Integrated evaluation of aquatic organism responses to metal exposure: gene expression, bioavailability, toxicity and biomarker responses - BIOTOXMET (MUL/FFoQSI-contribution)

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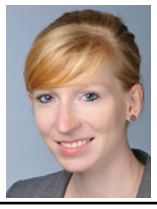
2 Austrian Competence Centre for Feed and Food Quality, Safety and Innovation, FFoQSI GmbH
Technopark 1D, 3430 Tulln, Austria

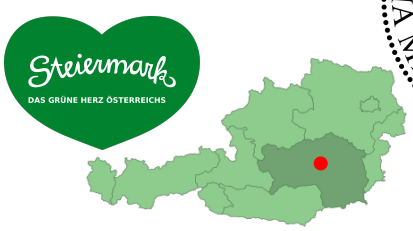
3 University of Natural Resources and Life Sciences, Vienna, Department of Chemistry, Muthgasse 18, 1190 Wien, Austria

MONTANUNIVERSITÄT LEOBEN

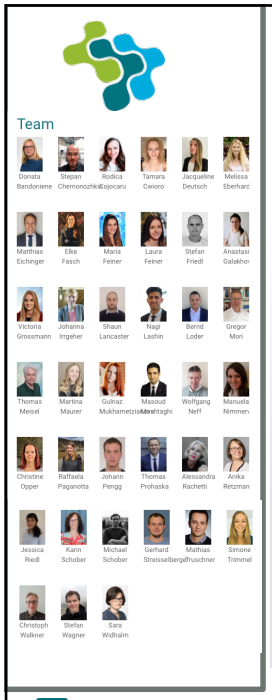

Montanuniversität Leoben
Students: 3.702 (WS 2019)
Staff: 1.272 (WS 2016)

Stadt Leoben
County: Steiermark
Inhabitants: 24.584 (1. Jän. 2019)



Bundesland Steiermark
Inhabitants: 1.243.052 (1. Jänner 2019)
Capital: Graz

Eisenerz / Eisenerzer Alpen (30 km ab LE)
Siderit-Bergbau
Abenteuer-Bergwerk



LS General and Analytical Chemistry

Bildquellen: Nu Instruments, Perkin Elmer, Agilent, Bruker, Pan Analytical, ESI
https://teceus.at

RESEARCH GROUPS

CHAIR GENERAL AND ANALYTICAL CHEMISTRY

ISOTOPIC-ANALYSIS
Leiterin: Irrgeher

Development of isotopic tools and application in material-, environmental-, geo- and life sciences.

CORROSION

Leiter: Mori

Fundamental research in corrosion and development of new technologies for corrosion protection

ELEMENTAL-ANALYSIS
Leiter: Meisel

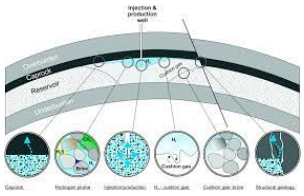
Development of analytical fingerprint methods for source determination, ore formation and certification of reference materials.

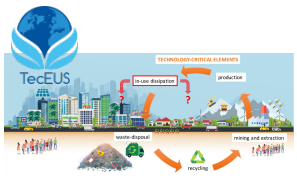
TECHNOLOGY-METROLOGY
Leiter: Prohaska

Development of novel technologies, characterization of novel materials and fundamental application of metrology.

LS General and Analytical Chemistry
selected MILESTONE projects

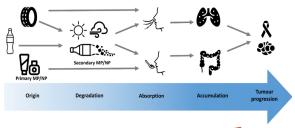
HyStorIES High Pressure Hydrogen Embrittlement	TECEUS Technological Critical Elements in Urban Spheres	ISOTRACE MS infrastructure for isotope research	nanoPLASTIC Health impact of micro and nanoplastic on cells





MC ICP-CC-MS

TIMS



Europäische Kommission

Hydrogen Storage In European Subsurface

FWF Der Wissenschaftsfonds.

EMPIR EURAMET

Das Land Steiermark

MONTAN UNIVERSITÄT LEOBEN

FWF Der Wissenschaftsfonds.

COMET Competence Centers for Excellent Technologies

Agilent Technologies

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Bildquellen: https://pubs.rsc.org/en/content/articlelanding/2021/ee/d0ee03536j#!divAbstract, https://teceus.at, https://www.nu-ins.com/; https://www.nu-ins.com/, Grafik: Thomas Meisel

LS General and Analytical Chemistry
Status Quo

- **Cooperations(MUL)**

DPT Allgemeine, Analytische und Physikalische Chemie, DPT Angewandte Geowissenschaften und Geophysik, DPT Kunststofftechnik, DPT Metallurgie, DPR Umwelt- und Energieverfahrenstechnik, DPT Werkstoffwissenschaft

- **Cooperations (national, international)**

UNIVERSITY OF CALGARY · BOKU · universität wien · TU WIEN · NUS National University of Singapore · UNI GRAZ · TU Graz

nhm · DERA Deutsche Rohstoffagentur · Helmholtz-Zentrum Geesthacht Zentrum für Material- und Küstenforschung · BAM · Kunst Historisches Museum Wien · ÖAW Österreichische Akademie der Wissenschaften · FFoQSI

OMV · LOCK · AUSTRIA AG · plansee GROUP · APPLIED SPECTRA · HILTI · Elemental Scientific · voestalpine

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Elemental and Isotopic Analysis at MUL

Agilent 4200
MP-AES

© agilent.com

Agilent 8800
ICP-MS-CRC-MS

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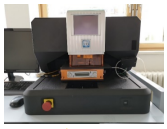
Nu Instruments NuTIMS
TIMS

© nu-ins.com

Nu Instruments Nu Plasma HR
MC ICP-MS

© nu-ins.com

ESI NWR 213
Laser-Ablation System



Perkin Elmer NexION 2000
ICP-CRC-MS

© perkinelmer.com

Perkin Elmer NexION 5000
ICP-MS-CRC-MS

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Nu Instruments Sapphire
MC ICP-CRC-MS

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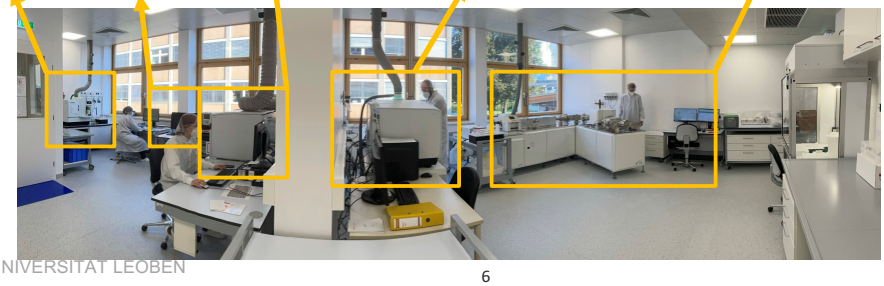

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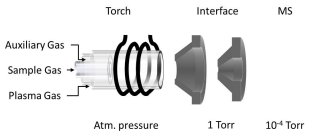
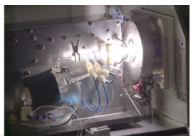
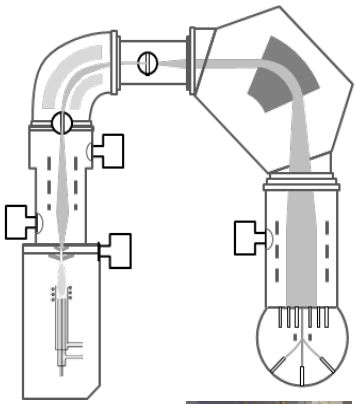
6

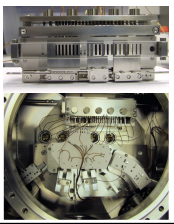
Multicollector Inductively Coupled Plasma Mass Spectrometry
MC ICP-MS

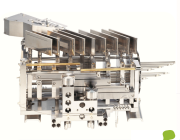




precision (2019): 0.0001 %







Prohaska T, Irrgeher J, Zitek A, Jakubowski N (eds) (2015) RSC, Cambridge

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AAC

Isotopic systems studied @MUL

isotopes with natural variation

X element with >1 stable isotope

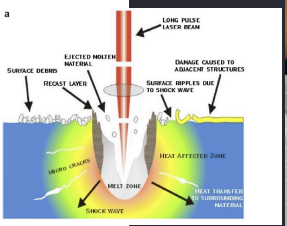
X element with only 1 stable isotope

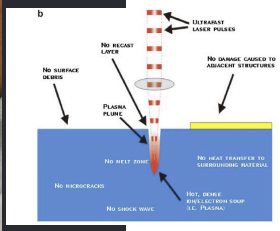
X element with only non stable isotopes

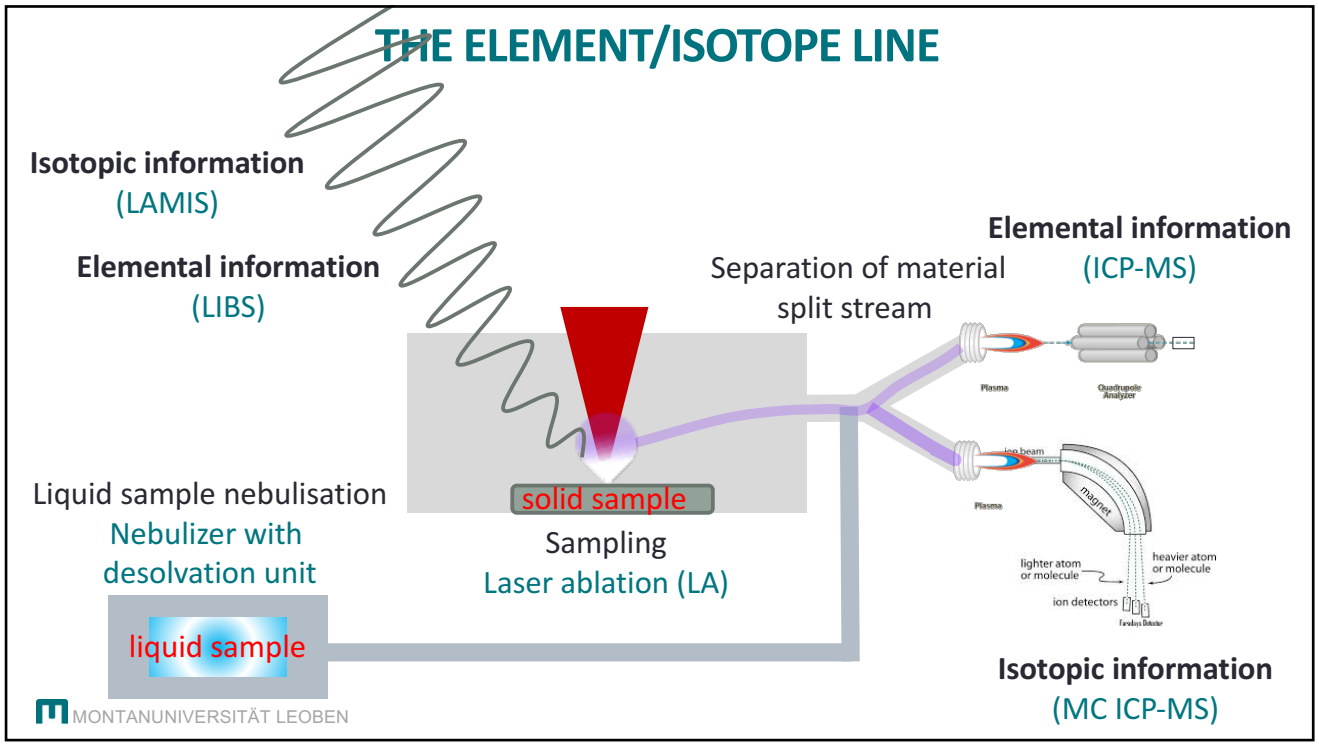
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

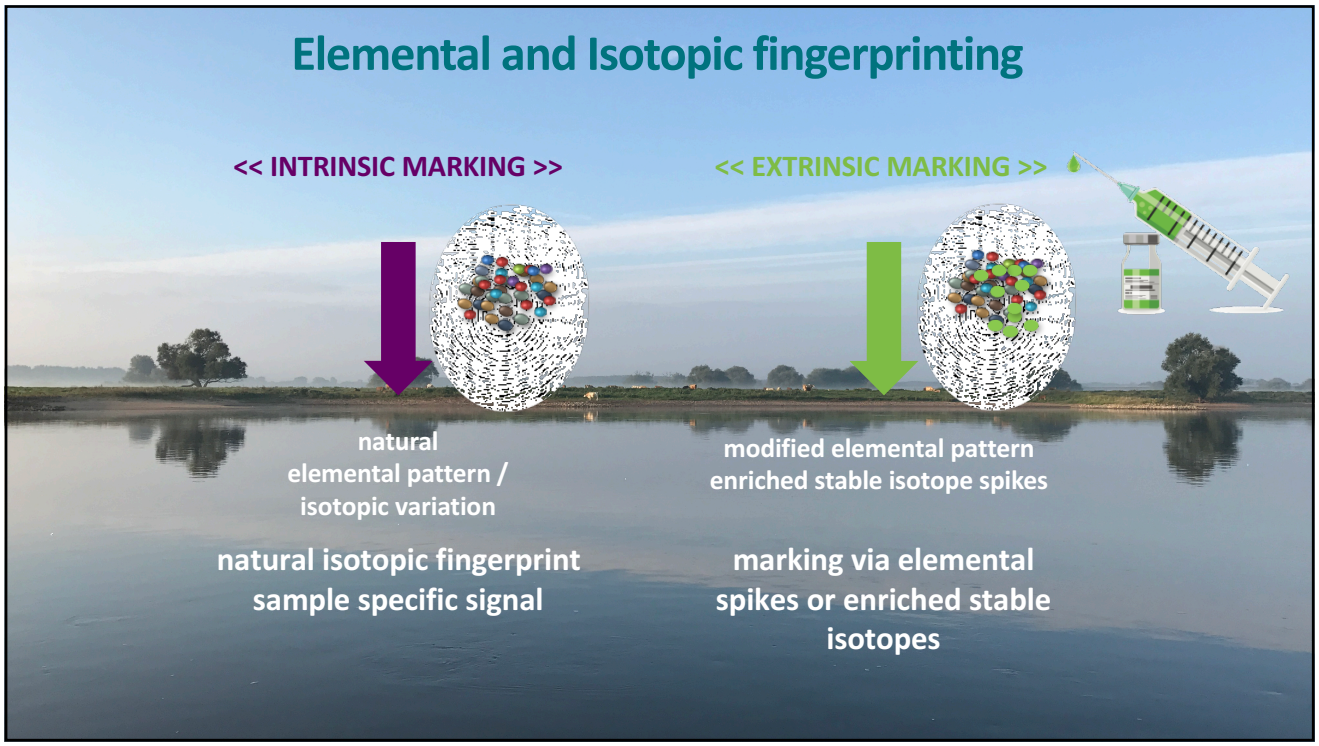
AAC

LA-ICP-MS





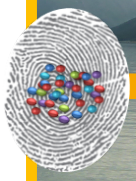

THE ELEMENT/ISOTOPE LINE
Isotopic information
(LAMIS)
Elemental information
(LIBS)
Separation of material
split stream
Elemental information
(ICP-MS)
Liquid sample nebulisation
Nebulizer with
desolvation unit
liquid sample
solid sample
Sampling
Laser ablation (LA)
Plasma
Quadrupole Analyzer
Plasma
magnet
lighter atom or molecule
heavier atom or molecule
ion detectors
Isotopic information
(MC ICP-MS)
MONTANUNIVERSITÄT LEOBEN


Elemental and Isotopic fingerprinting
<< INTRINSIC MARKING >>
<< EXTRINSIC MARKING >>
natural
elemental pattern /
isotopic variation
modified elemental pattern
enriched stable isotope spikes
natural isotopic fingerprint
sample specific signal
marking via elemental
spikes or enriched stable
isotopes

ISOTOPE RATIO ANALYSIS FOR FINGERPRINTING

<< Fingerprint-Method >>

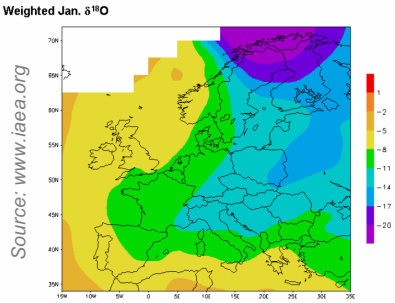
- oceanographic parameter (salinity, chlorophyll, ...)
- physical parameter (pH, T, *p* ...)
- chemical species (Gd, As, P, Sn, Hg, Br ...)
- multielement pattern (REE, Pb, Cd, Zn, Cu, U, ...)
- stable isotopes (I) (C, O, H, N, S)
- stable isotopes (II) (B, Sr, Zn, Nd, Mo, Pb, ...)

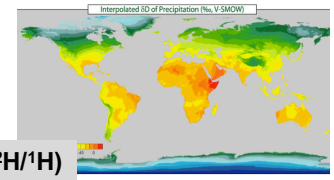


- identification of sources, transport pathways and sinks of contaminants, matter,...
- differentiate between natural and anthropogenic sources
- understand impacts of extreme events and their short and mid-term effects

ELEMENTAL AND ISOTOPIC DISTRIBUTION MAPS - ISOSCAPES

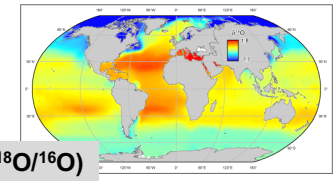
- distribution maps of isotopes for aquatic and terrestrial systems
- spatially resolved explicit predictions of distributions of chemical and physical parameters in a Geographic Information System (GIS).
- first presented by Jason West and Gabriel Bowen in 2005





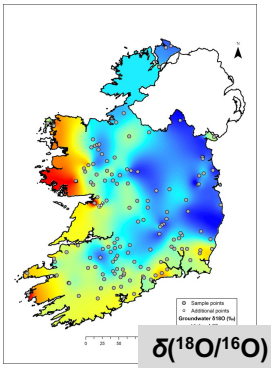
$\delta(^2H/^1H)$

http://www.animalmigration.org/stable_isotopes/index.htm

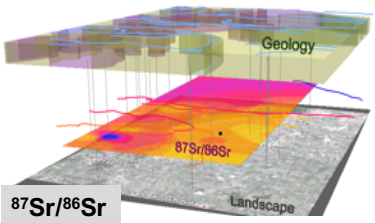


$\delta(^{18}O/^{16}O)$

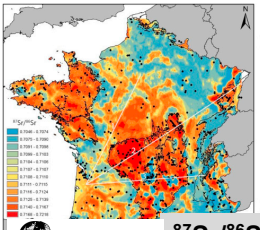
https://keltonmcmahon.sites.ucsc.edu/page-builder/ocean-isoscapes/



$\delta(^{18}O/^{16}O)$



$^{87}Sr/^{86}Sr$



IRHUM

$^{87}Sr/^{86}Sr$

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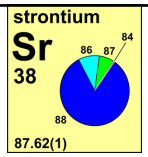
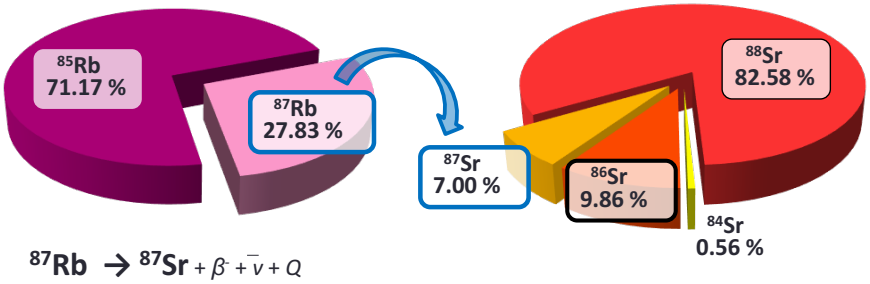


Sr isotopic system

Rubidium **Strontium**

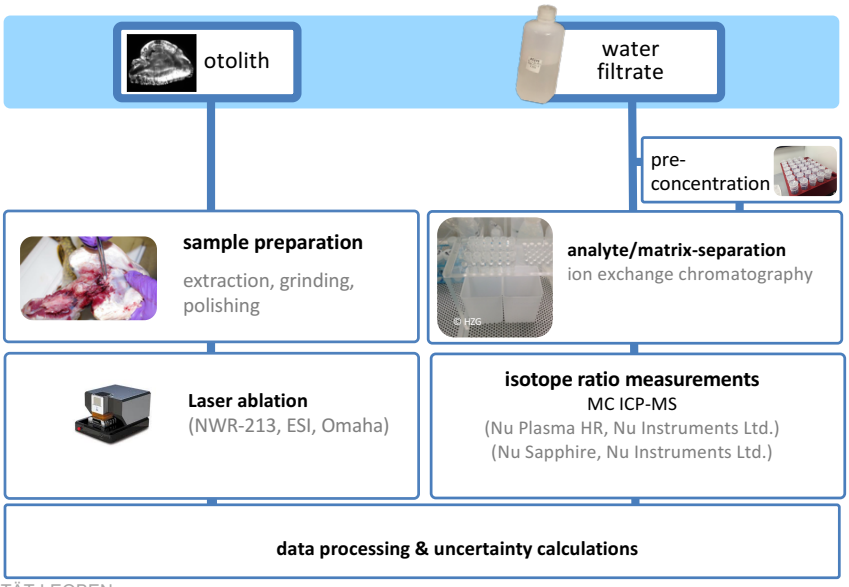


$^{87}Rb \rightarrow {}^{87}Sr + \beta^- + \bar{\nu} + Q$

$T_{1/2}$ … half life ($T_{1/2}$ = 48.8 x 10^9 a)

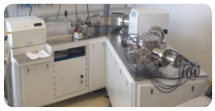
Variation of $^{87}Sr/^{86}Sr$ with geological origin
- geochemical composition
- geological age

Experimental protocol - Example



Sr isotopic analysis via MC ICP-MS

Sample preparation



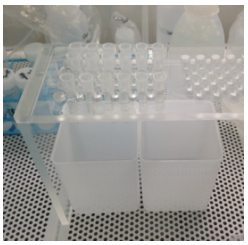
- Requires a measurement solution containing only the analyte
- Sr isotopic composition suffers from isobaric and polyatomic spectral interferences

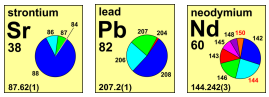
Sr
$^{84}Kr^{+}$, $^{86}Kr^{+}$, $^{87}Rb^{+}$, REE^{2+}, Ca-dimers, Ca-argides

- Substantial amounts of matrix elements (Ca, Mg, Na etc) can lead to signal suppression and changes in the instrumental isotopic fractionation

ANALYTE / MATRIX SEPARATION

- Chromatography (LP, HP)
  - **Off line separation**
  - On line separation
  - **Automated separation**
- Gas phase separation
  - Evaporation
  - Hydride formation
- Membrane separation
- Diffusive Gradient in Thin Films (DGT)

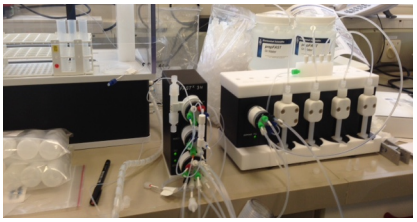


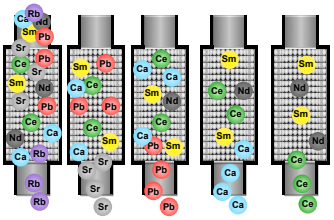


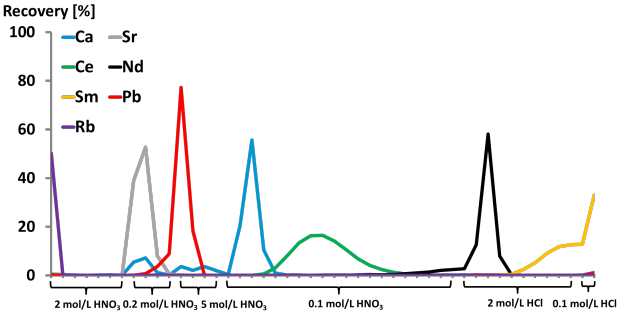
Analyte/matrix separation
ESI prepFAST-MC™ system

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

prep*FAST-MC*
(ESI Elemental Scientific)
resin: Sr, Pb, Nd: Sr spec, DGA resin (EIChrom)







Retzmann A, Zimmermann T, Pröfrock D, Prohaska T, Irrgeher J, ANAL BIOANAL CHEM, 2017

Zimmermann T, Retzmann A, Schober M, Pröfrock D, Prohaska T, Irrgeher J, SPECTROCHIM ACTA B 2018

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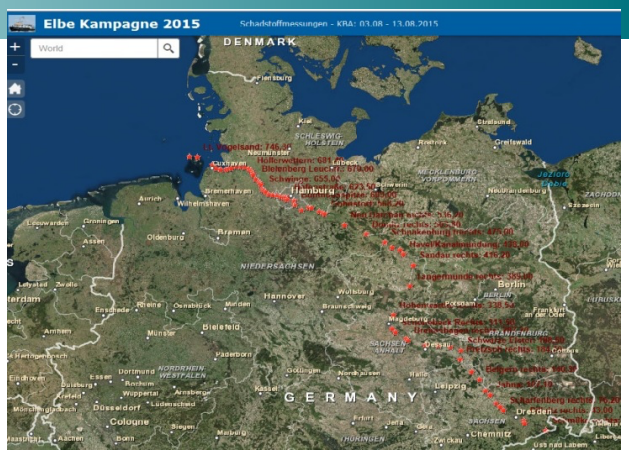
Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

German North Sea Catchment
Establishment of multi-element and isotopic landscapes

Johanna Irrgeher
Daniel Pröfrock & colleagues from Hereon



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MULTI-LAYER APPROACH – **SEDIMENT**: Multielemental and multi-isotopic data

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Highly dynamic area

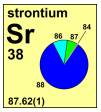
- Dredging / large deepening projects
- Ship traffic
- Dumping of harbour sediment
- Sediment transport by tidal pumping

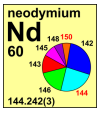
➢ Combination of multielemental fingerprinting and isotope ratio analysis
➢ Quantification of 48 elements and Sr, Nd and Pb isotope ratios in total sediment digest

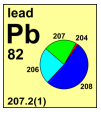
Reese, A., Zimmermann, T., Pröfrock, D., Irrgeher, J. (STOTEN 668 (2019) 512–523)

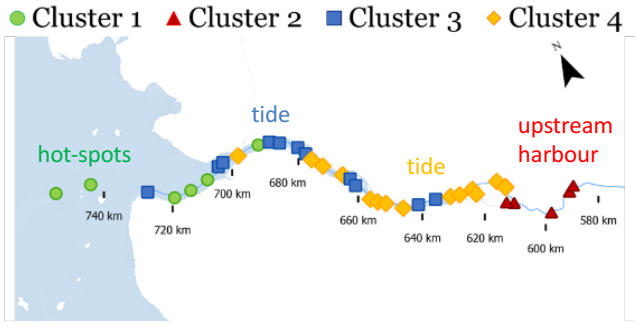
RESULTS – ELBE **SEDIMENT**: Sr-, Nd-, Pb-isotope ratios

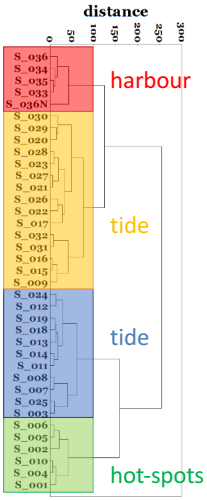
Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research











Clustering by

- $n(^{208}Pb)/n(^{204}Pb)$
- $n(^{87}Sr)/n(^{86}Sr)$
- Cr
- Rb
- Zn
- Mn

➢ **Basemap for river and harbor management**

Reese, A., Zimmermann, T., Pröfrock, D., Irrgeher, J. (STOTEN 668 (2019) 512–523)

ISOSCAPEs in MONGOLIA

LASS ICP-QMS/MC ICP-MS

Simultaneous multielement and isotope imaging by laser ablation split stream ICP-MS/MC ICP-MS to investigate fish migration

Prohaska, T., J.Irrgeher, and A.Zitek.
Journal of Analytical Atomic Spectrometry 31.8 (2016): 1612-1621.

Andreas Zitek
Johanna Irrgeher
Thomas Prohaska

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Contribution to BIOTOXMET

1.1.3. MEASUREMENT OF $^{87}Sr/^{86}Sr$ ISOTOPE RATIOS IN WATER

$^{87}Sr/^{86}Sr$ isotope ratios in the river water samples will be measured by double-focusing sector field MC ICP-MS (Nu Plasma HR, Nu Instruments, Ltd). External calibration will be performed by application of the reference material SRM986 SrCO3 (NIST). For isotope analysis, samples will be subjected to Rb/Sr separation procedure (Retzmann et al., 2017) using prepFAST–MC system (Elemental Scientific).

2.4. MEASUREMENT OF METAL CONCENTRATIONS IN FISH CALCIFIED STRUCTURES

Calcified structures will be cleaned by Milli-Q water and dried. Otoliths will be ground and polished. For each sample 4-6 scales will be prepared and mounted on small glass slides using adhesive tape and the scale with the most visible growth zones per sample will be analyzed. Measurement of metals will be conducted by connecting a laser ablation system (NWR193, Electro Scientific Industries) to an ICP-QMS (NexION 350D, PerkinElmer) and the laser lines will be taken through the middle of the hard tissues. Calcium, as a main element in the aragonite of otoliths and hydroxyapatite of scales, will be used as internal standard.

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