Detection of engineered cerium oxide nanoparticles in soils

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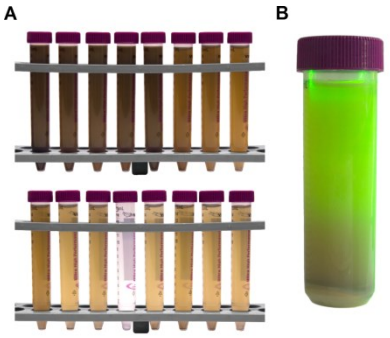

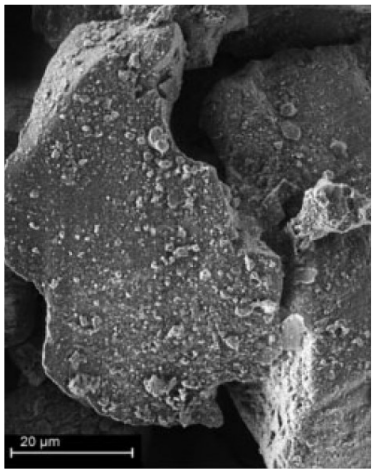

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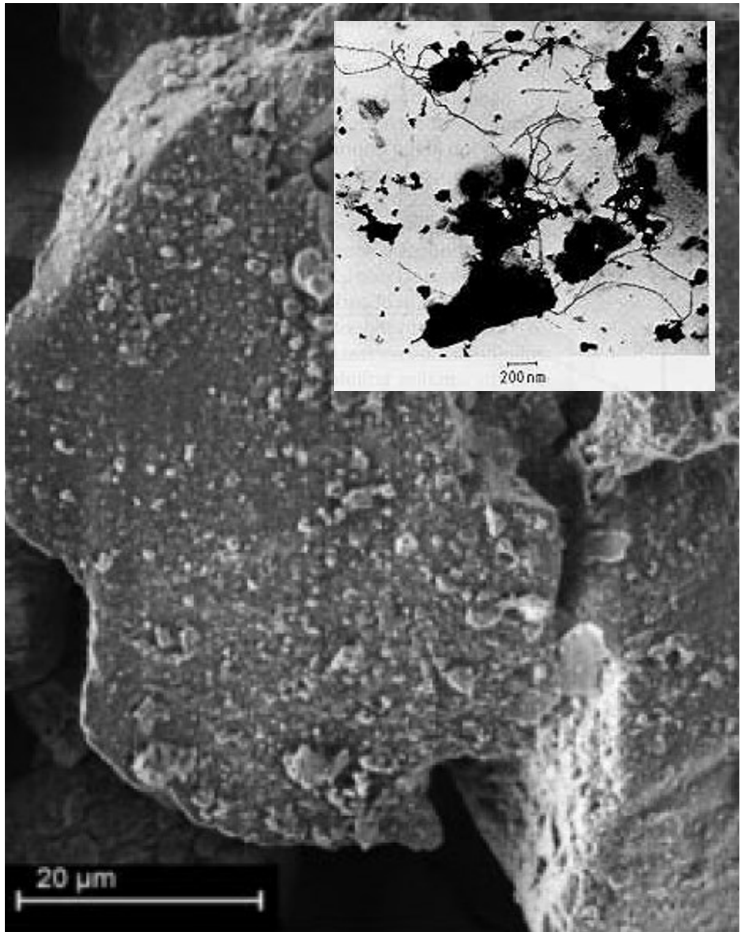
- identification as ENPs
- differentiation from natural background
- quantification in natural background

→ contrast is needed!

- usable difference between ENPs and NNPs
  - composition (low background elements)
  - purity (high element concentration per ENP)
  - elemental ratios (if specific for ENP or NNP)

  - isotopic signatures
  - particle shape
  - structure/composition
  - specific coating of ENPs
  - specific surface chemistry

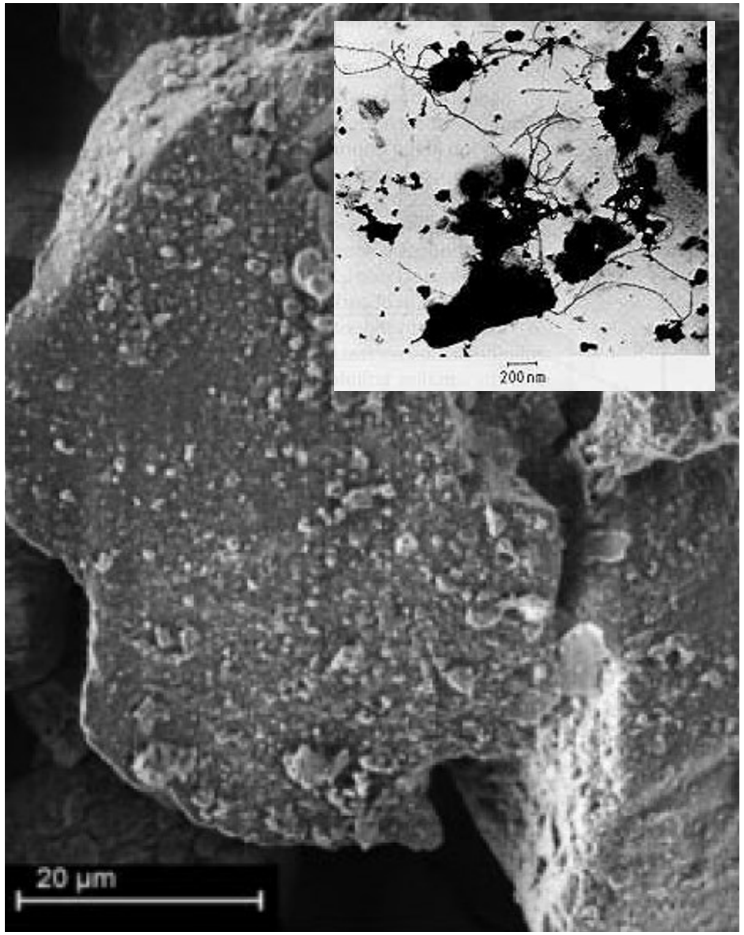


Von der Kammer (2012)

- identification as ENPs
- differentiation from natural background
- quantification in natural background

→ contrast is needed!

- usable difference between ENPs and NNPs
  - AuNPs ☺ (practically no background)
  - AgNPs ☺ (low to no background but speciation)
  - CeO_2-NPs ☹
  - TiO_2-NPs ☹ (have all high particulate background)
  - FeOx-NPs ☹
  - organic/carbonaceous NPs ☹



Von der Kammer (2012)

Find the fox!

ENP in tap water

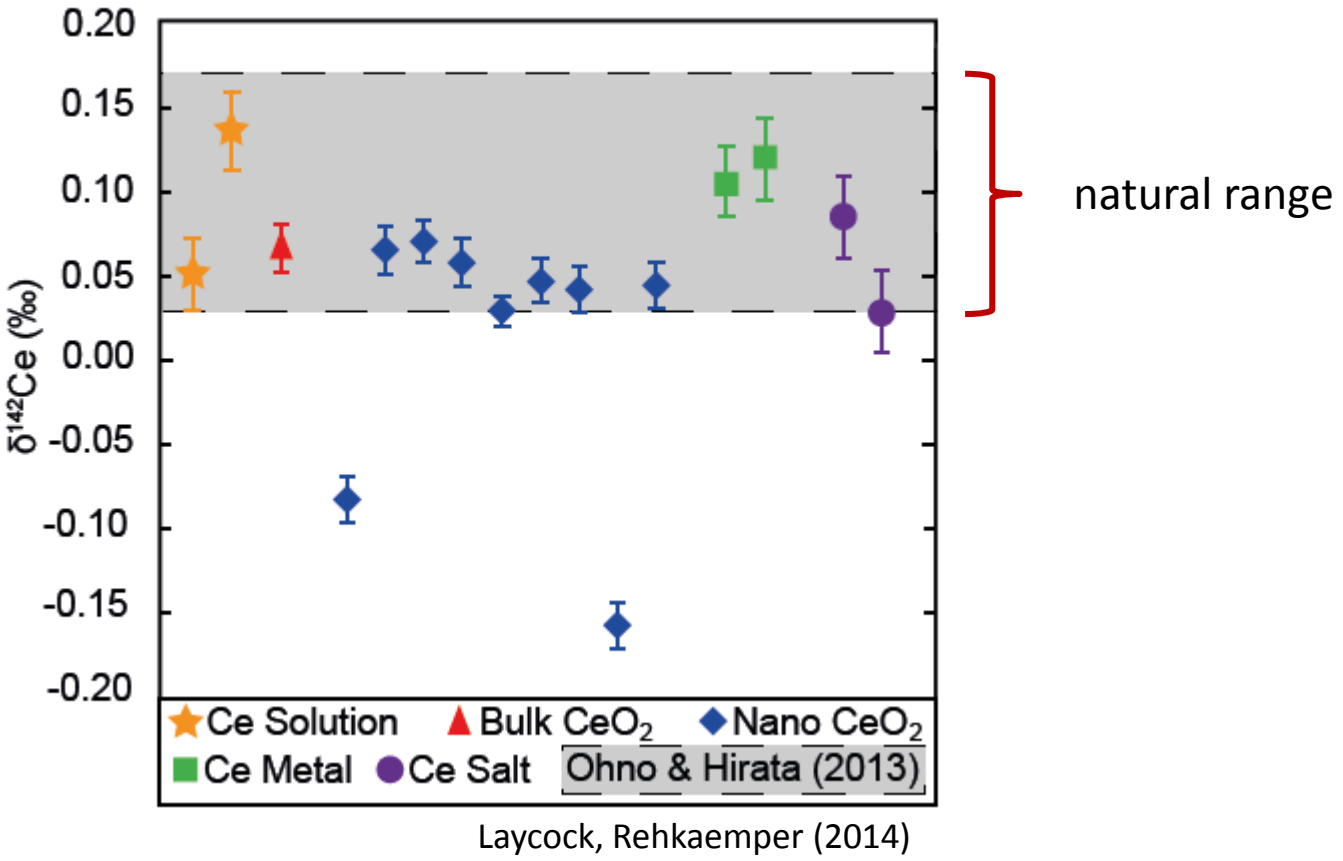
ENP in river water

ENP in soils & sediments

- natural CeO_2 nanoparticles are present in soils & sediments
- Ce concentrations range 10 – 100 **mg/kg**

- **Increase of bulk concentrations above local background?**
- **isotopic signatures ?**
- **elemental ratios ?**

Ce isotope ratios ($^{142}Ce/^{140}Ce$)

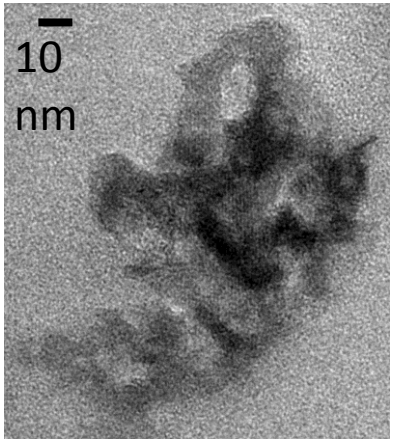


Laycock, Rehkaemper (2014)

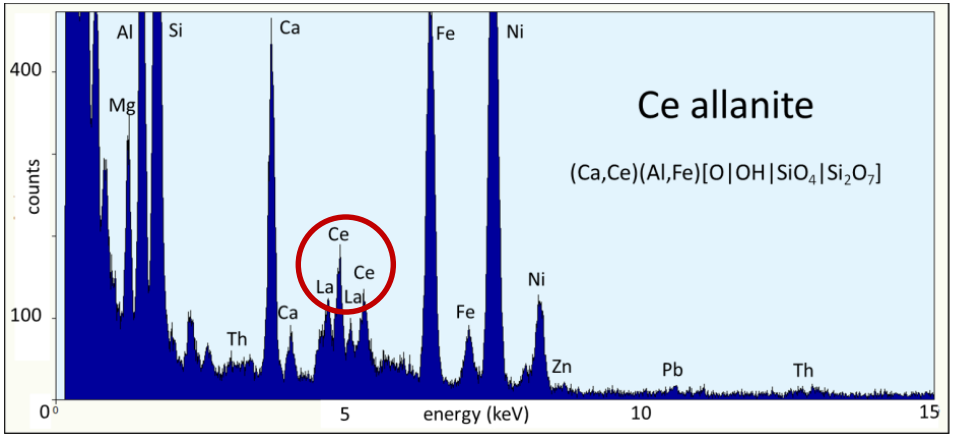
no usable isotopic fingerprint in products compared to natural soils and rock

CeO_2 nanoparticles

- Ce-ENPs have a high purity (other rare earth elements appear only in traces)
- natural background comes with La, Nd, Th and other REE



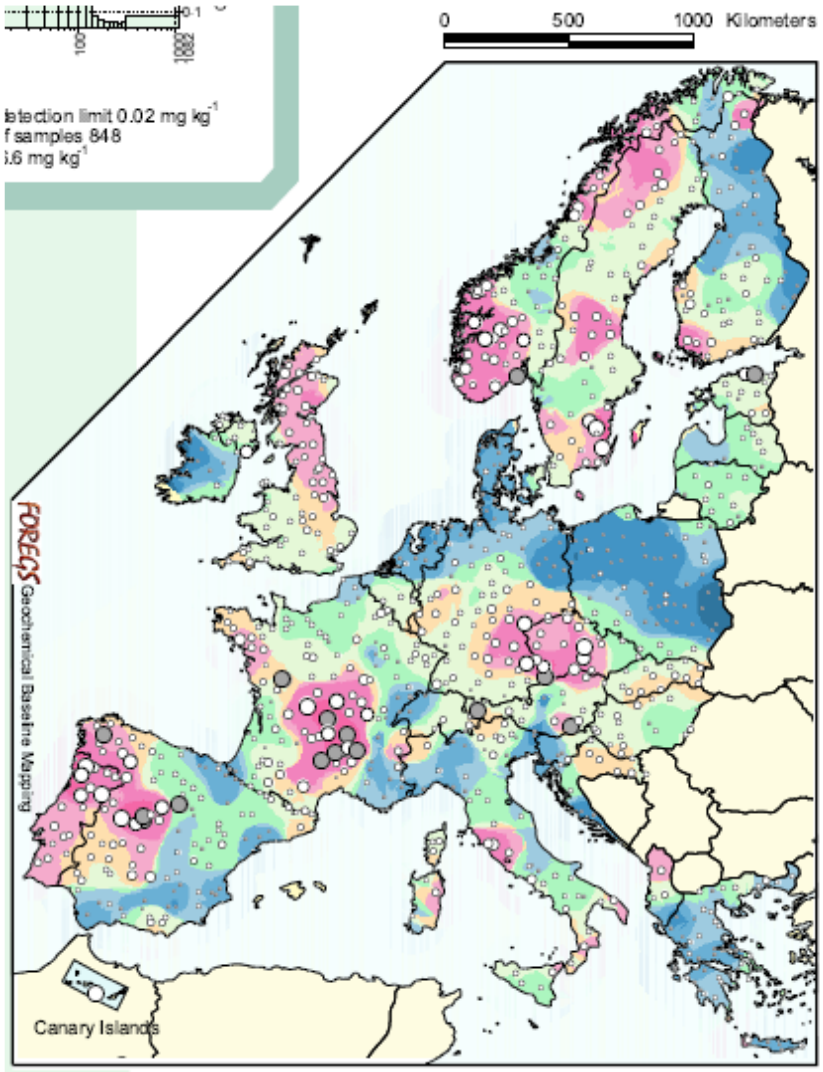
natural CeO_2 contains La, Nd, Th…



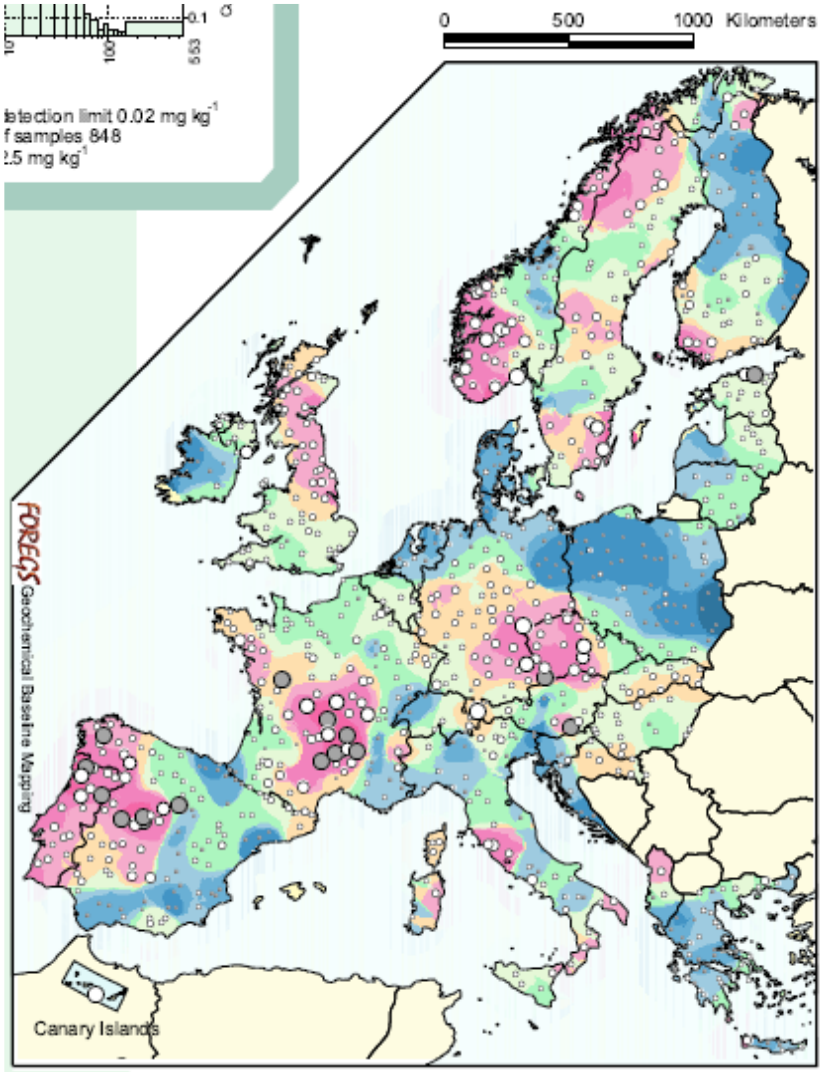
Ce containing nanoparticle from Clark Fork River bank sediment (Plathe et al.; Env Chem 2010)

elemental ratios (e.g. Ce/La) to identify natural background

Ce in floodplain sediments



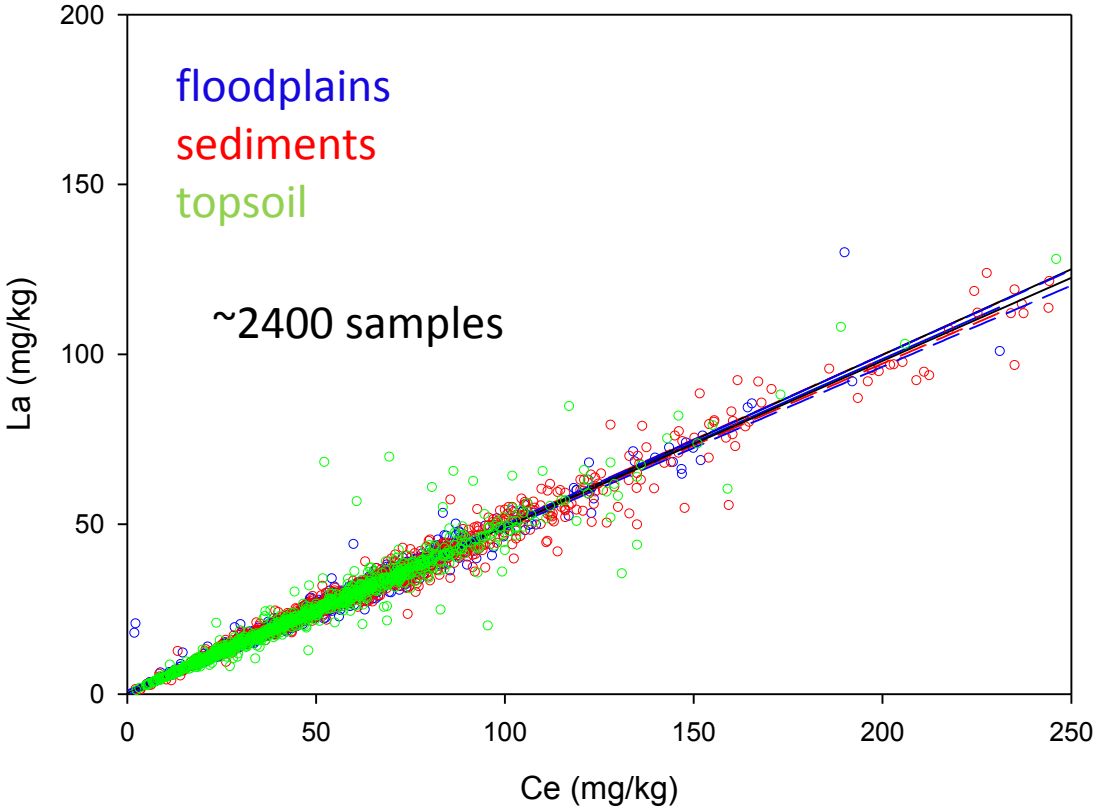
La in floodplain sediments



figures from FOREGS baseline mapping project

CeO_2 nanoparticles

La over Ce concentrations according to FOREGS database



hypothesis:

Ce/La ratios can be used

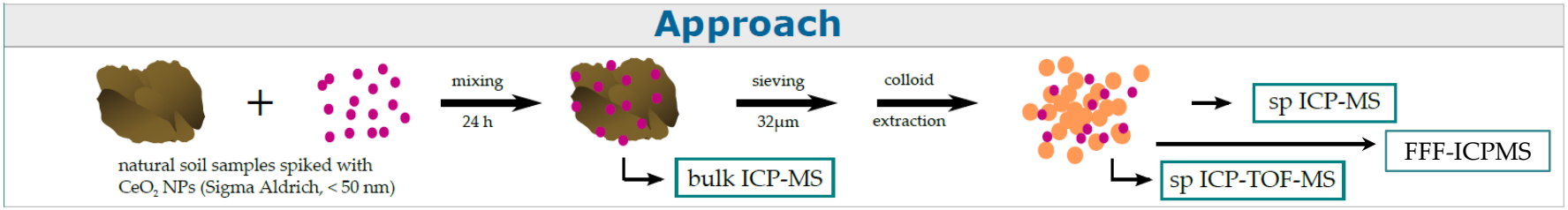
to identify natural background

to separate ENPs & NNPs

FOREGS database
v.d. Kammer et al. ET&C 2012

	factor Ce/La	SD	mean (mg/kg)
floodplains	2.0140	0.1404	53.7
sediments	2.0403	0.1658	82.9
topsoils	2.0439	0.2464	52.2

CeO_2 NP analysis in soil matrix – general approach

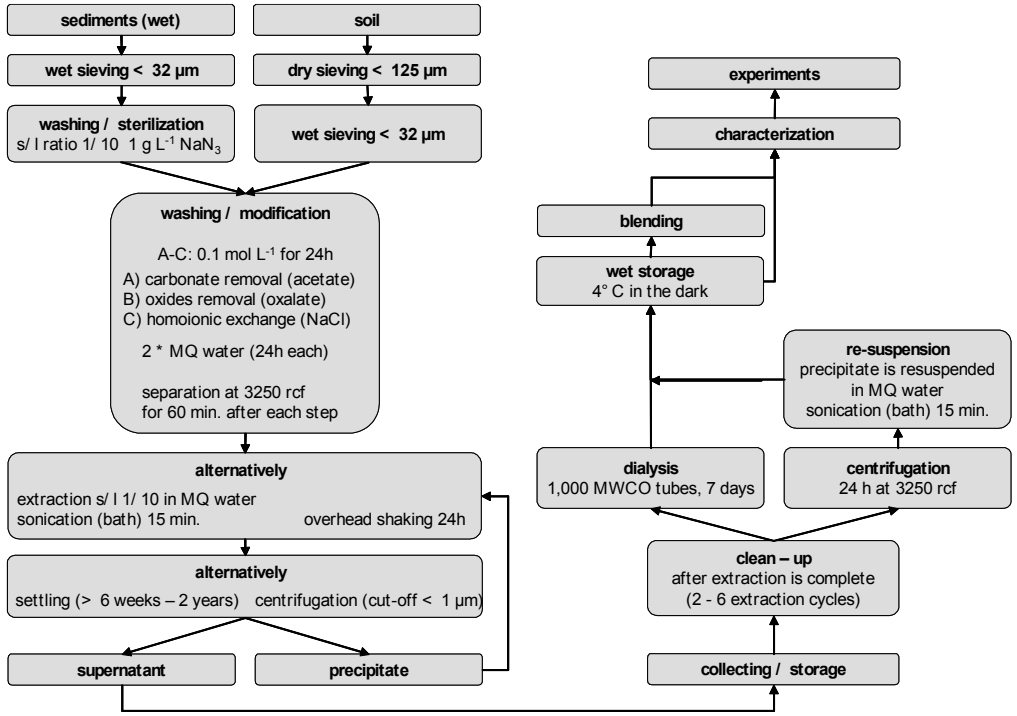


spiking of natural soil samples

natural background 74 mg/kg (Ce)

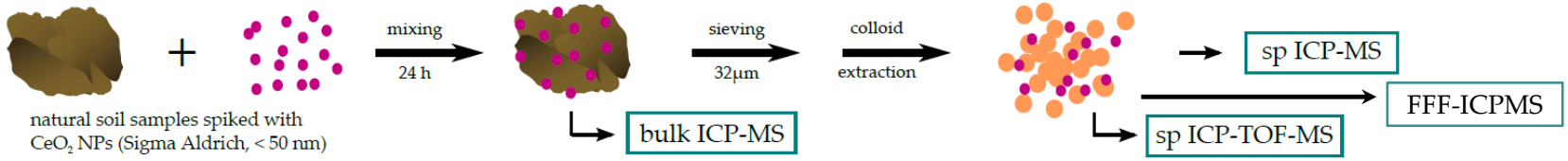
SPK0	+ 0
SPK1	+ 0.004 mg/kg Ce-ENPs
SPK2	+ 0.04 mg/kg
SPK3	+ 0.4 mg/kg
SPK4	+ 4 mg/kg
SPK5	+ 40 mg/kg
SPK6	+ 400 mg/kg

colloid/nanoparticle extraction procedure

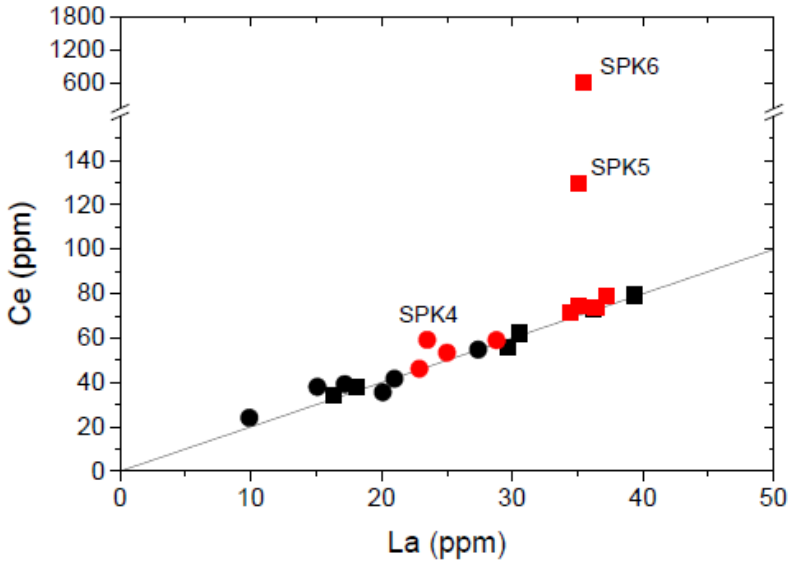


CeO_2 NP analysis in soil matrix – bulk analysis

Approach



A: Bulk analysis of Ce:La ratios in natural and contaminated soils



in colloidal extracts CeO_2 yields are

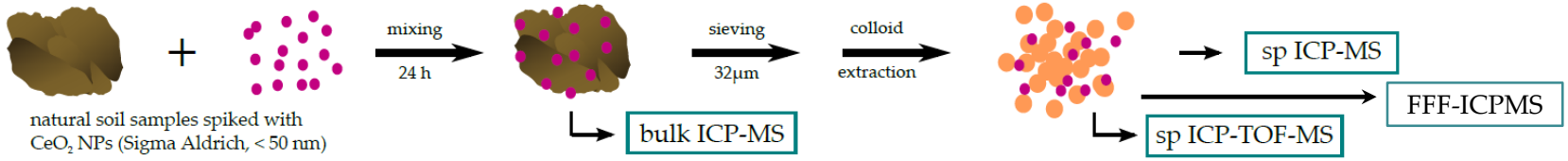
16% in the unspiked and low concentration spikes

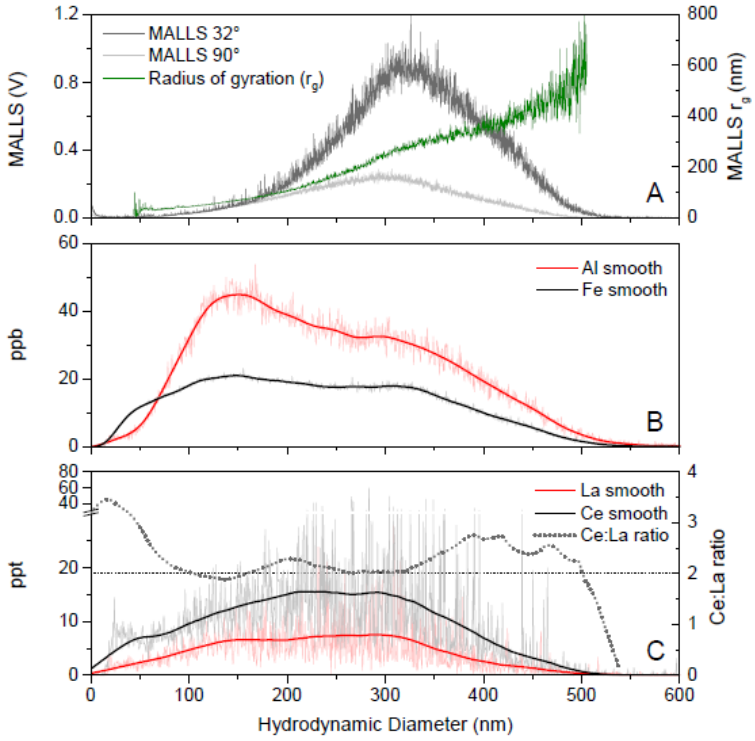
24% in the 40 ppm spike

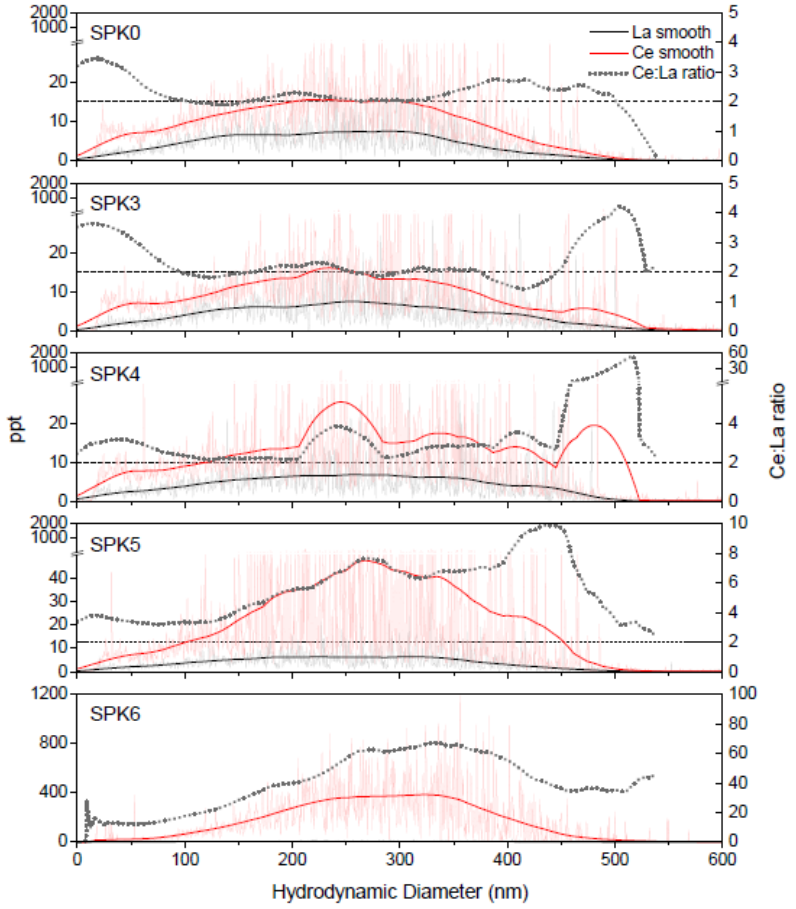
34% in the 400 ppm spike

CeO_2 NP analysis in soil matrix – FFF-ICPMS

Approach







single particle analysis

selective & specific counting techniques

- elemental composition & morphology (EM)
- single element derived particle size (spICPMS)

→ time resolved ICPMS

→ quadrupole instruments: only single isotope monitored

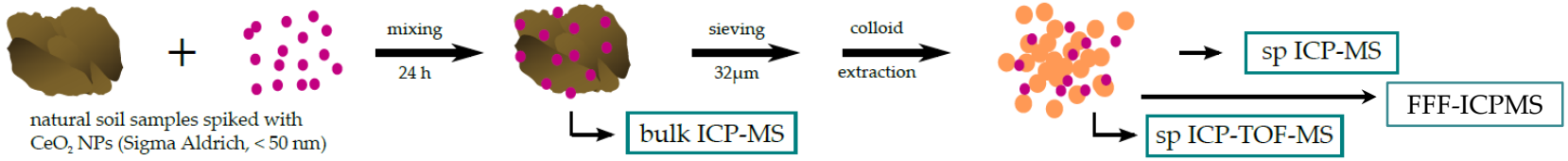
1) single spike mode (read intervals 1 – 10 ms)
2) high resolution event monitoring (read intervals ~ 100 µs)

→ fast scan quadrupole: theoretically 2 isotopes could be monitored

→ Time of Flight instruments: multiple isotope monitoring
event monitoring at ~ 30 µs resolution

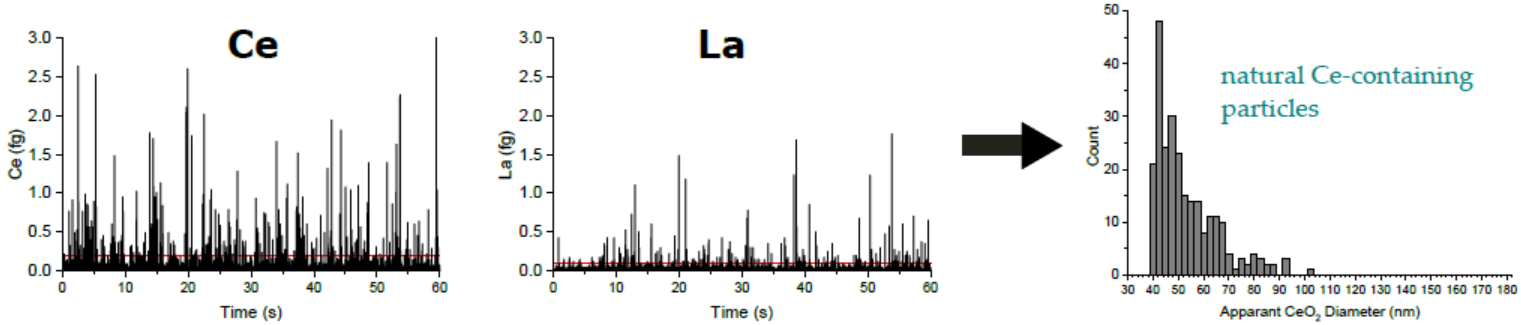
CeO_2 NP analysis in soil matrix – sp-ICPMS

Approach

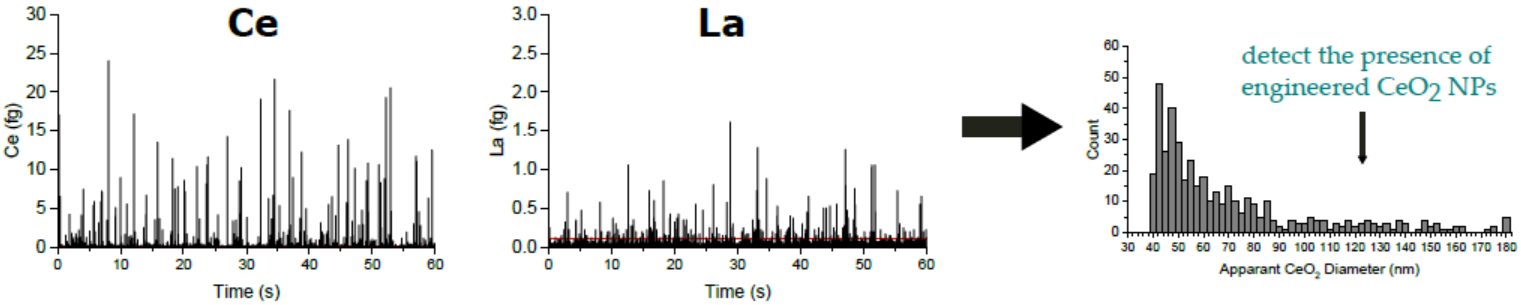


B: Single-element single-particle ICP-MS of colloidal extracts

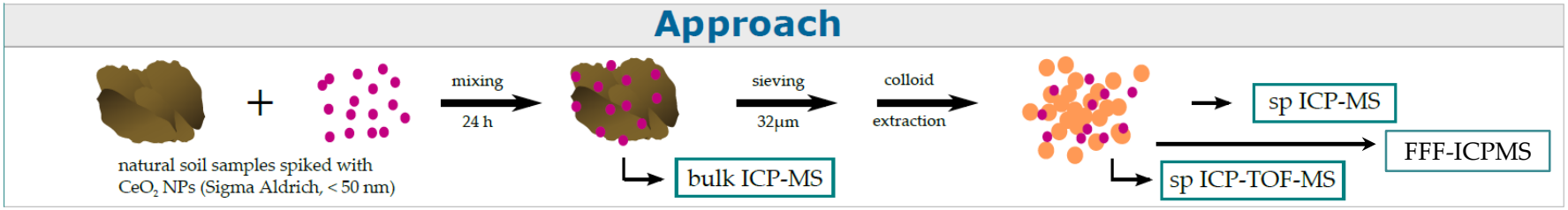
colloidal extract of uncontaminated natural soil

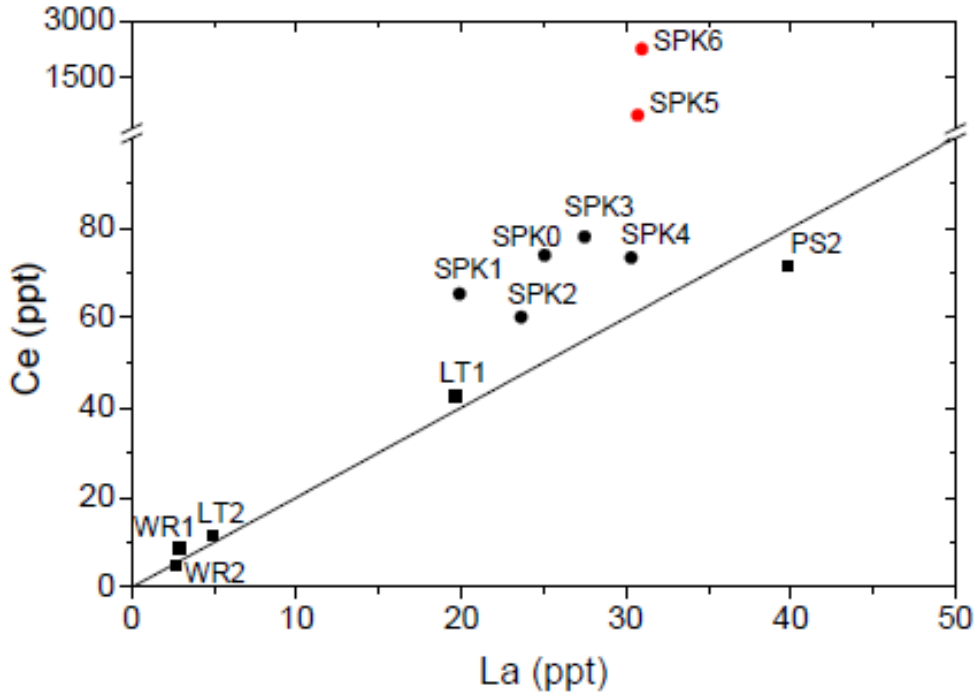


colloidal extract of soil spiked with 40 ppm CeO_2 NPs

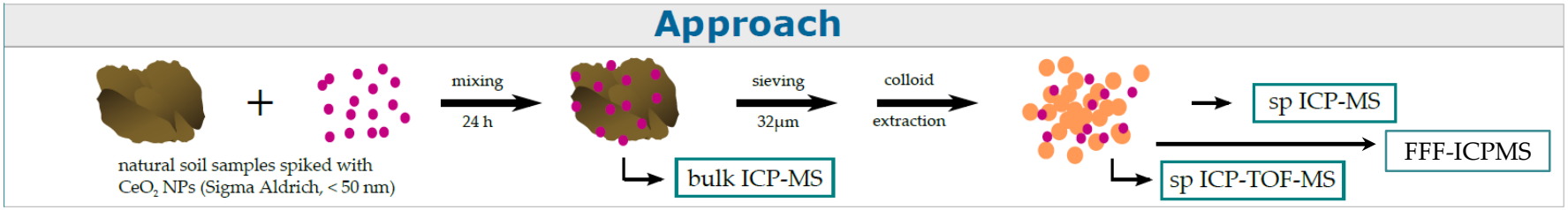


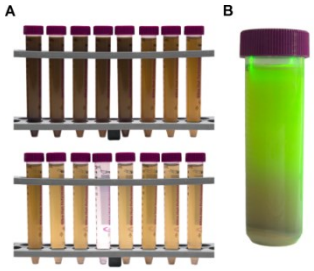
CeO_2 NP analysis in soil matrix – sp-ICPMS





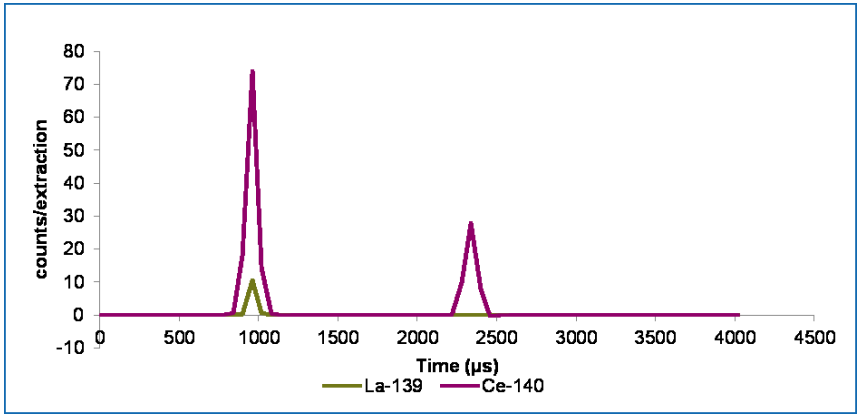
CeO_2 NP analysis in soil matrix – sp-ICPMS concept

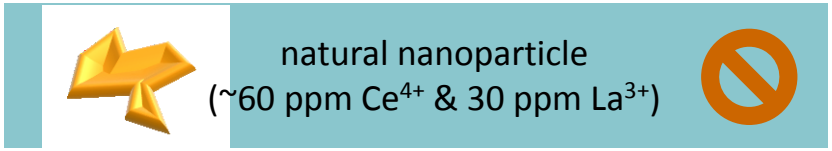


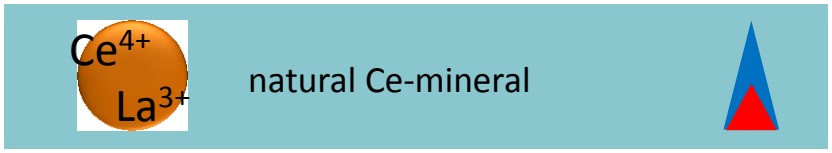


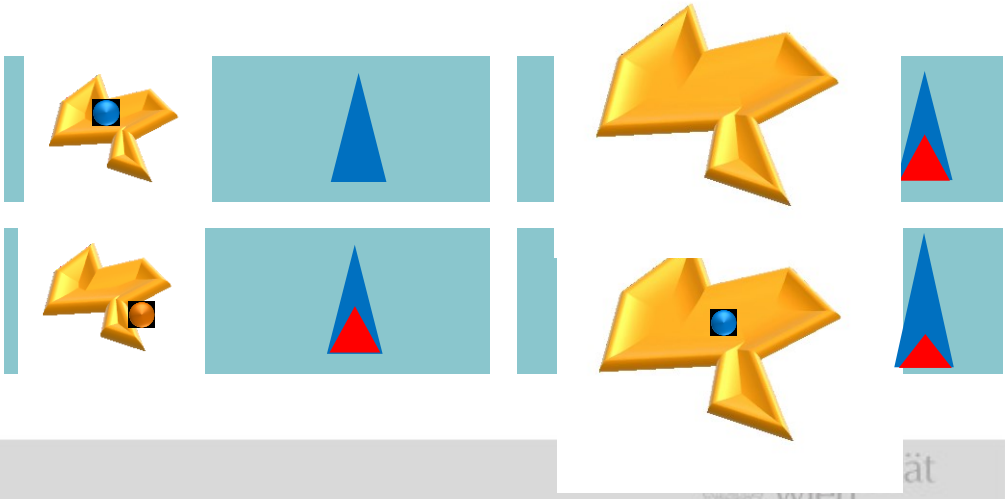
fast scan qpol-ICPMS

sp-ICP-TOFMS

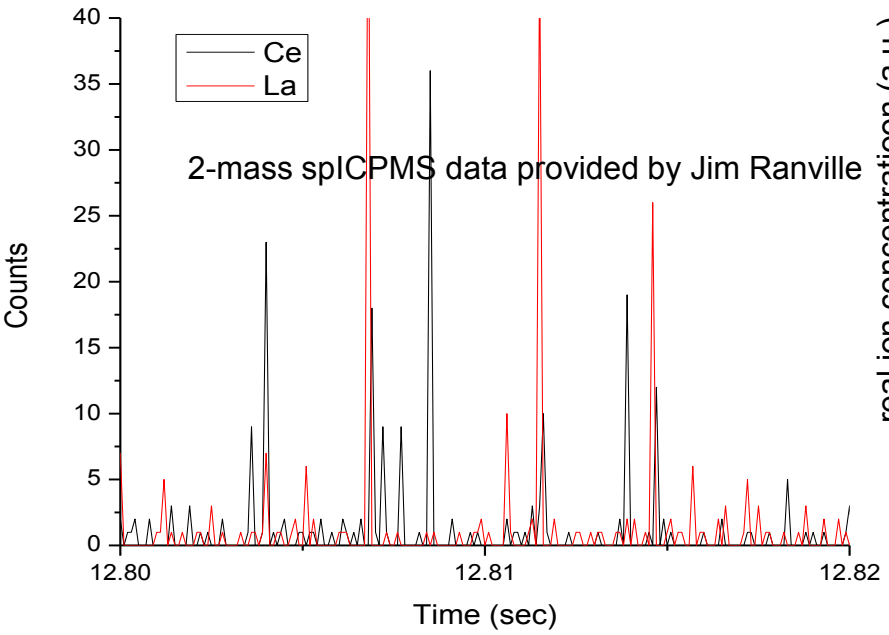


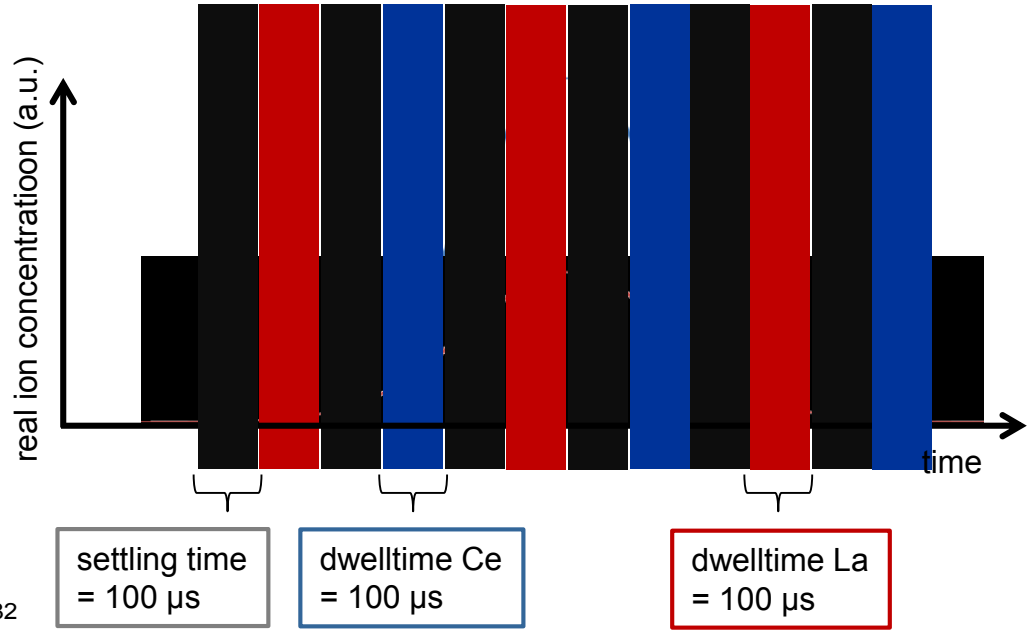




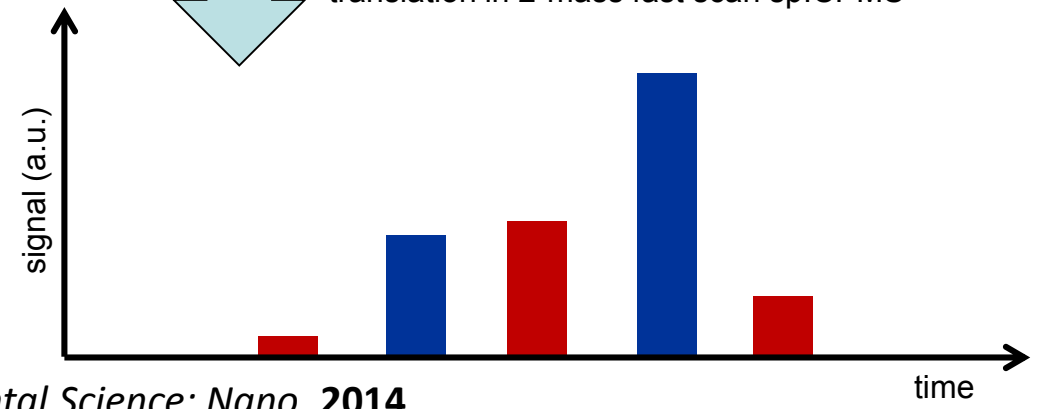


Ce & La signals in fast scan & switching spICPMS





translation in 2-mass fast scan spICPMS



Ce/La ratio of 1.7 : 1 measured in the colloidal bulk is not found in 2-mass spICPMS on single peak level

But averaging 20,000 data points of 2-mass spICPMS delivers a ratio of 1.6 : 1

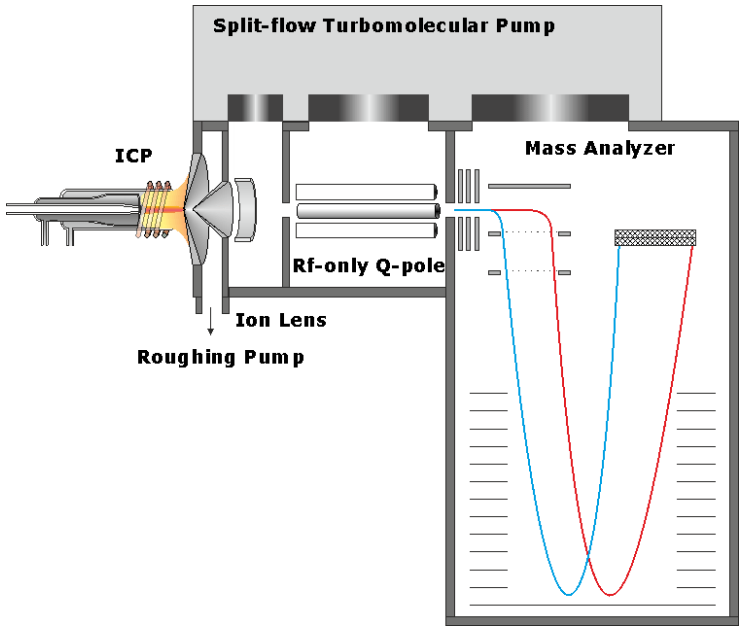
Montaño, Ranville, vd Kammer et al. *Environmental Science: Nano*, **2014**

CeO_2 NP analysis in soil matrix – sp-TOF -ICPMS

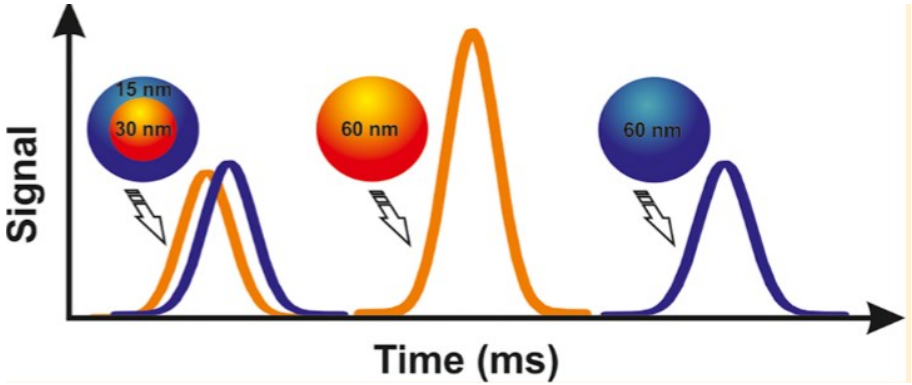
possible solution:

ICP-TOF-MS

simultaneous, high speed detection of multiple elements

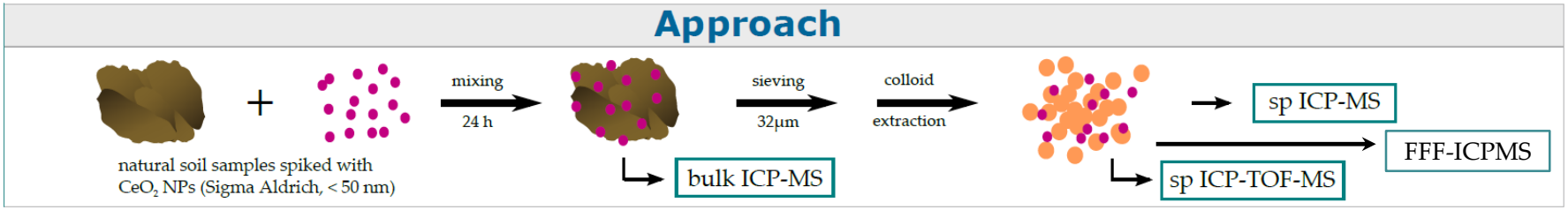


simultaneous single particle detection of ^{107}Ag and ^{197}Au
time resolution 33 µs



Borovinskaya et al. 2014

CeO_2 NP analysis in soil matrix – sp-TOF -ICPMS



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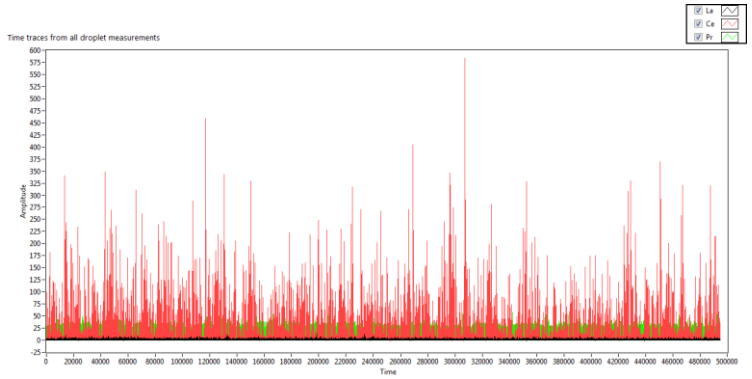
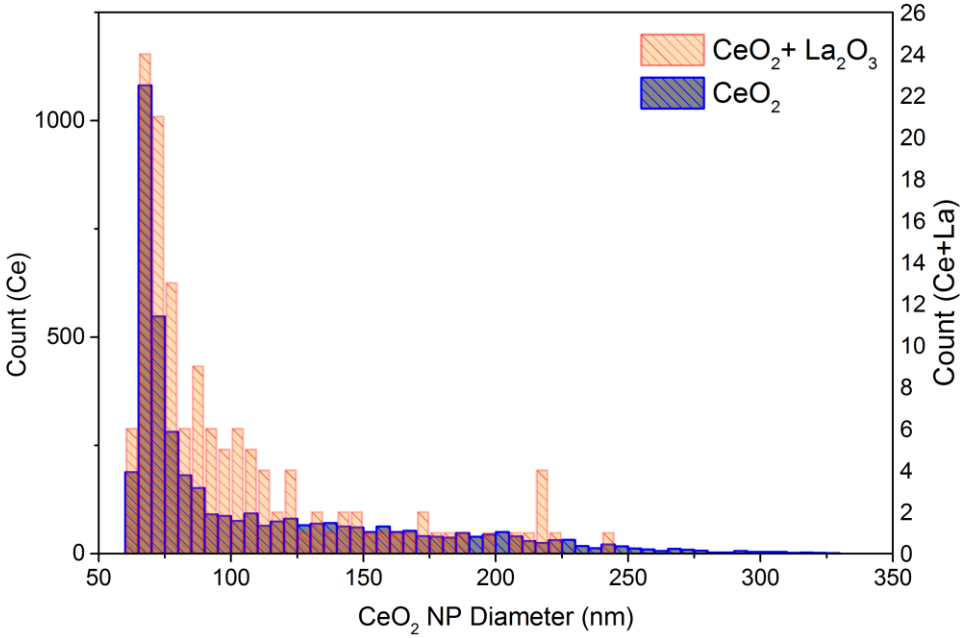


highest spike (SPK6)



size cut-offs:
Ce: 67 nm
La: 57 nm both due to dissolved background

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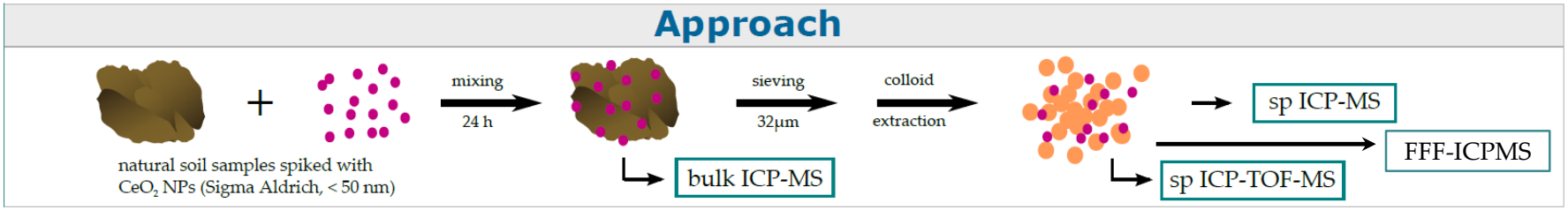
CeO_2 NP analysis in soil matrix – sp-TOF -ICPMS



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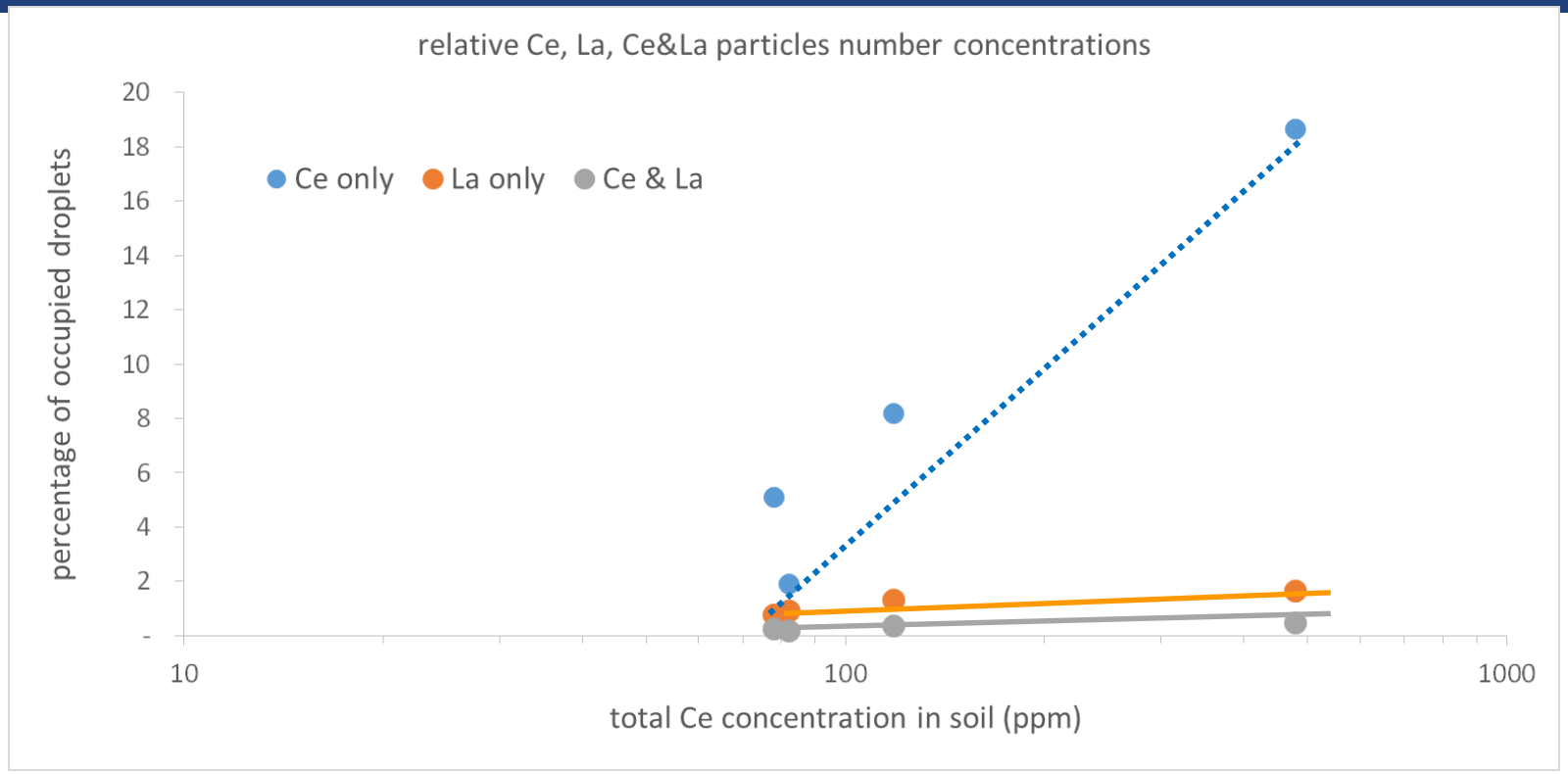

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Conclusions

Ce/La elemental ratios enable identification of manufactured CeO_2 NPs in natural background

NP extractions from soils show recoveries around 20% (often seen…)

Current limits for CeO_2 NPs are 5-10% of the natural background values

single element sp-ICPMS shows potential for better sensitivity (on N and Ce/La mass ratios)

fast scan 2-element sp-ICPMS identification is qualitative only

sp-TOF-ICPMS shows great potential

- still need to improve particle size limits
- need adaption of data treatment (identification and concentration is priority, not size)

Acknowledgement

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ETH zürich

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