

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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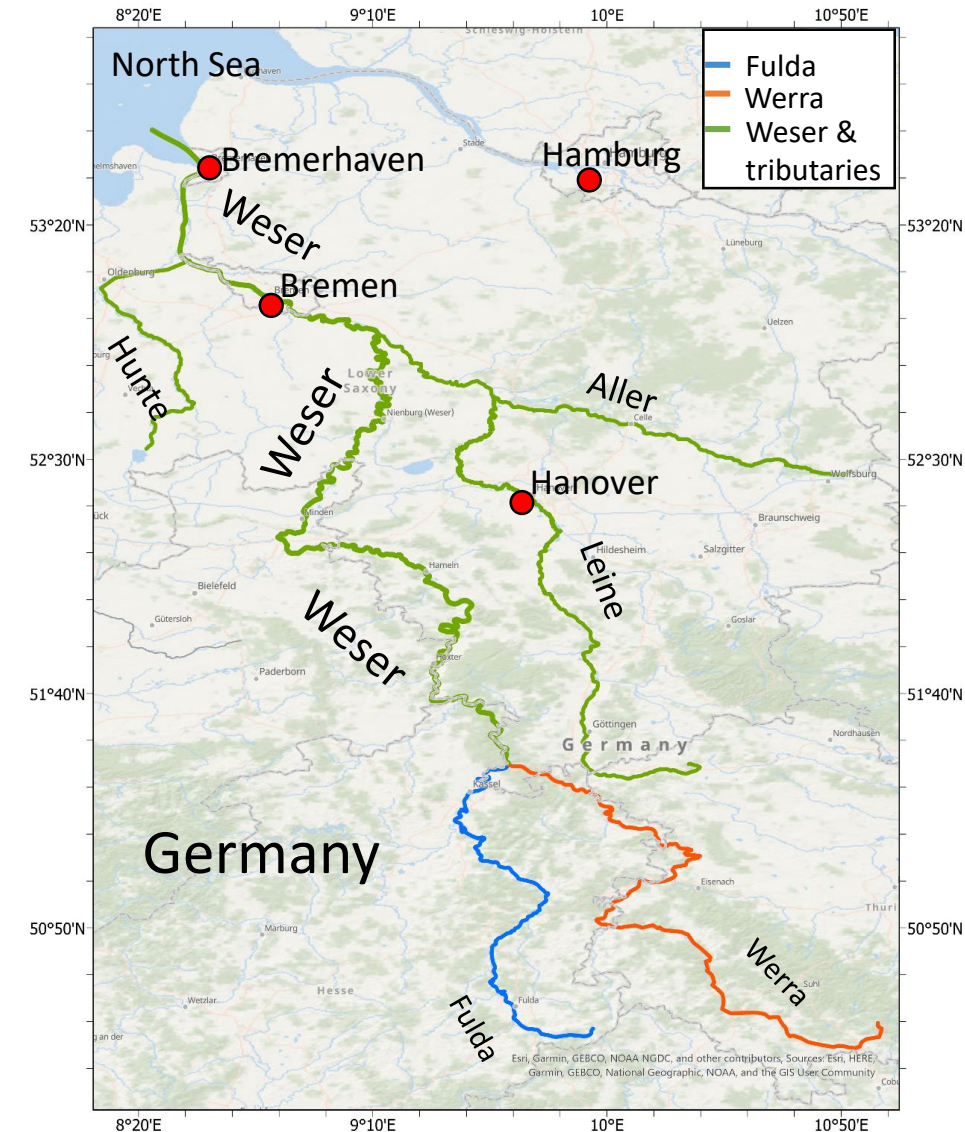
BACKGROUND AND AIMS OF STUDY

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.



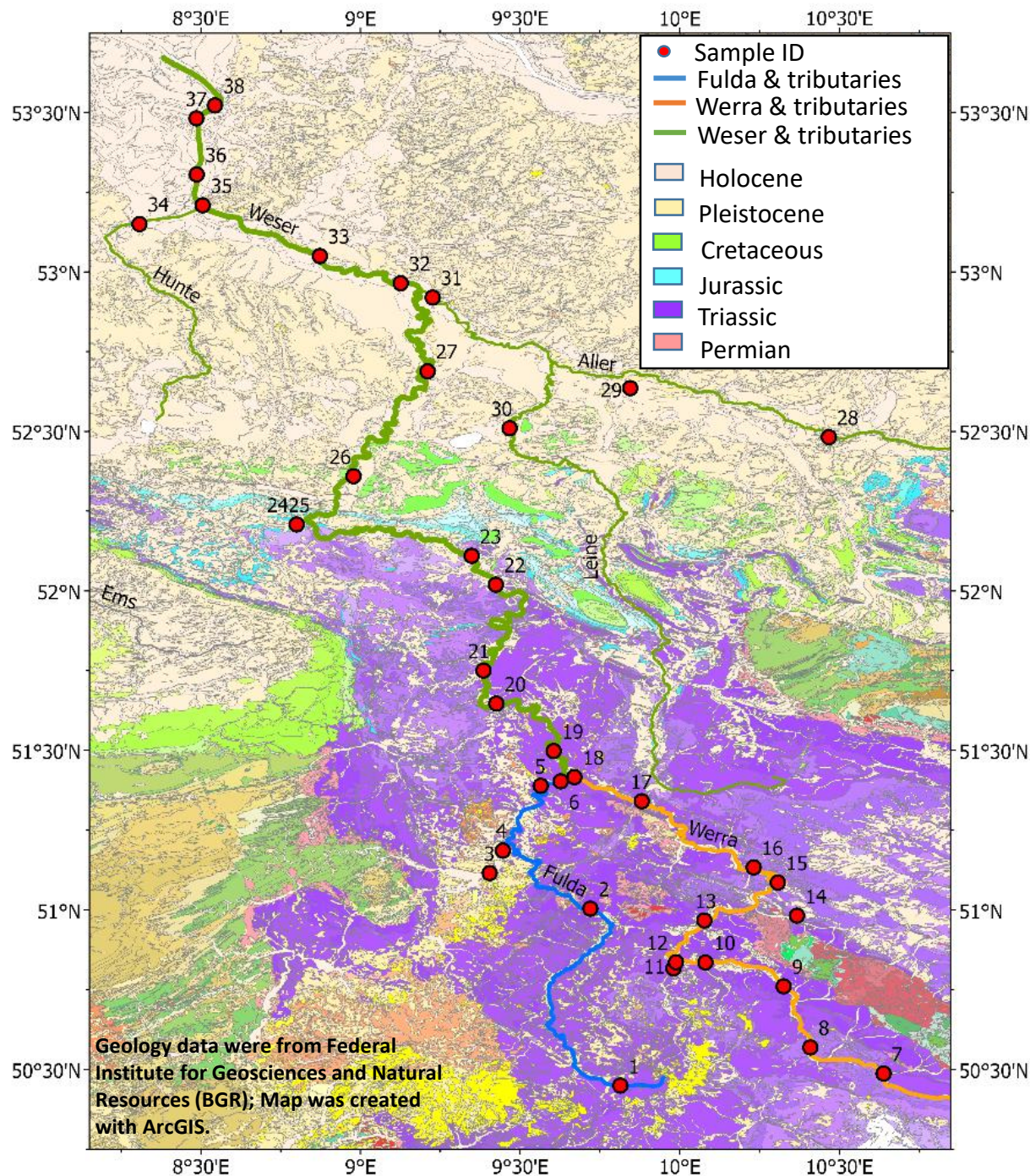
Study site and material

Weser River:

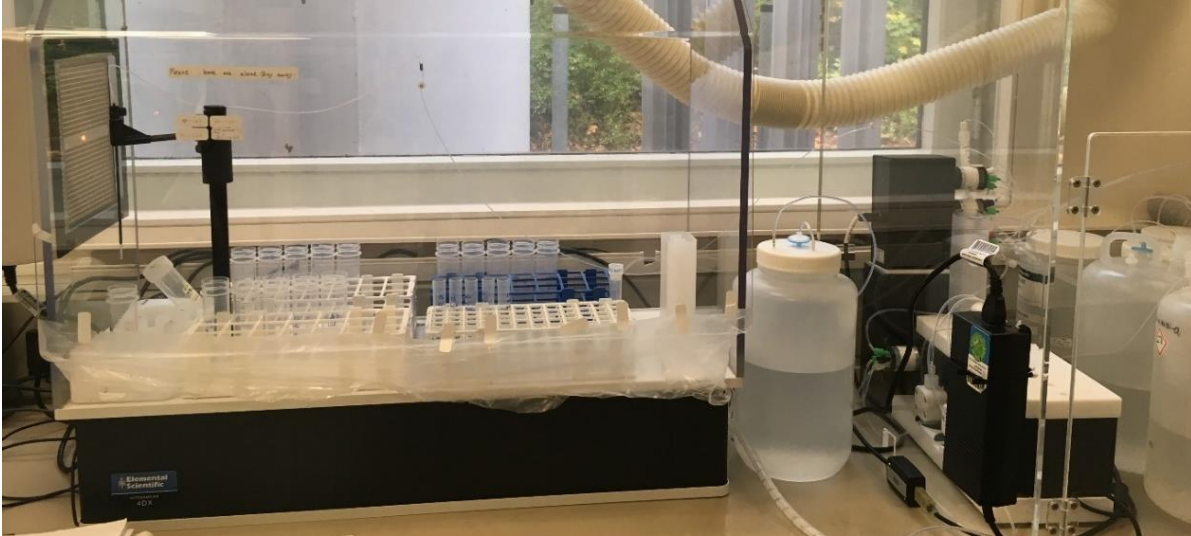
- Hydrological settings:
 - Drainage basin: 46339 km²;
 - Length: 451.4 km (751 km including Werra);
 - Mean annual discharge: 327 m³/s;
 - Headwaters: Fulda and Werra;
 - The largest tributary: Aller, and is historically polluted by mining activities in Mount Harz.
- Geological settings:
 - Fulda (sample 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.



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



Analytical methods

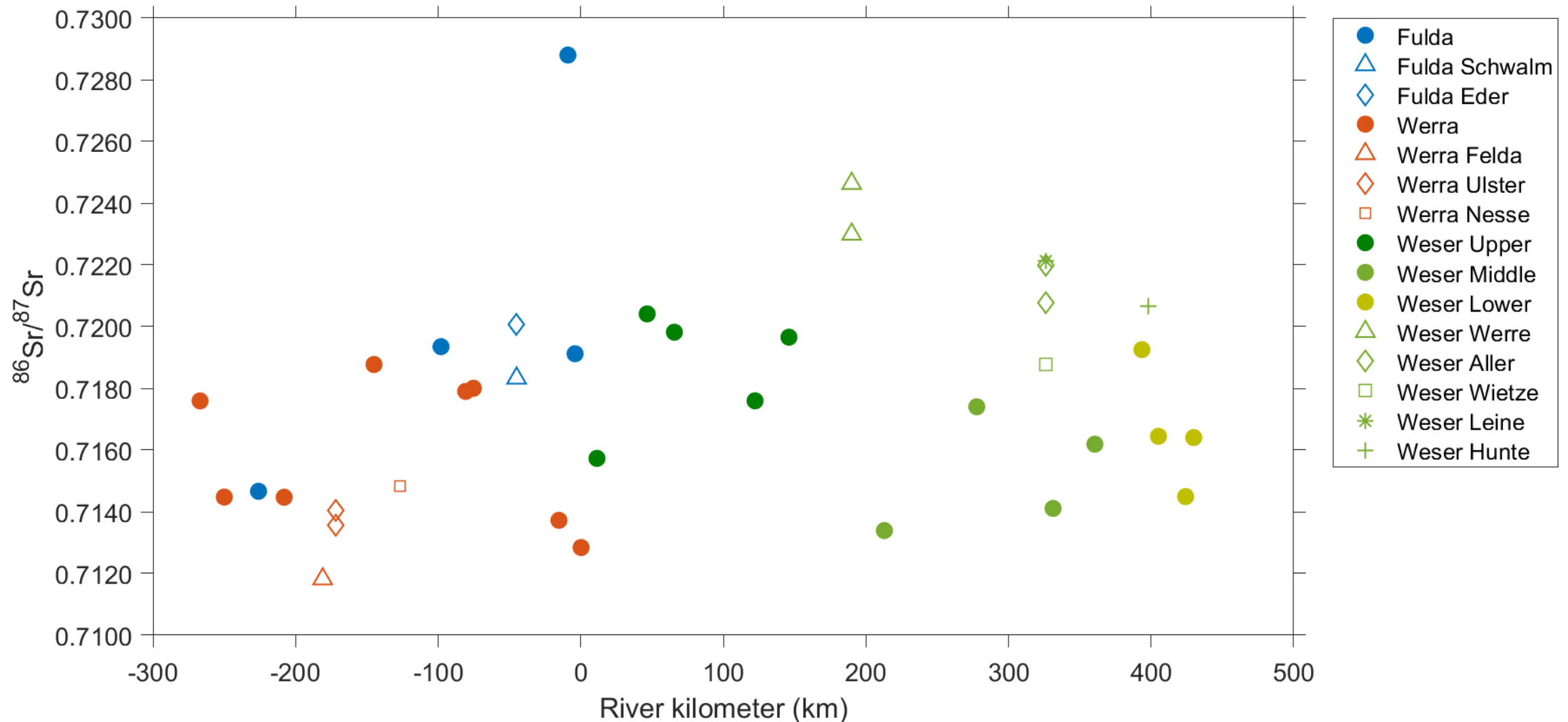
- Sr, Nd, Pb isotope analysis :
 - **Fully automated** prepFAST sample purification: cost- and time-effective compared with conventional bench-top purification (Retzman et al. 2017, Anal. Bioanal. Chem.);
 - Nu II MultiCollector-InductivelyCoupledPlasma-MassSpectrometry (MC-ICP-MS): reliable, high-precision isotope data generation.
- Elemental composition:
 - Quadrupole ICP-MS (8800 Triple Quad, Agilent Technologies, Japan).

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

$^{87}\text{Sr}/^{86}\text{Sr}$ range: 0.71182 - 0.72880

River Weser: 0.71339 - 0.72041

Mean 2 standard deviation (2se): ± 0.00013

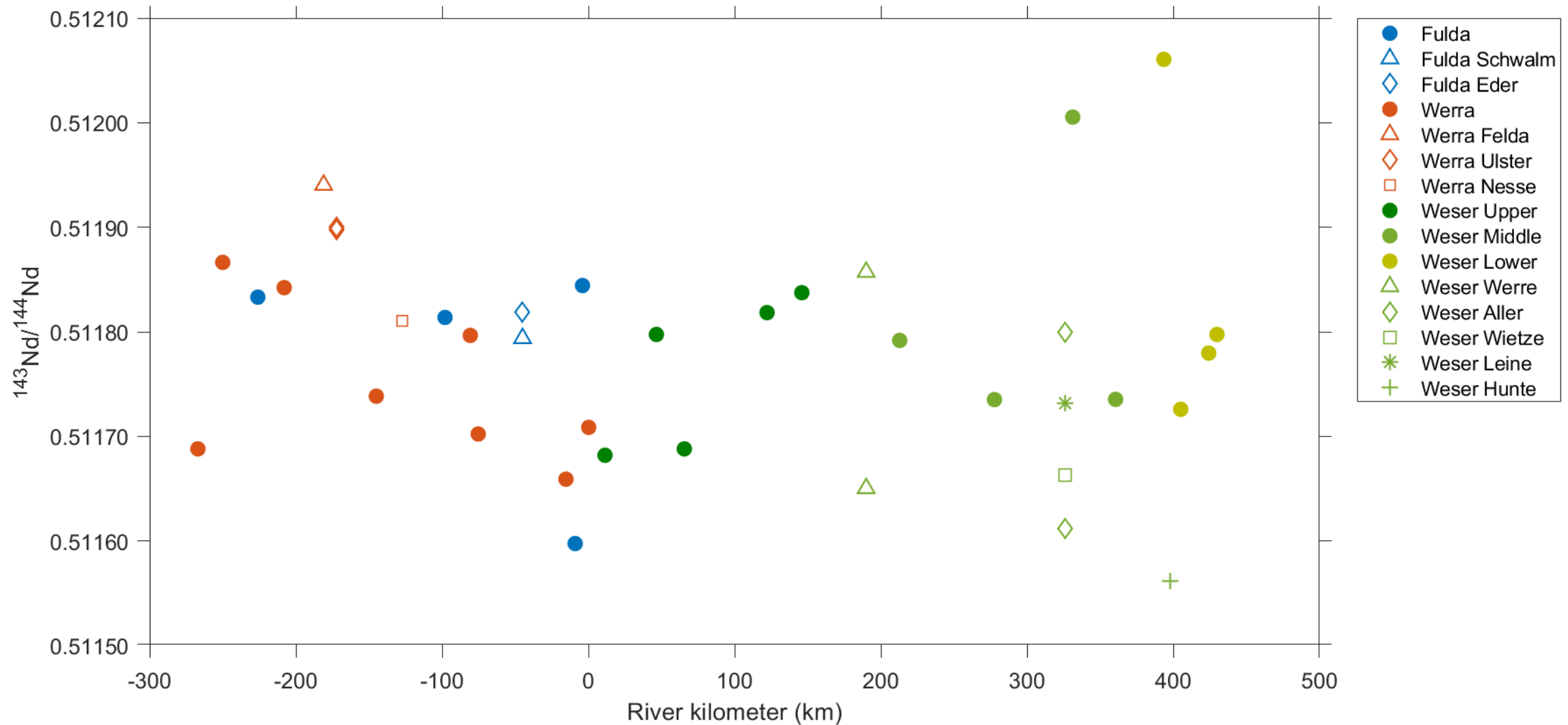


Result: $^{143}\text{Nd}/^{144}\text{Nd}$

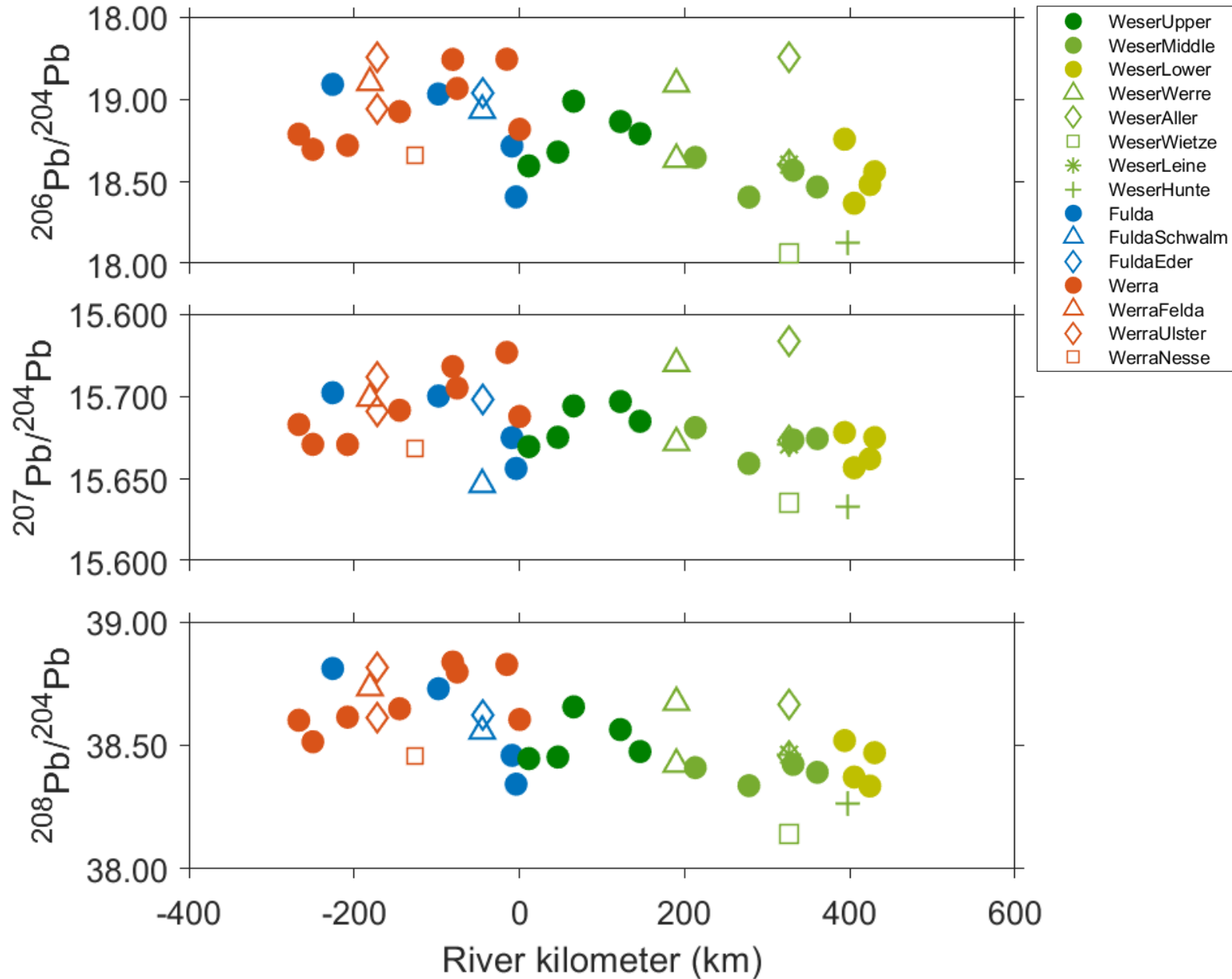
$^{143}\text{Nd}/^{144}\text{Nd}$ range: 0.511561 – 0.512061

River Weser: 0.511682 - 0.512061

Mean 2se: ± 0.000032



Result: Pb isotopes



$^{206}\text{Pb}/^{204}\text{Pb}$ range: 18.226 to 18.703

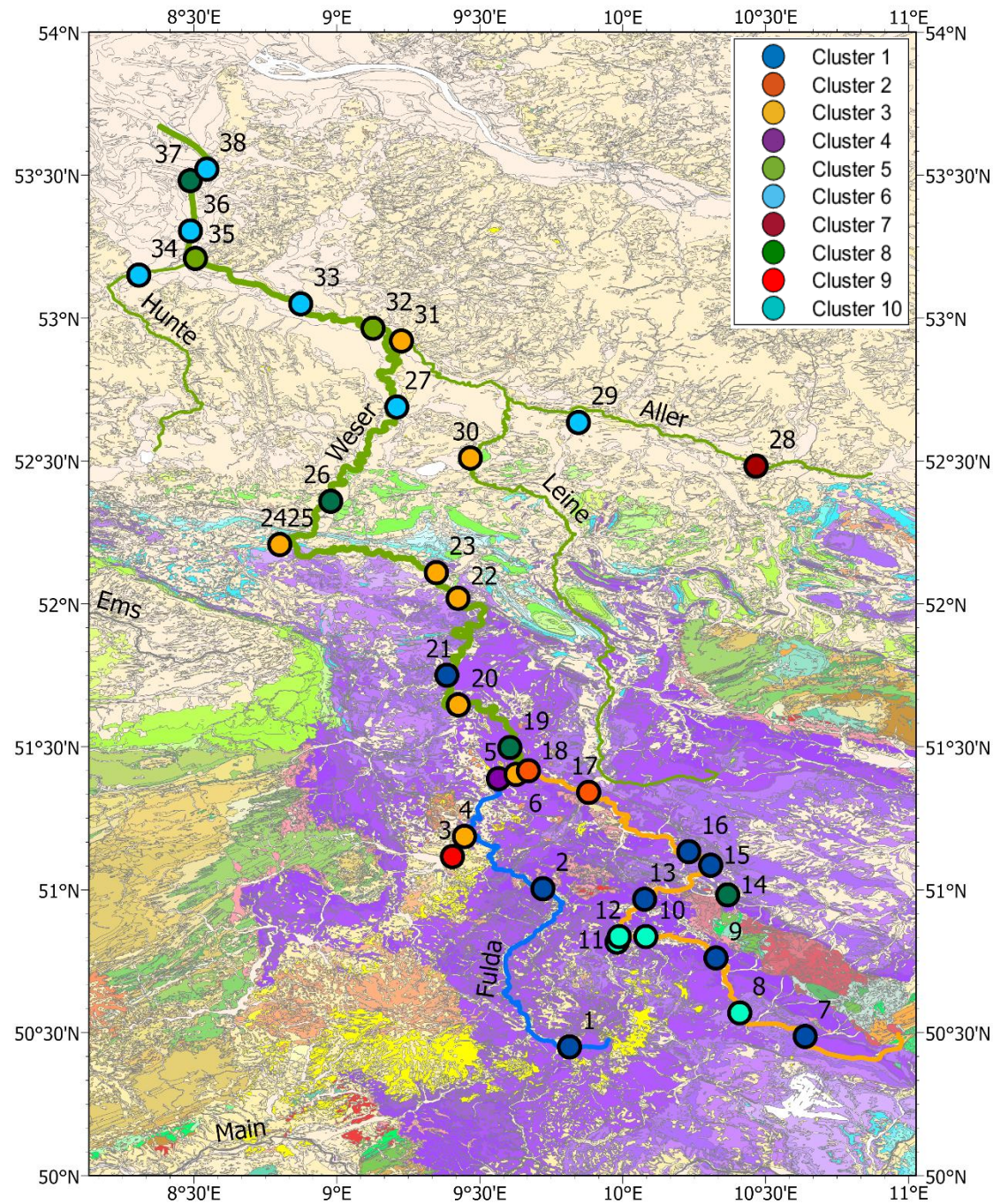
Mean 2se: ± 0.030

$^{207}\text{Pb}/^{204}\text{Pb}$ range : 15.613 to 15.653

Mean 2se: ± 0.0033





$^{208}\text{Pb}/^{204}\text{Pb}$ range: 38.144 to 38.837

Mean 2se: ± 0.051

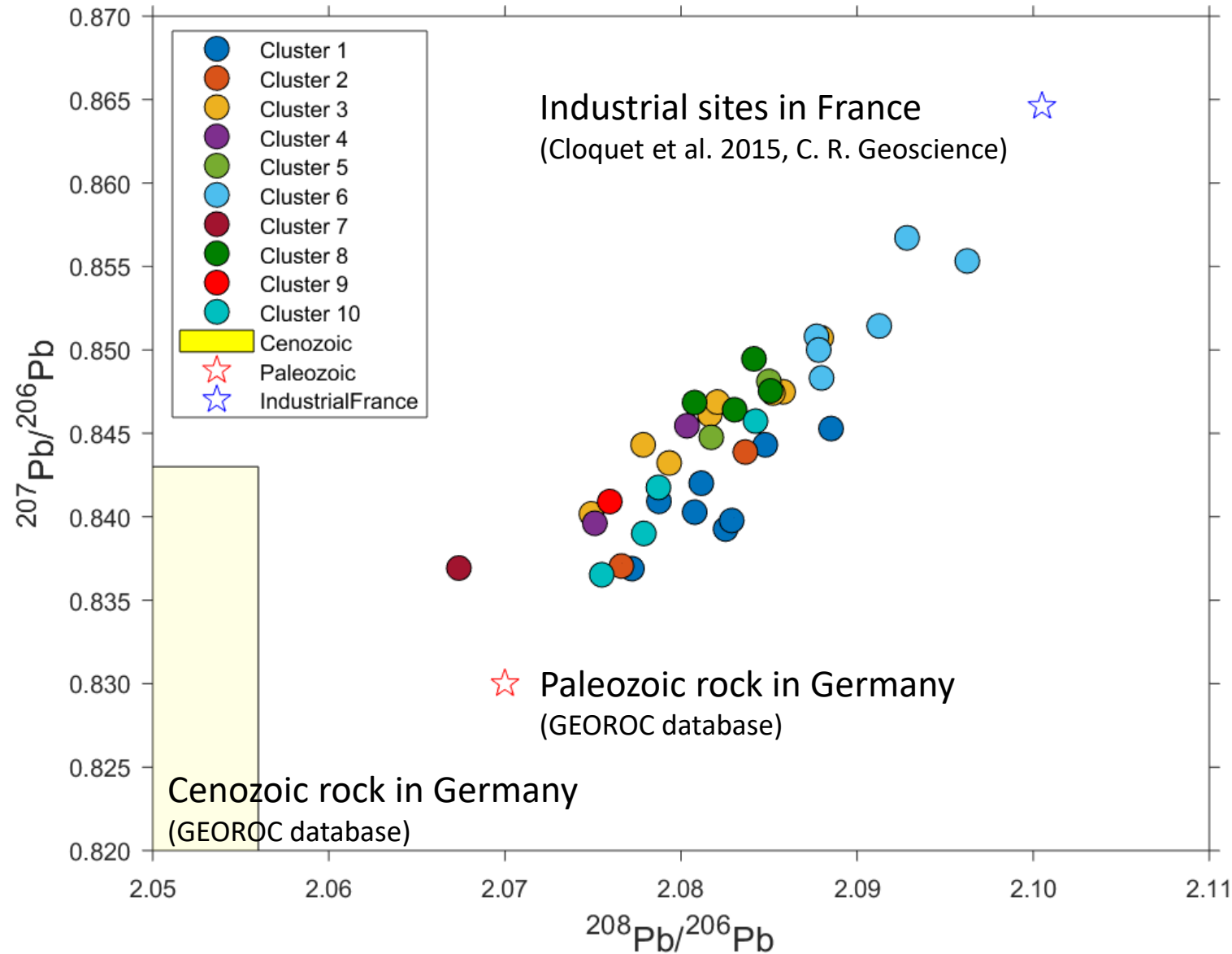


Unsupervised K-means Cluster Analysis

- K-means cluster analysis (KCA) was performed with Matlab using $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ 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.

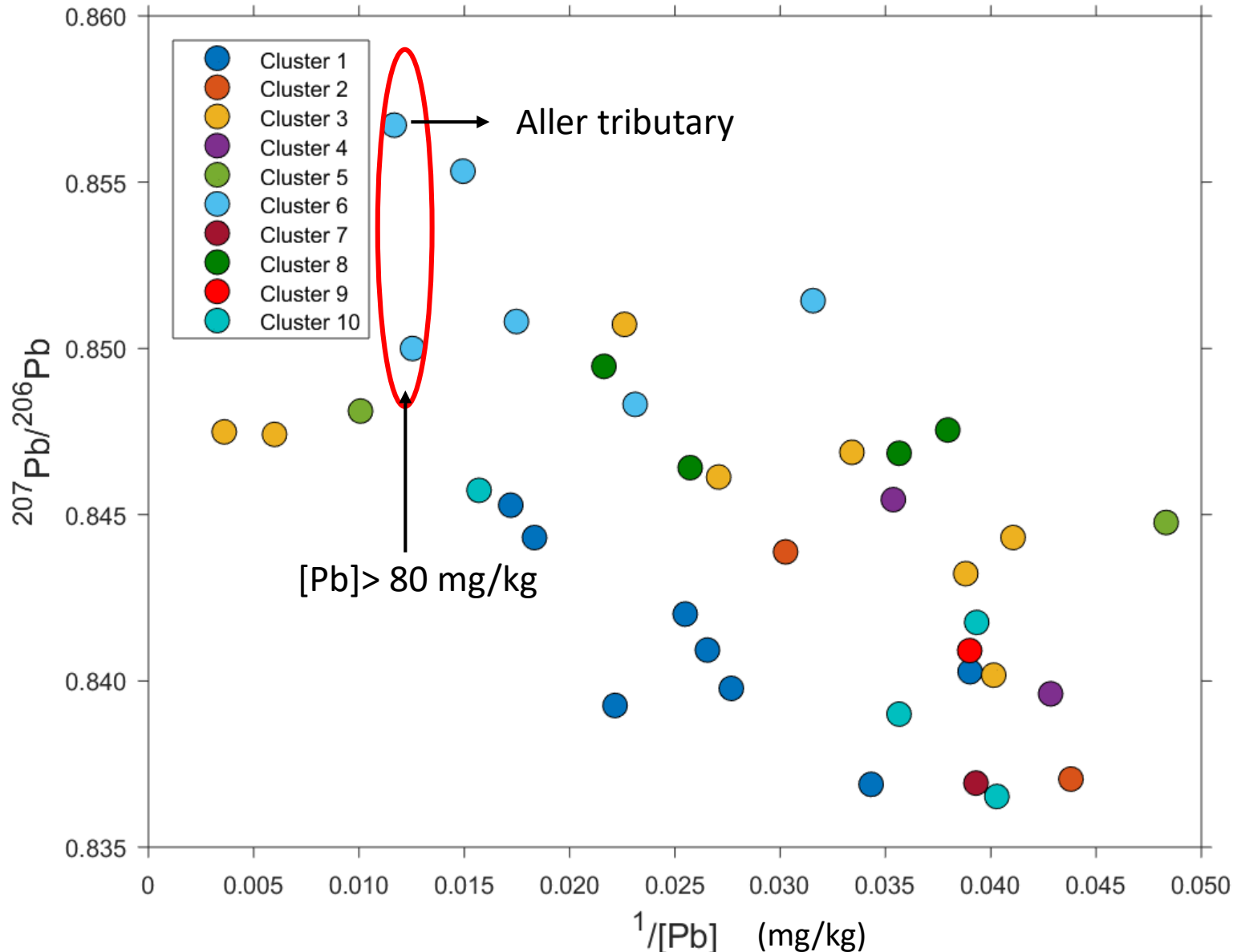
Geographic region	Main cluster	Cluster symbol
Lower and Middle Weser	Cluster 6	
	Cluster 5	
Upper Weser	Cluster 3	
Fulda and Werra	Cluster 1	

Identifying Natural v.s. **Anthropogenic** signals



- KCA revealed a cluster, cluster 6, with features distinctively different from other clusters: $^{207}\text{Pb}/^{206}\text{Pb}$ (0.848-0.857) and $^{208}\text{Pb}/^{206}\text{Pb}$ (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 ($[\text{Pb}]$):

- 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.

- 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 $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$) 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 from 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.