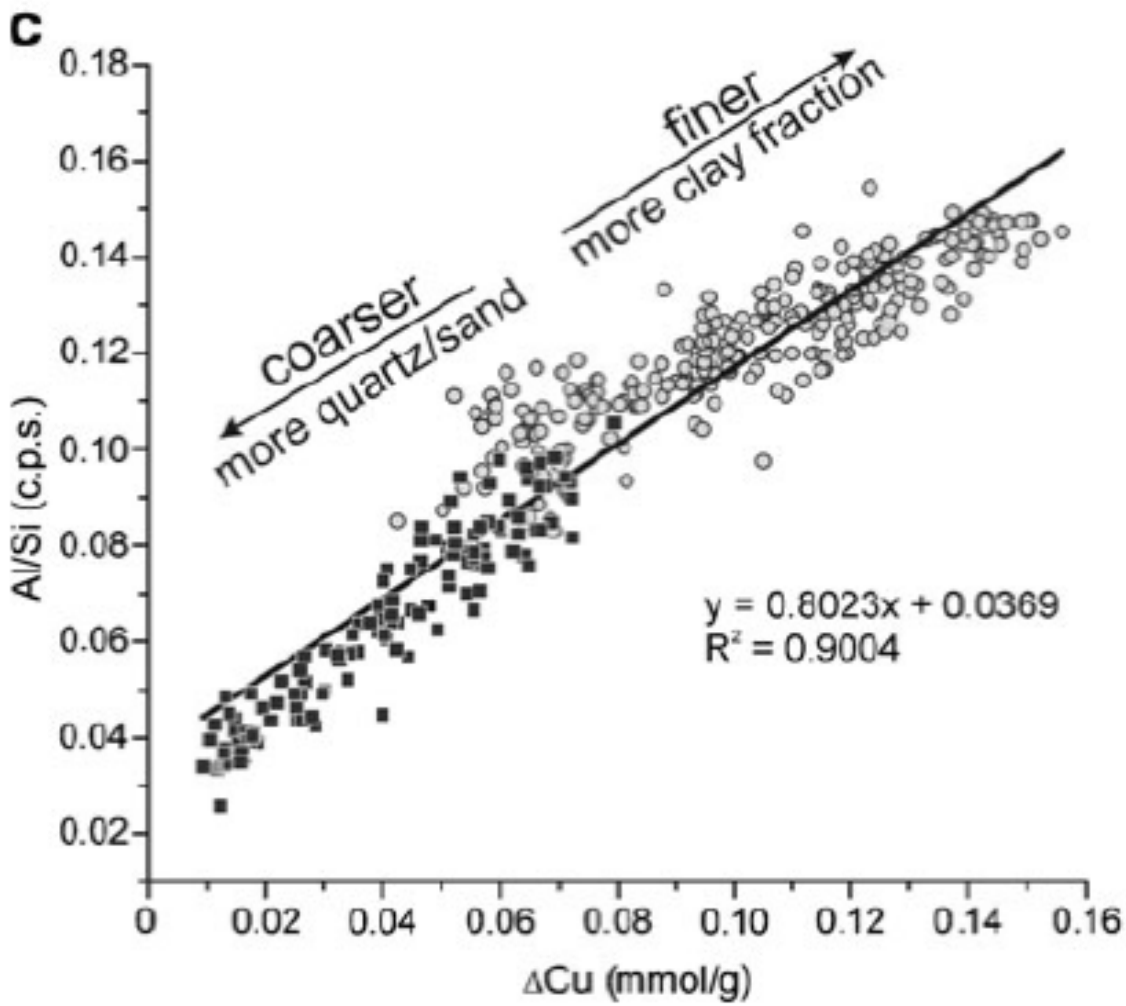
Geochemical meaning of grain size : normalizing of target elements (pollutants) to lithogenic grain-size sensitive elements



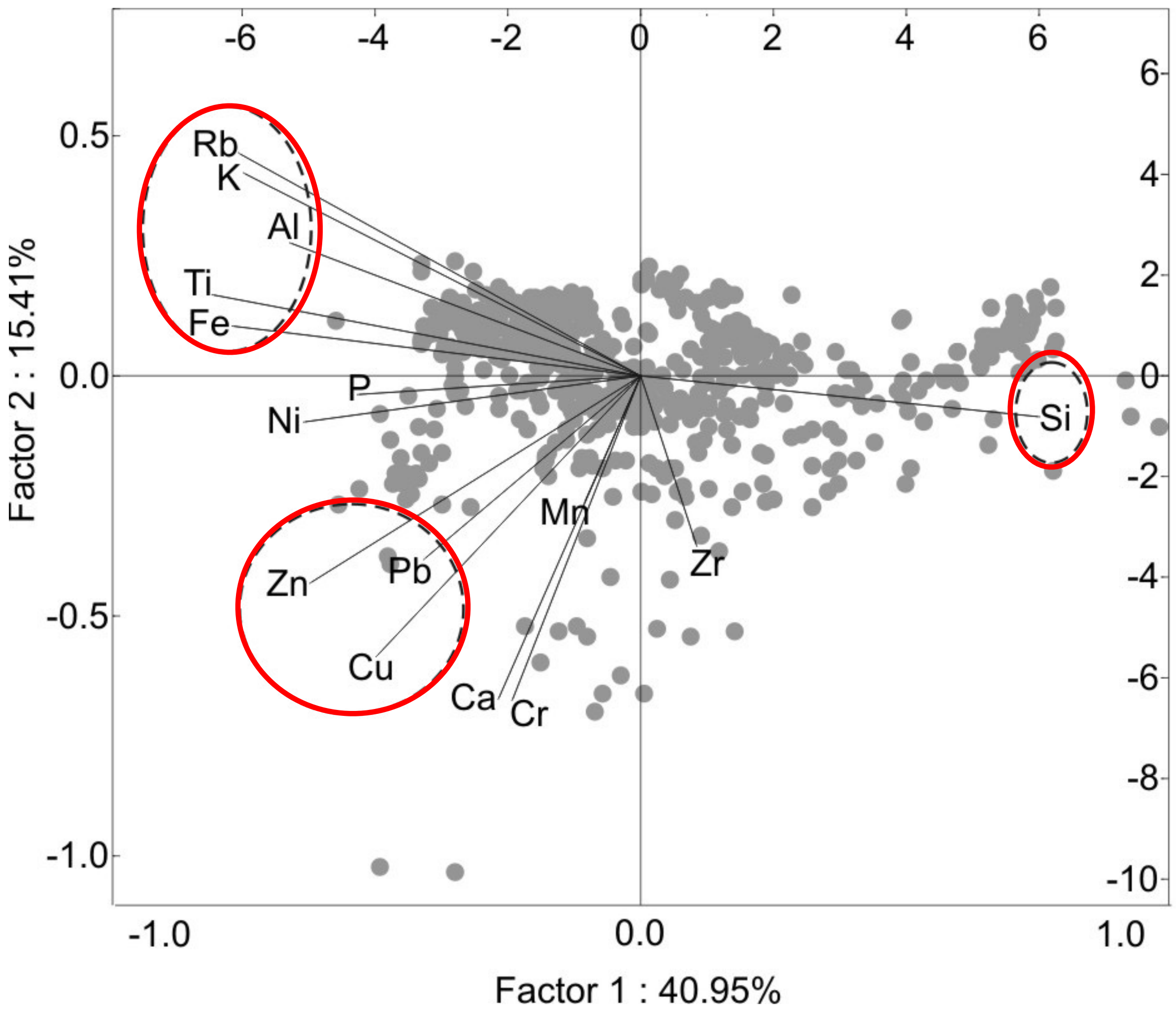
Al/Si: a useful geochemical proxy of grain size:

- **Al** carried mainly by **phyllosilicates**, fine-grained fraction; **Si** carried mainly by **quartz and feldspar** grains, coarse fraction

- **Al/Si vs cation exchange capacity** (CEC) – proxy of presence of clay minerals

- ***It is useful to normalize target elements to Al to filter out the effects of changing grain size***

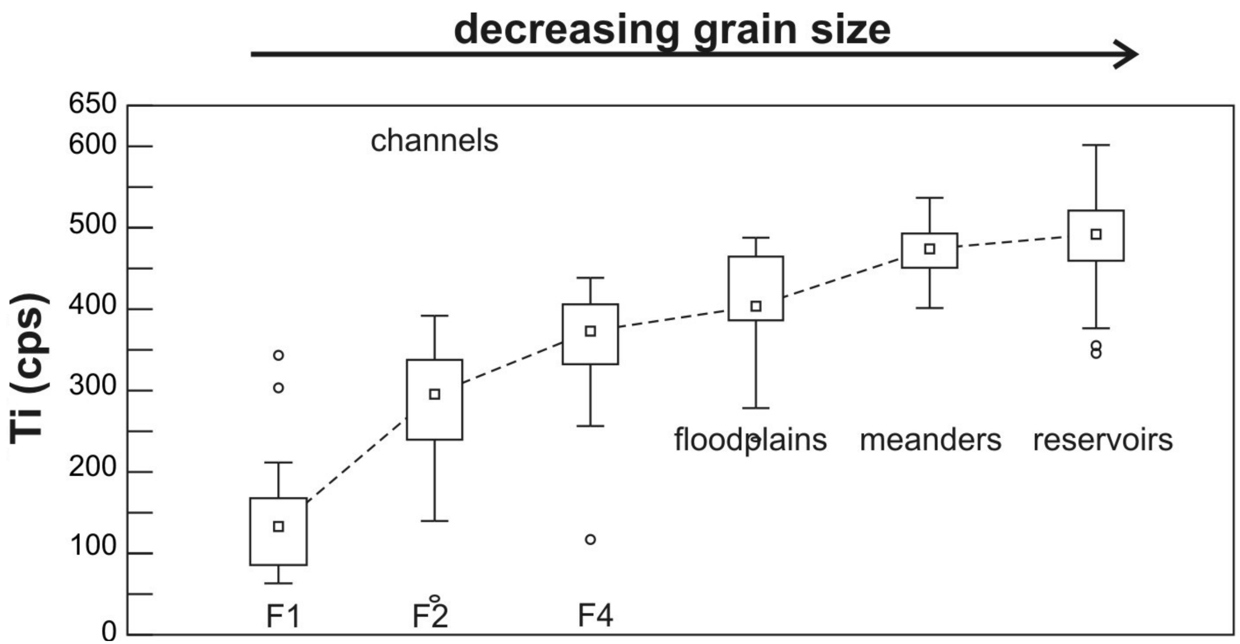
Element groups: PCA



PCA on raw (closed) data:

- **(1) Rb, K, Al, Ti, Fe**: lithogenic elements carried by fine-grained sediment fraction → suitable for normalizing
- **(2) Si**: lithogenic element carried by coarse-grained sediment fraction, anticorrelates with group (1)
- **(3) Pb, Zn, Cu, Cr**: elements at least partly related to anthropogenic contamination → toxic target elements
- ***We are looking for the best normalizing element***

Variation of lithogenic element concentrations across depositional environments



Tukey boxplots of element concentrations and element ratios (Al/Si; Al, Ti)

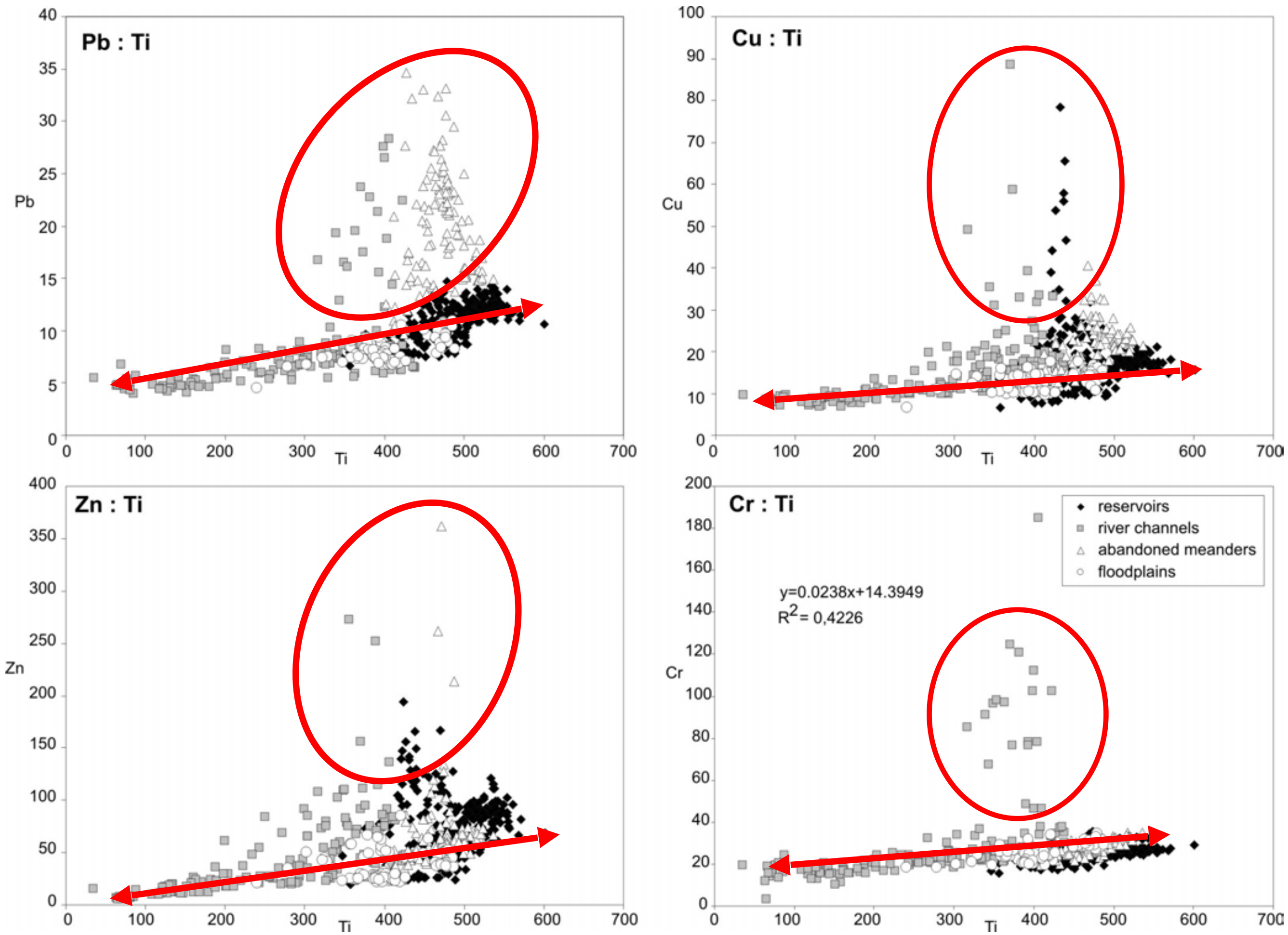
- **Lithogenic elements across depositional environments (coarse-grained channel fill /F1/ through to distal dam reservoirs)**

- ***We are looking for the best***

Titanium is the best proxy of grain size

"Local" testing for the best lithogenic denominator is needed, it is not always Al !

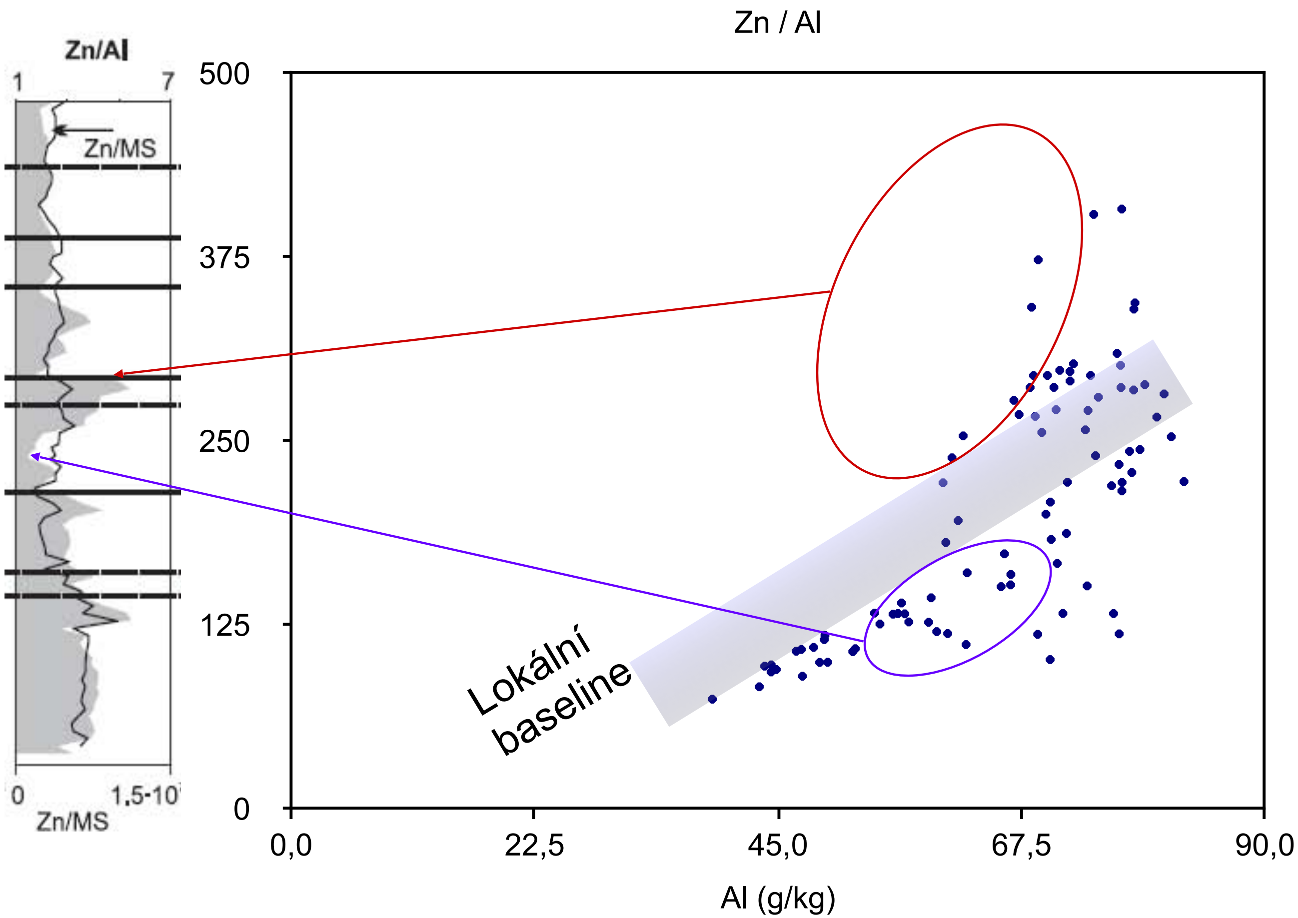
Background functions of Ti-normalized concentrations (Pb, Cu, Zn, Cr):



Distinct data structure:

- **Regions of linear covariance of Pb,Zn,Cu,Cr with Ti → lithogenic concentrations**
- **Outliers → added (anthropogenic) concentrations**
- ***How to separate these two regions ?***

What is the meaning of baseline ?



- **Pre-industrial concentrations ?**
- **Safe depths ?**
- **Average grain size ?**
- → interpretation first, then calculation of EFs or
- → first calculation and then interpretations ?
- → looking for suitable statistical procedure

Geochemical background and threshold: a statistical approach

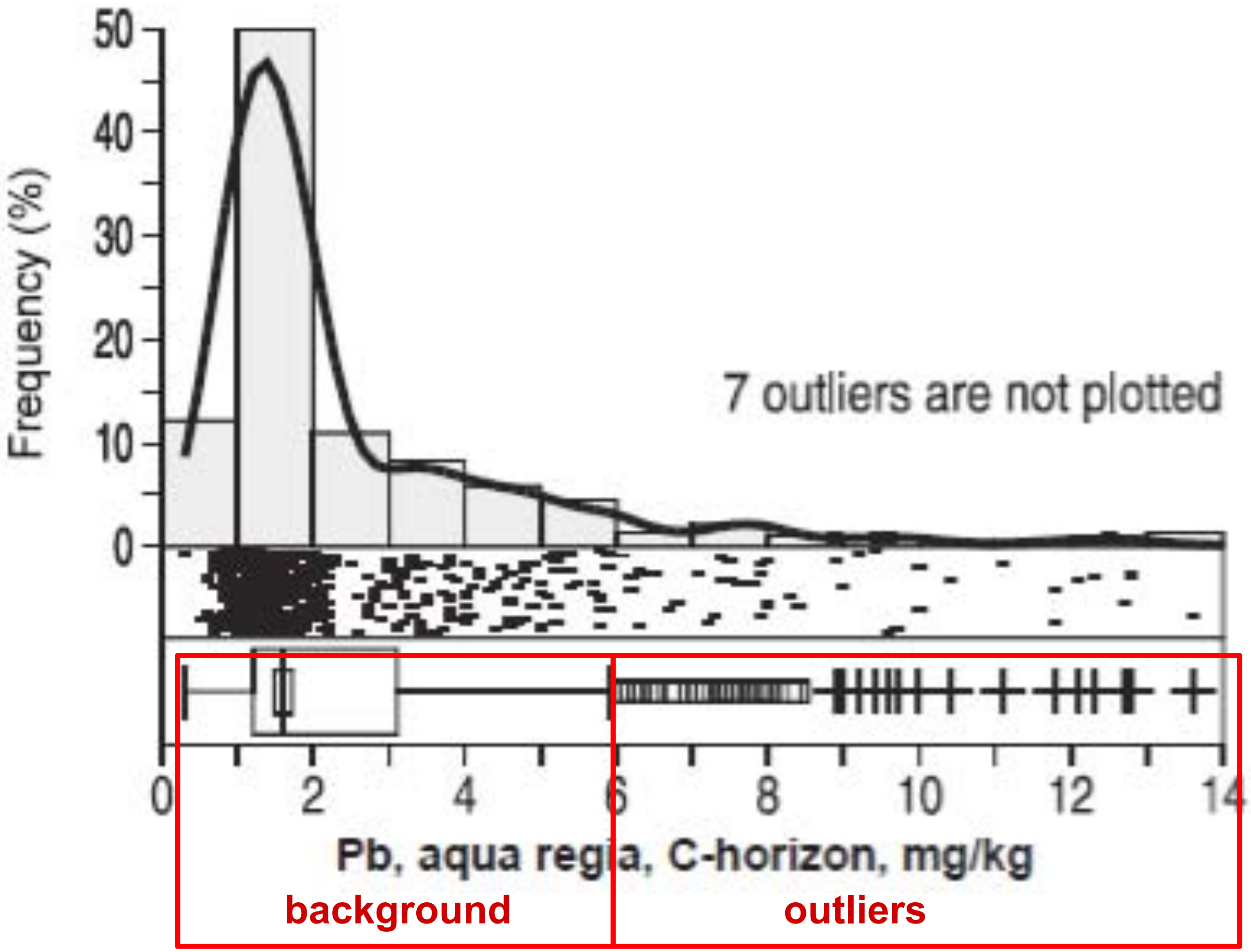
Soil data

- Histogram
- Density scattergram
- Tukey box-and-whisker plot

Background + threshold

- Mean +/- 2σ
- Median +/- 2σ
- Median + upper and lower whisker

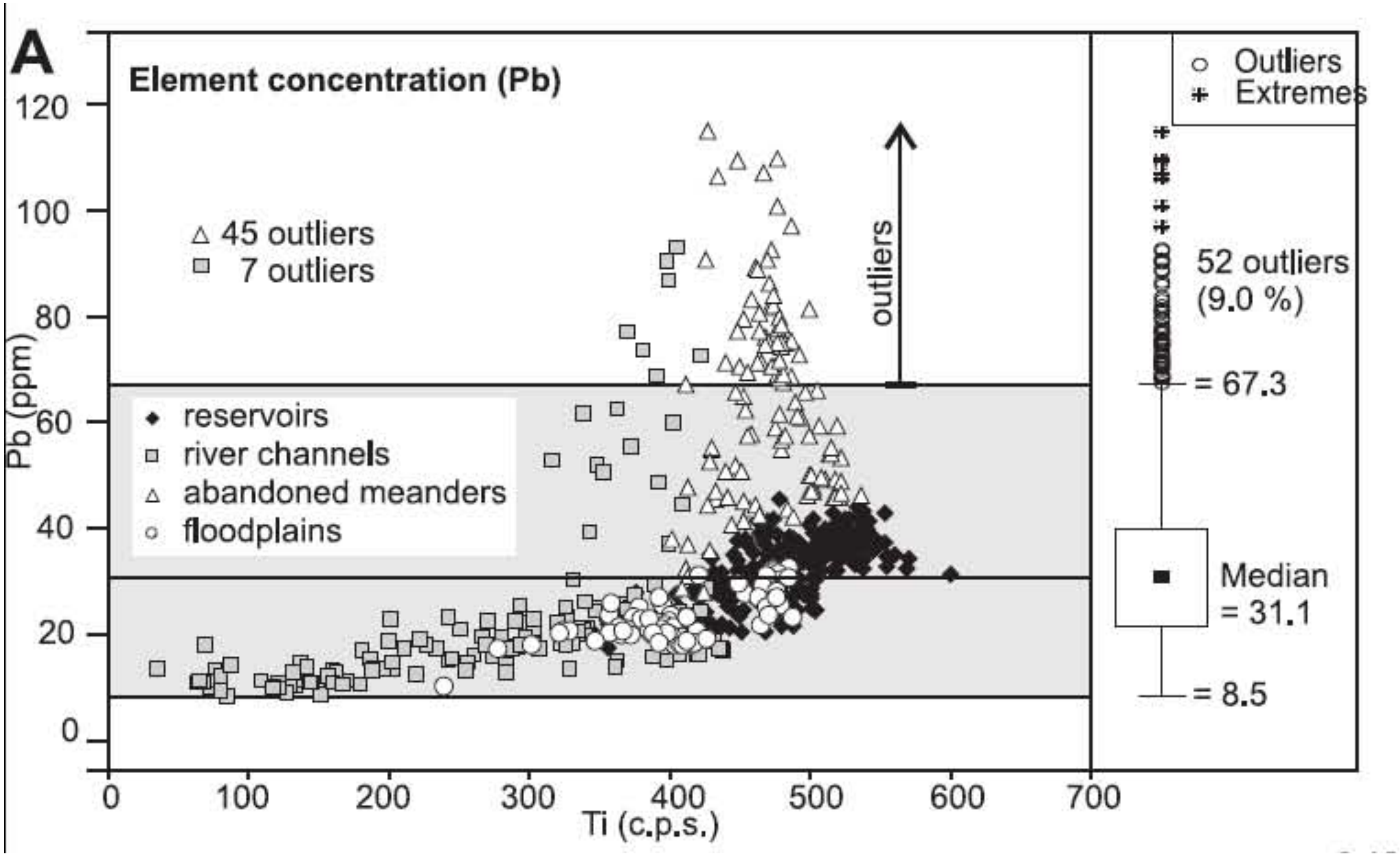
Outliers → geochemical anomalies



C. Reimann et al. / Science of the Total Environment 346 (2005) 1–16

Graphical representation of background function: Pb vs Ti scatter plots + boxplots

Pb concentrations



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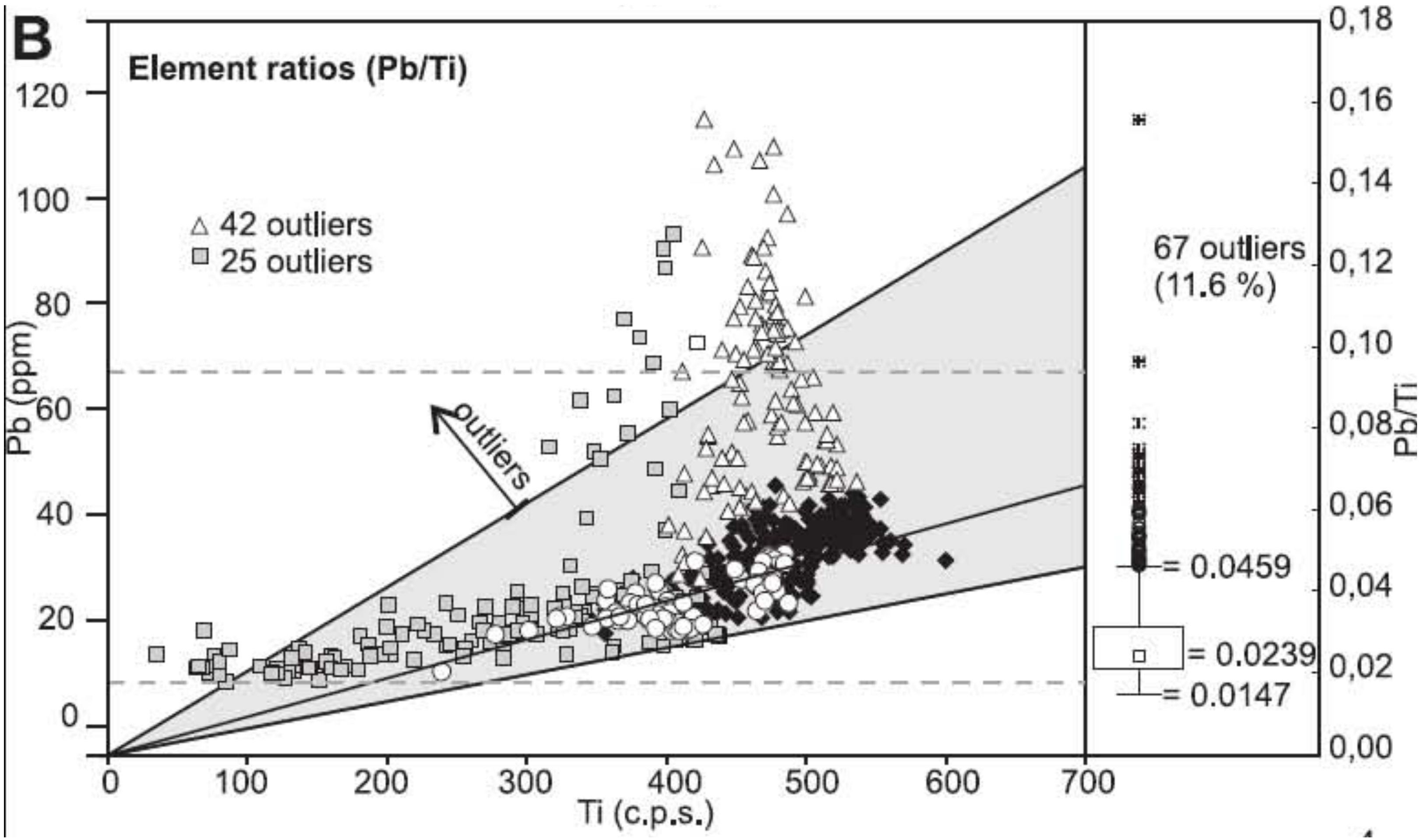
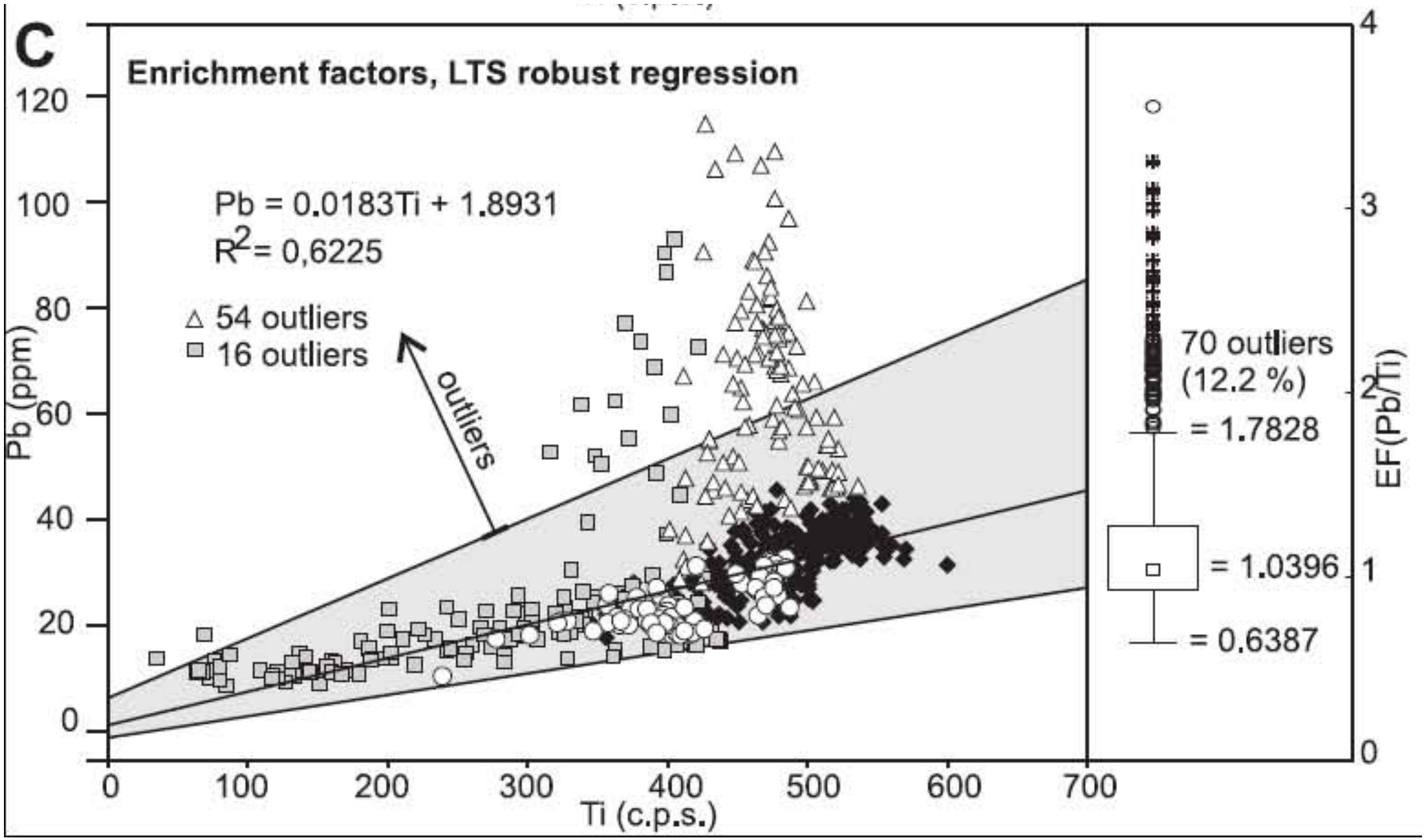
Pb / Ti ratios



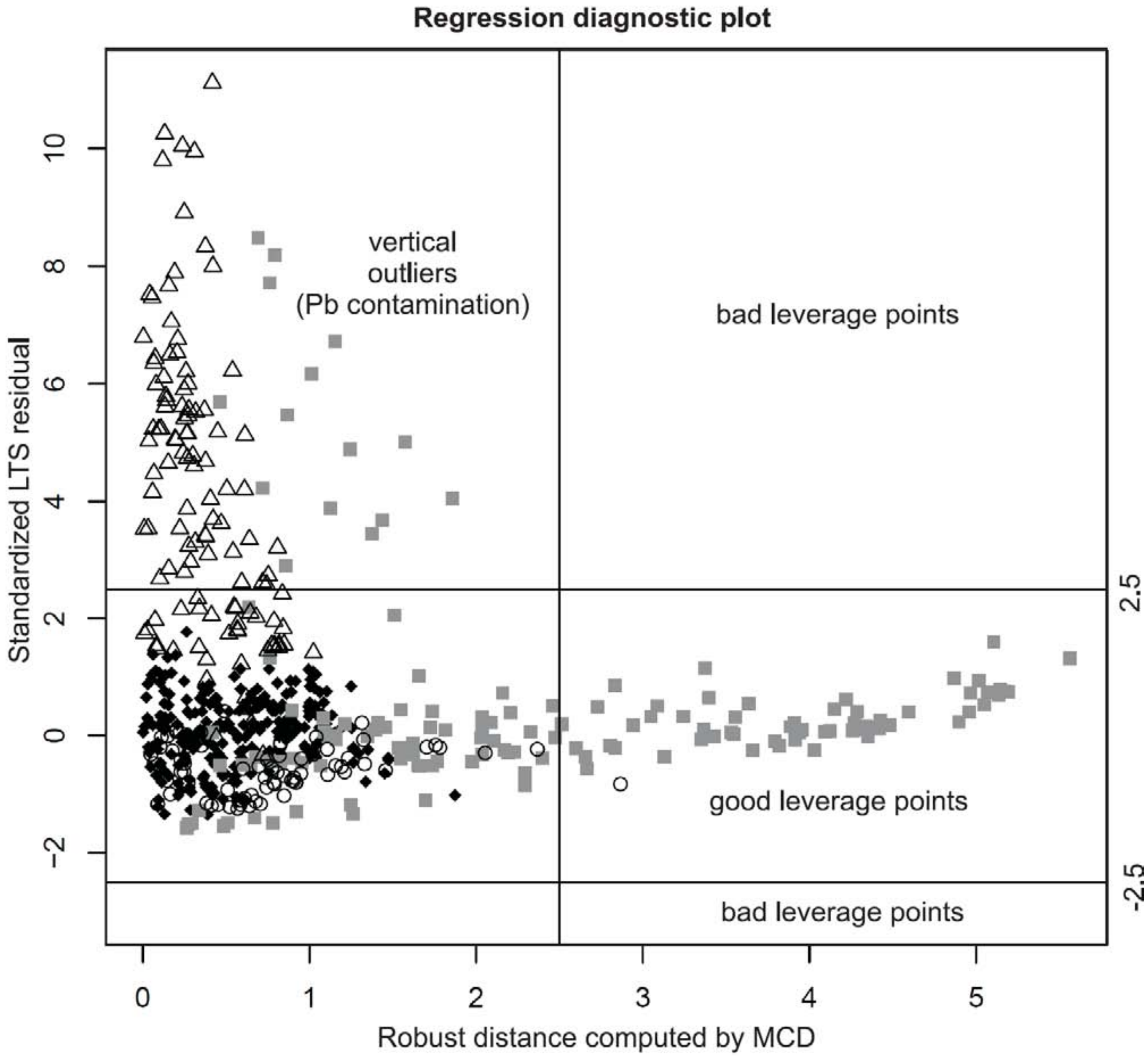
Graphical representation of background function: Pb vs Ti scatter plots + boxplots

EFs Pb/Ti, robust LTS regression



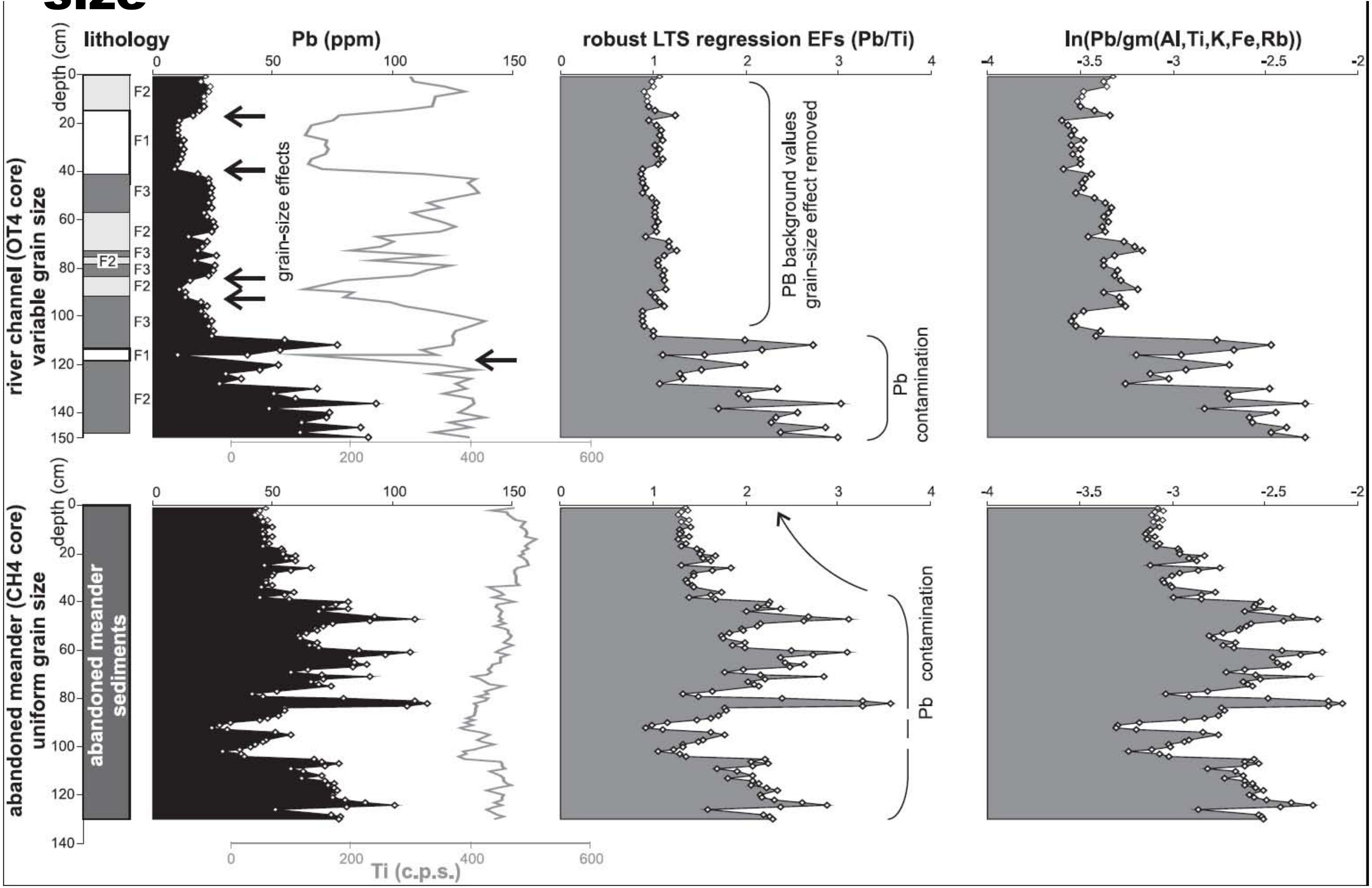
LTS (least trimmed squares) regression diagnostic plot

Pb / Ti ratios



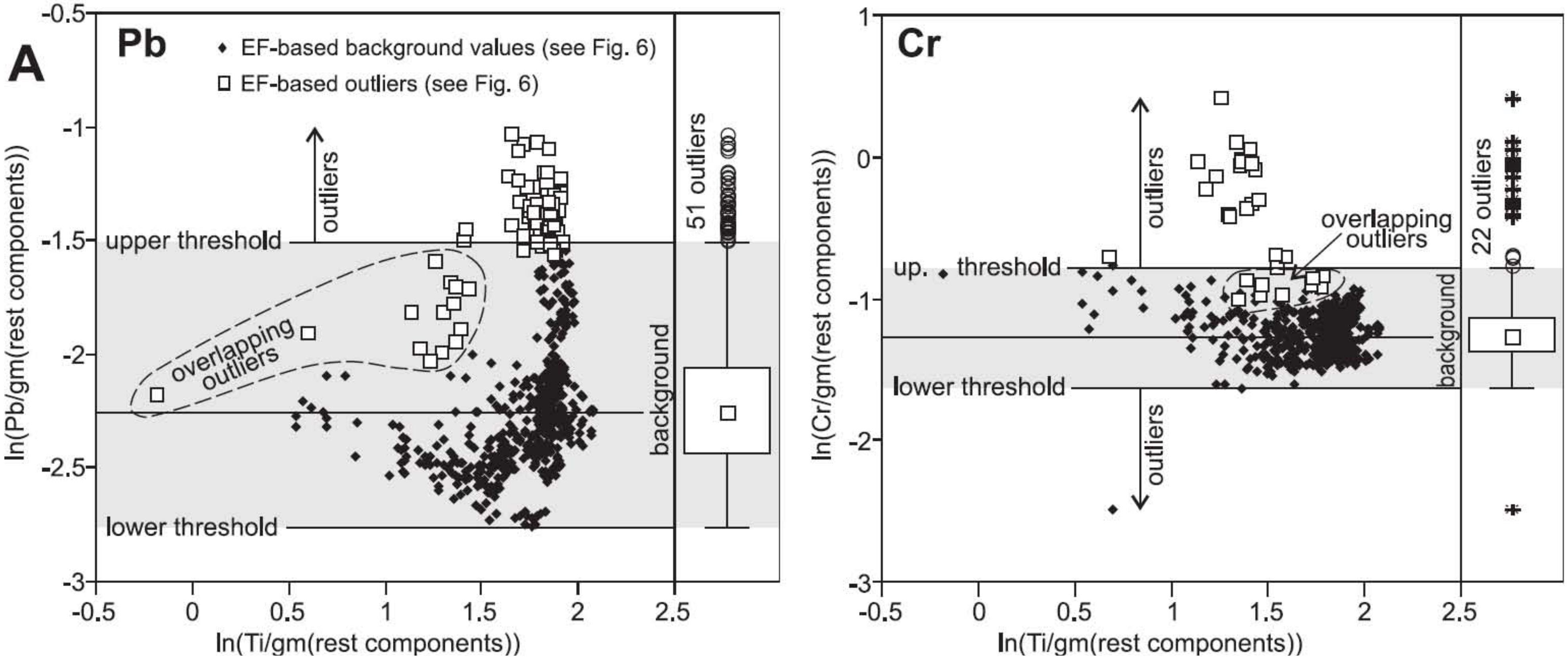
LTS regression is a safe, objective method for baseline calculation

Smoothing of Pb vertical trends due to grain size



Geochemical data are always closed (sum up to unity); danger of “spurious correlation“

Log-ratio approach to geochemical background



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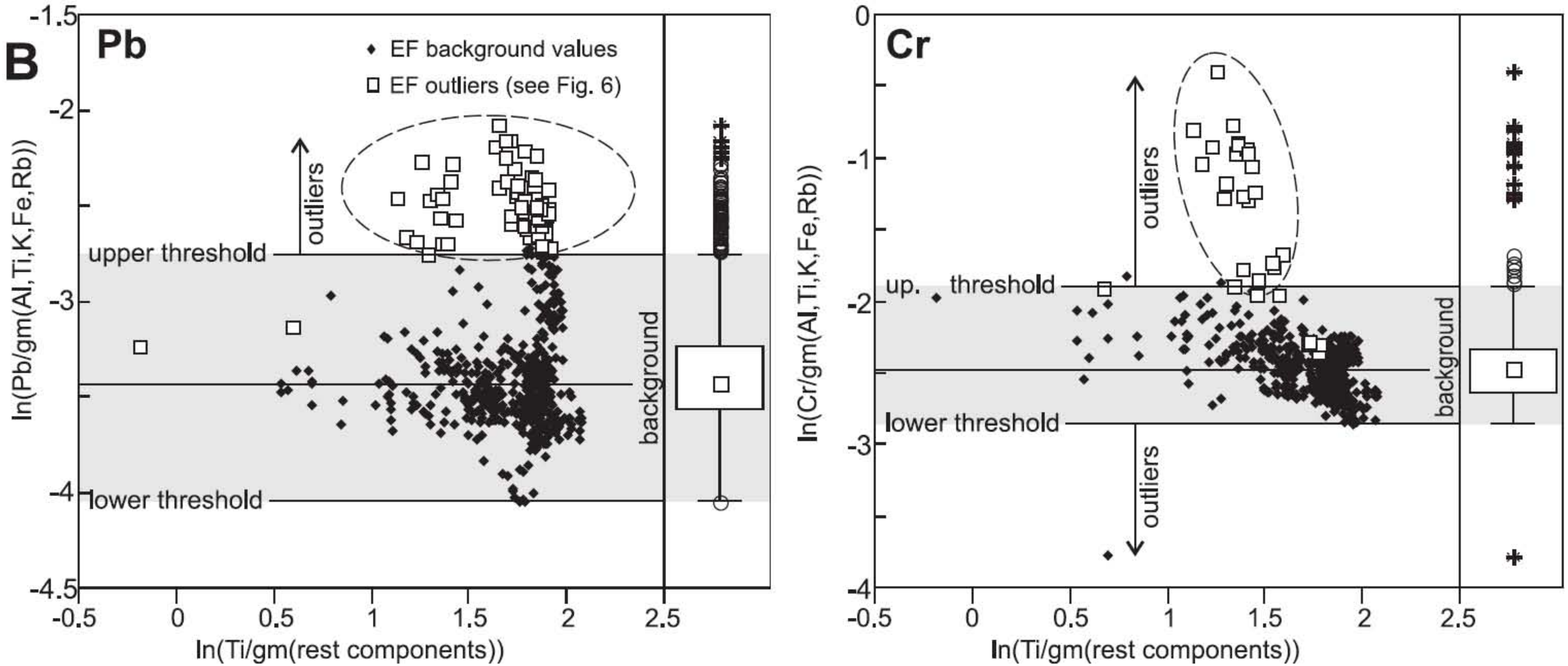

… take-home messages:

- subsurface sediment architecture critical
- water table depth
- geophysical and petrophysical tools
- “safe depth“ for definition of local geochemical background can be dangerous misconception
- objective statistical tools: LTS regression, log-ratio analysis

Thank you very much !