Development, Analysis und Assessment of Processes

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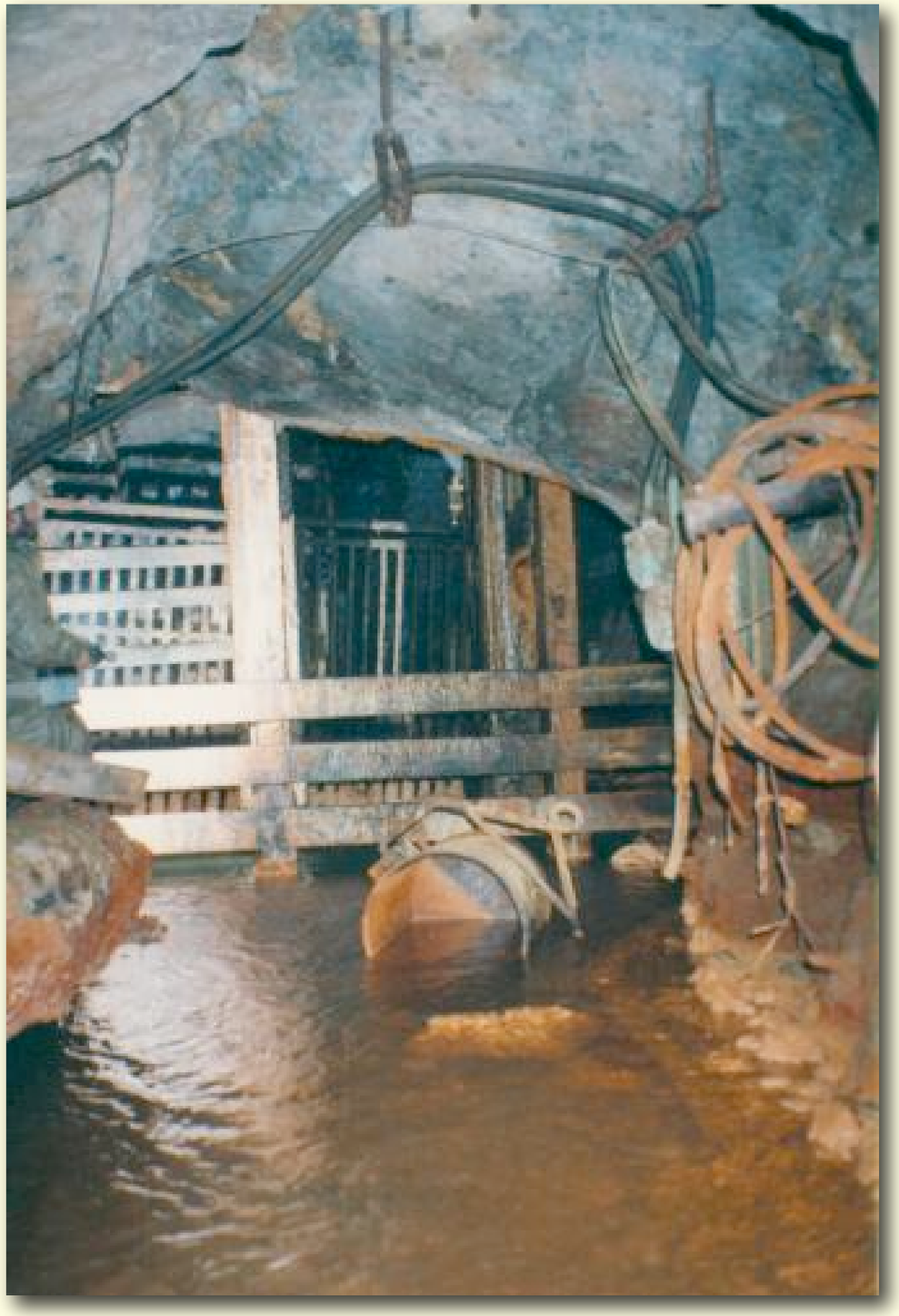
Environmental Science & Technology

EVISA Workshop on: Mercury speciation analysis

The basis for sound risk assessment, and optimized remediation strategies for contaminated soils, sediments and sludge

Why speciation: the origin



Problems with Mine Effluents
in the German Ore Mountains

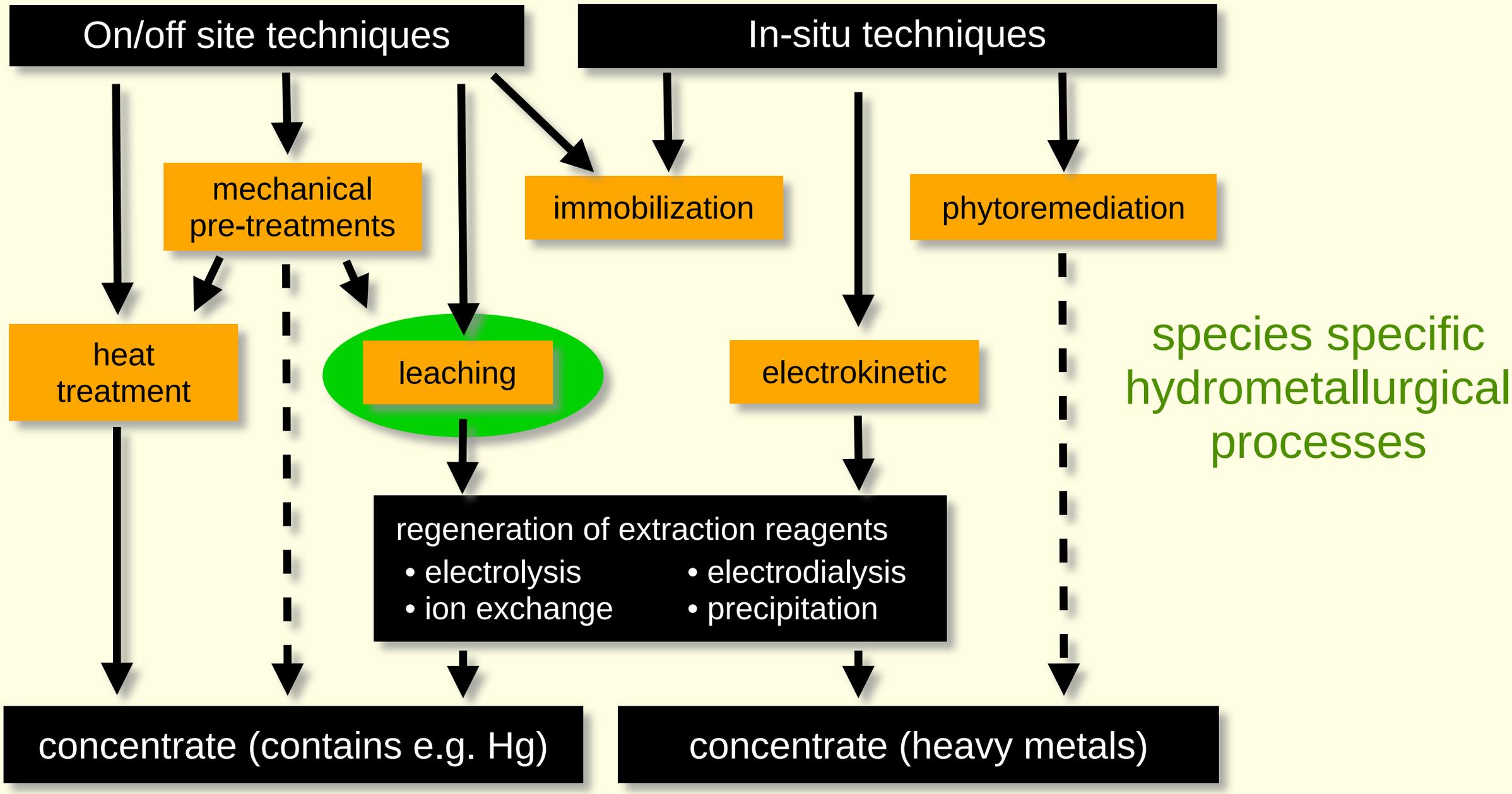
Why speciation: transportation I

Why speciation: transportation II

Why speciation: dislocation

Dredging in Hamburg Harbor

Remediation of Heavy Metal Polluted Soils



Why speciation?

criteria for risk estimation for environment:

⇒ **concentration** of heavy metals

⇒ **toxicity** of the respective heavy metals for plants and creatures

⇒ **chemical form** of heavy metals

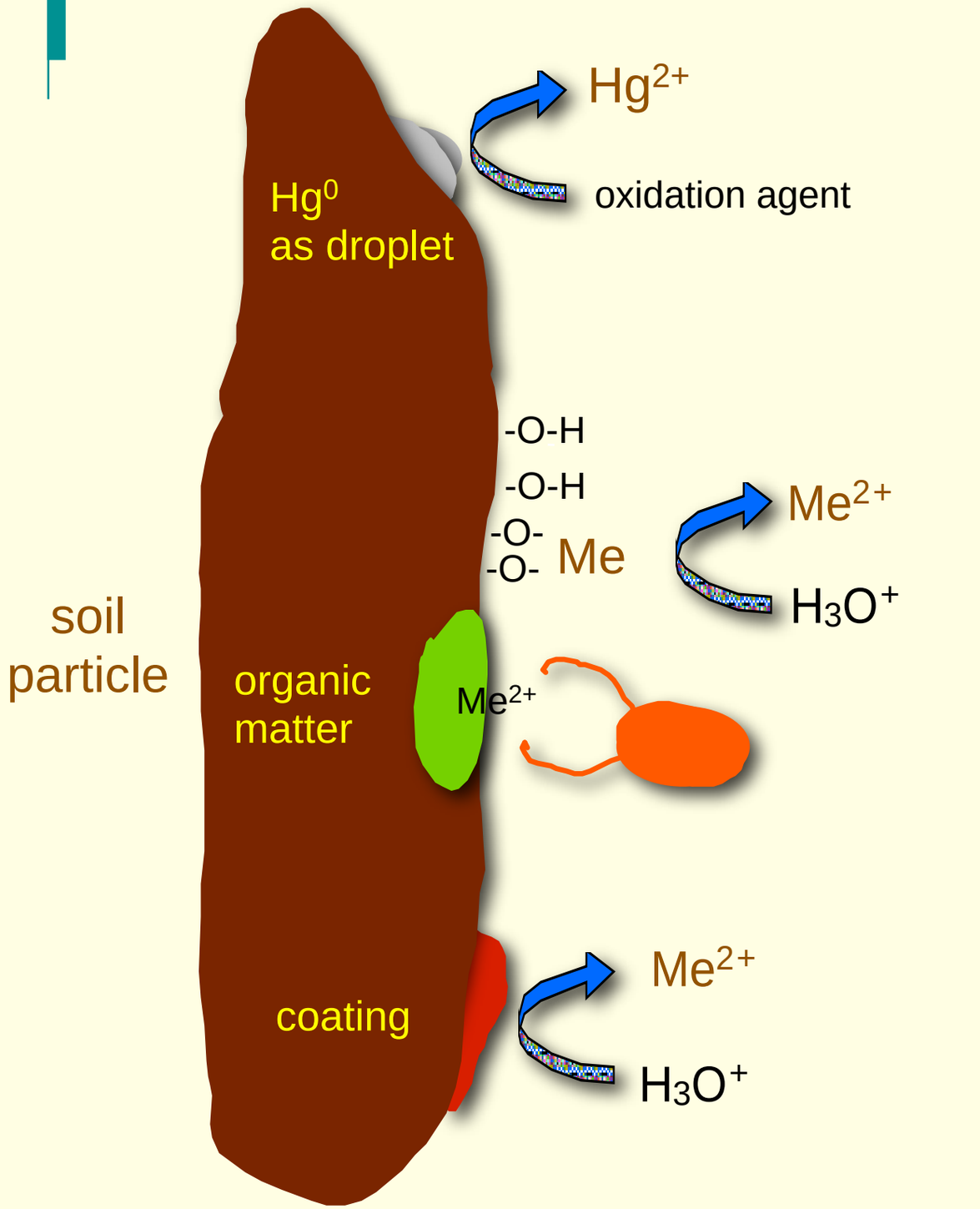
Cr^{3+} -> LD_{50} = 1870 mg/kg

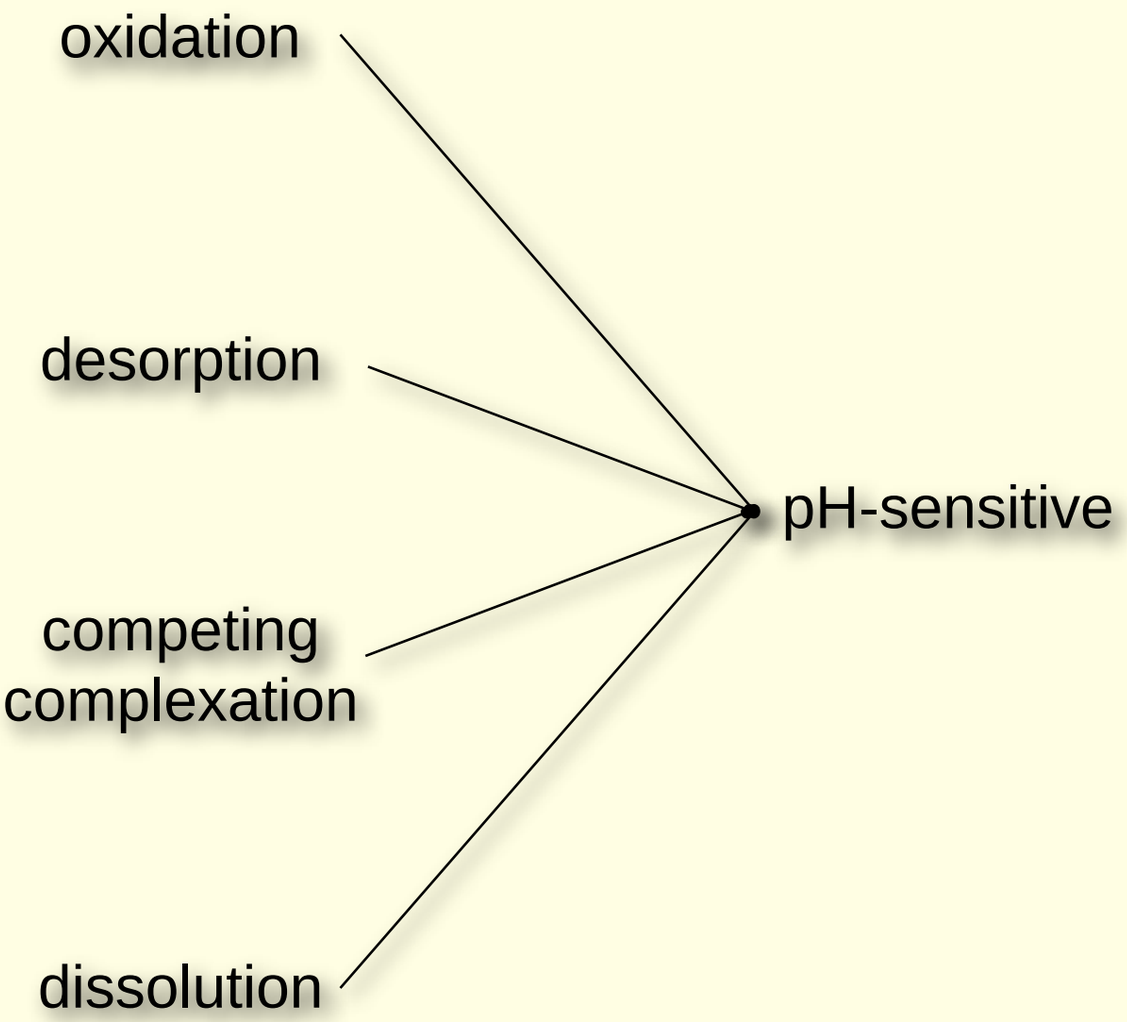
Cr^{6+} -> LD_{50} = 50 mg/kg, carcinogen

urgency of remediation

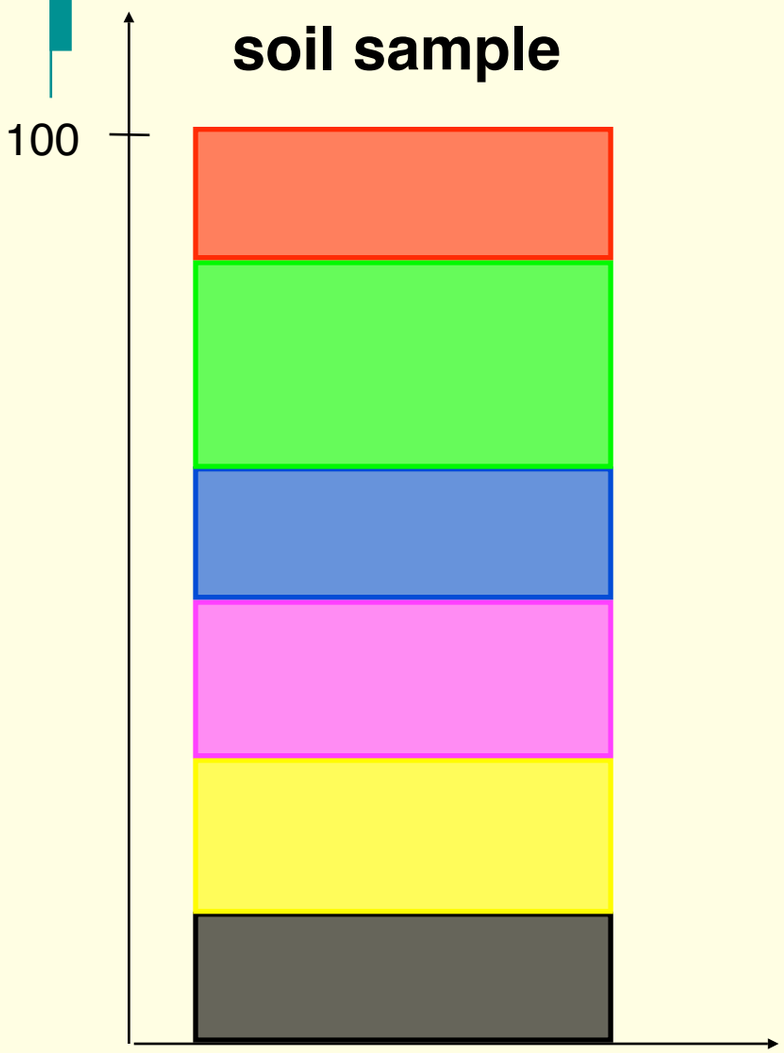
which remediation technique

Mechanisms of Metal Extraction from Soil





sequential extractions



solvent	fraction
NH_4Ac, pH 7	easily exchangeable
HAc/ NaAc, pH 5	bound to carbonates
$NH_2OH \cdot HCl$, pH 2	easily reducible
$(NH_4)_2Ox$/ Na_2Ox	moderately reducible
H_2O_2 / NH_4Ac	oxidizable
HNO_3	residual fraction

advantages:

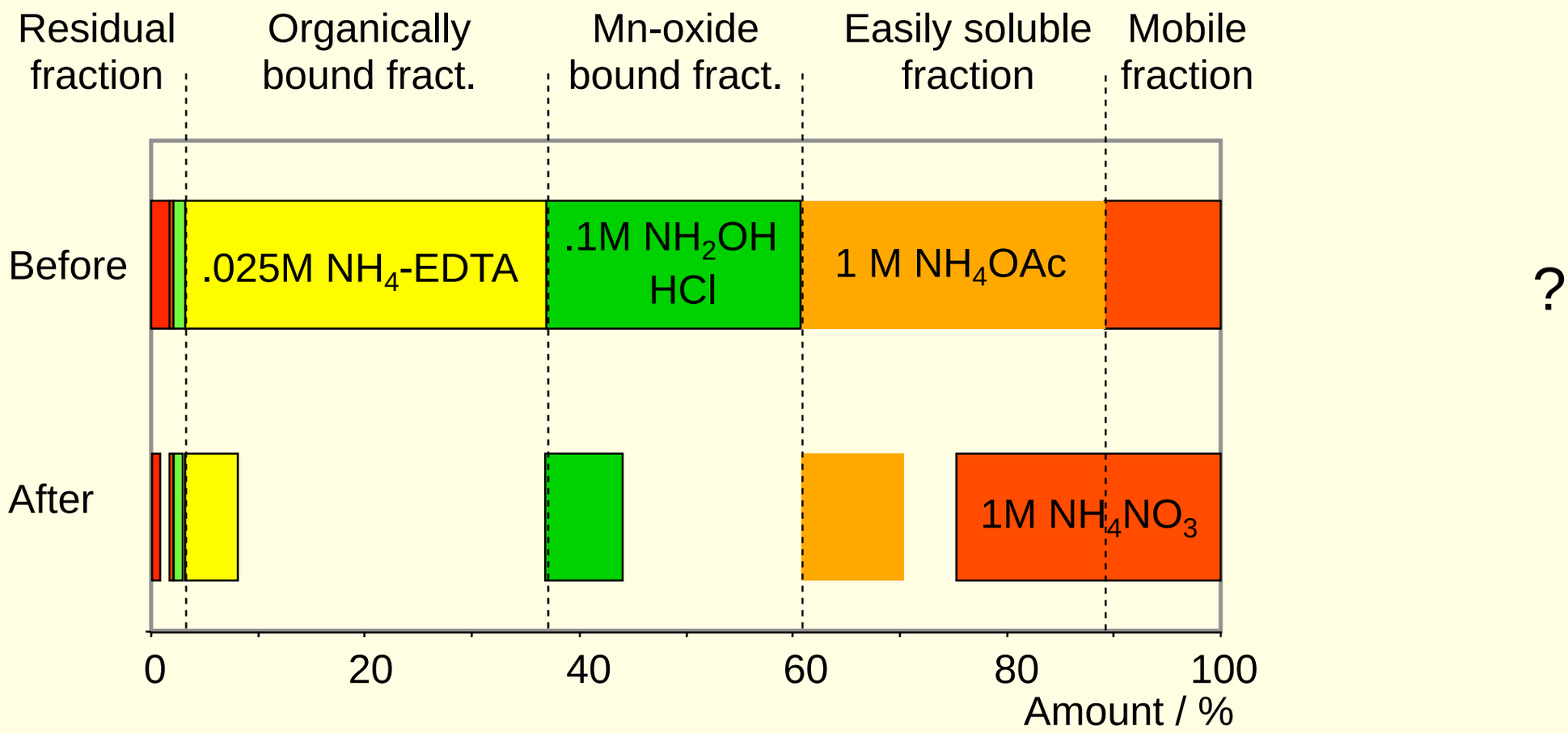
- easily and inexpensive to perform
- frequently used in environmental science

disadvantages:

- solvents are not selective for one species
- strong evidence of alterations of the composition of the sample during the first steps => artefacts

Pb species before & after leaching

Sequential extraction | instrumental analysis



Explanation: **Even if the clean-up targets are reached, the situation might be worse as it was before the treatment due to increased mobility of the pollutants.**

Direct instrumental speciation

problem

possibility to separate the analyte from matrix

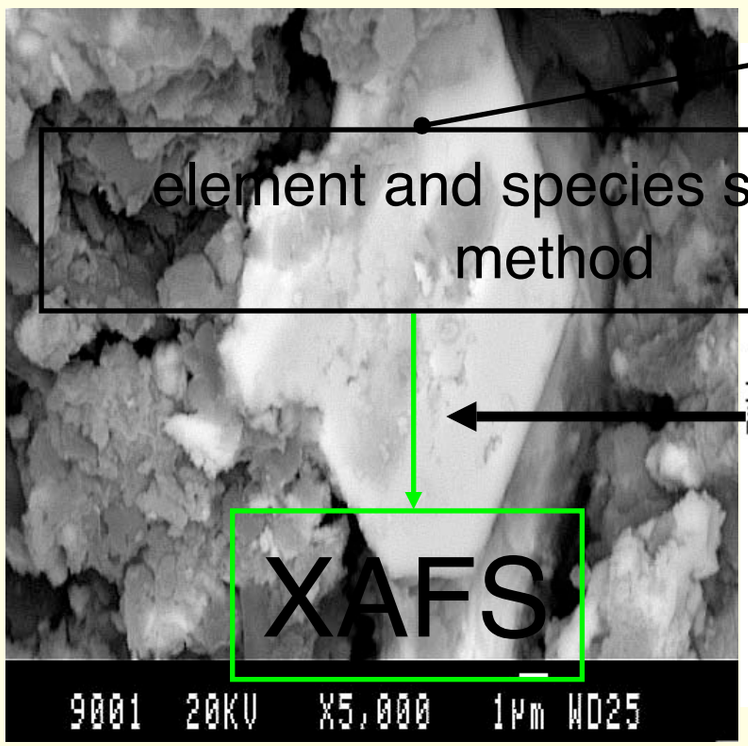
yes

extraction, derivatisation, GC/AAS

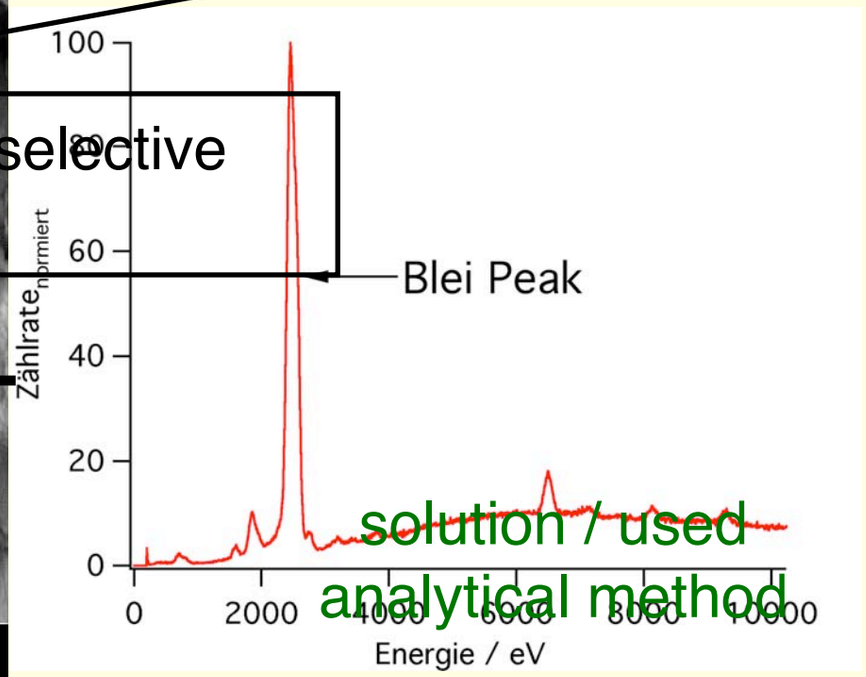
no

analytical method has to be used in presence of the matrix

element and species selective method



XAFS

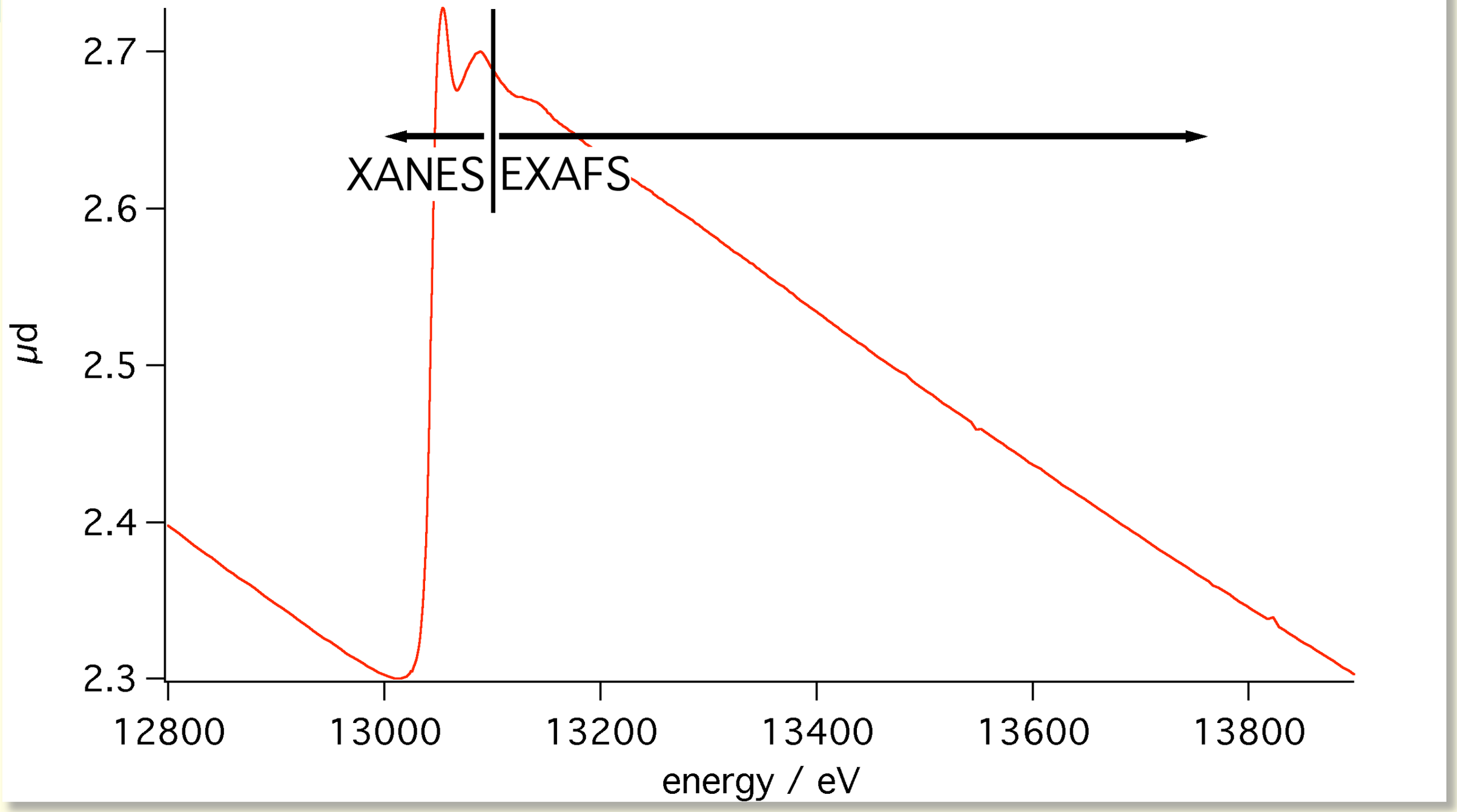


solution / used analytical method

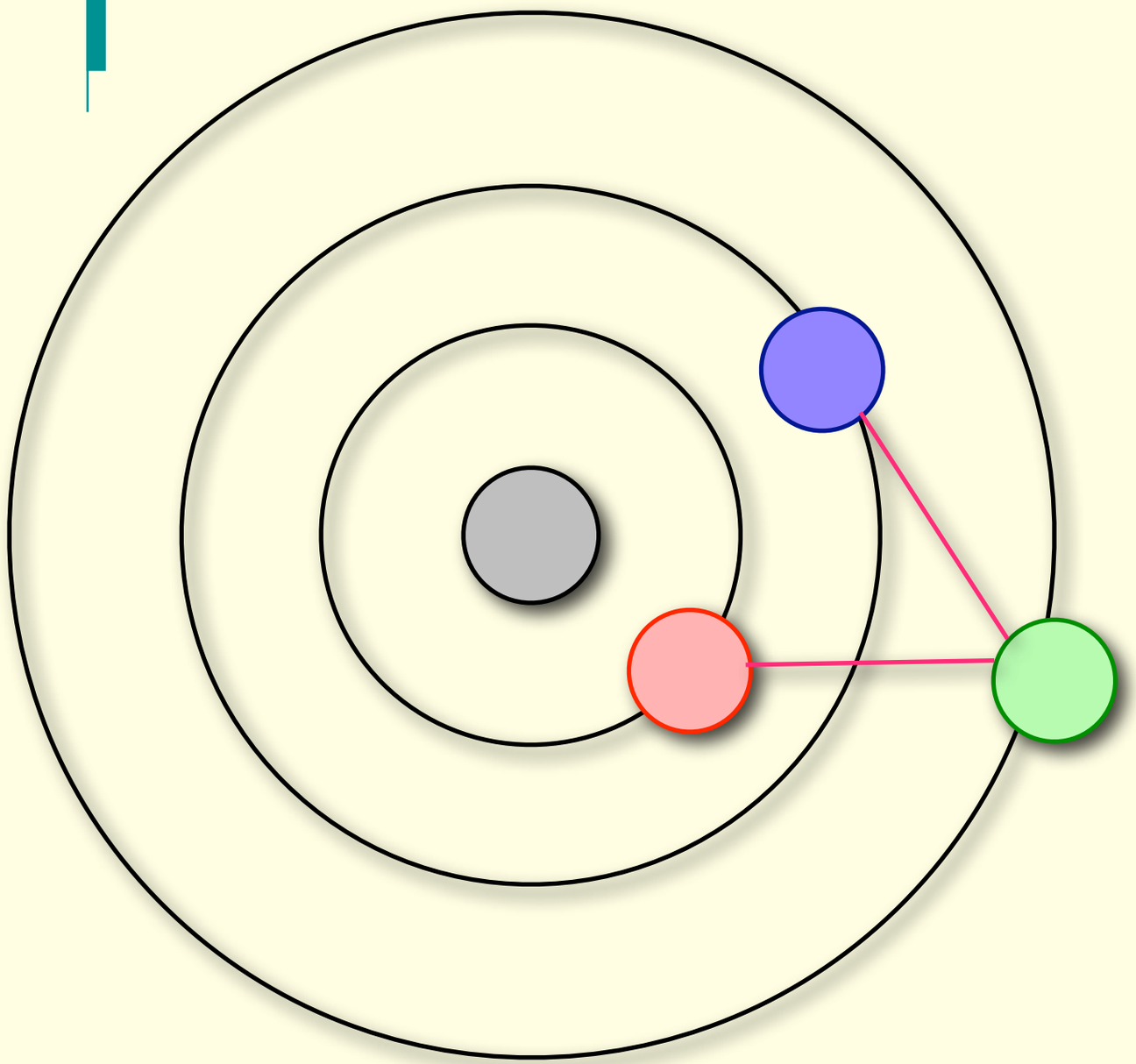
method with high spatial resolution

REM / EDX

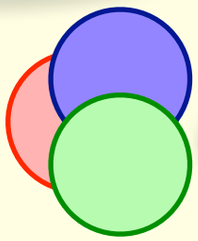
XAFS - XANES, EXAFS



information by XAFS



central atom



neighboring atoms

XRD => **L**ong **R**ange **O**rder

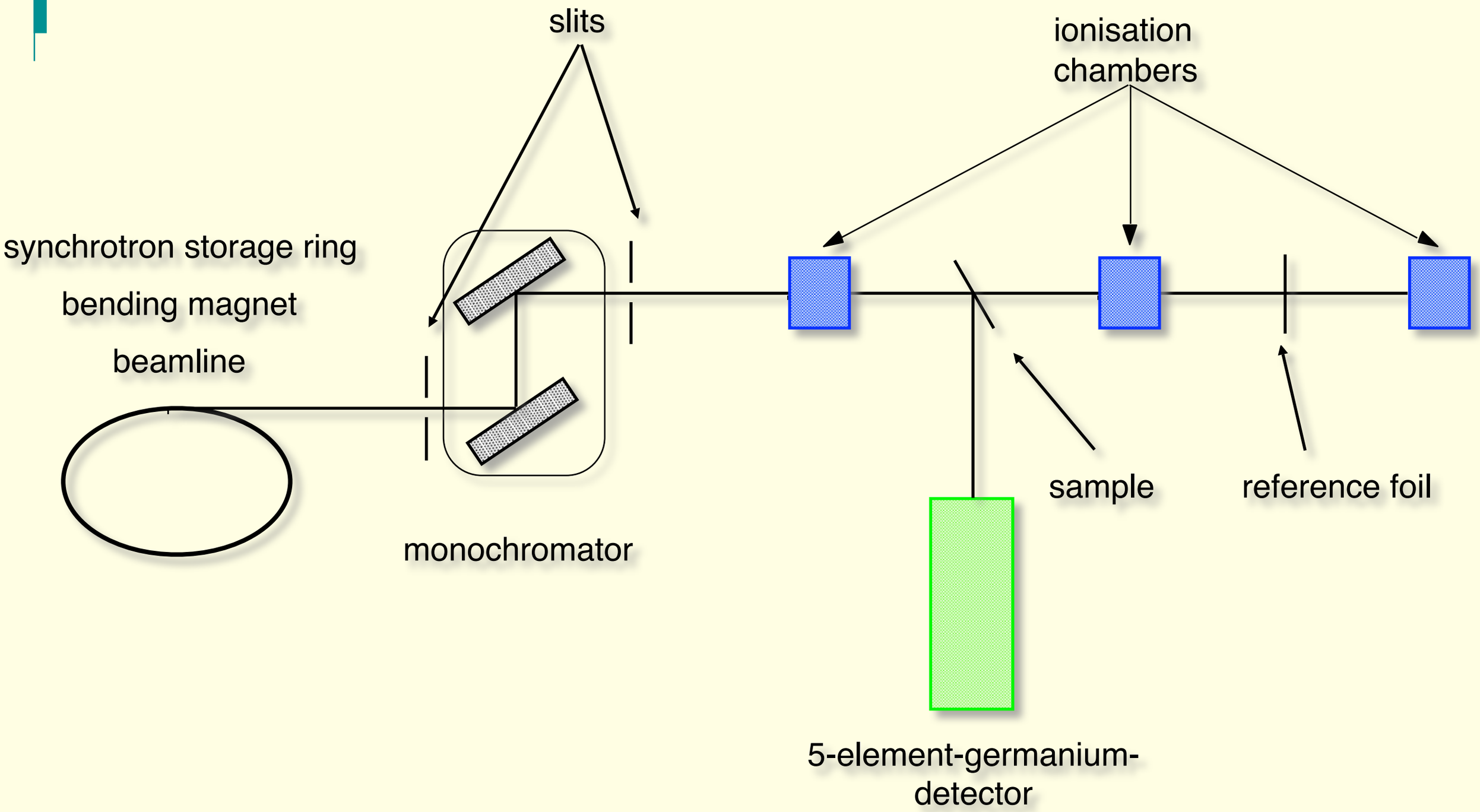
XAFS => **S**hort **R**ange **O**rder

information about:

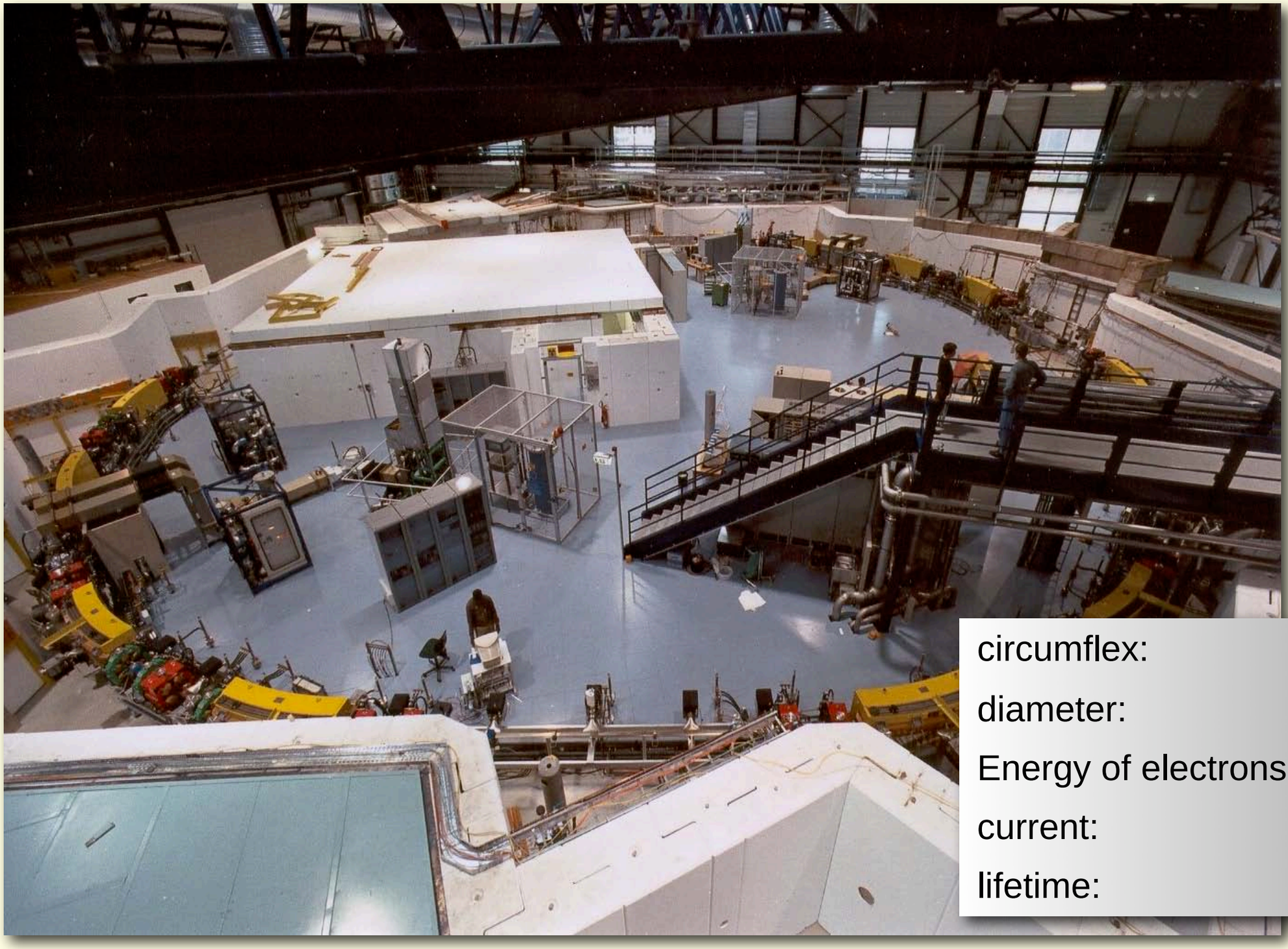
- distance
- nature
- number of neighboring atoms

- site symmetry
- electronic configuration

set-up of standard experiment



ANKA



circumflex:	110.4 m
diameter:	ca. 35 m
Energy of electrons:	2.5 GeV
current:	ca. 200 mA
lifetime:	> 20 h

beamlines at ANKA

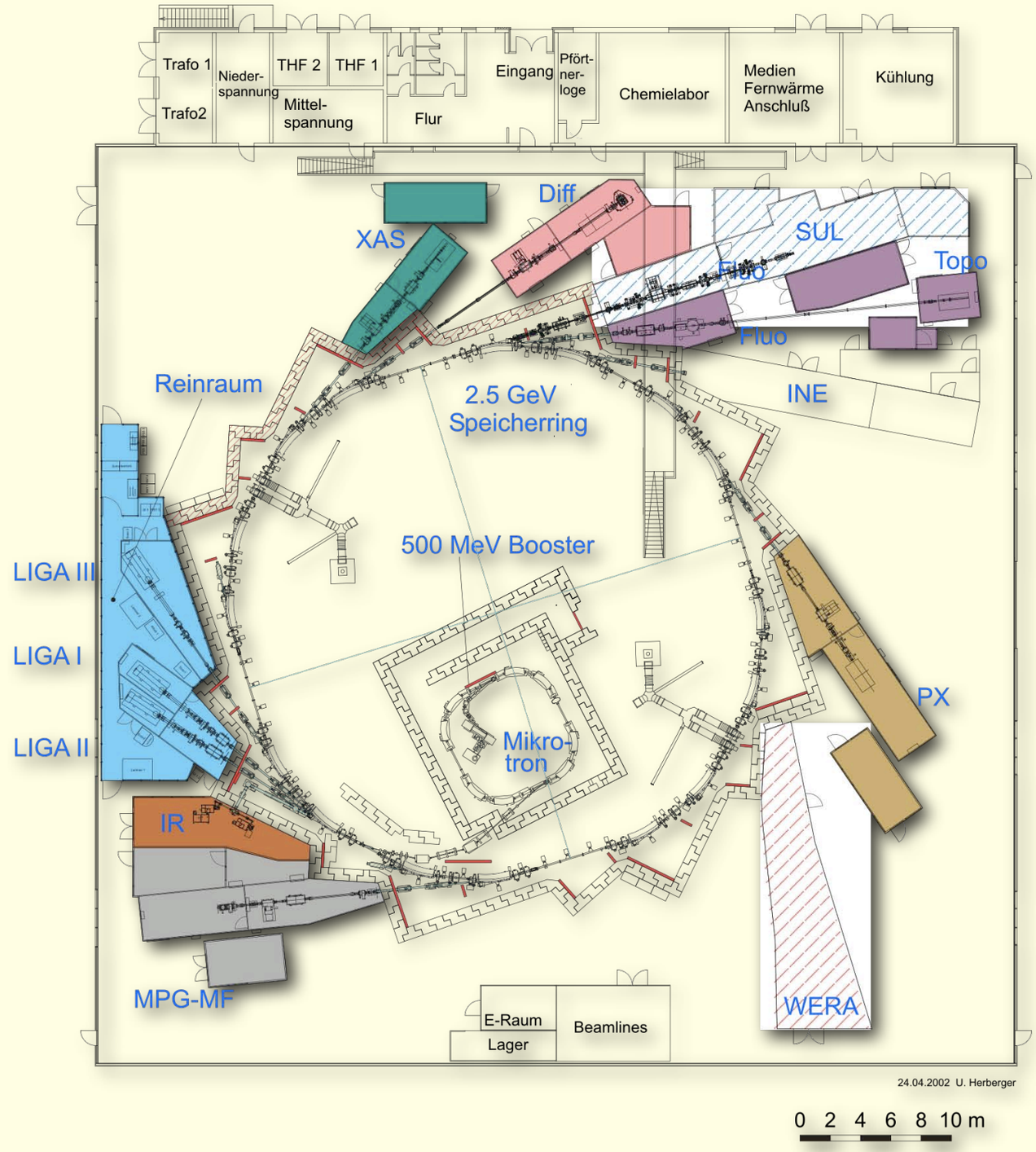
micro fabrication

- deep x-ray lithography

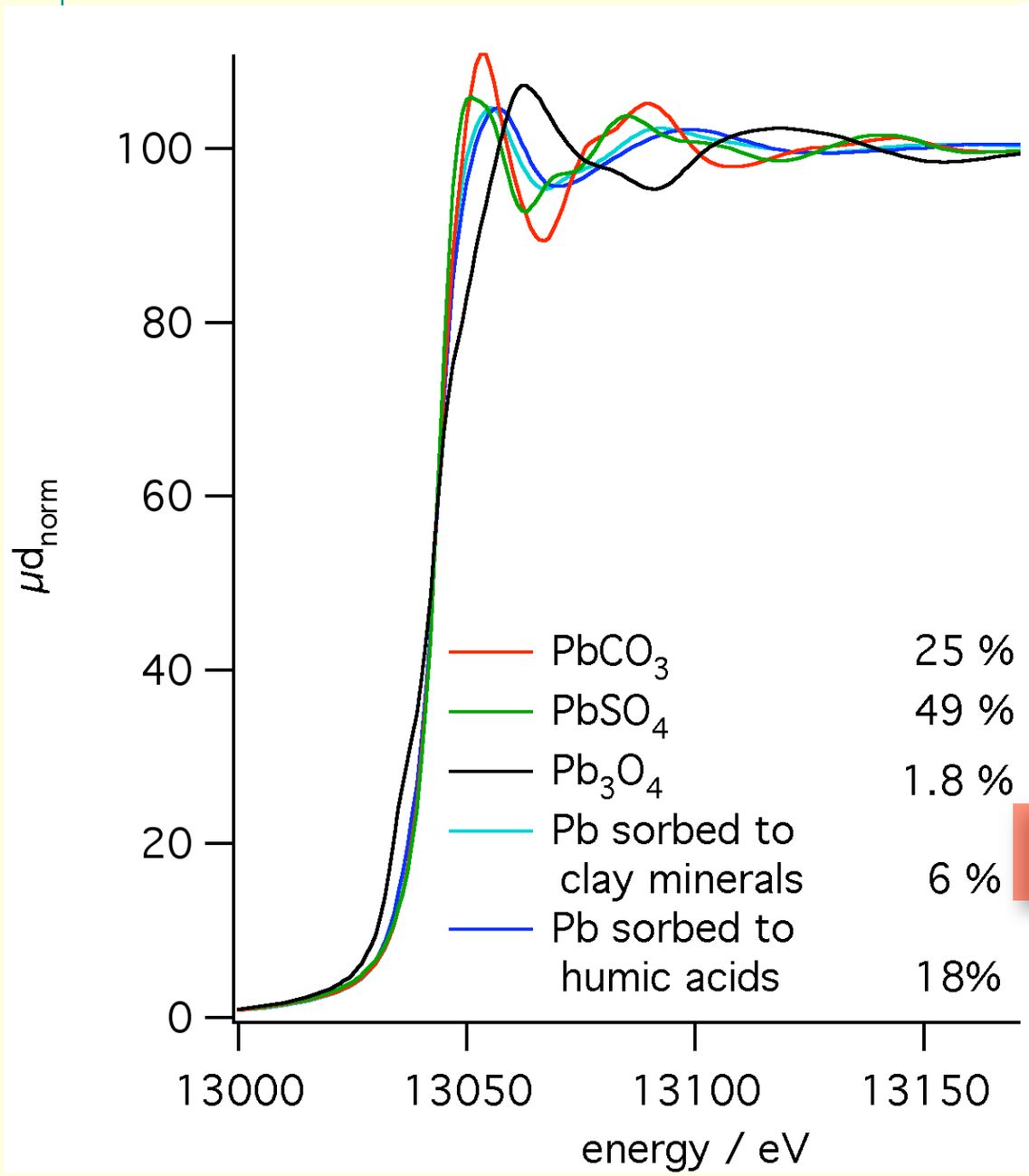
analytical beamlines

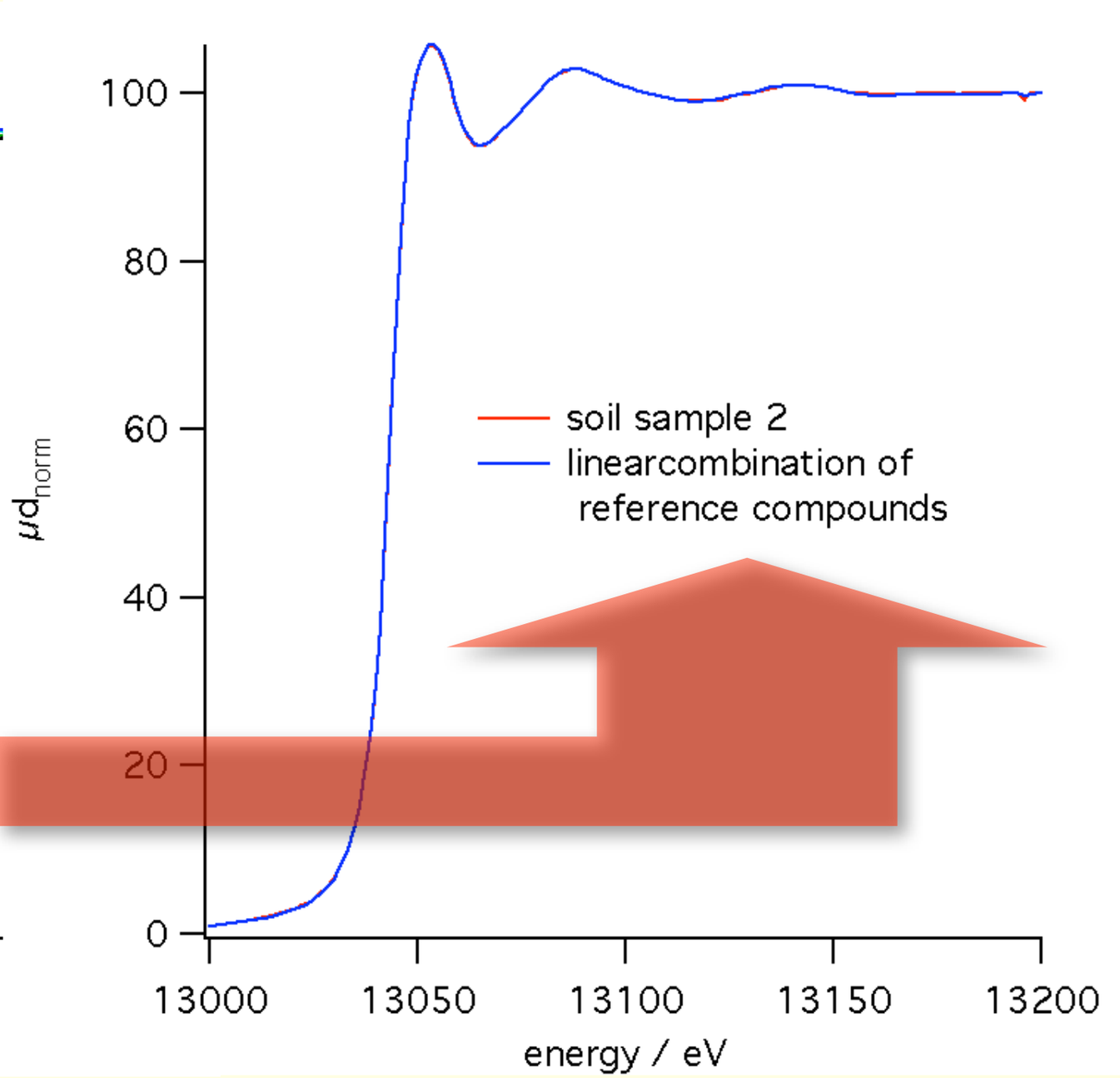
in use

- XAS
- Diffraction
- SUL-X (in commissioning)
- Fluo-Topo (in split)
- INE
- SCD
- WERA
- MPG MF
- IR (IR2 2007)



soils sample + linear combinations



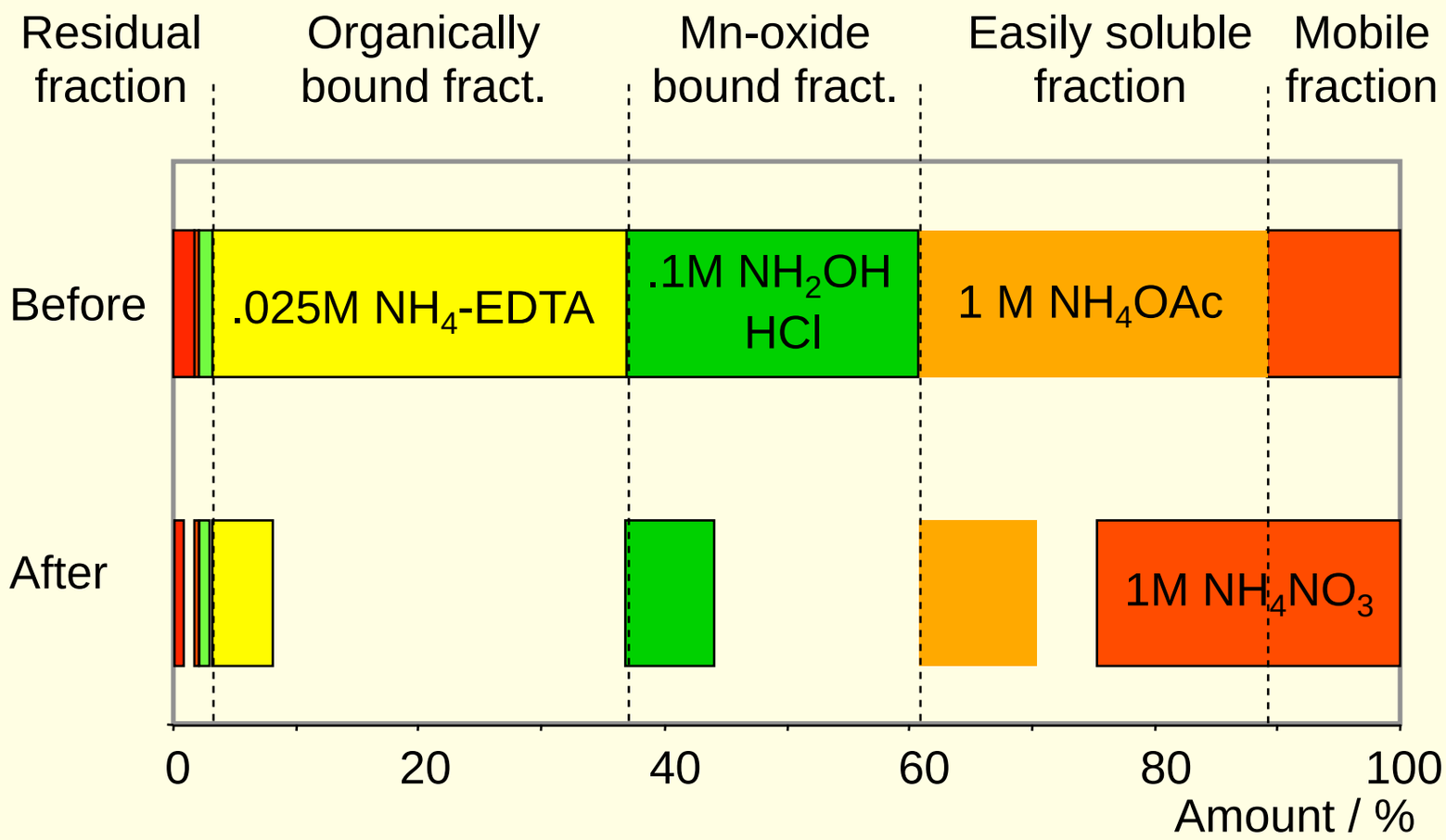


Hg contaminated sample

spectra had to be removed

Pb species before & after leaching

Sequential extraction | XAFS

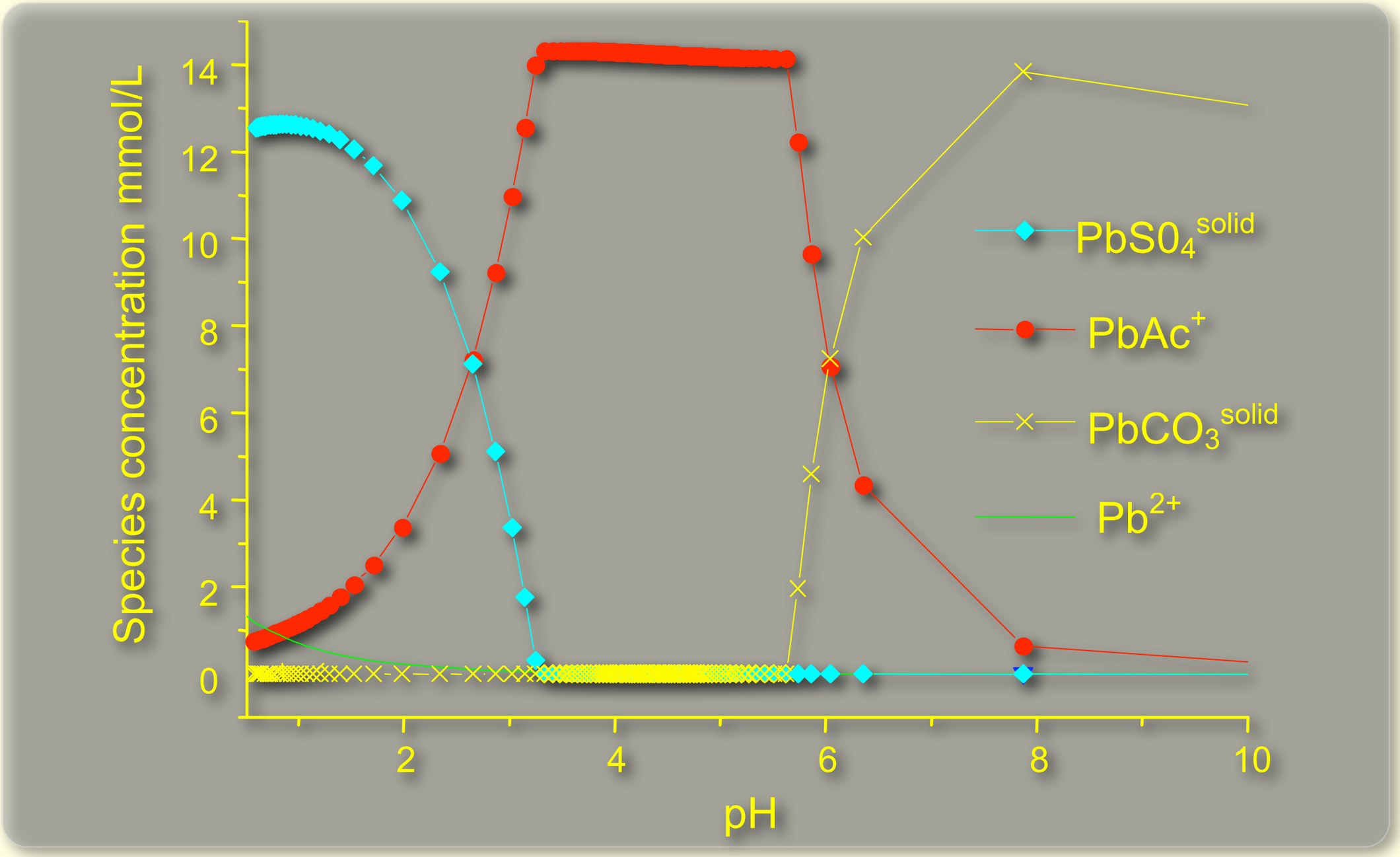


$PbSO_4$	32.3 %
$PbCO_3$	21.4 %
Pb-humic-subst.	46.3 %

$PbSO_4$	13.8 %
$PbCO_3$	2.0 %
Pb-montmorrillonite	17.5 %

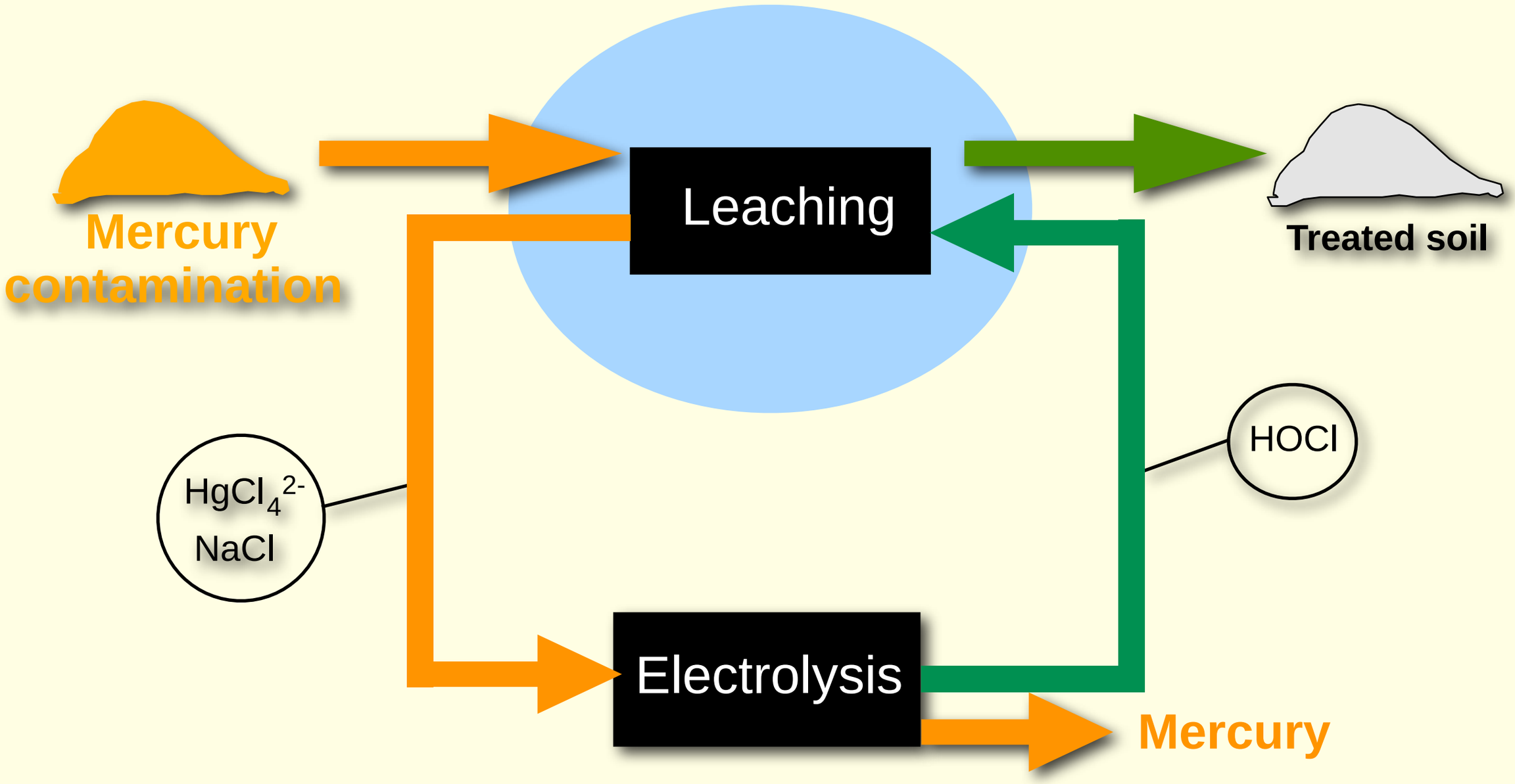
Explanation: **Even if the clean-up targets are reached, the situation might be worse as it was before the treatment due to increased mobility of the pollutants.**

Calculated distribution of Pb-species

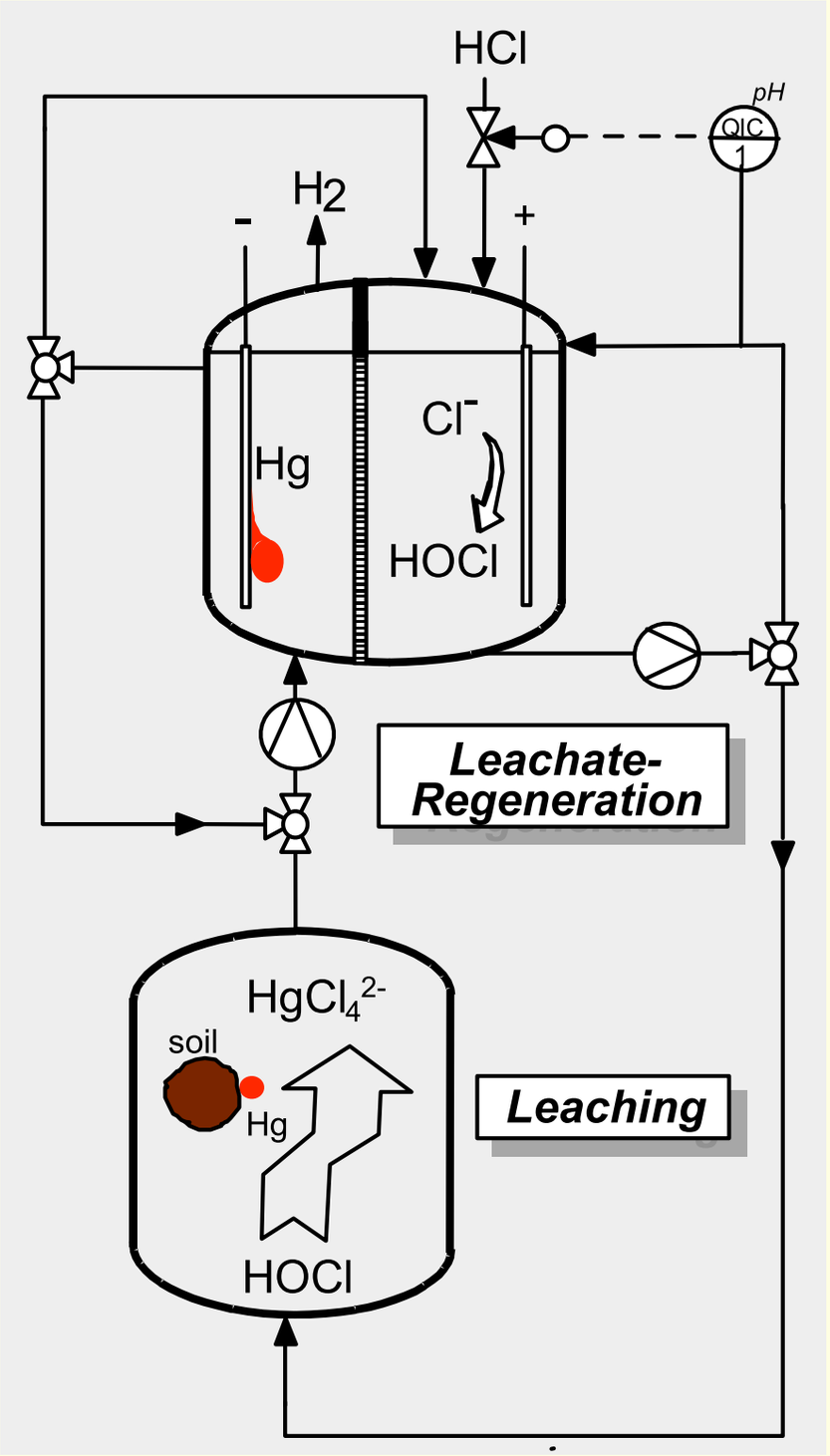


Calculated distribution of Pb-species suspended or dissolved in a acetate solution containing also sulfate and carbonate

Redox-Activated Leaching of Mercury Polluted Soil



reaction mechanism



Anodic reaction 1: $H_2O - 2\ e^- + Cl^- \rightarrow ClO^- + 2\ H^+$

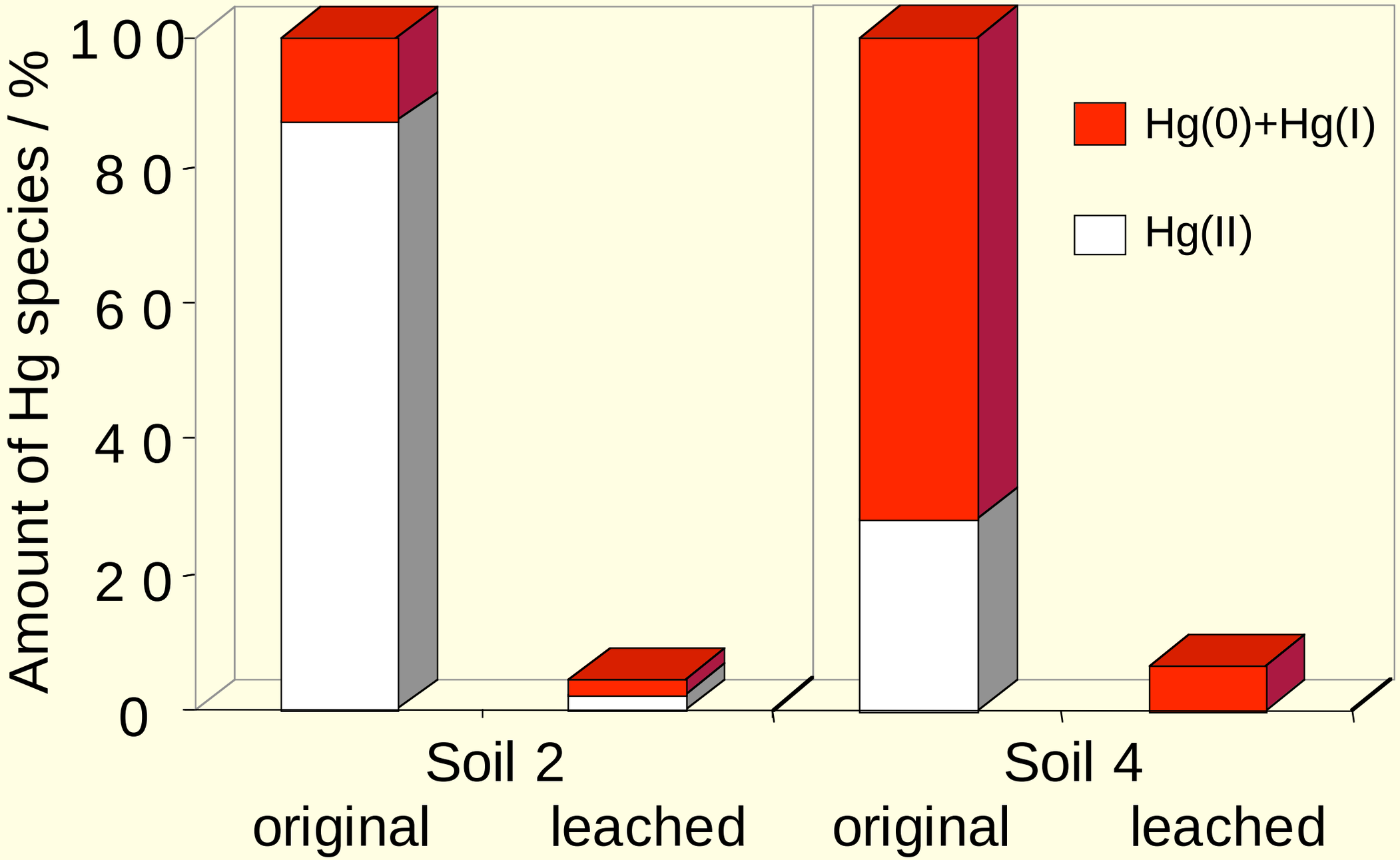
Anodic reaction 2: $H_2O - 2\ e^- \rightarrow \frac{1}{2}\ O_2 + 2\ H^+$

$$Hg + HOCl + 3\ Cl^- + H^+ \rightarrow HgCl_4^{2-} + H_2O$$

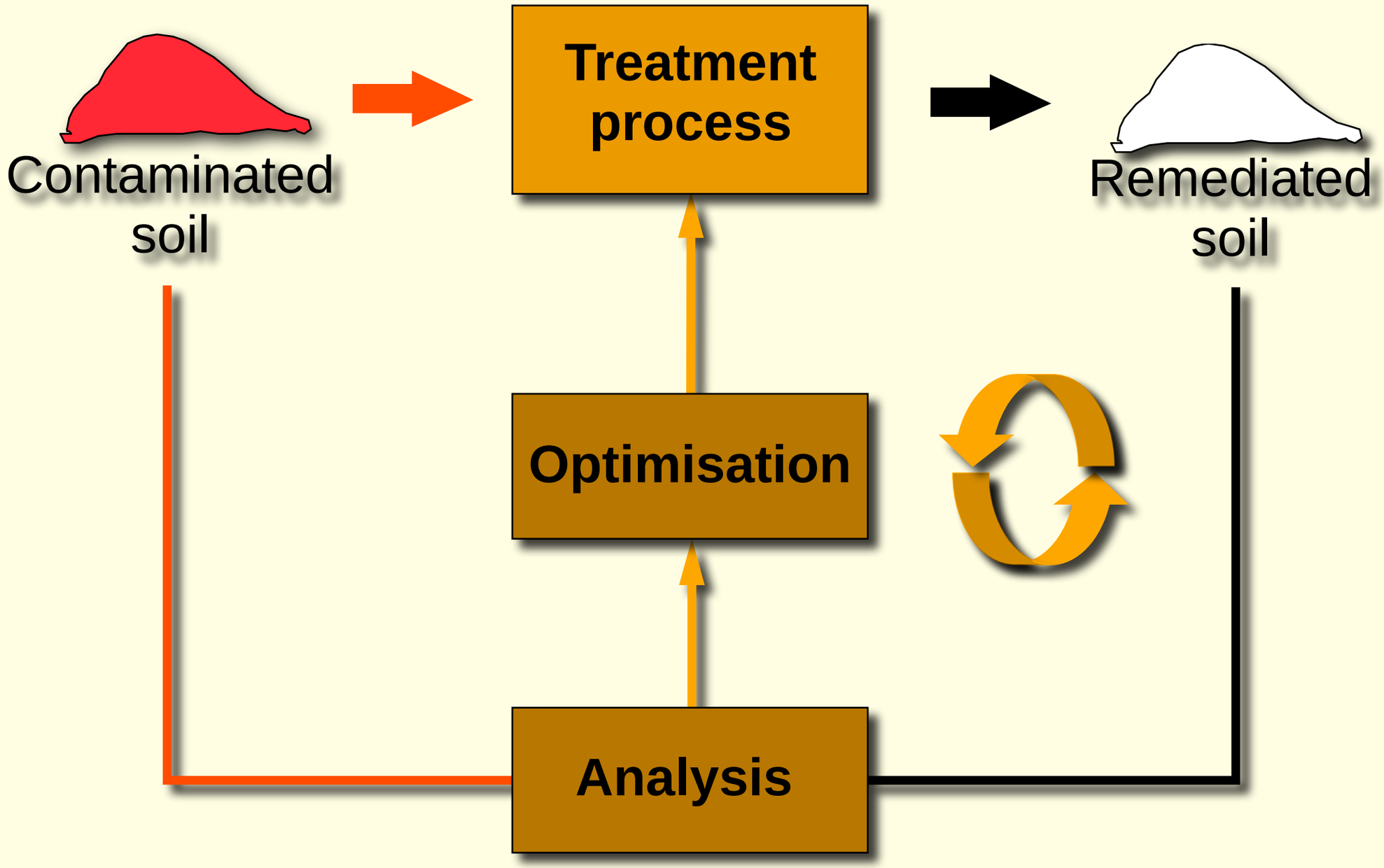
Cathodic reaction 1: $HgCl_4^{2-} + 2\ e^- \rightarrow Hg^0 + 4\ Cl^-$

Cathodic reaction 2: $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$

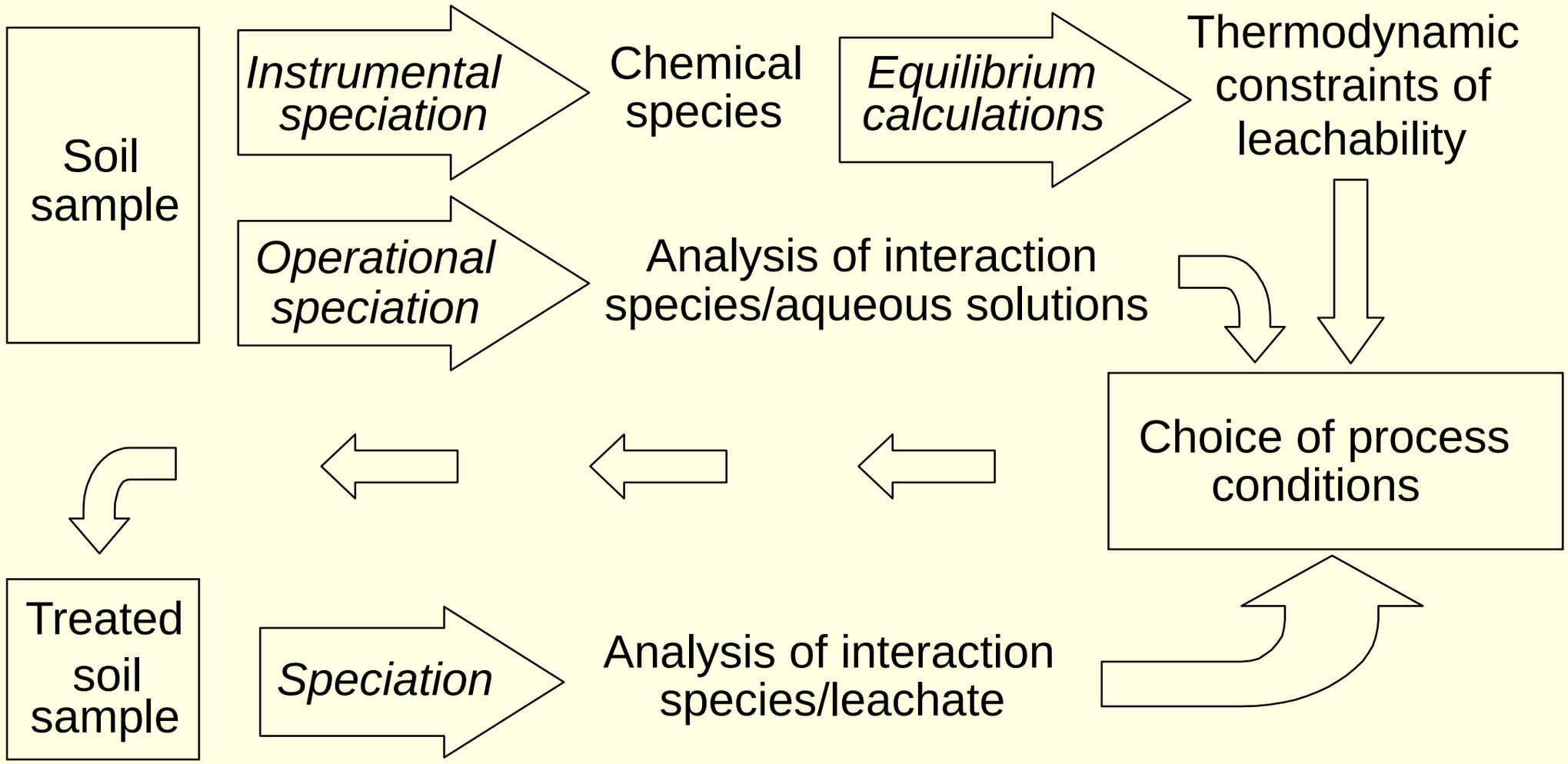
Distribution of mercury species in soils 2 and 4 before and after a single leaching step using an NaCl/HOCl-solution



Optimization of Selectivity



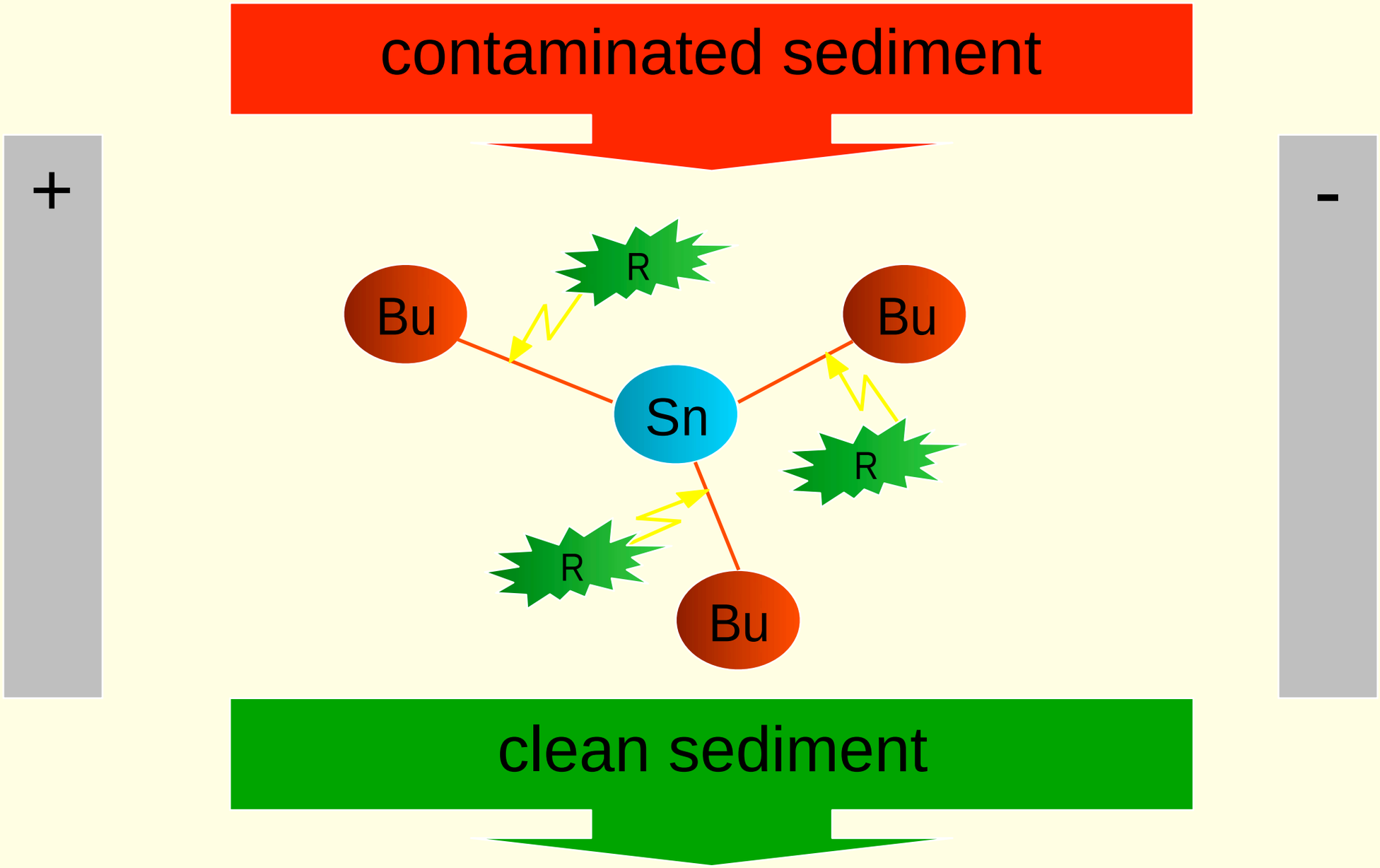
Optimization of Selectivity



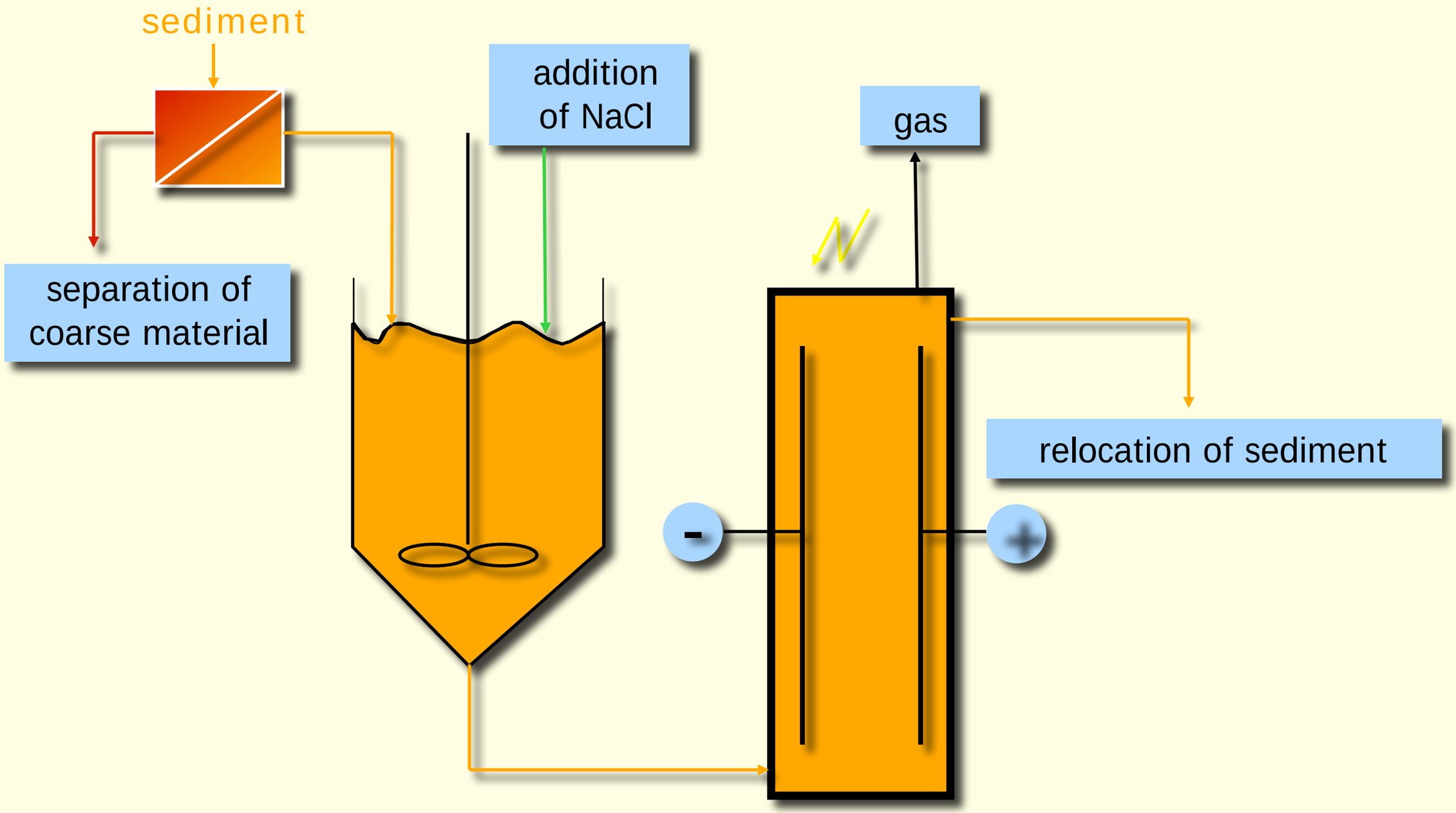
Instrumental speciation: X-ray absorption fine structure spectroscopy (XAFS)

Integrated Process Development for Dredged Material

Example III: TBT-Degradation



Process Scheme



Units

Laboratory Cell

Process Unit with Reactor Volume of 30 L

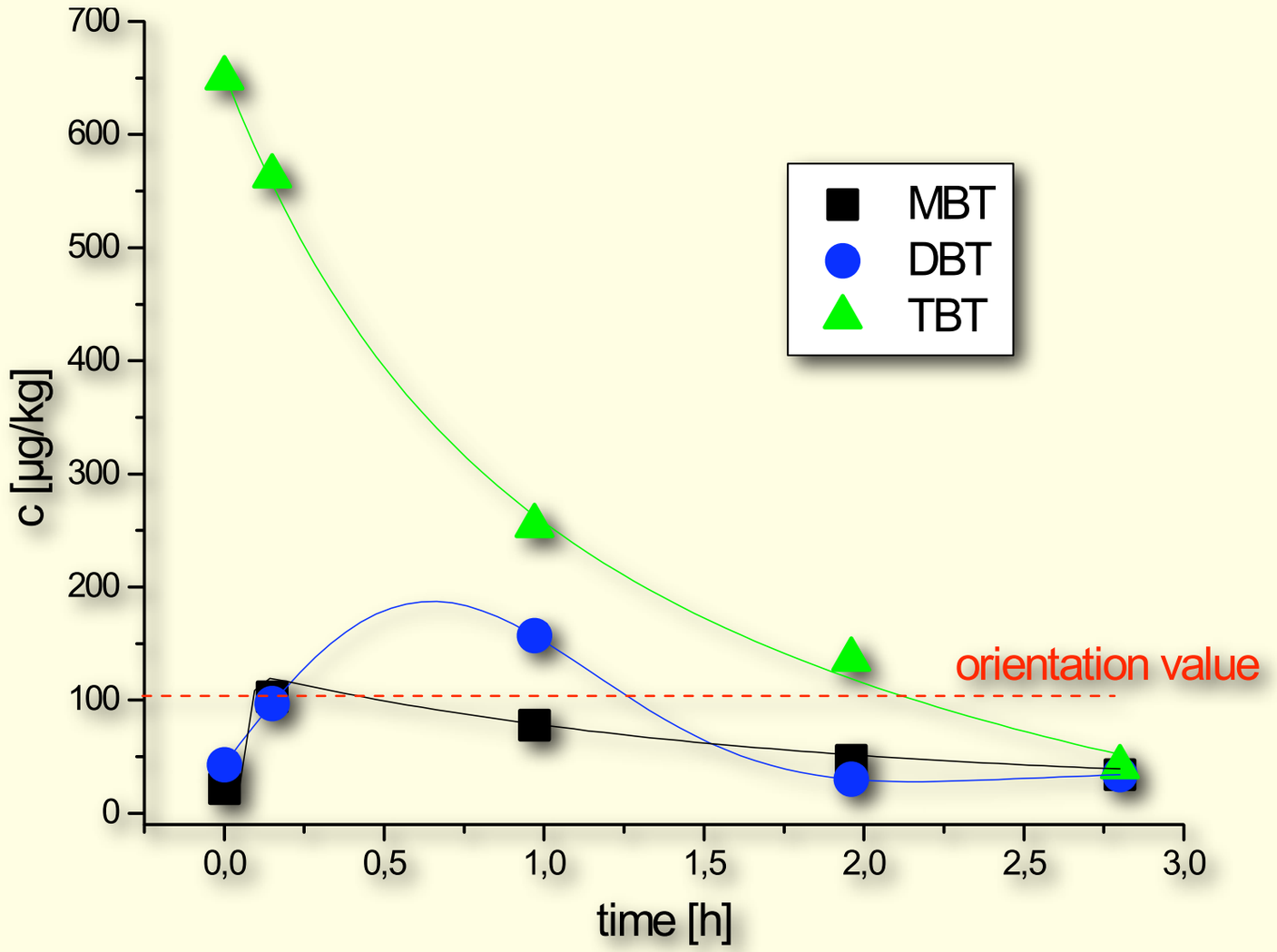
Pilot Plant

Pilot Plant

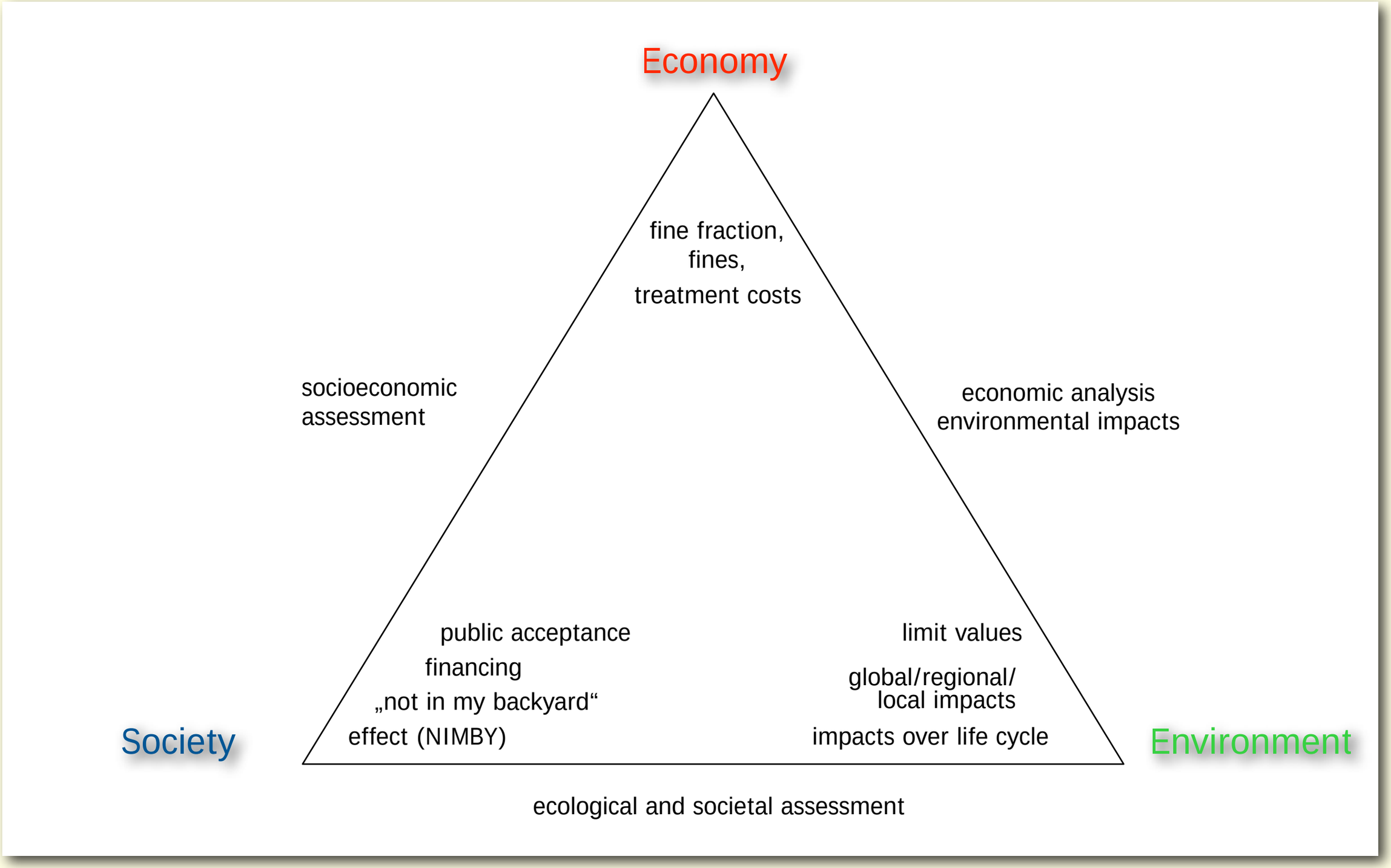
Pilot Plant

Pilot Plant

Butyltin Degradation in Technical Scale Unit (Fine Sand)



Assessment Criteria for Sustainable Remediation Processes

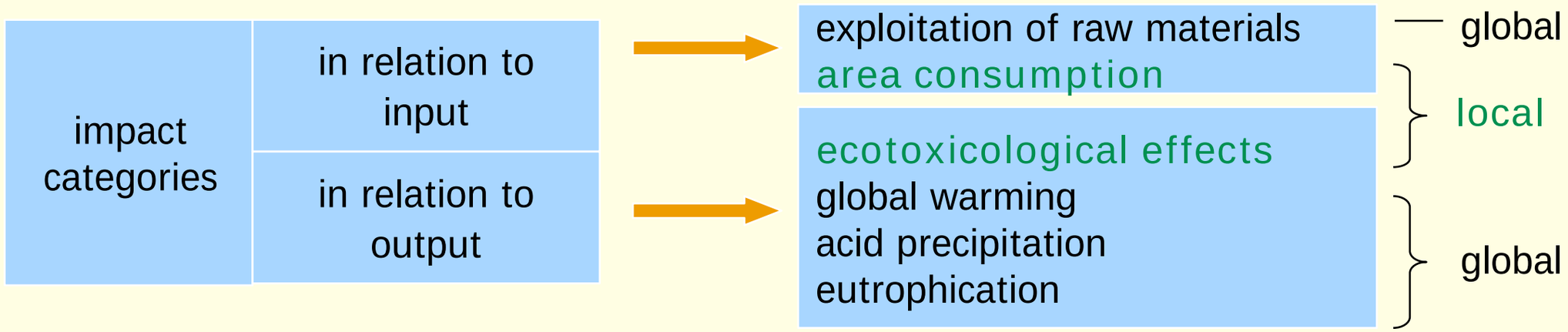


Phases of Life-Cycle Assessment

- definition of the framework and goals
  - system boundaries, i.e. “from cradle to grave”; system operation conditions
  - applied processes: important for process comparison

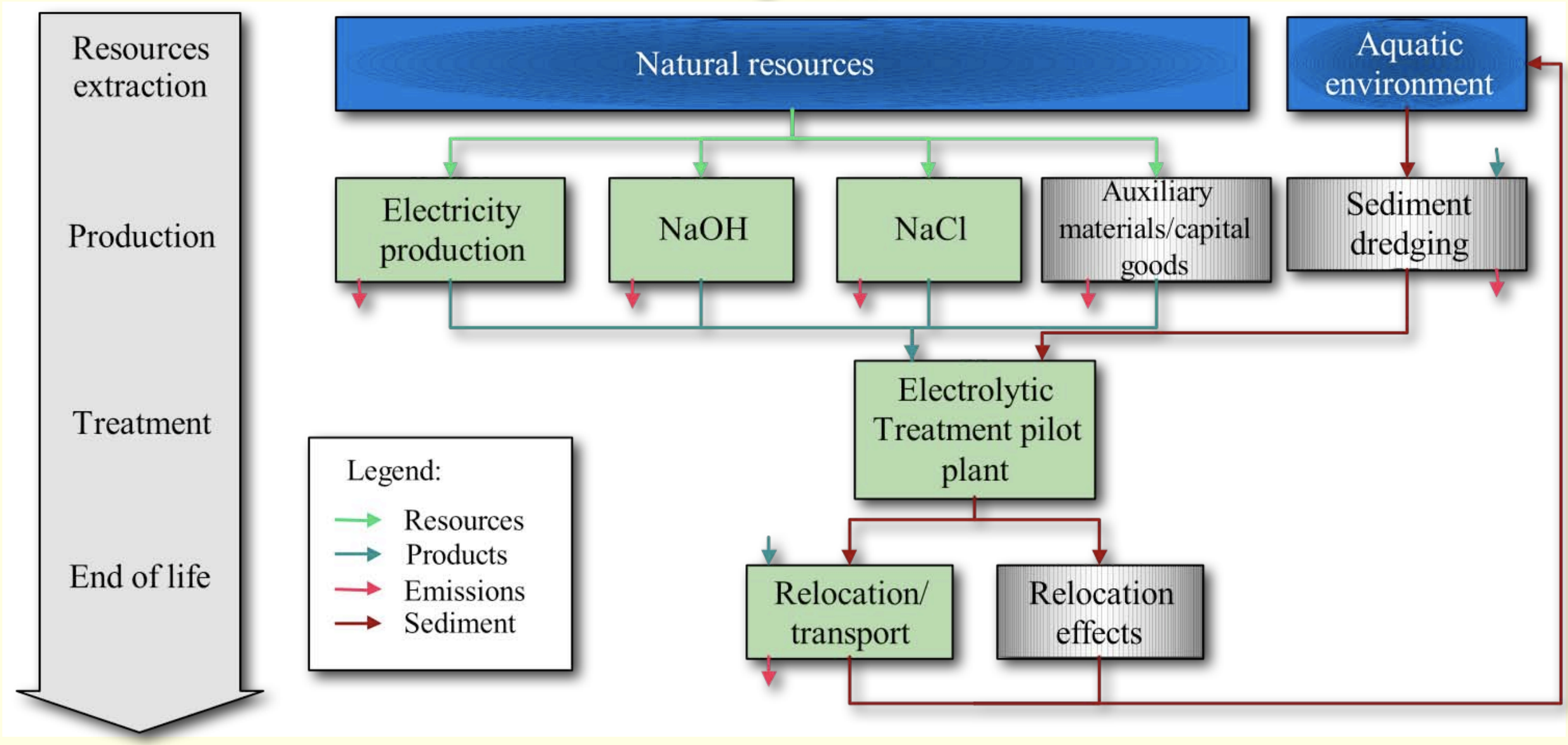
- inventory analyses (life cycle inventory analysis (LCI))
  - system inputs and outputs quantification in relation to single processes

- assessment (life cycle impact assessment (LCIA))
  - classification/characterization



- interpretation
  - evaluation, critical examination, validation, etc.

Product System:
Dredged Materials, Raw Materials, Treatment, Disposal



Conclusion Life-Cycle Assessment

Sustainable development, assessment and optimization of treatment technology requires integration of
economic, ecological and social criteria

Challenge
integrating design and combined application of these criteria

Open questions

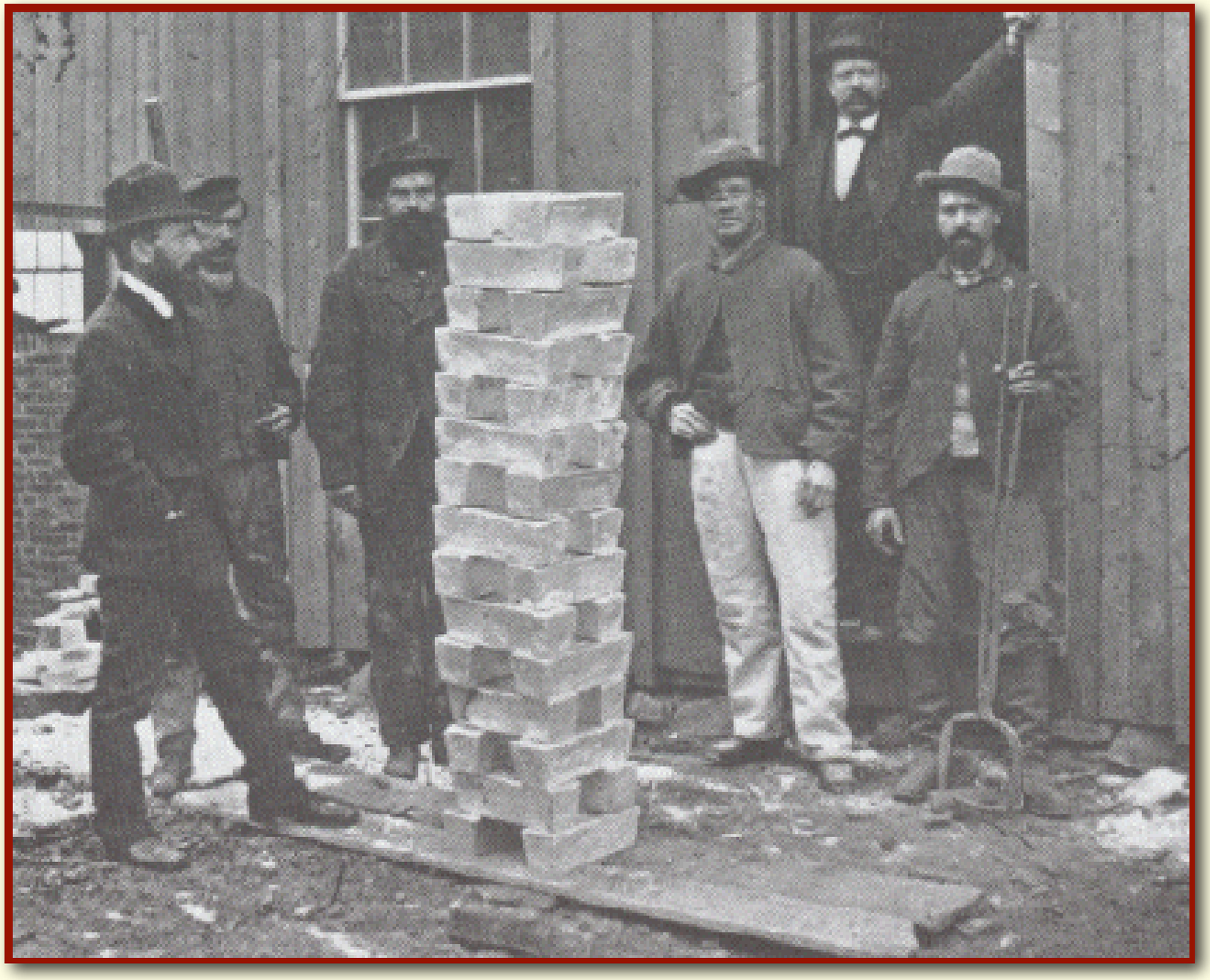
- which indicators?
- quantification and normalization of indicators?
- weighting and integration of indicators?
- methodical uncertainties?
- consequences for decision processes?

=> interdisciplinary research

Conclusion

- Why speciation is important
- speciation with XAFS
- process optimization
- Life-Cycle Assessment

helpless experts looking at heavy metal loaded soil ? ...



Thanks to

Prof. Dr.-Ing Wolfgang Calmano

Dipl.-Ing. Eduardo Arevalo

Dipl.-Ing. Arne Keller

Dr. Heinz Stichnothe

Prof. Dr.-Ing. Jorg Thöming

and Dr. Edmund Welter

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