Sr-Nd-Pb fingerprints of River Weser (Germany) and its implication to trace anthropogenic impacts - towards an automated and unsupervised analytical approach

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BACKGROUND AND AIMS OF STUDY

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Weser River System:

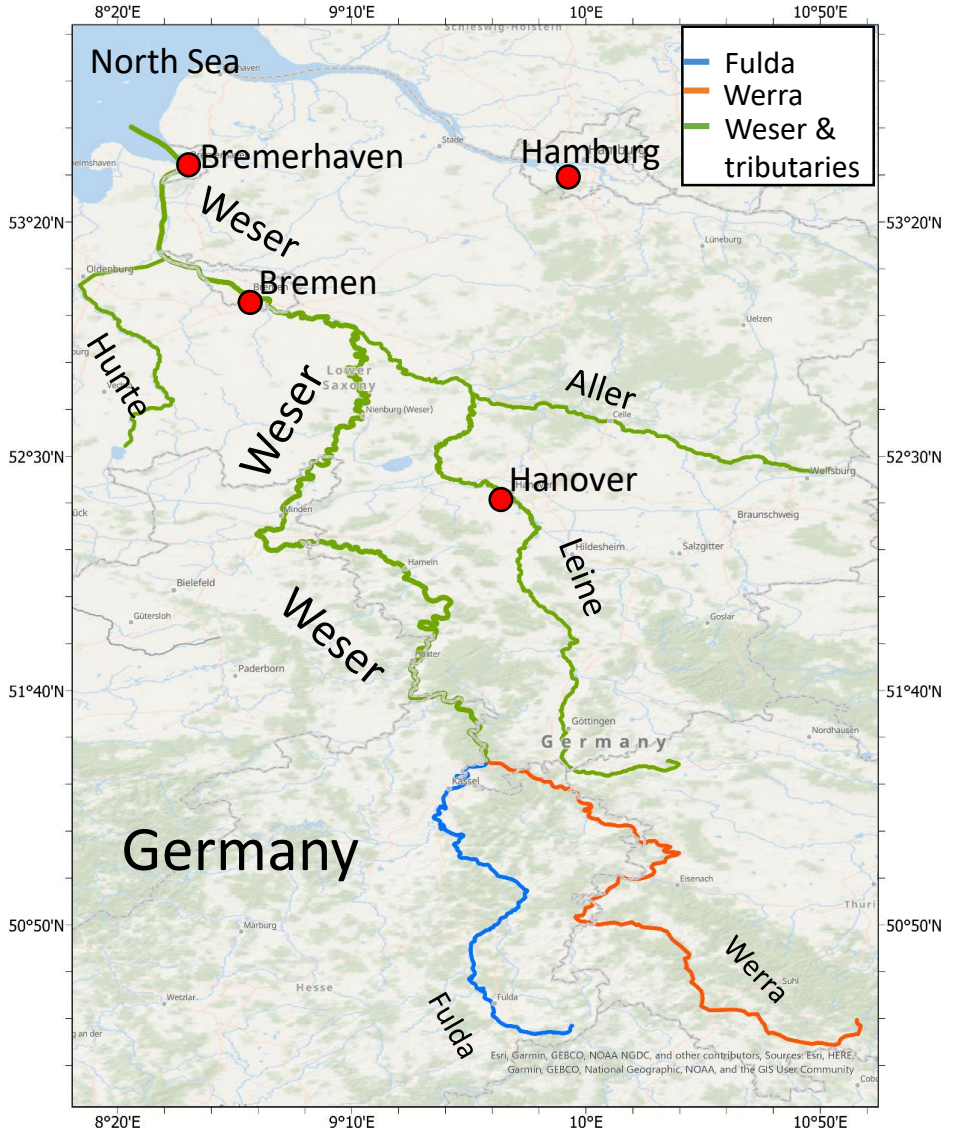
- The largest river entirely located in Germany;
- Discharge into the North Sea;
- Historically polluted and still under the modern pressure of human activities (e.g. agriculture, mining) and extreme climate events (e.g. flooding).

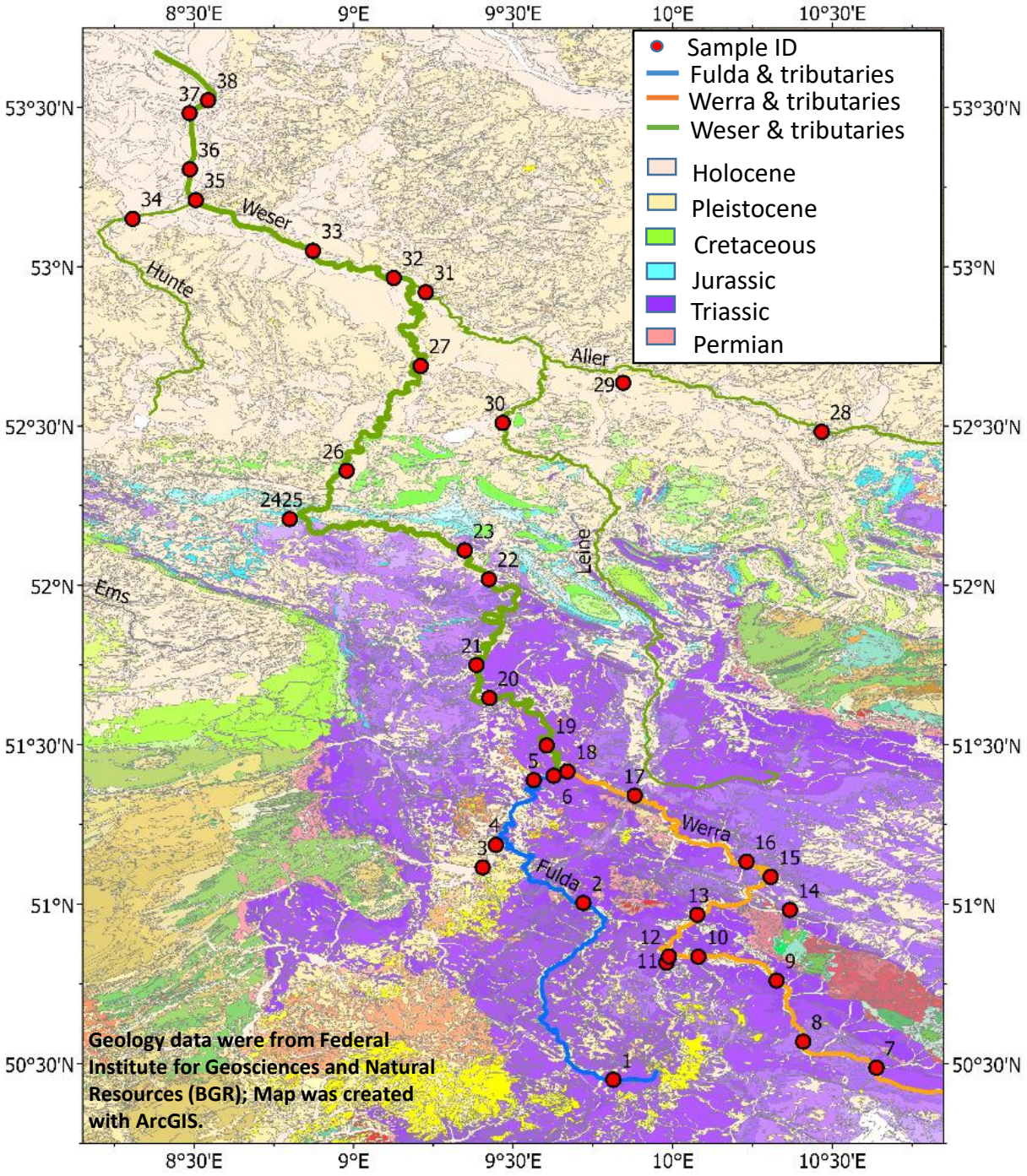
Aims:

- To map Sr, Nd, Pb isotopes for the Weser river system- the first such dataset;
- To explore the potential of employing the unsupervised statistical analysis (k-means cluster analysis) of the isotope data as a tool to

- identify natural versus anthropogenic processes of the Weser river system;

- trace anthropogenic sources and transport.





Study site and material

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Weser River:

- Hydrological settings:
  - Drainage basin: 46339 km^2;
  - Length: 451.4 km (751 km including Werra);
  - Mean annual discharge: 327 m^3/s;
  - Headwaters: Fulda and Werra;
  - The largest tributary: Aller, and is historically polluted by mining activities in Mount Harz.
- Geological settings:
  - Fulda (sample 1-6) and Werra(sample 7-18): Paleozoic-Mesozoic rocks;
  - Upper Weser (sample 19-23): Mesozoic rocks;
  - Middle Weser (sample 26-27, 32-33) and Lower Weser (sample 35-38): Pleistocene- Holocene sedimentary rocks;

Study Material:

- 38 sediment samples were collected along Weser and its tributaries (Hunte, Aller, Leine, Werre) and headwaters, Fulda and Werra.

Analytical methods

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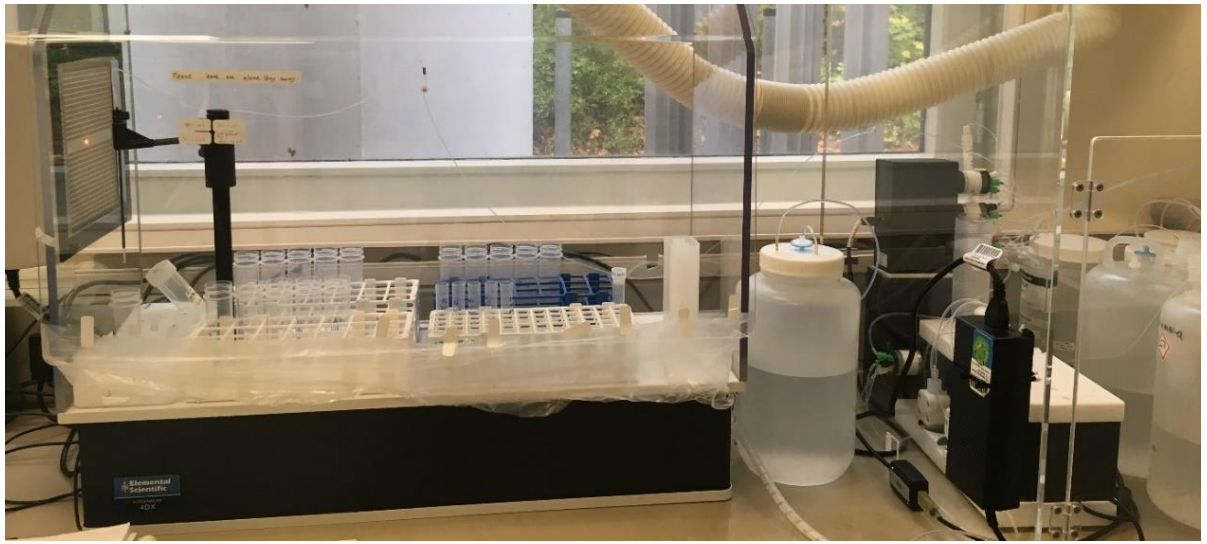
prepFAST-MC (Elemental Scientific, USA)
in Class 100-1000 clean laboratory, HZG, Germany



Nu II MC-ICP-MS (Nu instruments, UK)
in Class 100-1000 clean laboratory, HZG, Germany

- Sr, Nd, Pb isotope analysis :

  - Fully automated prepFAST sample purification: cost- and time-effective compared with conventional bench-top purification (Retzman et al. 2017, Anal. Bioanal. Chem.);

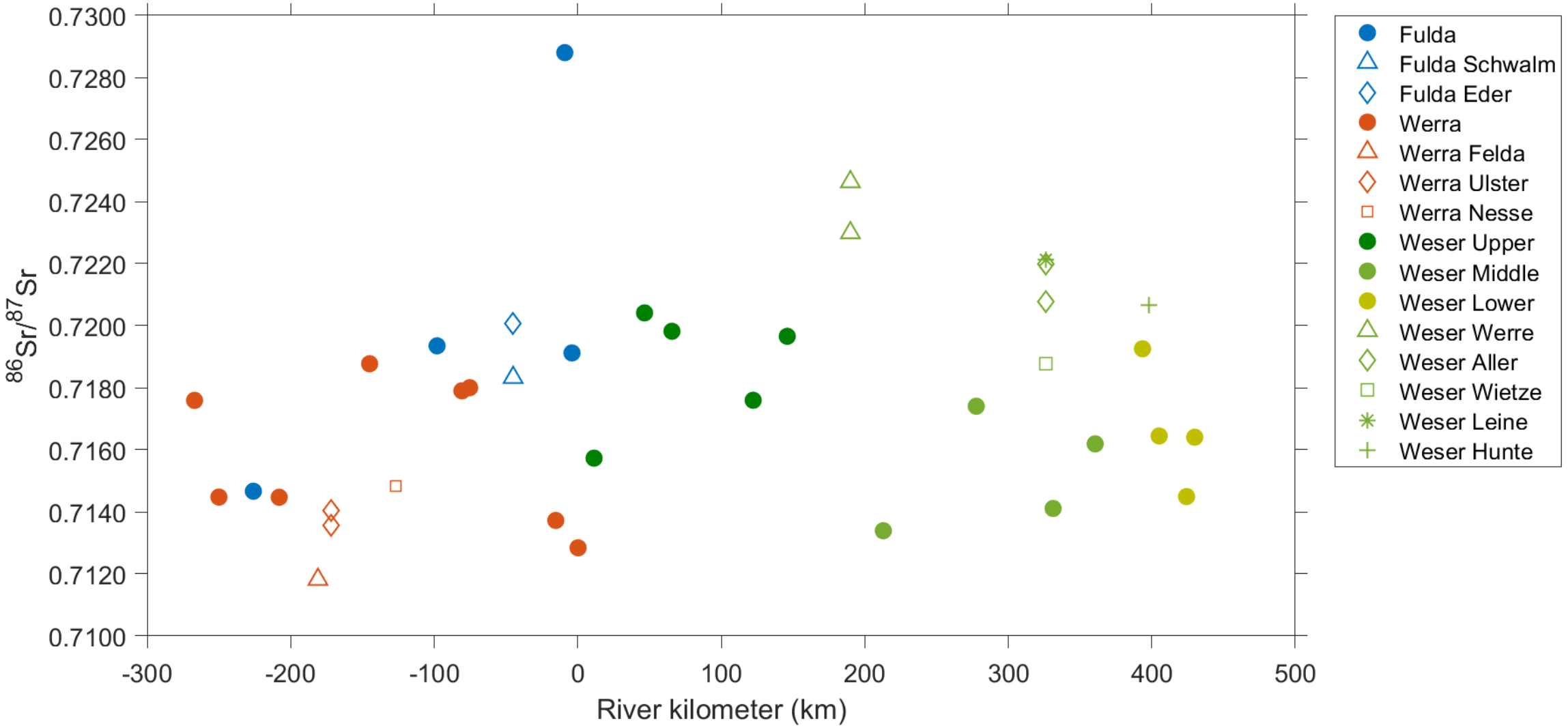
  - Nu II MultiCollector-InductivelyCoupledPlasma-MassSpectrometry (MC-ICP-MS): reliable, high-precision isotope data generation.

- Elemental composition:

  - Quadrupole ICP-MS (8800 Triple Quad, Agilent Technologies, Japan).

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

$^{87}Sr/^{86}Sr$ range: 0.71182 - 0.72880
River Weser: 0.71339 - 0.72041
Mean 2 standard deviation (2se): ±0.00013

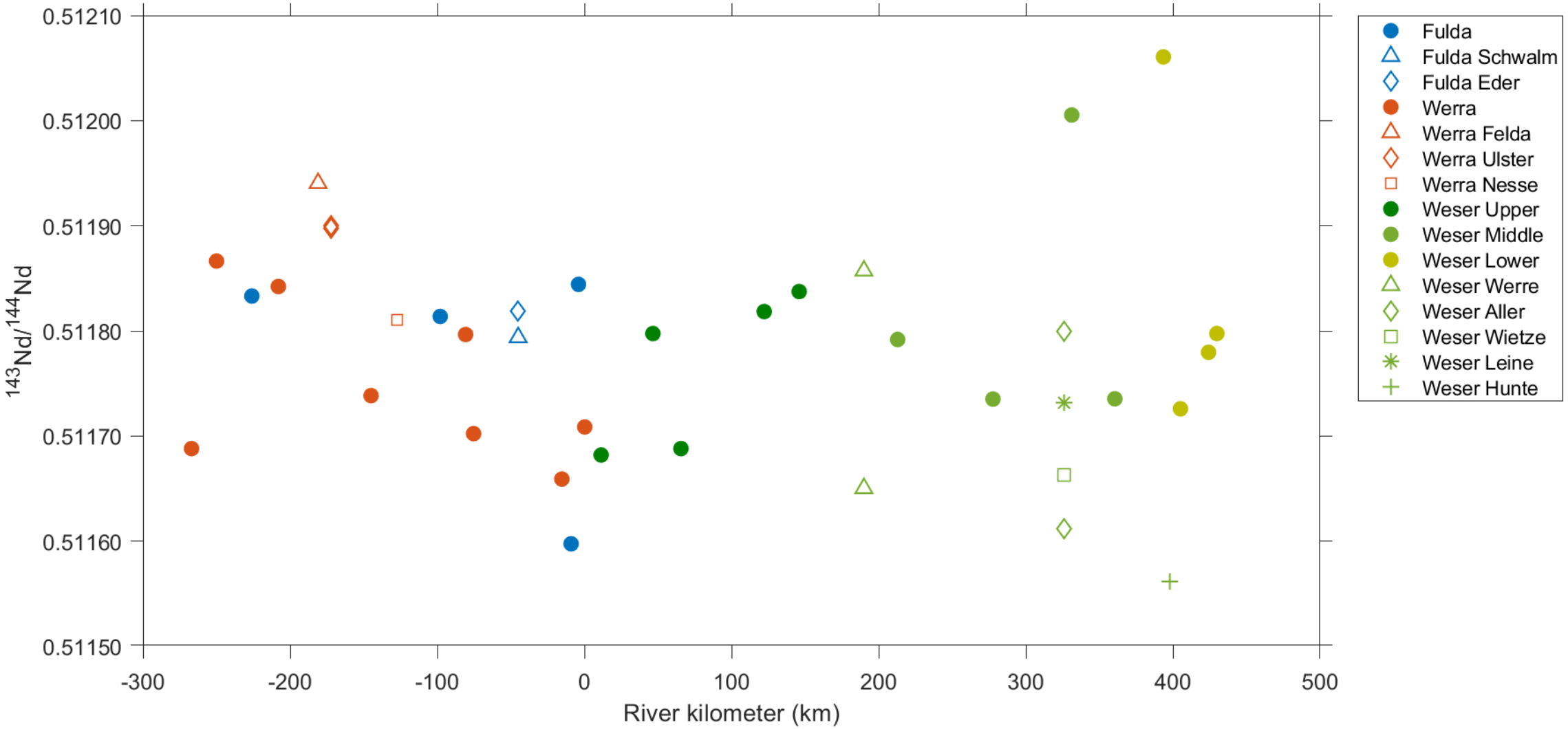


Result: $^{143}Nd/^{144}Nd$

$^{143}Nd/^{144}Nd$ range: 0.511561 – 0.512061

River Weser: 0.511682 - 0.512061

Mean 2se: ±0.000032



Result: Pb isotopes

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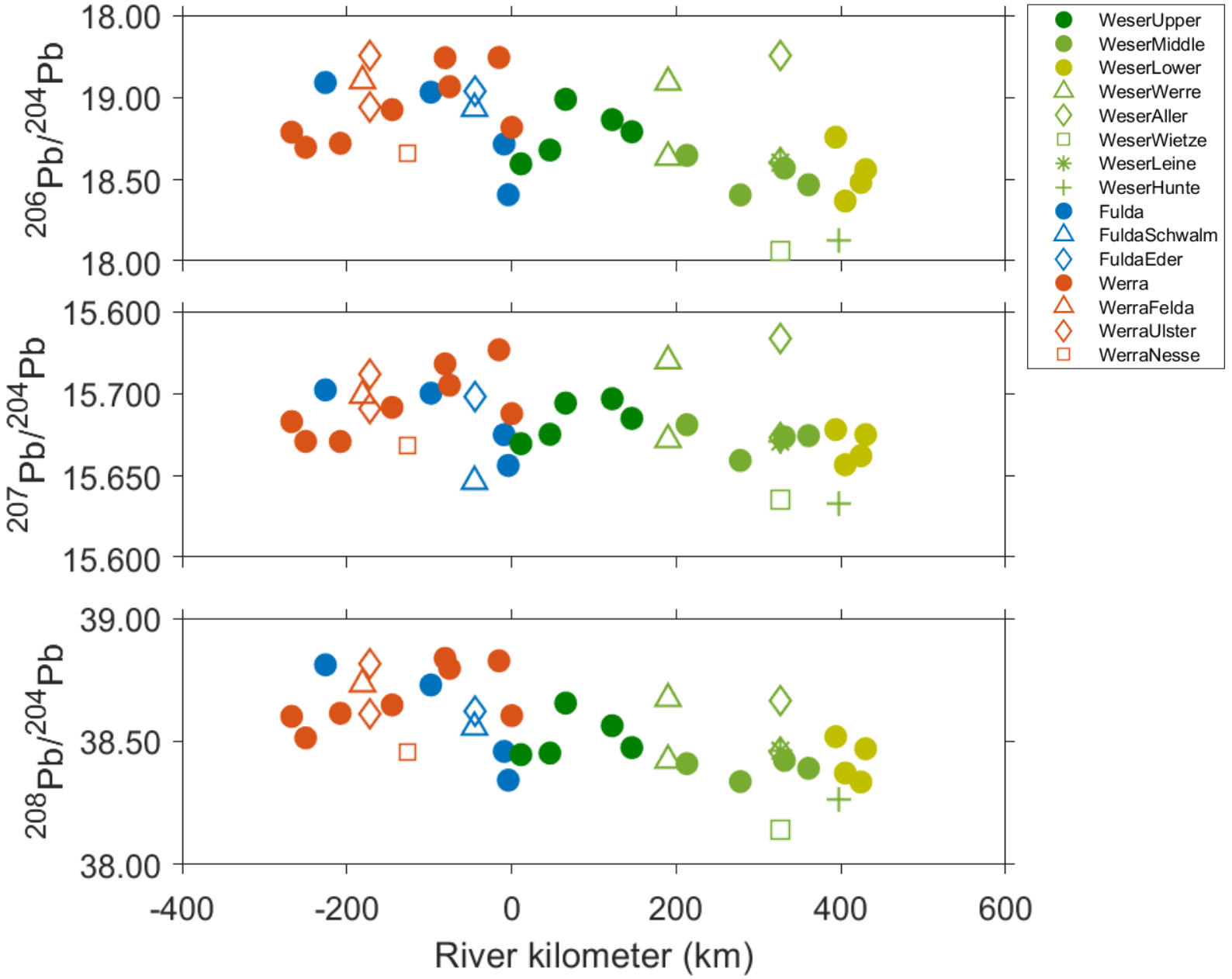

$^{206}Pb/^{204}Pb$ range: 18.226 to 18.703
Mean 2se: ±0.030

$^{207}Pb/^{204}Pb$ range : 15.613 to 15.653
Mean 2se: ±0.0033

$^{208}Pb/^{204}Pb$ range: 38.144 to 38.837
Mean 2se: ±0.051

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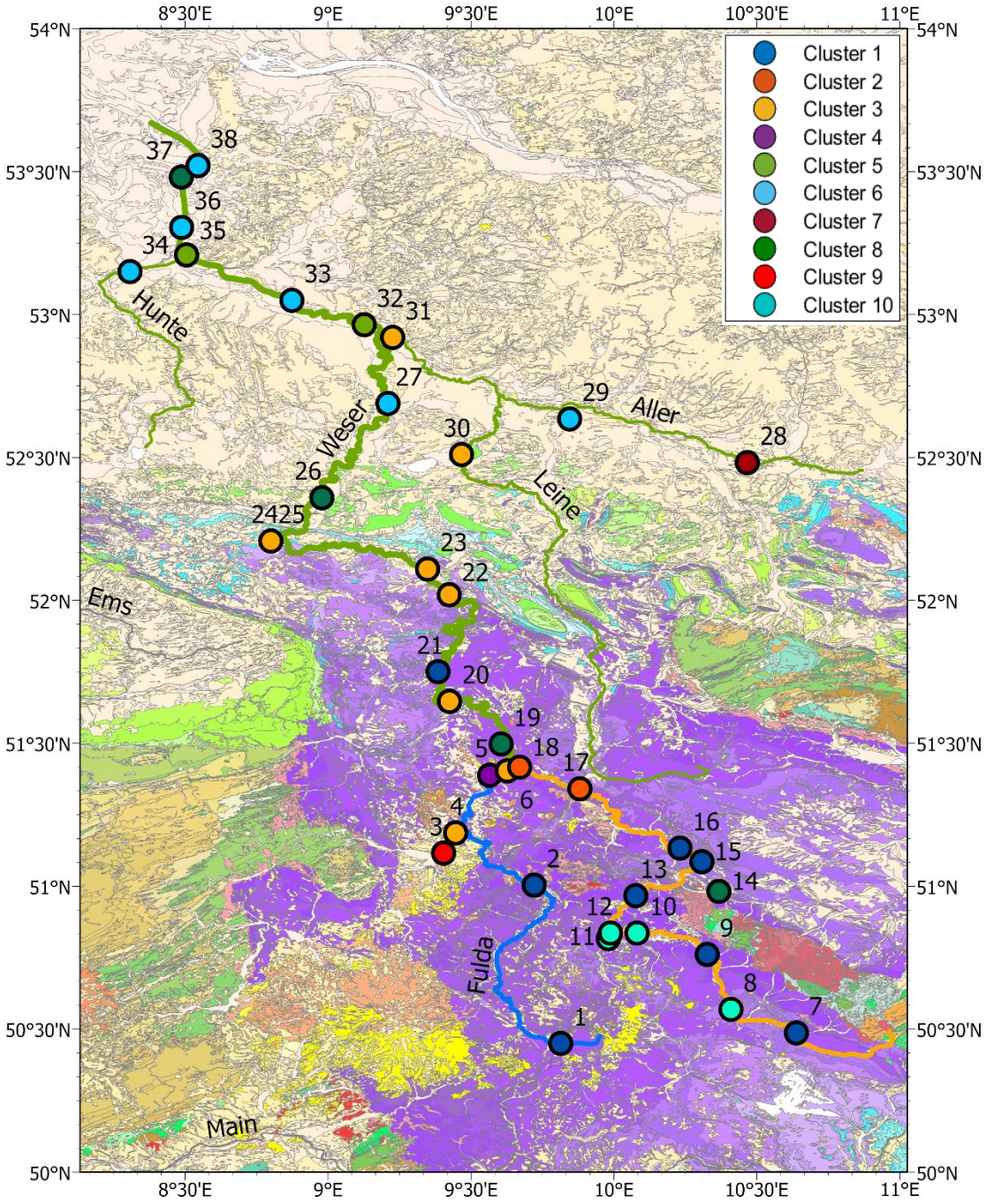
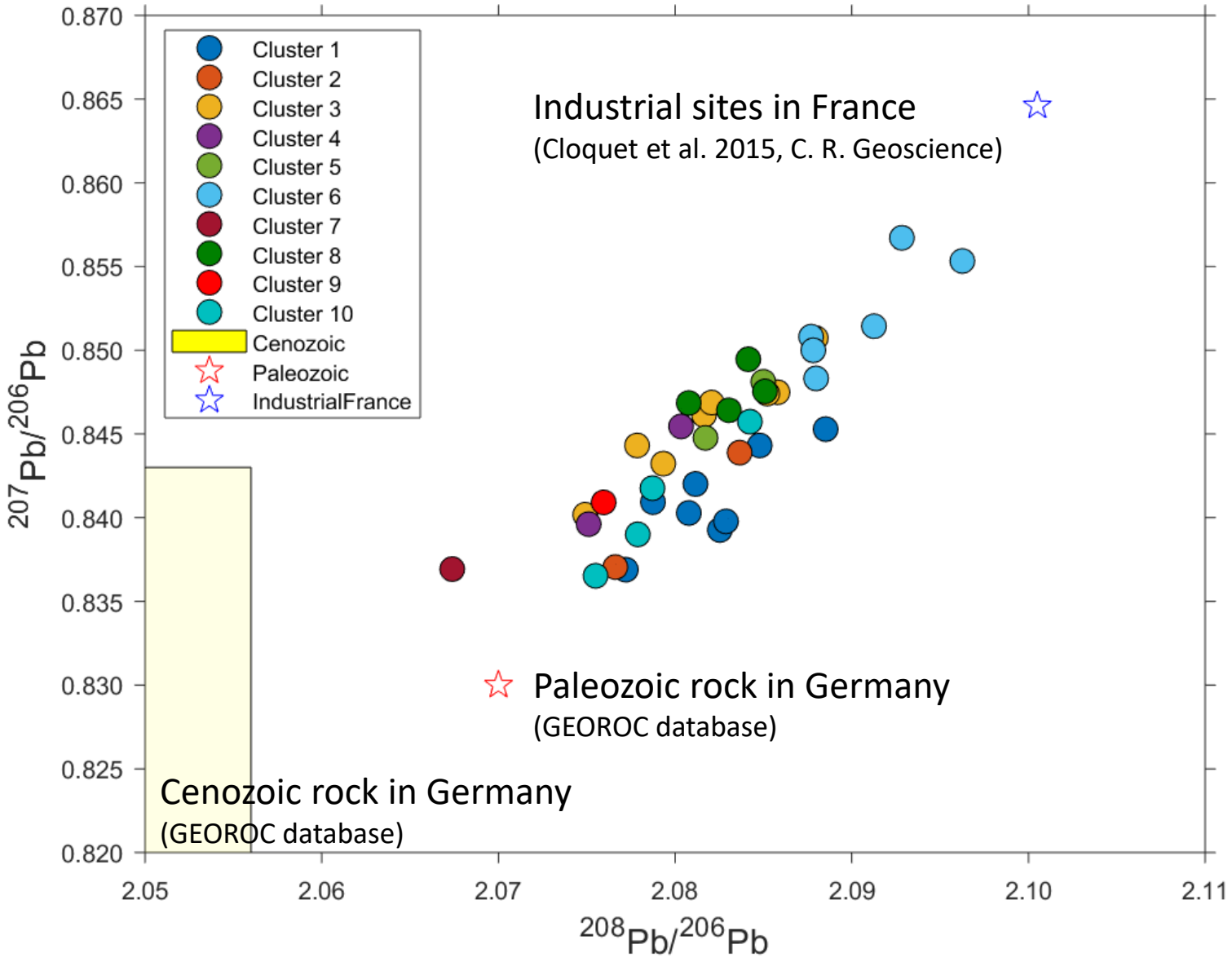
Unsupervised K-means Cluster Analysis



- K-means cluster analysis (KCA) was performed with Matlab using $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios;
- Data were standardized (mean=0, standard deviation=1) and whitened before KCA;
- The optimal cluster number was evaluated with Silhouette , CalinskiHarabasz, and Gap criteria;
- An optimal cluster number of 10 was obtained, and KCA was conducted with a replicate of 10,000 to converge.
- Samples were partitioned into 10 clusters shown on the map.

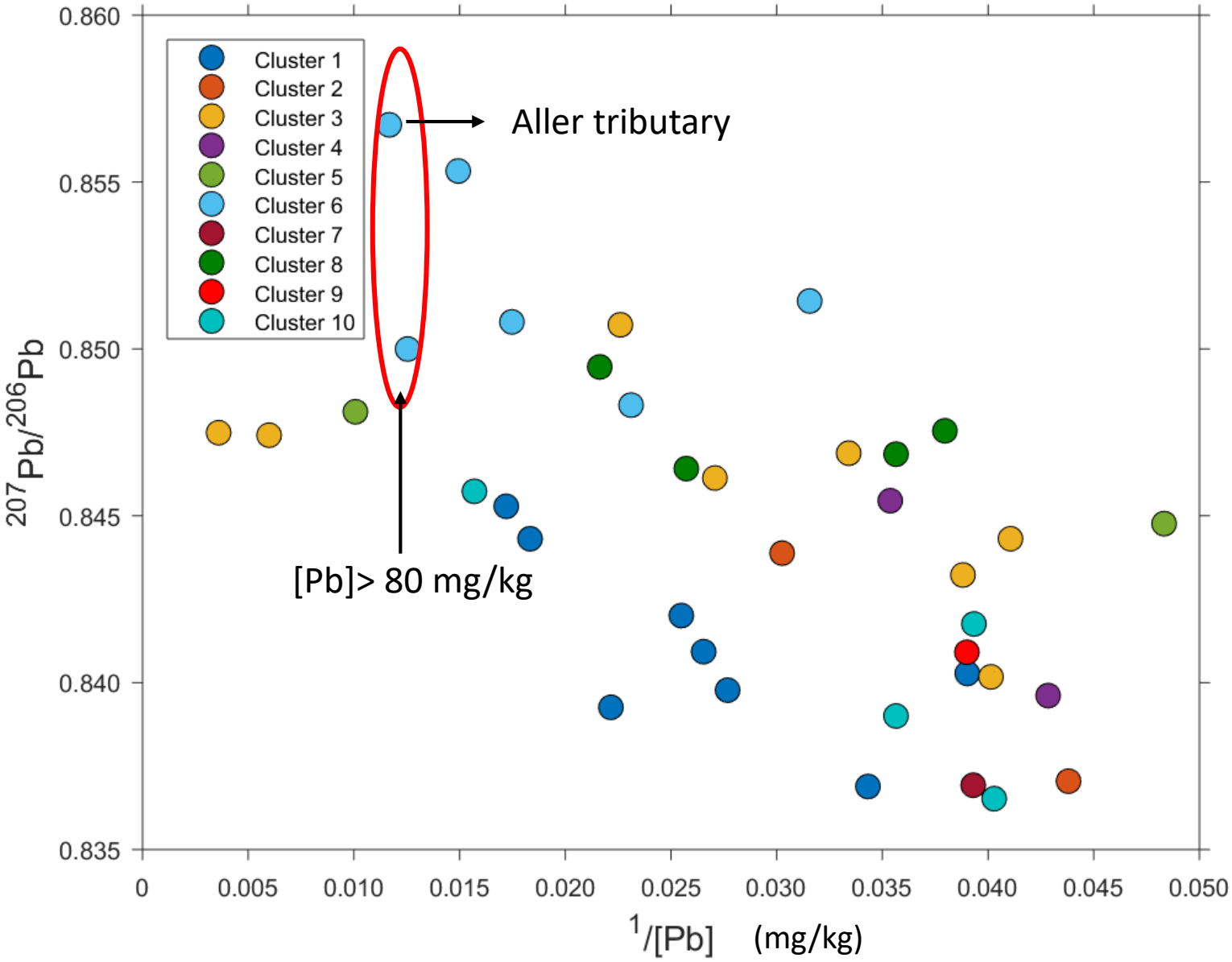
Geographic region	Main cluster	Cluster symbol
Lower and Middle Weser	Cluster 6	
	Cluster 5	
Upper Weser	Cluster 3	
Fulda and Werra	Cluster 1	

Identifying Natural v.s. Anthropogenic signals



- KCA revealed a cluster, cluster 6, with features distinctively different from other clusters: $^{207}Pb/^{206}Pb$ (0.848-0.857) and $^{208}Pb/^{206}Pb$ (2.088-2.096) fall within the higher range;
- Cluster 6 can be identified as an Anthropogenic cluster:
  - Cluster 6 includes samples collected in regions draining a geologically young basin (Pleistocene-Holocene), but deviates significantly from the range of Holocene Pb isotopic ratios;
  - The distinctive feature (high Pb isotopic ratios) of Cluster 6 can only be explained by a significant anthropogenic input.

Tracing anthropogenic source and transport



2 samples from cluster 6 with very high Pb concentrations ([Pb]):

- Geographic location:
  one sample collected from River Aller tributary, the other from River Weser after the joining of Aller.

- Indicative of anthropogenic signal from Aller, and is to some extent being transported to the River Weser.

- Suggests other anthropogenic sources to other samples in the cluster with no significantly high Pb concentrations.

SUMMARY

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- Fully-automated sample purification system and high-precision MC-ICP-MS were employed to generate the first Sr, Nd, Pb isotope dataset from 38 sediment samples along River Weser, its tributaries and headwaters (Fulda and Werra);
- Unsupervised K-means cluster analysis (KCA) was performed on the Sr, Nd, and Pb isotope data, resulting in samples being partitioned into 10 clusters;
- KCA results reveal a distinctive cluster (high $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$) indicative of significant anthropogenic influence in the Middle to Lower Weser region;
- High Pb concentrations correspond to 2 samples in the anthropogenic cluster, and signal an anthropogenic source originating form River Aller, a heavily polluted area very likely due to the historical mining activities in Harz;
- Anthropogenic signal from River Aller is transported to River Weser after joining of Aller, but the lower regions of River Weser is affected by other sources anthropogenic influence.

Thank you for your attention!

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We would like to hear about your comments.

REFERENCES

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Retzmann, A., Zimmermann, T., Pröfrock, D., Prohaska, T., Irrgeher, J., 2017. A fully automated simultaneous single-stage separation of Sr, Pb, and Nd using DGA Resin for the isotopic analysis of marine sediments. Analytical and Bioanalytical Chemistry 409, 5463-5480.

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