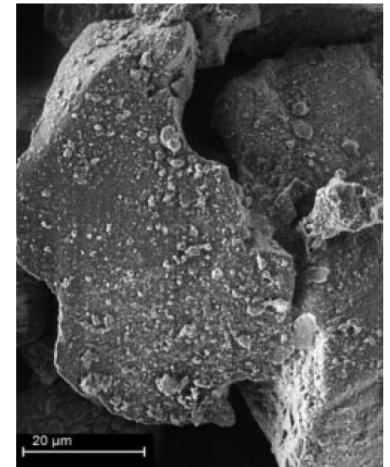
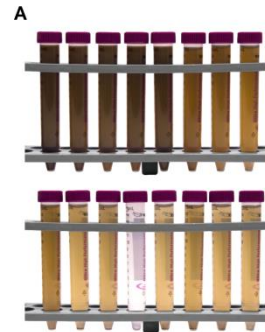


Detection of engineered cerium oxide nanoparticles in soils

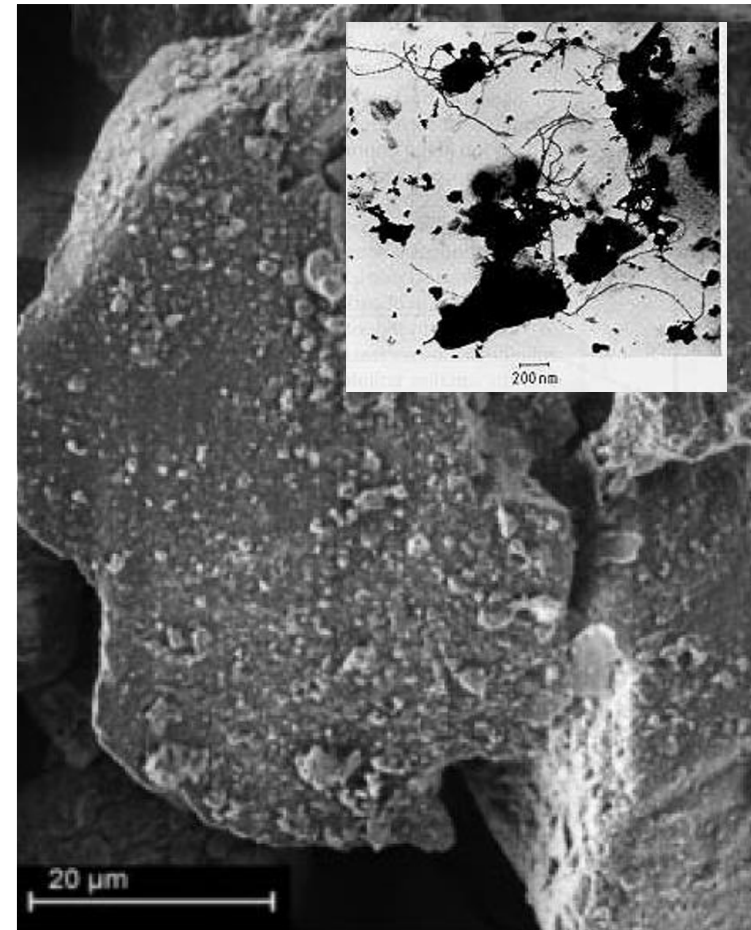
Frank von der Kammer
Antonia Praetorius
Willi Fabienke
Thilo Hofmann



- 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

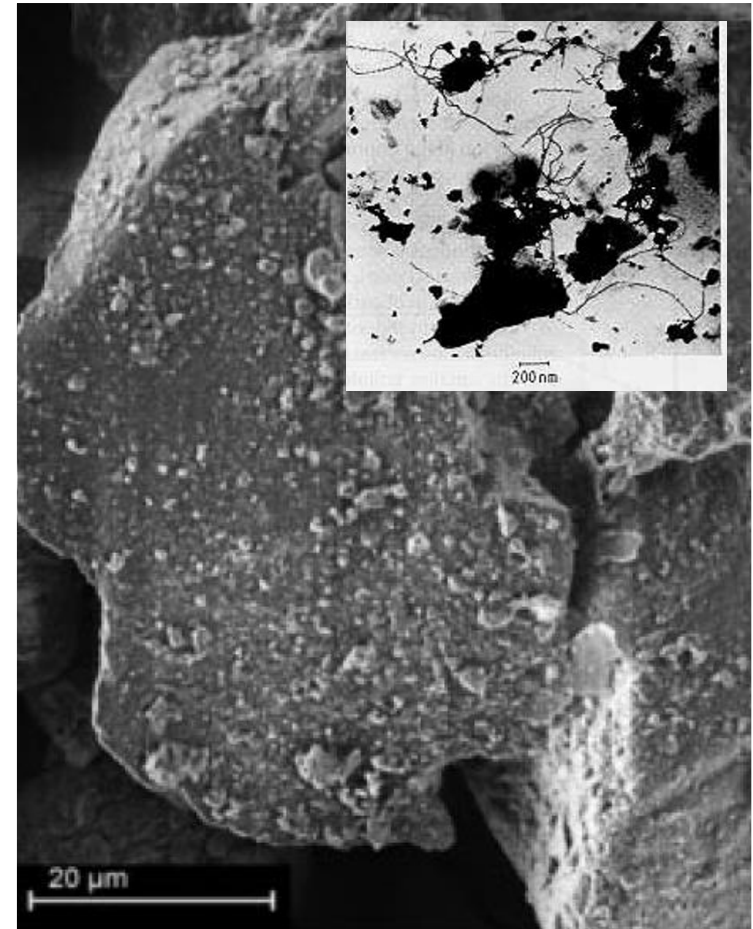


Von der Kammer (2012)

- 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



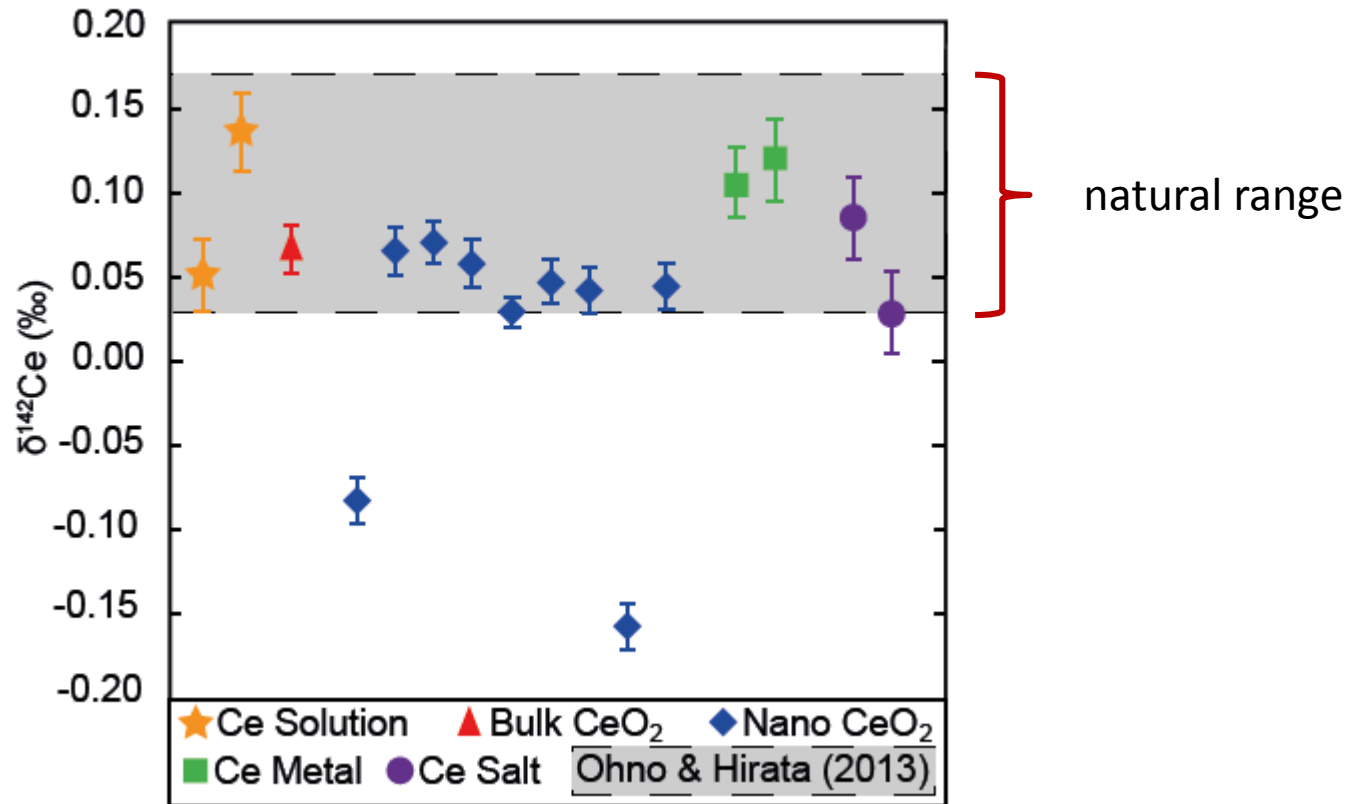
ENP in river water



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 ($^{142}\text{Ce}/^{140}\text{Ce}$)



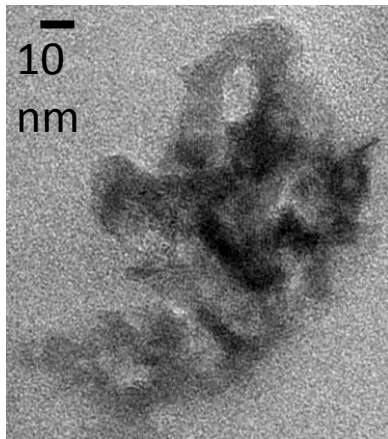
Laycock, Rehkaemper (2014)



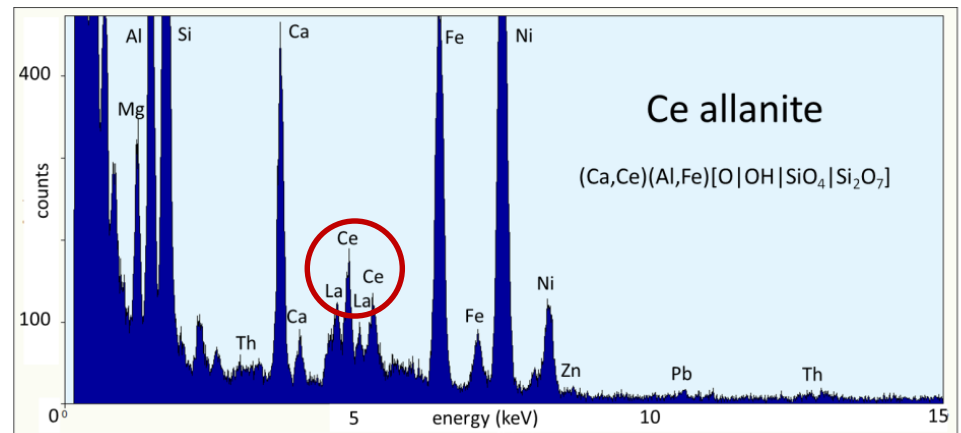
no usable isotopic fingerprint in products compared to natural soils and rock

CeO₂ 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



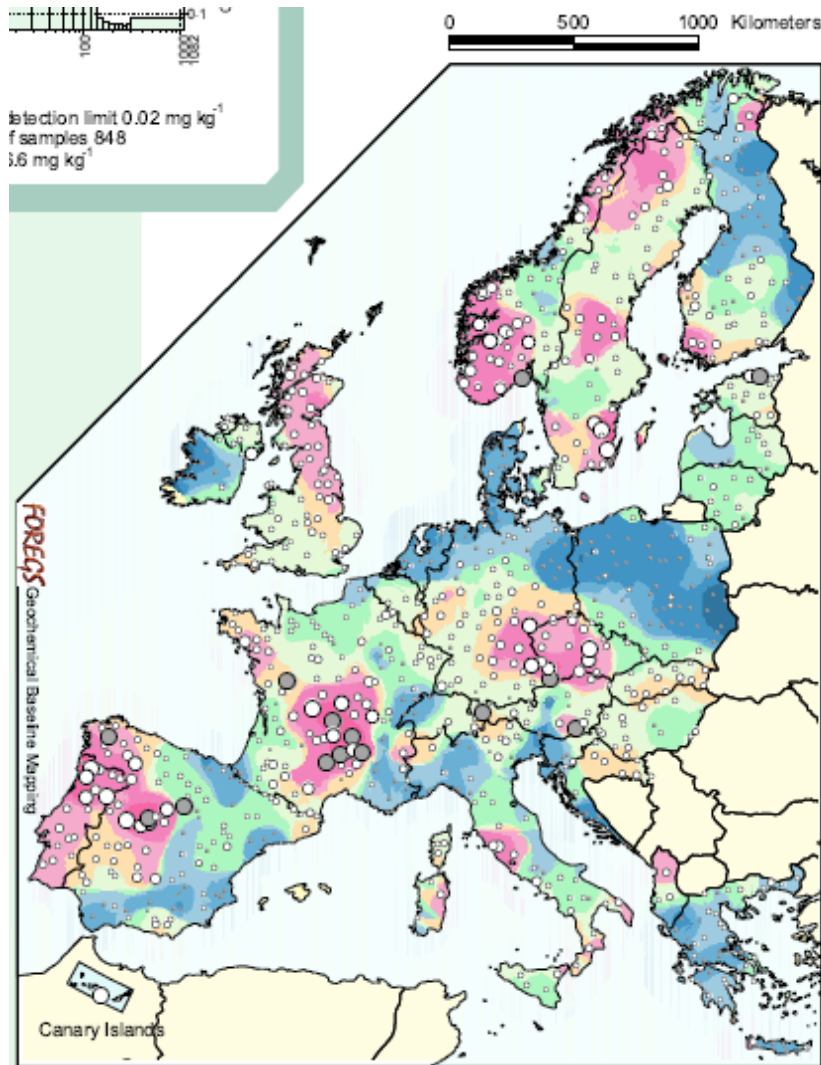
natural CeO₂ contains
La, Nd, Th...



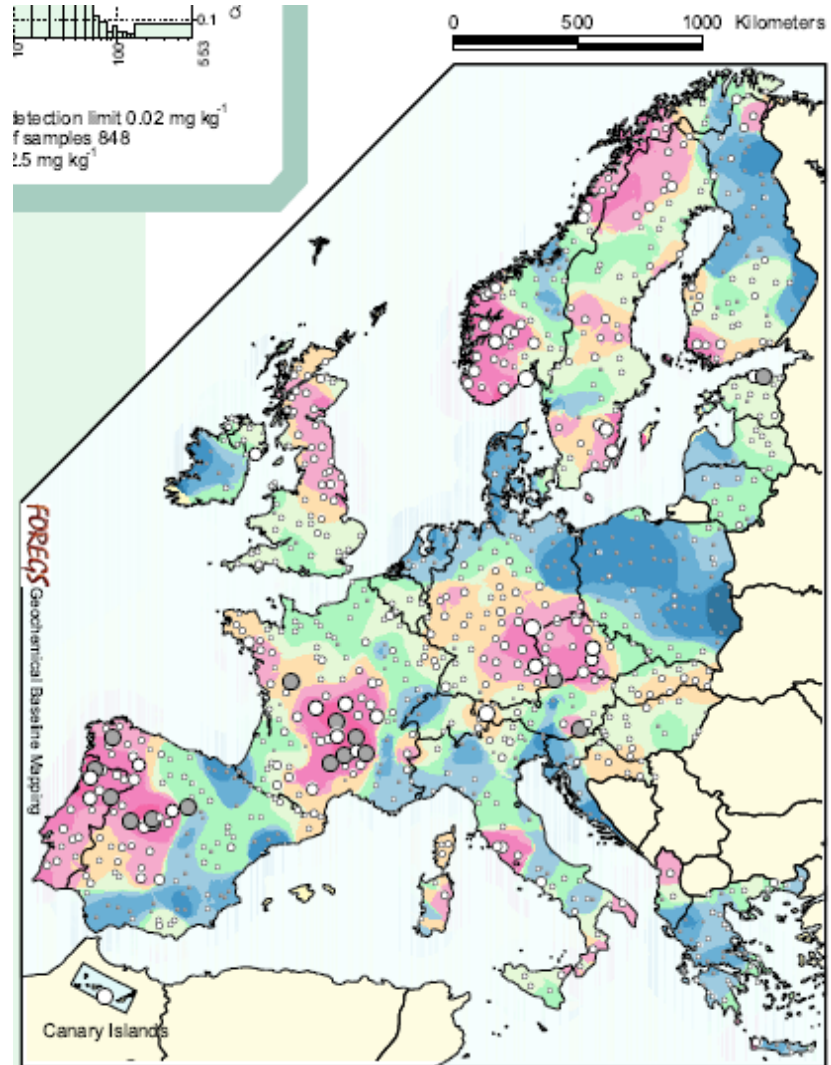
Ce containing nanoparticle from Clark Fork River bank sediment
(Plathe et al.; Env Chem 2010)

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

Ce in floodplain sediments

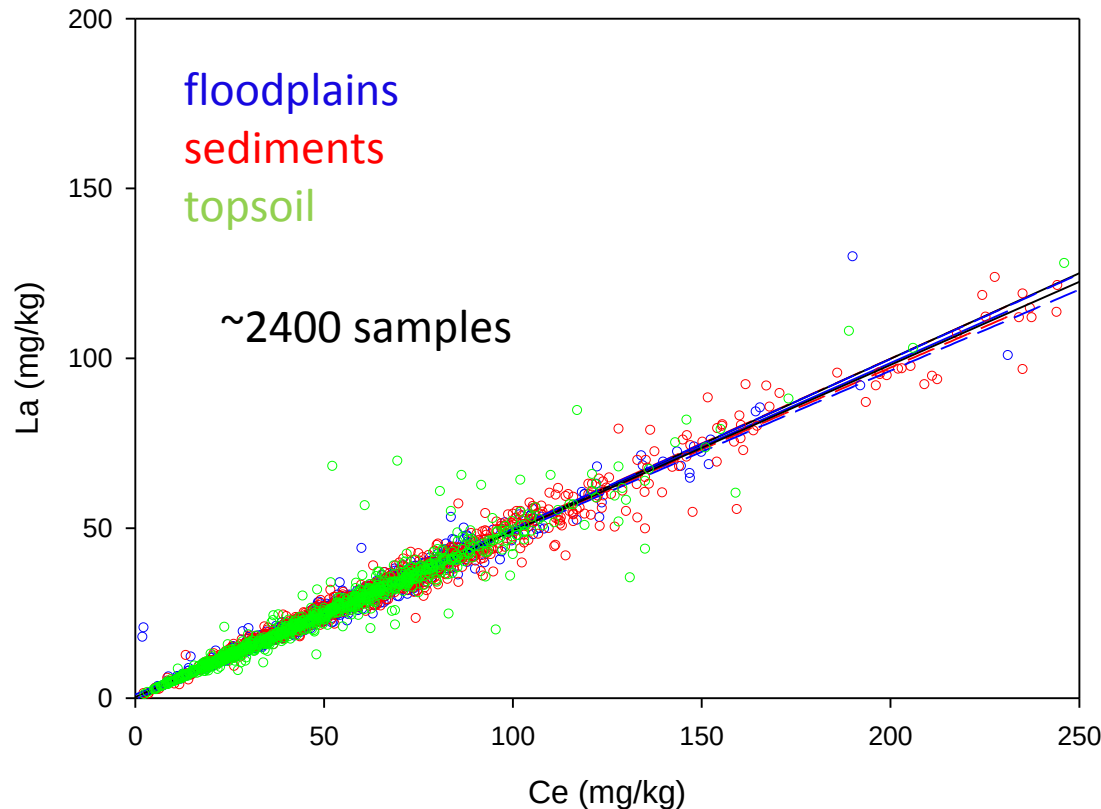


La in floodplain sediments



CeO₂ nanoparticles

La over Ce concentrations according to FOREGS database



hypothesis:

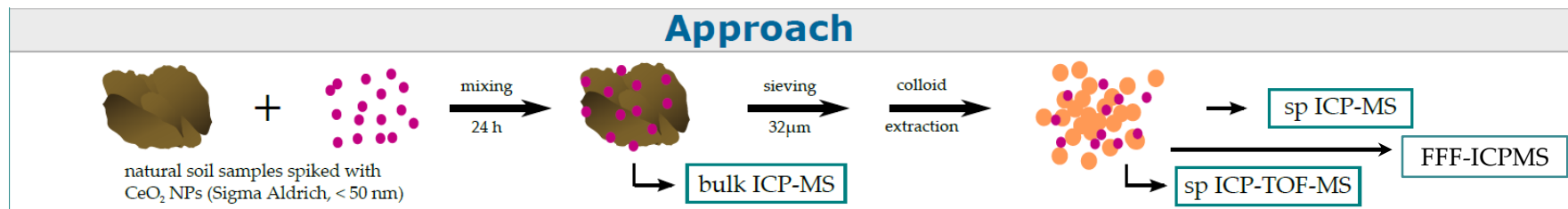
Ce/La ratios can be used
to identify natural background
to separate ENPs & NNPs

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

CeO₂ NP analysis in soil matrix – general approach



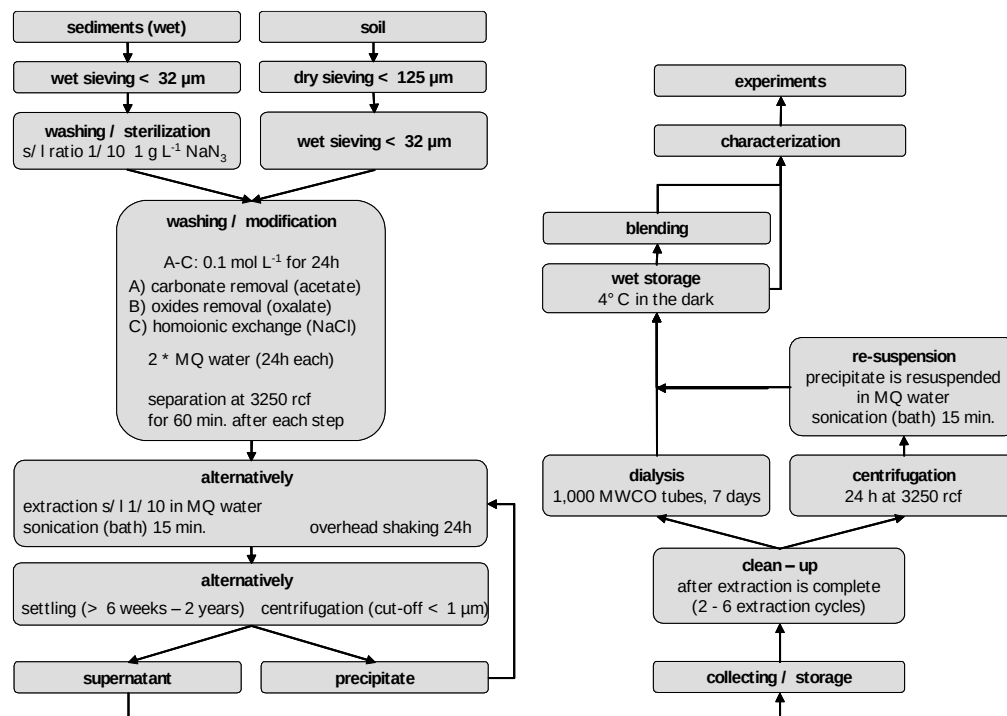
spiking of natural soil samples



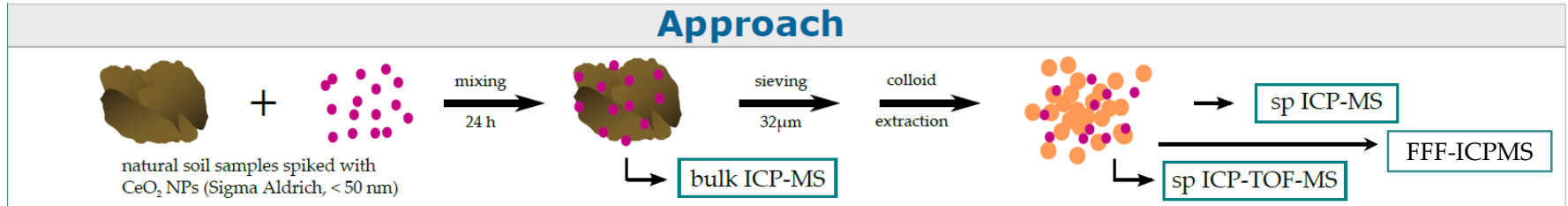
natural background 74 mg/kg (Ce)

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

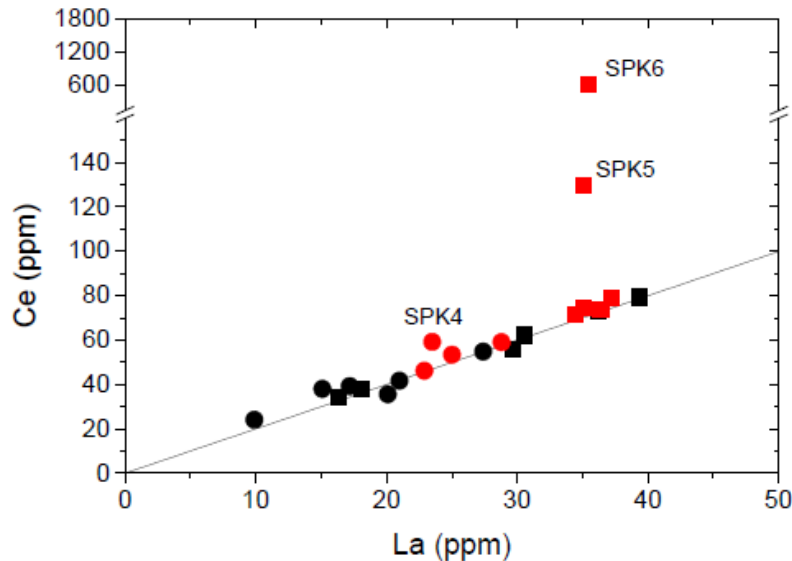
colloid/nanoparticle extraction procedure



CeO₂ NP analysis in soil matrix – bulk analysis



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



in colloidal extracts CeO₂ yields are

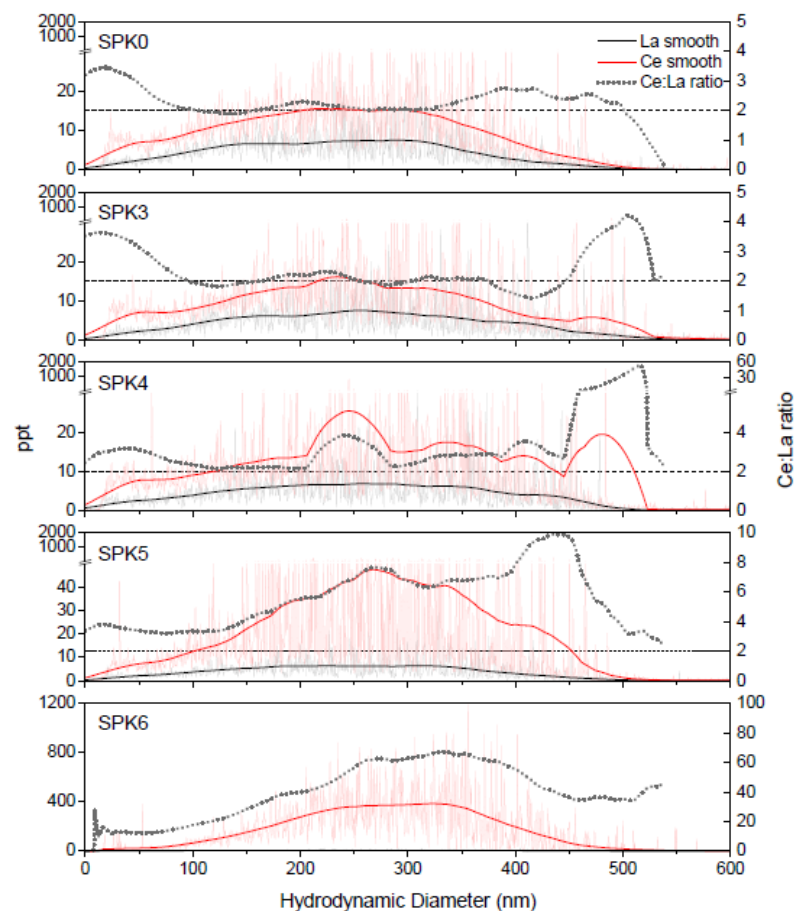
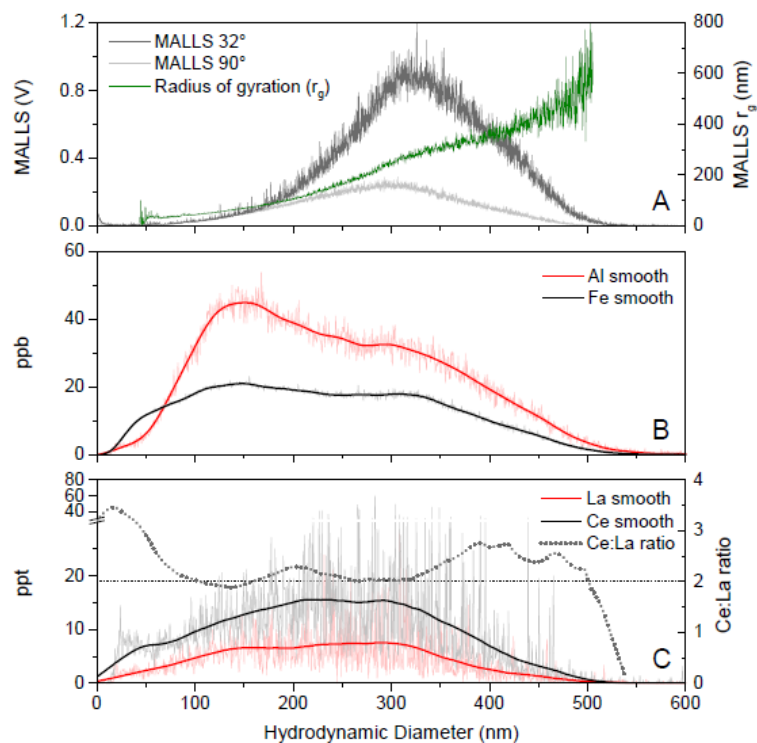
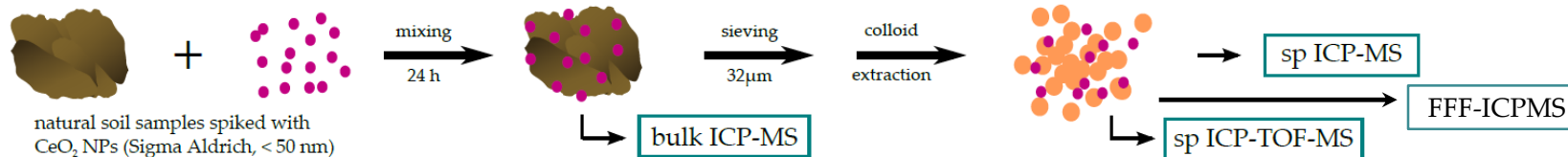
16% in the unspiked and low concentration spikes

24% in the 40 ppm spike

34% in the 400 ppm spike

CeO₂ 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

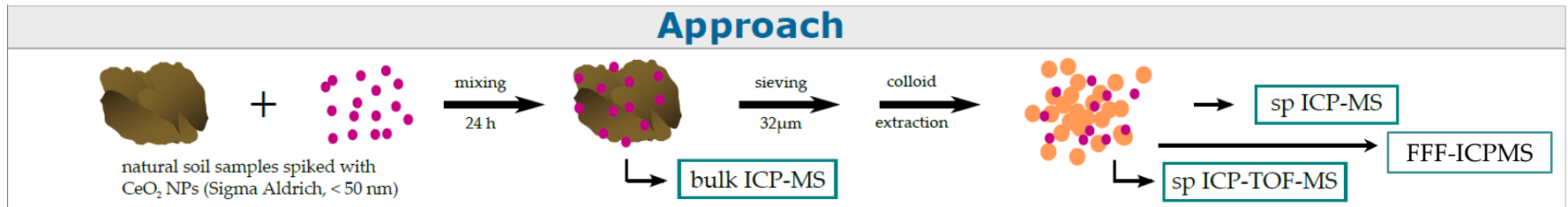
→ quadrupole instruments: only single isotope monitored

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

→ fast scan quadrupole: theoretically 2 isotopes could be monitored

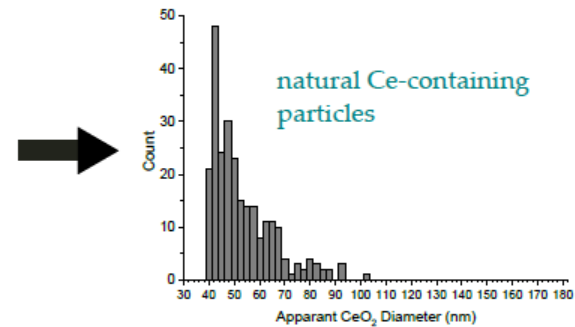
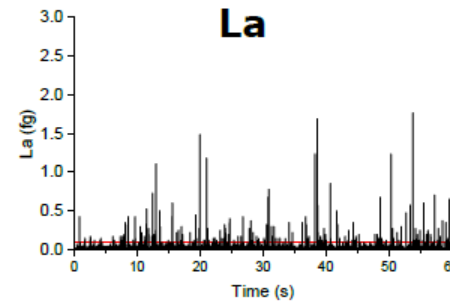
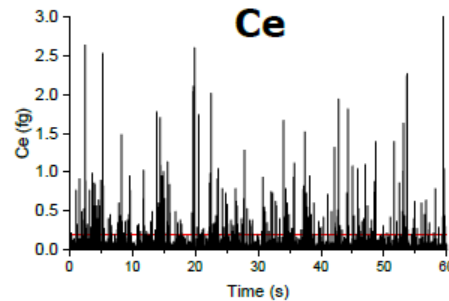
→ Time of Flight instruments: multiple isotope monitoring
event monitoring at ~ 30 μ s resolution

CeO₂ NP analysis in soil matrix – sp-ICPMS

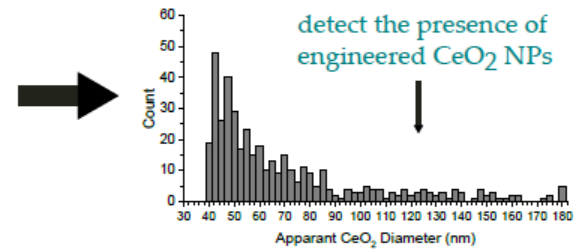
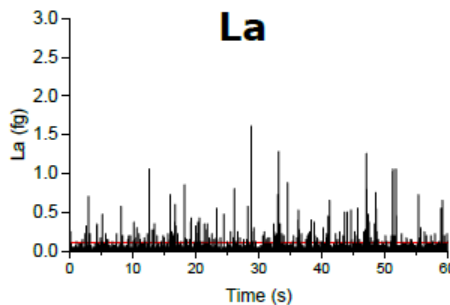
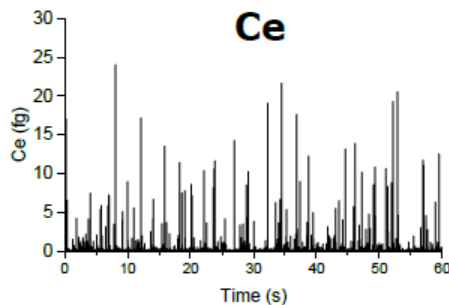


B: Single-element single-particle ICP-MS of colloidal extracts

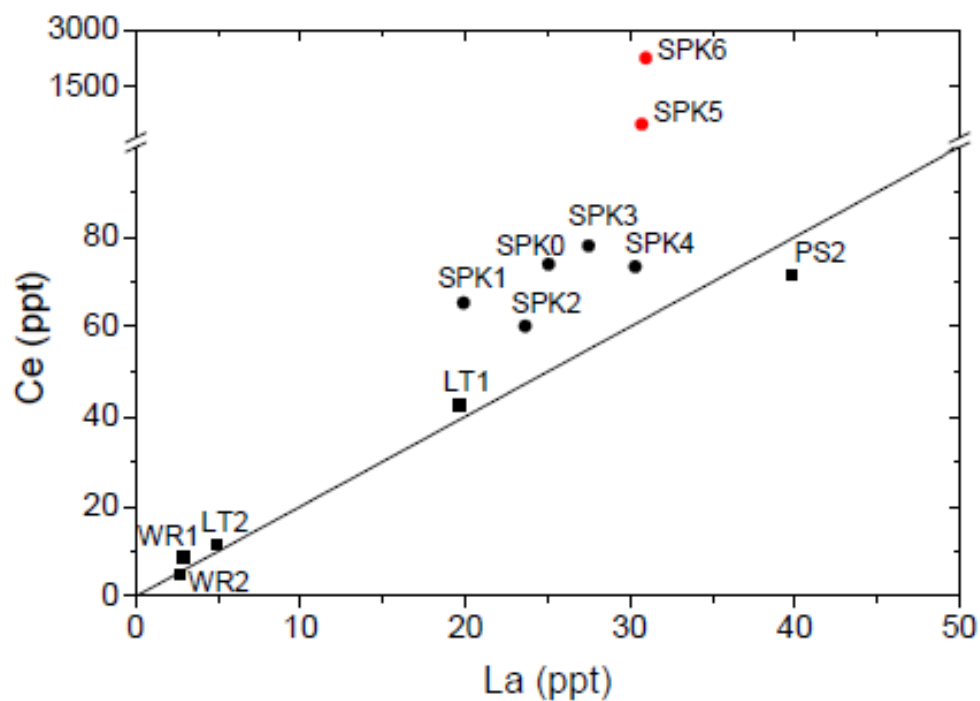
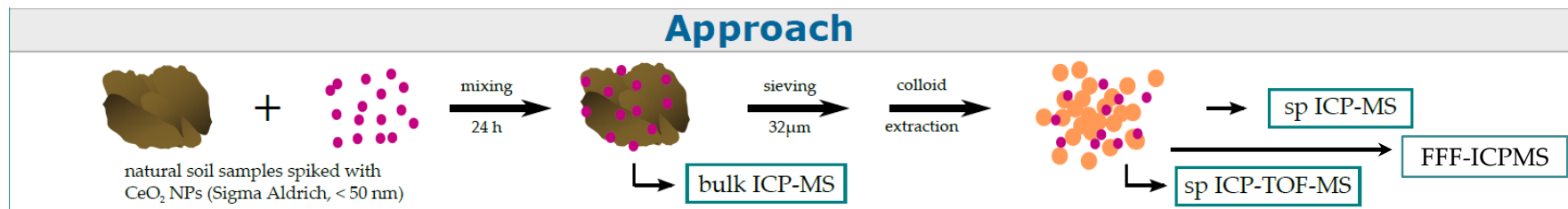
colloidal extract of
uncontaminated
natural soil



colloidal extract of
soil spiked with
40 ppm CeO₂ NPs

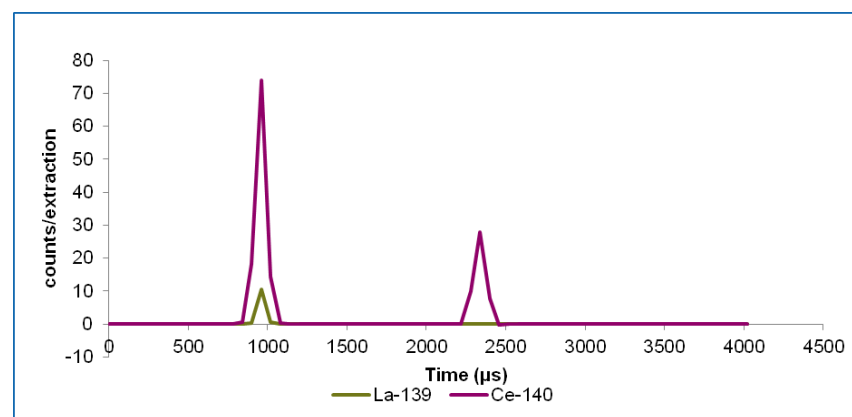
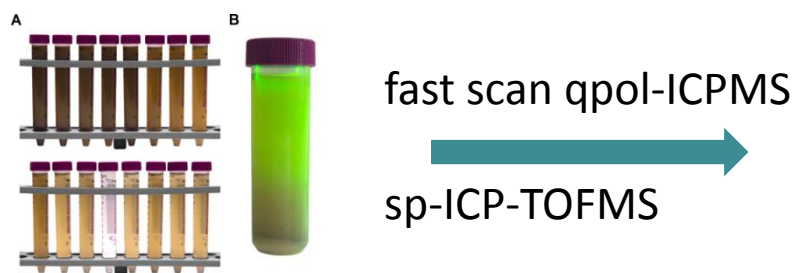
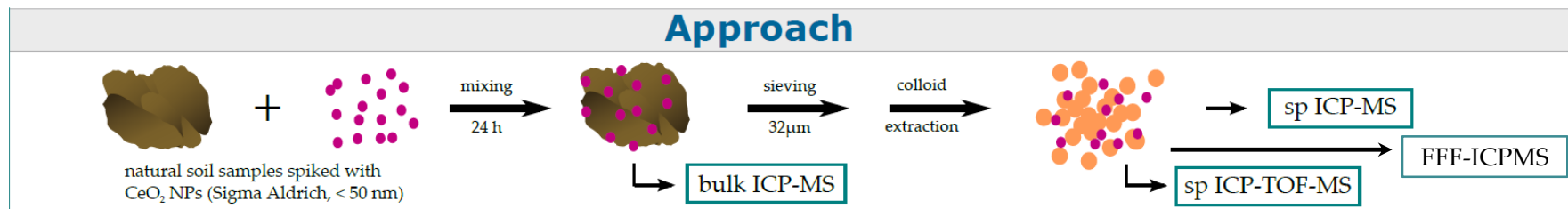


CeO₂ NP analysis in soil matrix – sp-ICPMS

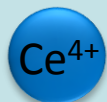


CeO₂ NP analysis in soil matrix – sp-ICPMS concept

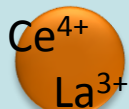
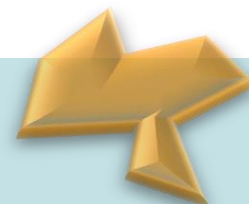
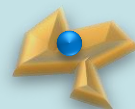
Approach



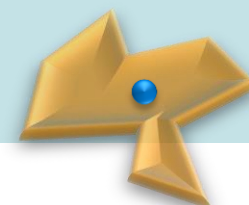
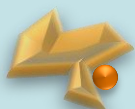
natural nanoparticle
(~60 ppm Ce⁴⁺ & 30 ppm La³⁺)

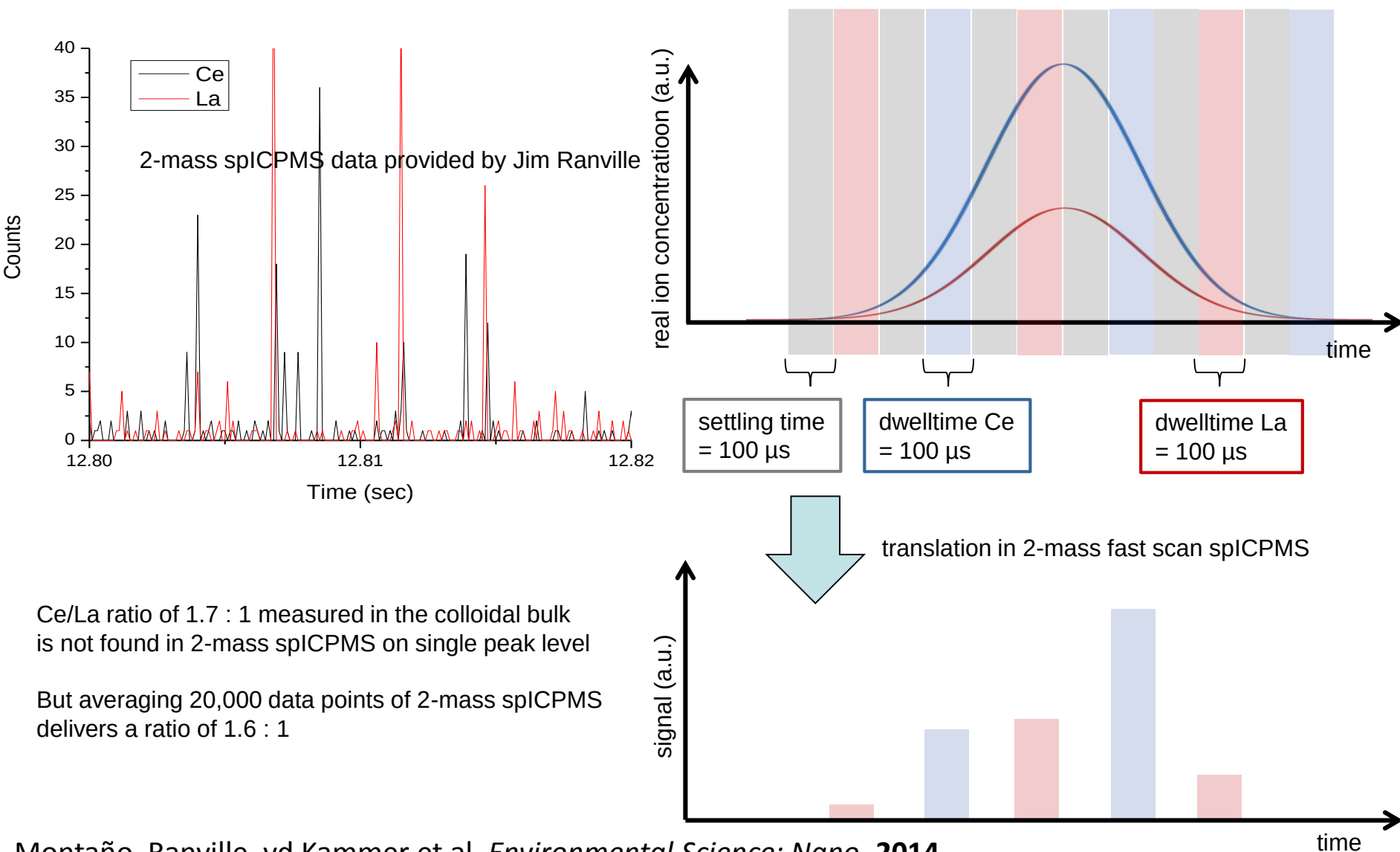


engineered CeO₂ NP



natural Ce-mineral



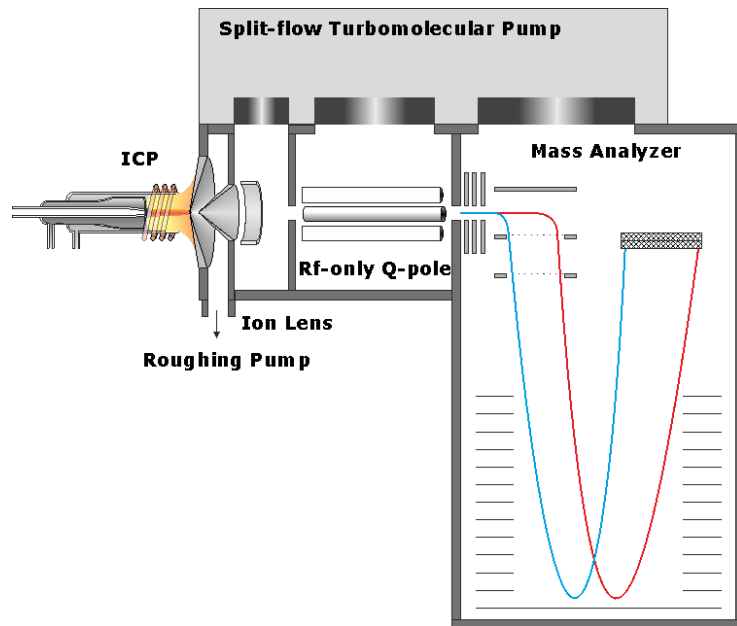


CeO₂ NP analysis in soil matrix – sp-TOF -ICPMS

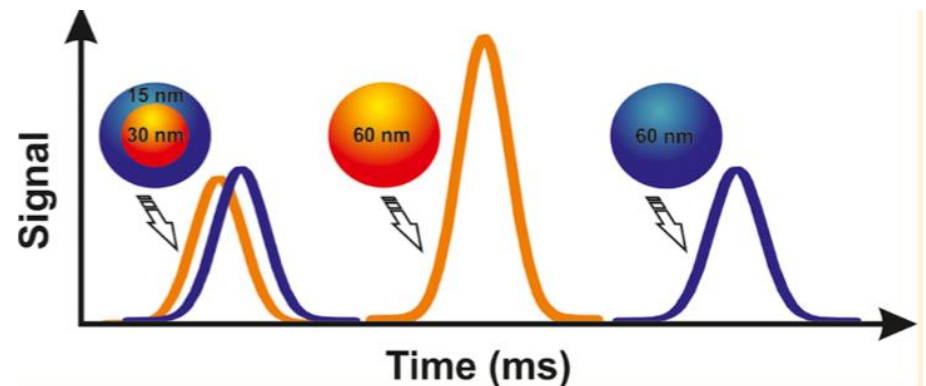
possible solution:

ICP-TOF-MS

simultaneous, high speed detection of multiple elements

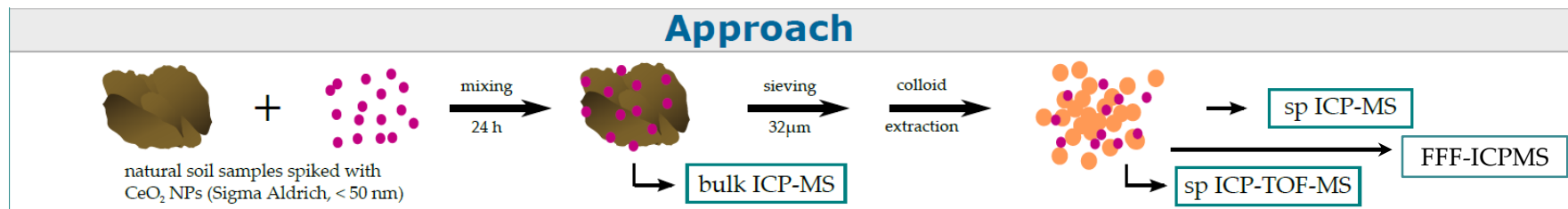


simultaneous single particle detection of
 ^{107}Ag and ^{197}Au
time resolution 33 μs

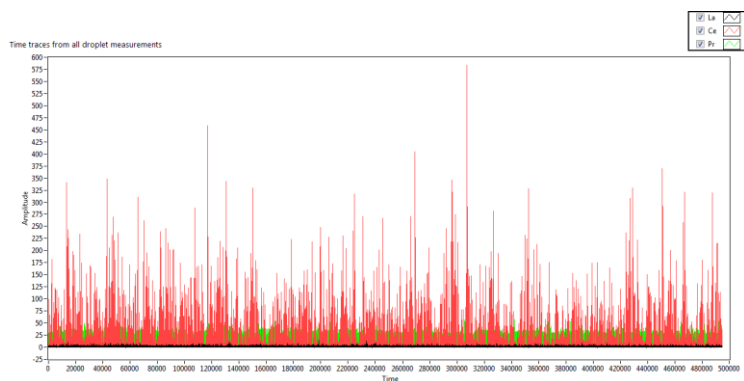


Borovinskaya et al. 2014

CeO₂ NP analysis in soil matrix – sp-TOF -ICPMS



ETH zürich



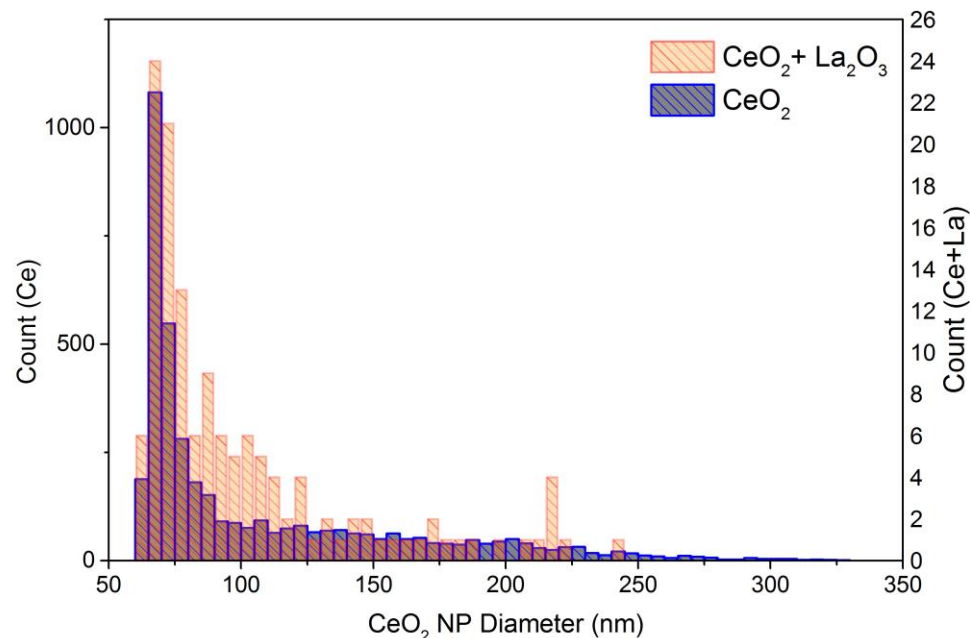
highest spike (SPK6)



size cut-offs:

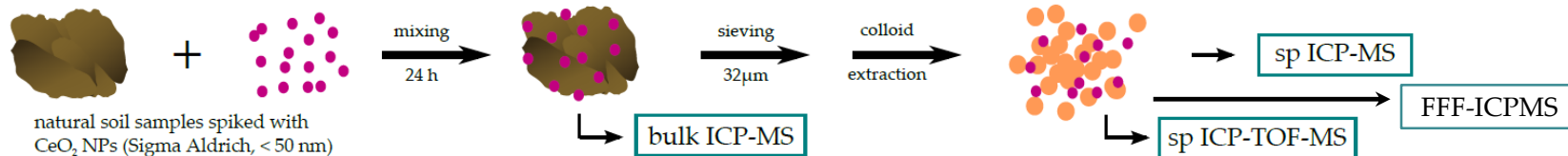
Ce: 67 nm

La: 57 nm both due to dissolved background

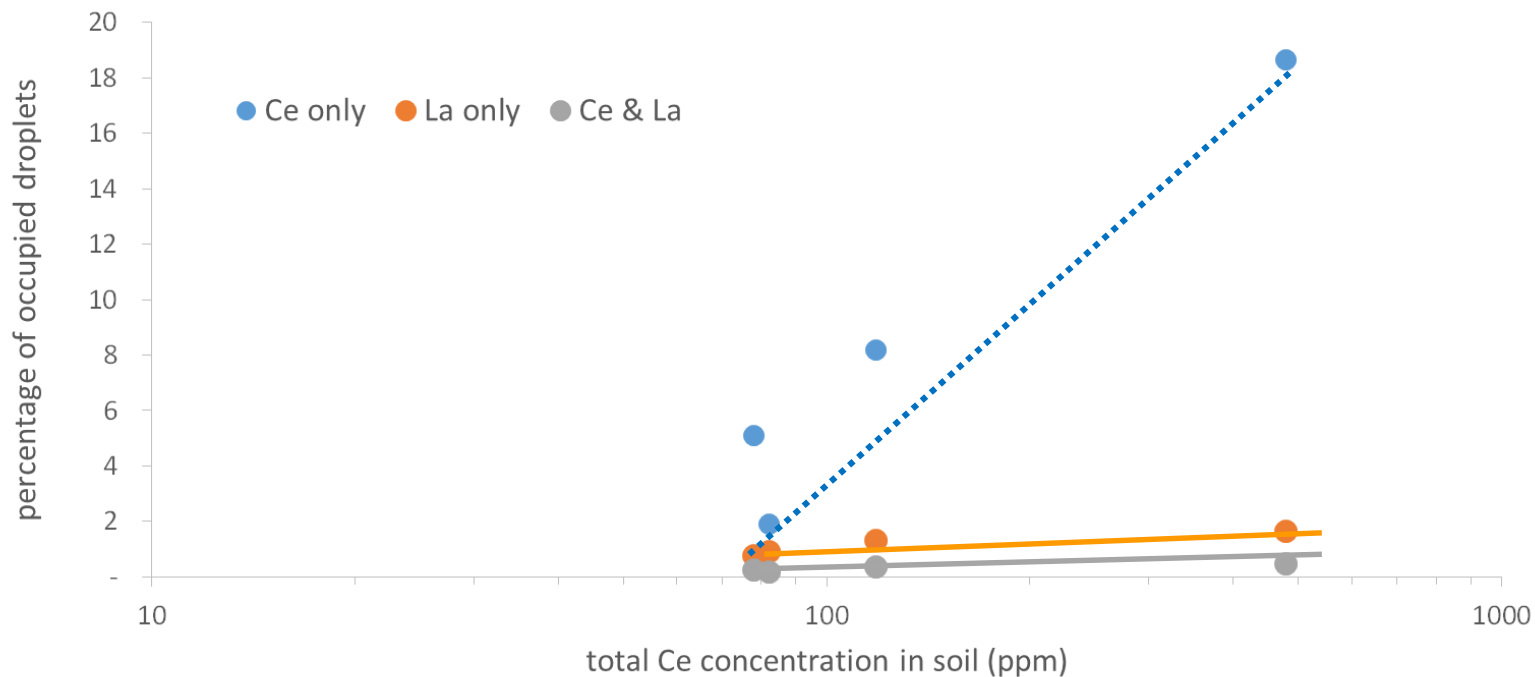


CeO₂ NP analysis in soil matrix – sp-TOF -ICPMS

Approach



relative Ce, La, Ce&La particles number concentrations



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)



Antonia Praetorius



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Elisabeth Neubauer



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wien



vienna university
environmental geosciences



ETH zürich

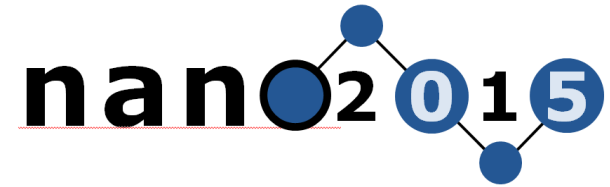
Alex Gundlach-Graham
Olga Borovinskaya
Detlev Günther

Thank you!

funding was provided by

Austrian FFG: DetectNano

ICEENN 2015 - 10th anniversary – 6.-10. September 2015
International Conference on the Environmental Effects of
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