Oral Presentation GQ 19, Liège

Department of Engineering Geology and Hydrogeology
RWTH Aachen University

M. Sc. Uwe Boester

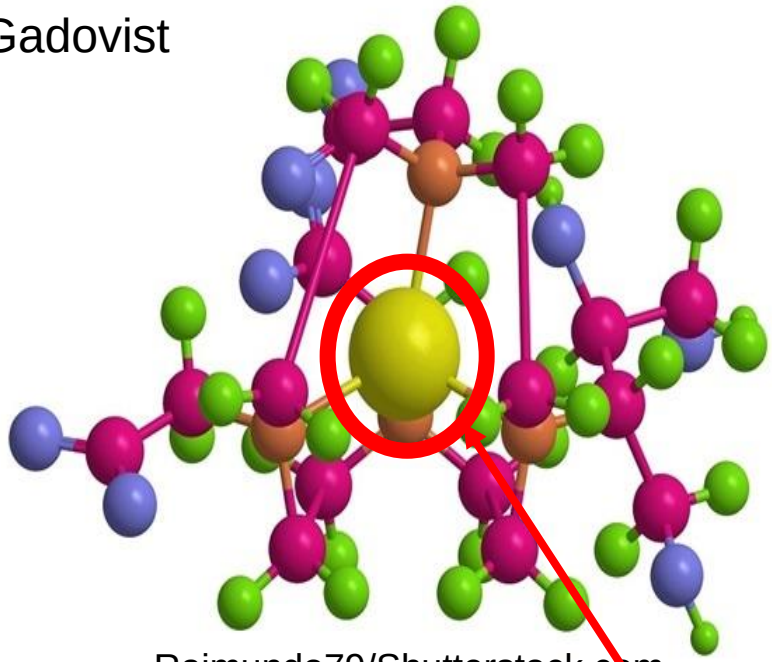
Using Gadolinium as Environmental Tracer for Groundwater-Surface Water Interaction

Outline

1) Anthropogenic Gadolinium
2) Study Site
3) Gd Background in Surface Water and Groundwater
4) Anthropogenic Gd as Tracer for Surface Water Infiltration
5) Correlation with Other Anthropogenic Contaminants
6) Conclusion

1) Gadolinium (Gd)

Gadovist



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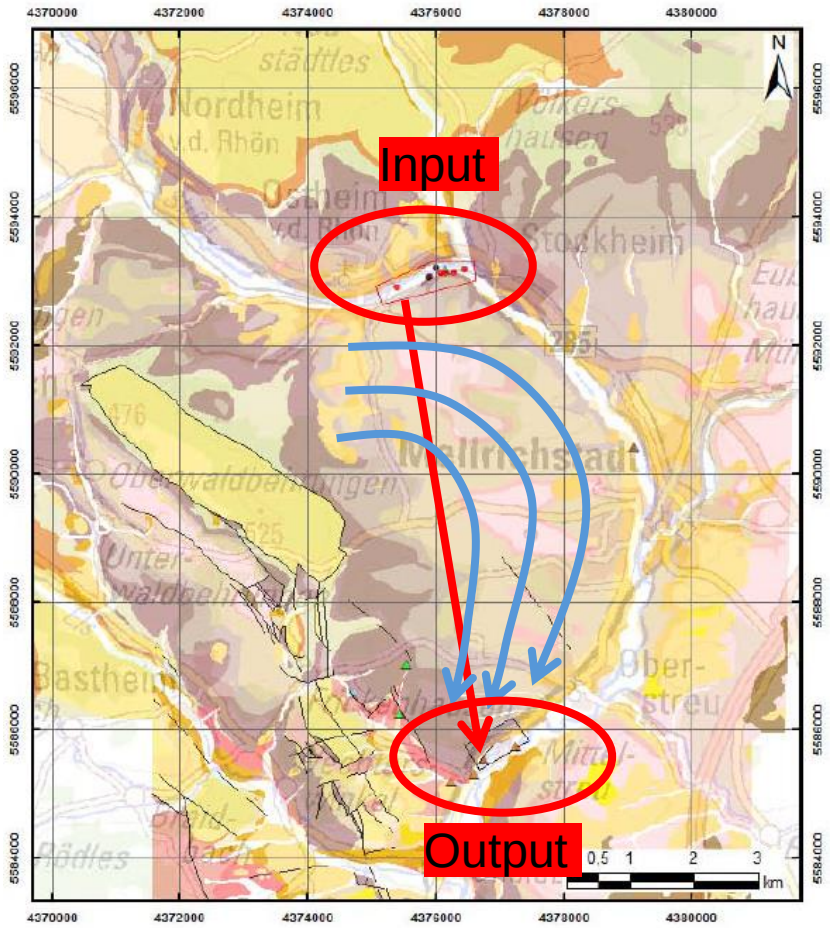
Central Ion in MRT-contrast agents

2) Study Site

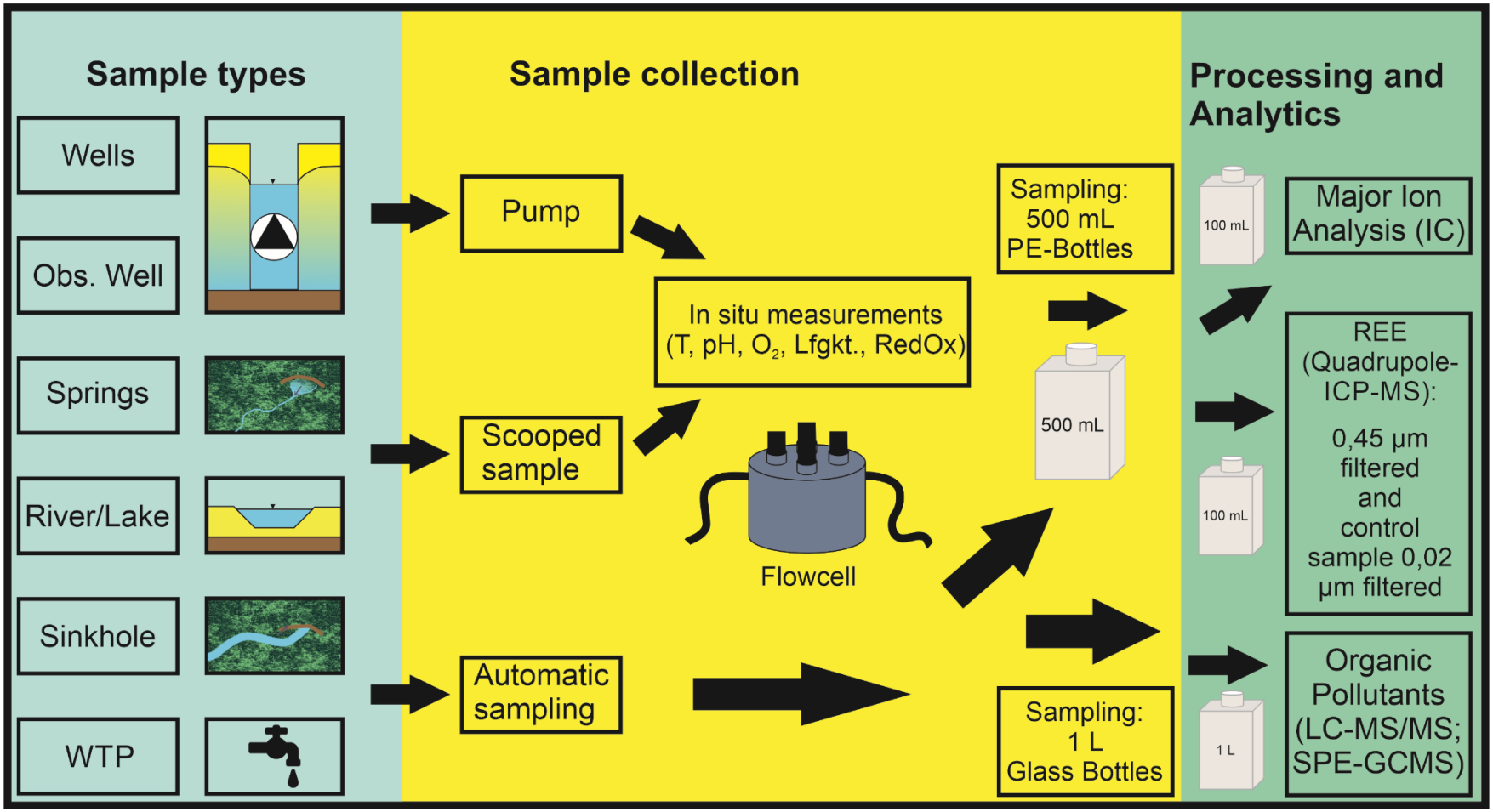

OSTHEIM V.D.RHÖN
Stockheim
Sinkhole
N
Springs
Hendungen
Unsleben
Wollbach

2) Study Site: Geology, Karst



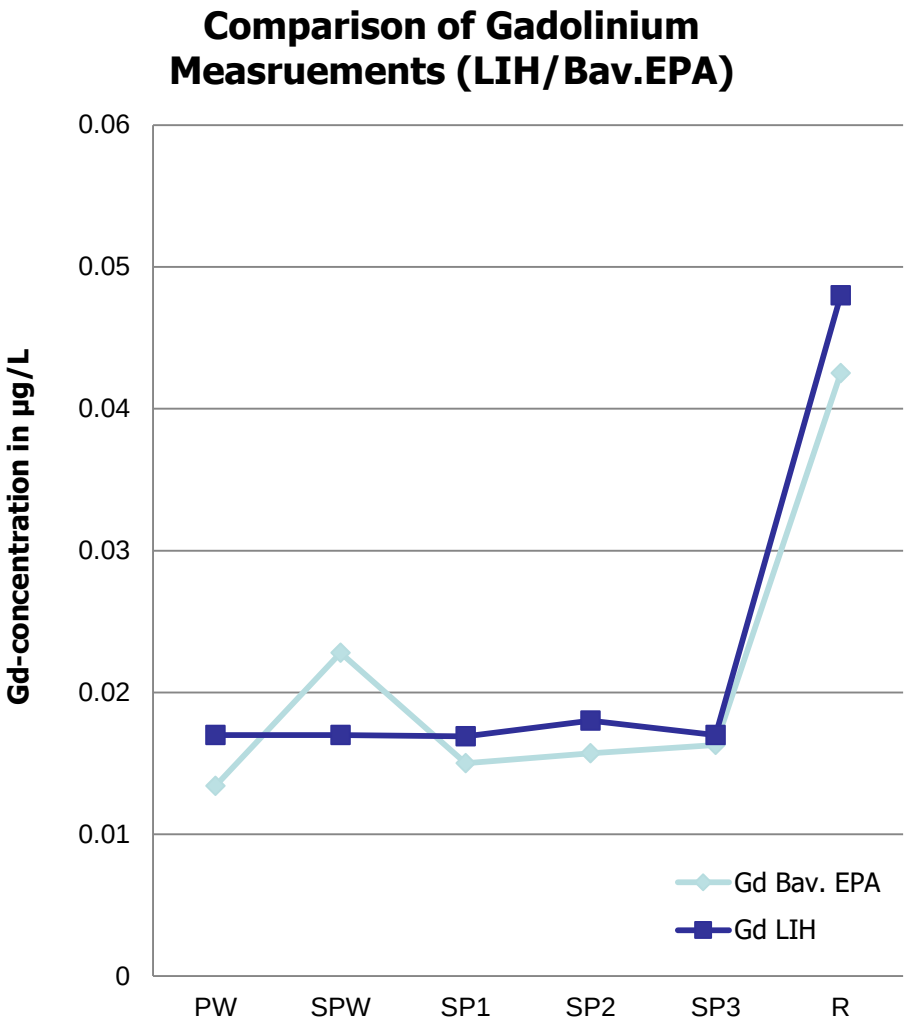
- Cuesta
- Triassic solid rocks
- Local aquifer (Muschelkalk) shows karstification (red)
  - Input: surface water at a sinkhole
  - Output: groundwater at springs
- Groundwater flow direction follows the River (blue)

2) Sampling

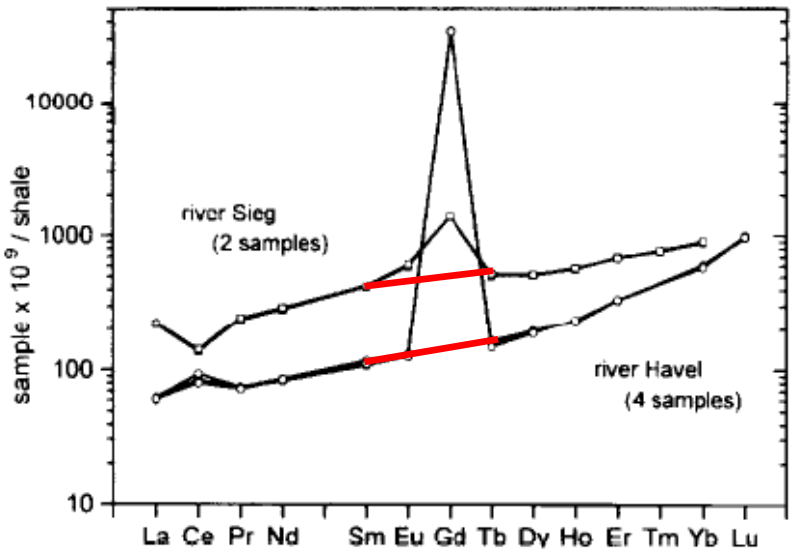

Sample types
Wells
Obs. Well
Springs
River/Lake
Sinkhole
WTP
Sample collection
Pump
Scooped sample
Automatic sampling
In situ measurements (T, pH, O_2, Lfgkt., RedOx)
Flowcell
Sampling: 500 mL PE-Bottles
500 mL
Sampling: 1 L Glass Bottles
Processing and Analytics
100 mL
100 mL
1 L
Major Ion Analysis (IC)
REE (Quadrupole-ICP-MS): 0,45 µm filtered and control sample 0,02 µm filtered
Organic Pollutants (LC-MS/MS; SPE-GCMS)

2) Sampling Campaigns

- First sampling: test of the analytical method (Quadrupole-ICP-MS) July 2017
  - Comparison with the method used at the Bavarian EPA
- February 2018: one week sampling at the sinkhole and the water treatment plant (WTP)
- May-June 2018: three weeks of automated probing at the sinkhole and WTP



3) Gd Background in Surface Water and Groundwater



$$\frac{Gd_{SN}}{Gd_{SN}*} = \frac{Gd_{SN}}{(0{,}33 * Sm_{SN} + 0{,}67 * Tb_{SN})}$$

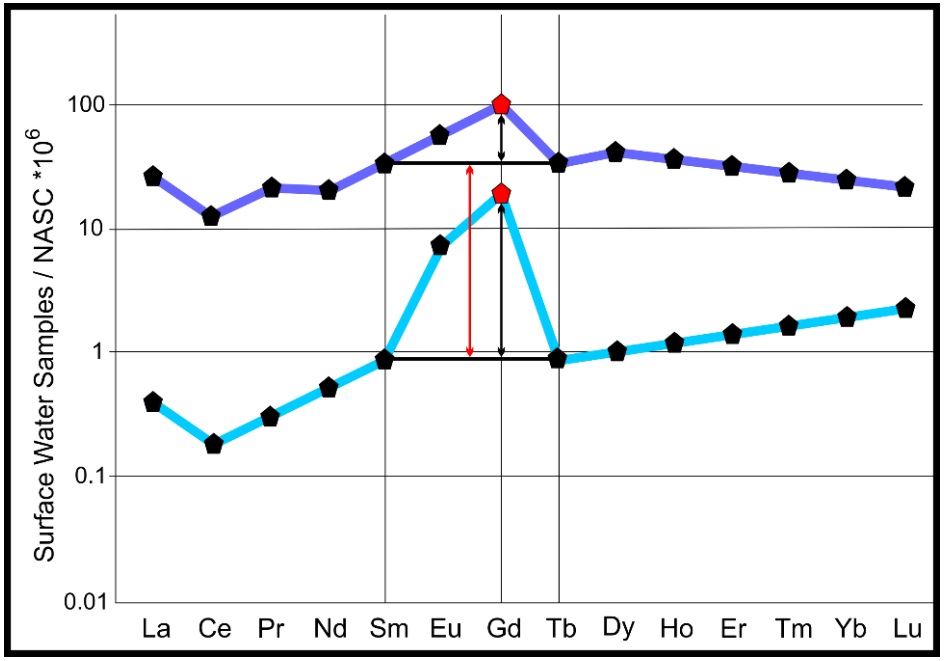
(Bau & Dulski 1996)

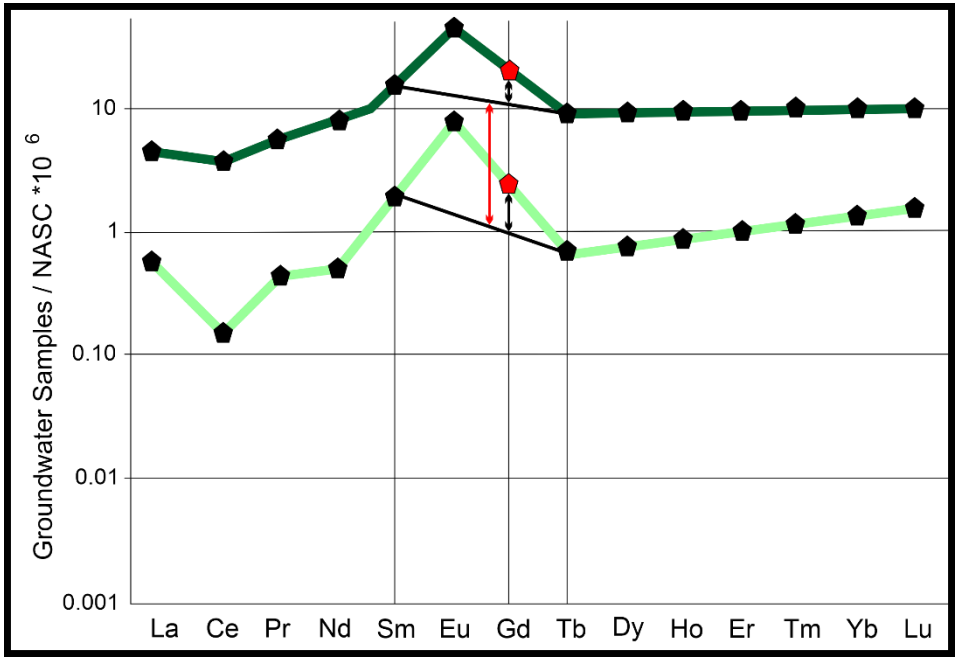
$$Gd_{geo} = \left(0{,}33 * \frac{Sm_{meas.}}{Sm_{UCC}} + 0{,}67 * \frac{Tb_{meas.}}{Tb_{UCC}}\right) * Gd_{UCC}$$

$$Gd_{anthr.} = Gd_{meas.} - Gd_{geo}$$

(Brünjes et al. 2016)

3) Gd Background in Surface Water and Groundwater



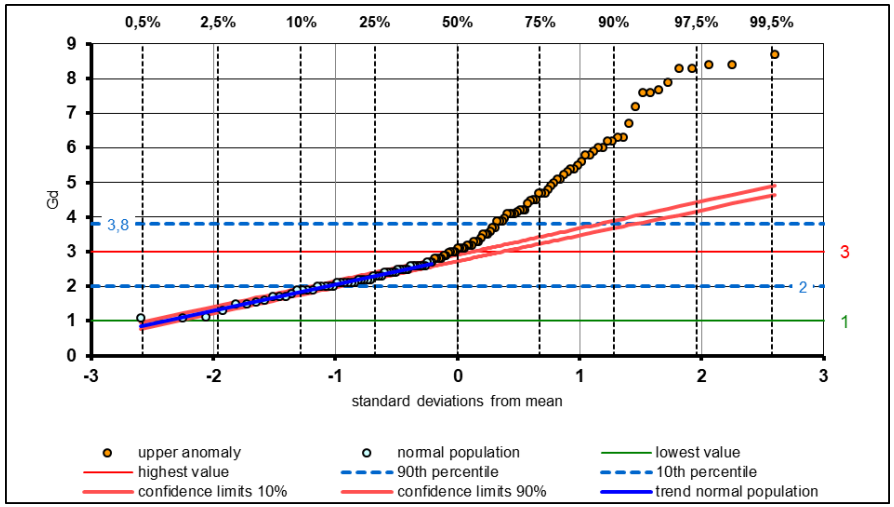


3) Statistical Background Calculation

- Anomaly distinction (Erhardt et al. 1996):
  - Assumption: normal distribution
  - Anomalies are defined as: 1.96 x std. dev.
  - Iterative reduction of the population → „normal value“
- Probability plot analysis (Lepeltier 1969)
  - Sum distribution put into a semilogarithmic: straight line if normally distributed
  - Using an Excel program (Wagner et al. 2011, Walter et al. 2012)
  - Slope variations show different cohorts

Unit	Background (ng/L)	Used for Calculation (n)	Samples per Unit (N)
All Samples	2.4	84	255
Luxemburg	1.5	5	24
Mittelstreu	2.4	73	215
Brombach Lake	2.3	3	16
Groundwater	2.4	67	139
Precipitation (Snow)	<1	4	4
Rivers, Lakes	9.6	73	105
Freshwater wells	2.2	5	7

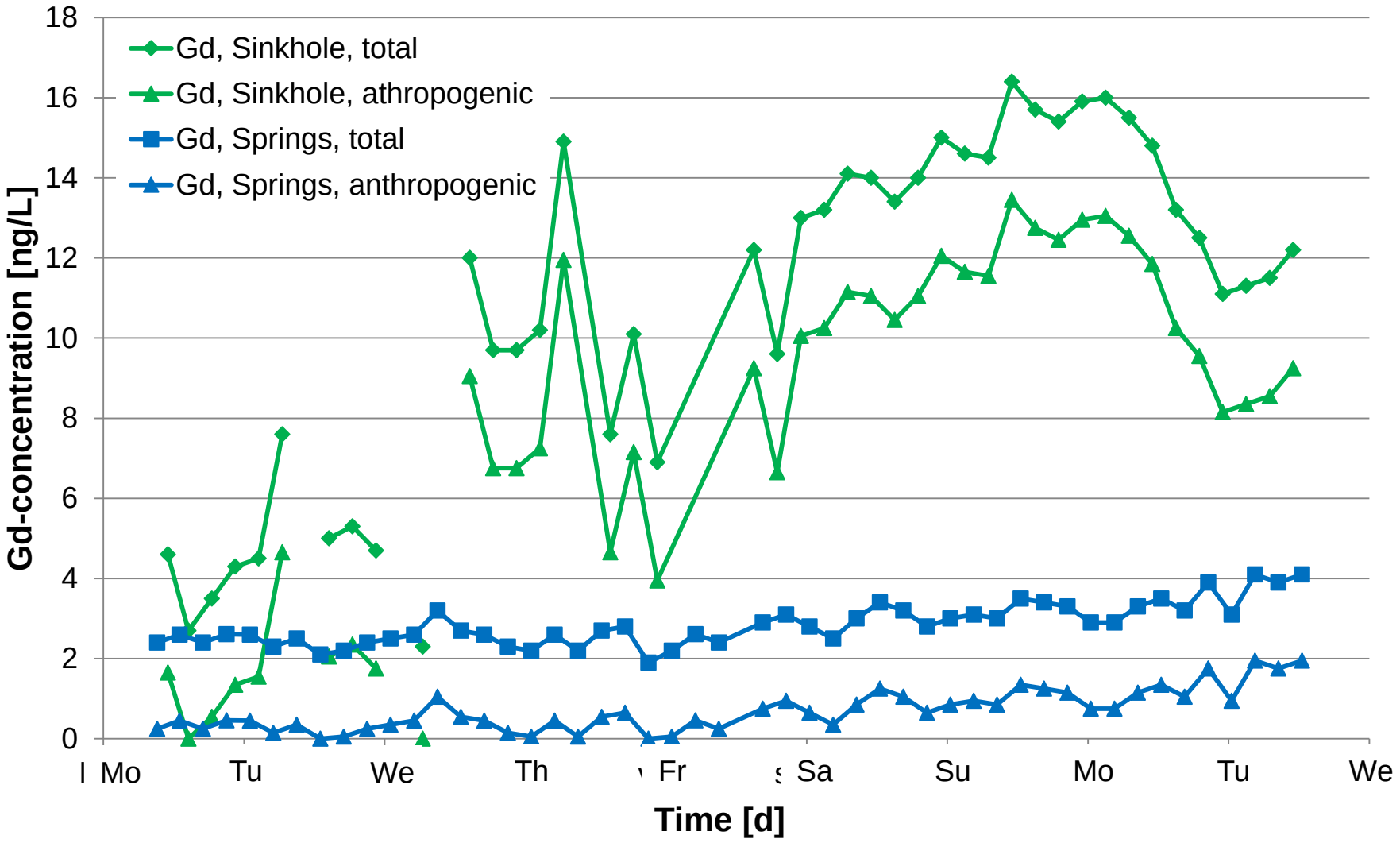
Entire data set



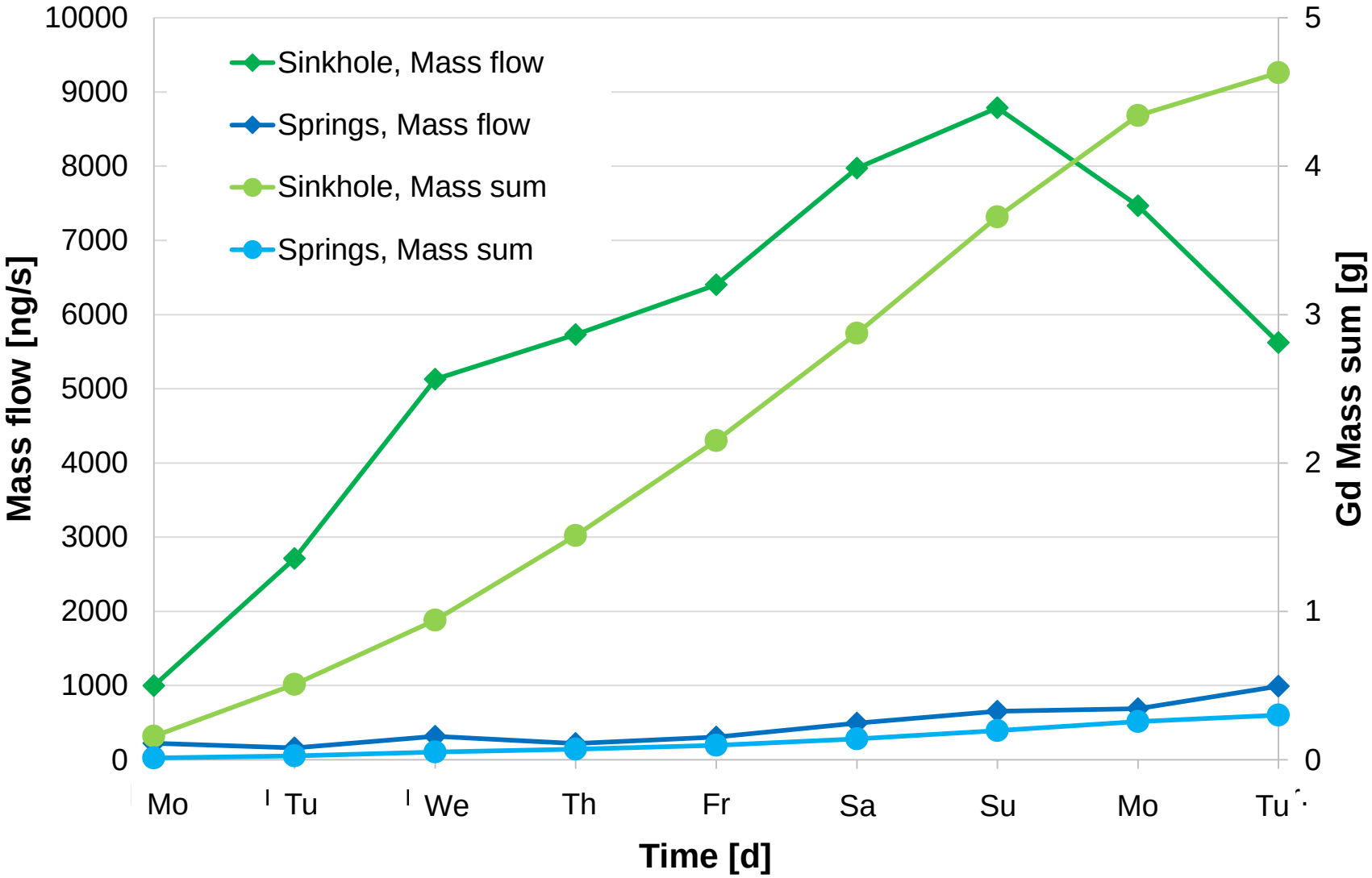
3) Gd Background in Surface Water and Groundwater

Eckhardt et al. 1996			
Study area	**Background [ng/L]**	**Background sample number**	**Total sample number**
All samples	**2.4**	**84**	**255**
Luxemburg	1.5	5	24
Brombachsee	2.3	3	16
Mittelstreu WTP	2.4	73	215
Mittelstreu Catchment			
Mittelstreu Streu			
Probability Plot (Walter et al. 2012)			
All samples	**3.8**	**133**	**255**
Luxemburg	2.2	5	13
Brombachsee	2.6	10	16
Mittelstreu WTP	2.15	15	83
Mittelstreu Catchment	3.27	13	48
Mittelstreu Streu	2.95	9	76

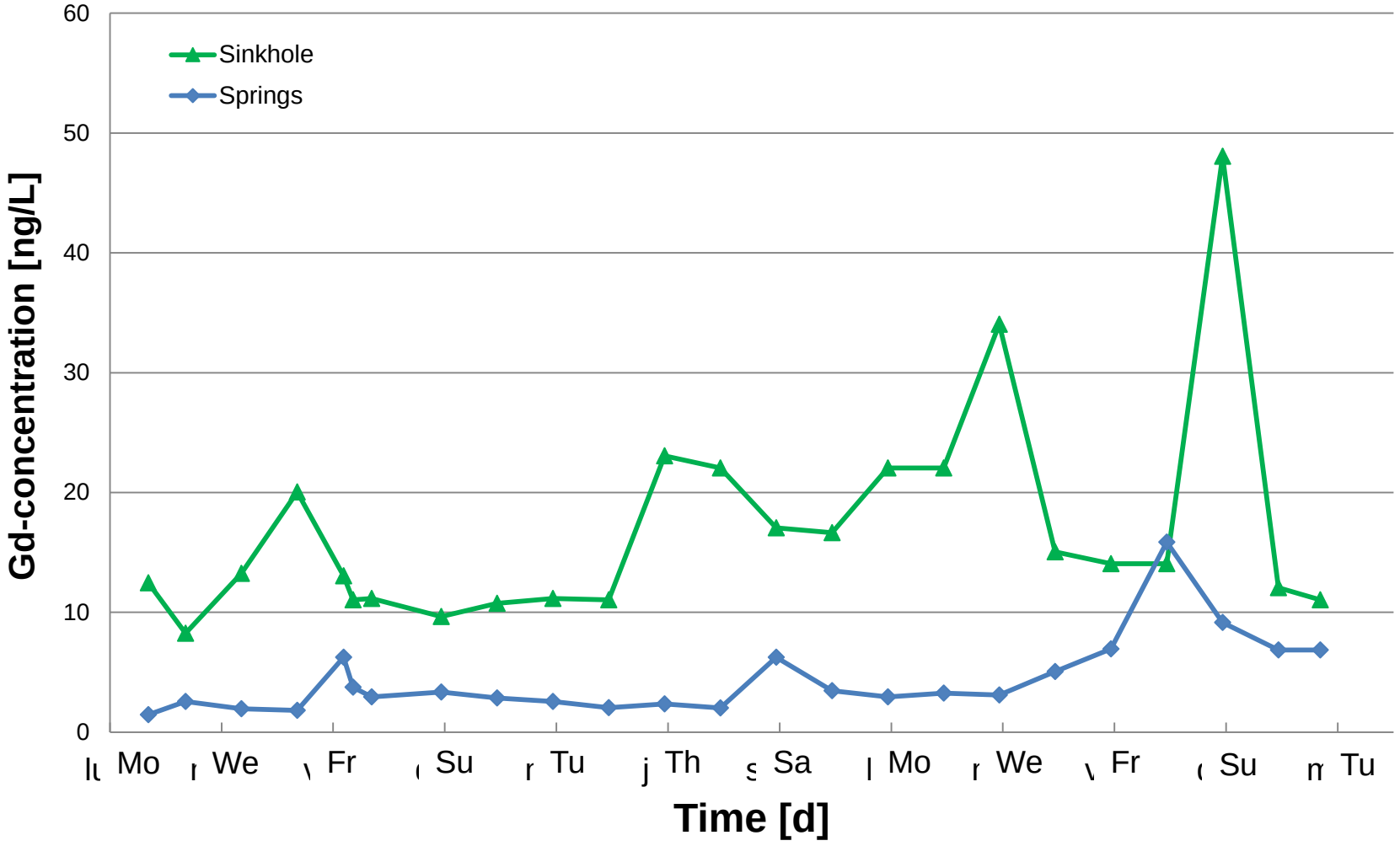
4.) Anthropogenic Gd Infiltration, Karst, Winter



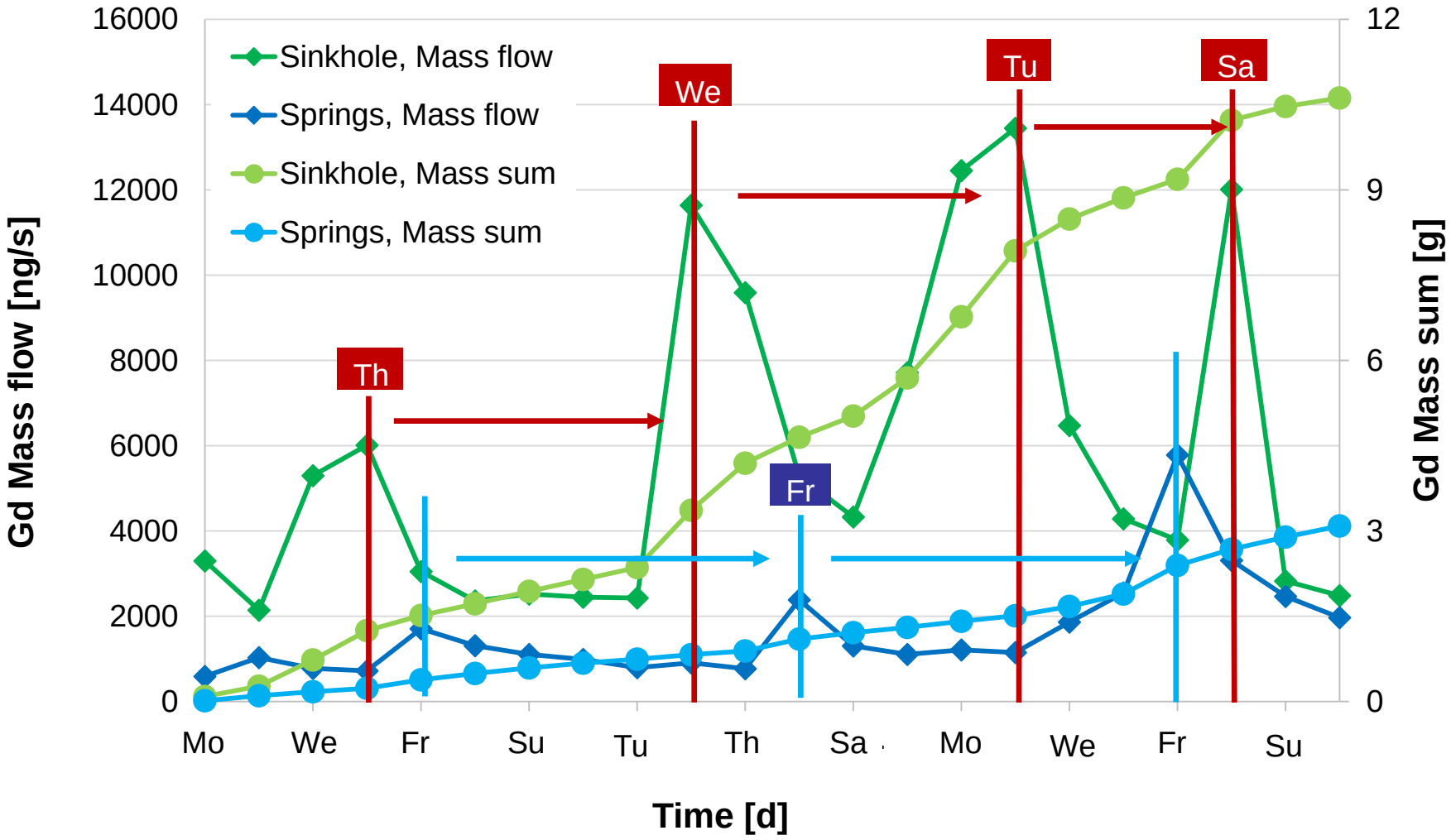
4.) Mass Flow and Gd-Mass sum, Winter



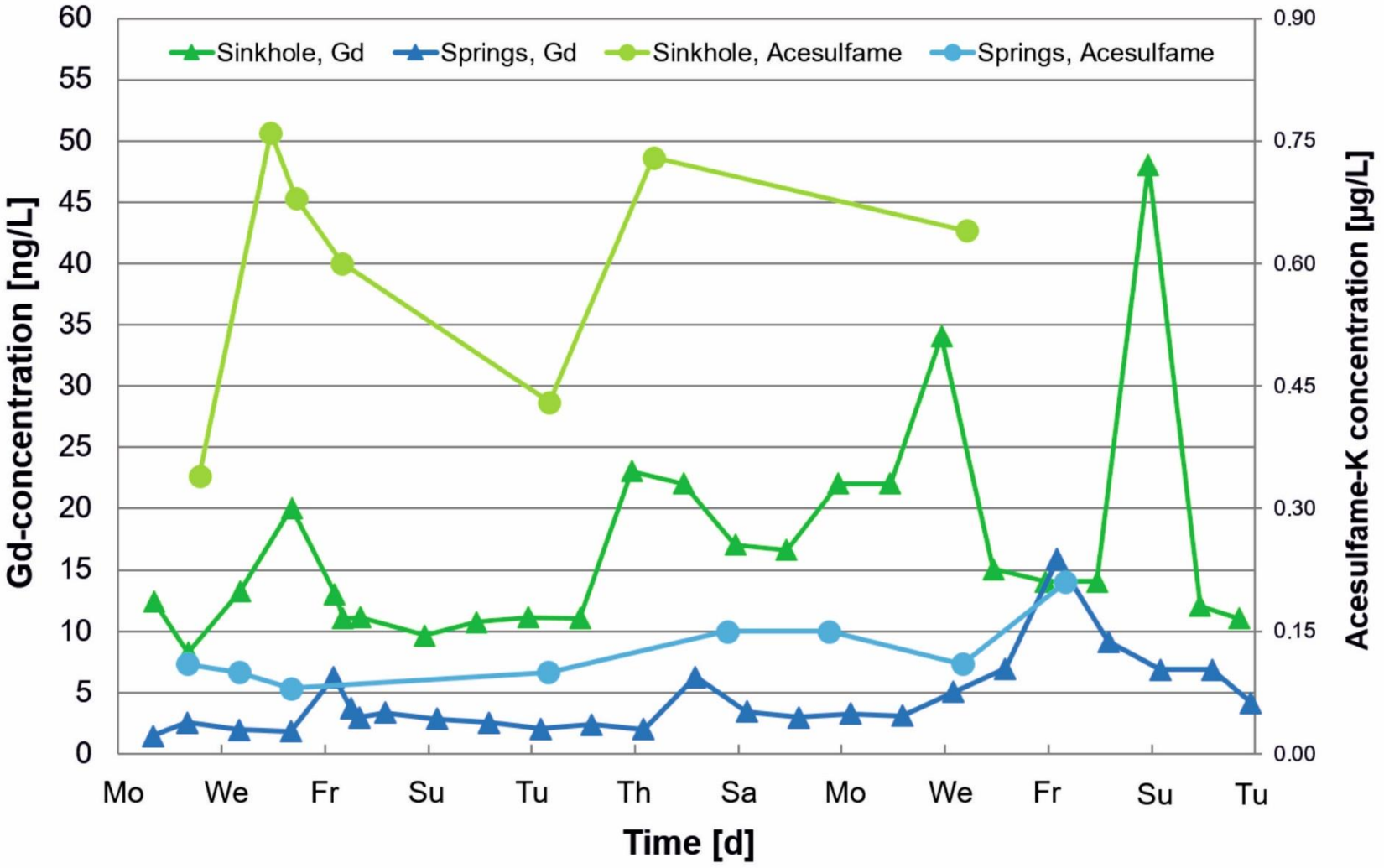
4.) Anthropogenic Gd Infiltration, Karst, Summer



4.) Mass Flow and Gd-Mass sum, Summer



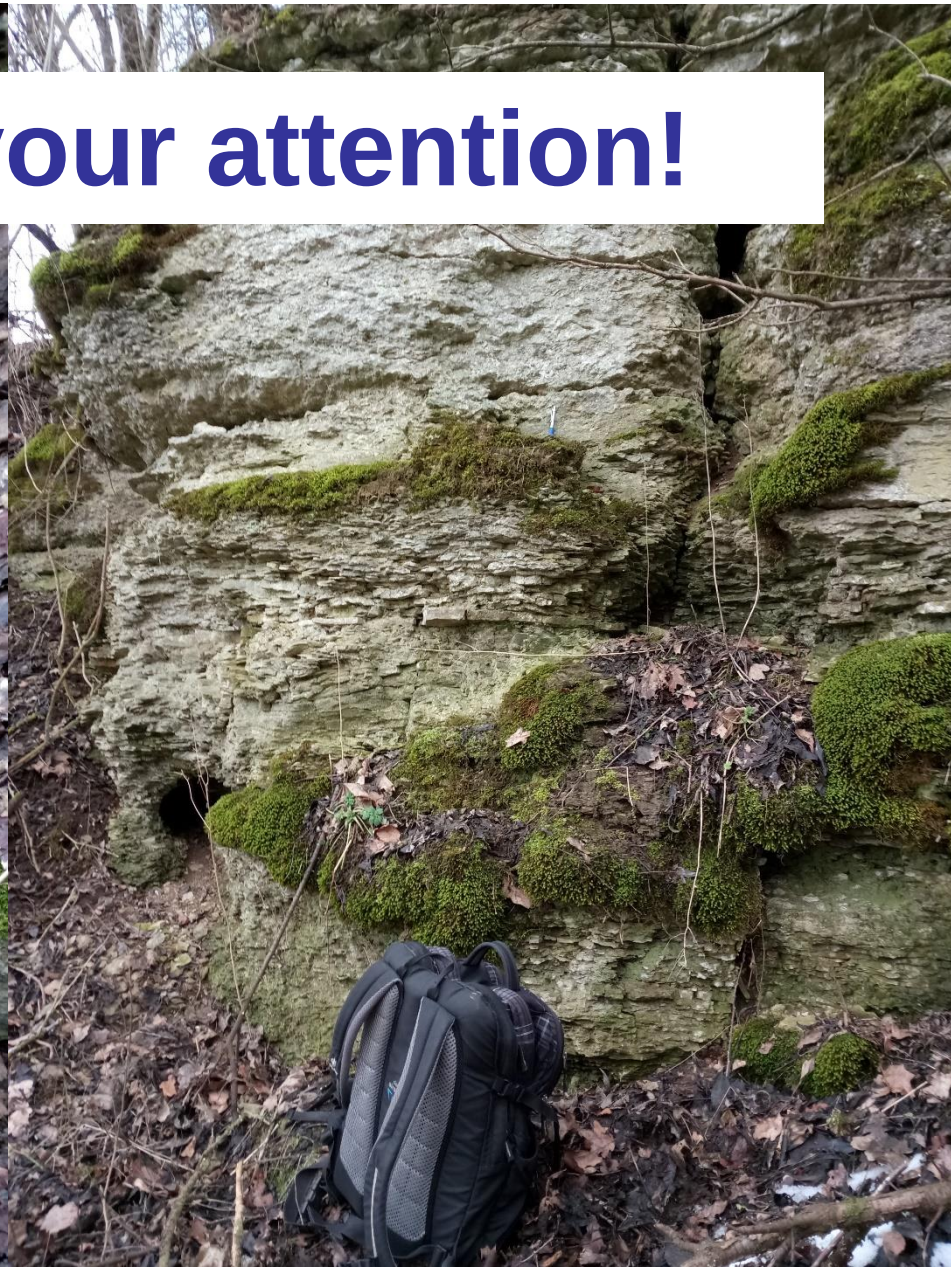
5) Correlation of Gd and Acesulfame-K



6) Conclusion

- Statistical background calculation: probability plot
- Surface water shows a cyclic Gd-signal in the river “Streu”
- Groundwater: the anthropogenic Gd-signal is attenuated
  - Groundwater velocity: 125 m/d
  - 60 days from sinkhole to spring
  - Dilution, adsorption etc.
- Dry weather conditions with low groundwater recharge
  - Less dilution leads to a higher Gd-signal
  - More stable runoff conditions
- Gd can be used as environmental tracer for surface water interaction with groundwater
  - Mixing calculations (Volume)
- Correlation of Gd with Acesulfame-K

Thank you for your attention!



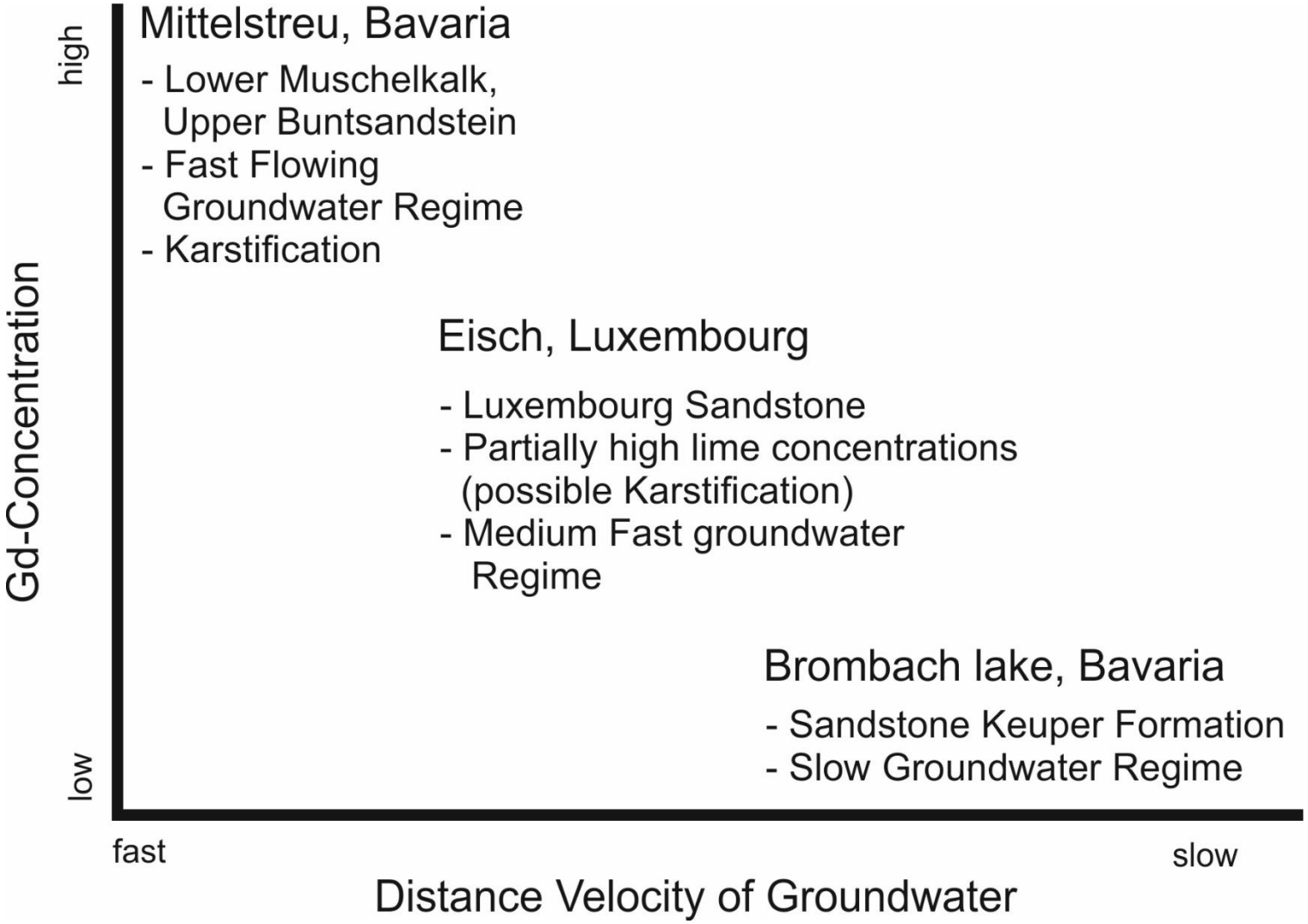
5) Literature

- Bau, M., Dulski, P. (1996): Anthropogenic origin of positive gadolinium anomalies in river waters. *Earth and Planetary Science Letters,* 143(1-4), p. 245–255.
- Brünjes, R.; Bichler, A; Hoehn, P.; Lange, F. T.; Brauch, H.J.; Hofmann, T. (2016): Anthropogenic gadolinium as a transient tracer for investigating river bank filtration. *The Science of the total Environment,* 571, p. 1432-1440.
- Erhardt W, Höpker KA, Fischer I (1998) Verfahren zur Bewertung von immissionsbedingten Stoffanreicherungen in standardisierten Graskulturen. V: Auswertung und Darstellung von Meßergebnissen aus Bioindikationsverfahren. Z Umweltchem Ökotox 8 : 237–240.
- Wagner, B.; Walter, T.; Himmelsbach, T.; Clos, P.; Beer, A.; Budziak, D.; Dreher, T.; Fritsche, H-G.; Hübschmann, M.; Marczinek, S.; Peters, A.; Poeser, H.; Schuster, H.; Steinel, A.; Wagner, F.; Wirsing, G. (2011): Hydrogeochemische Hintergrundwerte der Grundwässer Deutschlands als Web Map Service. Grundwasser, 16(3), p. 155-162.

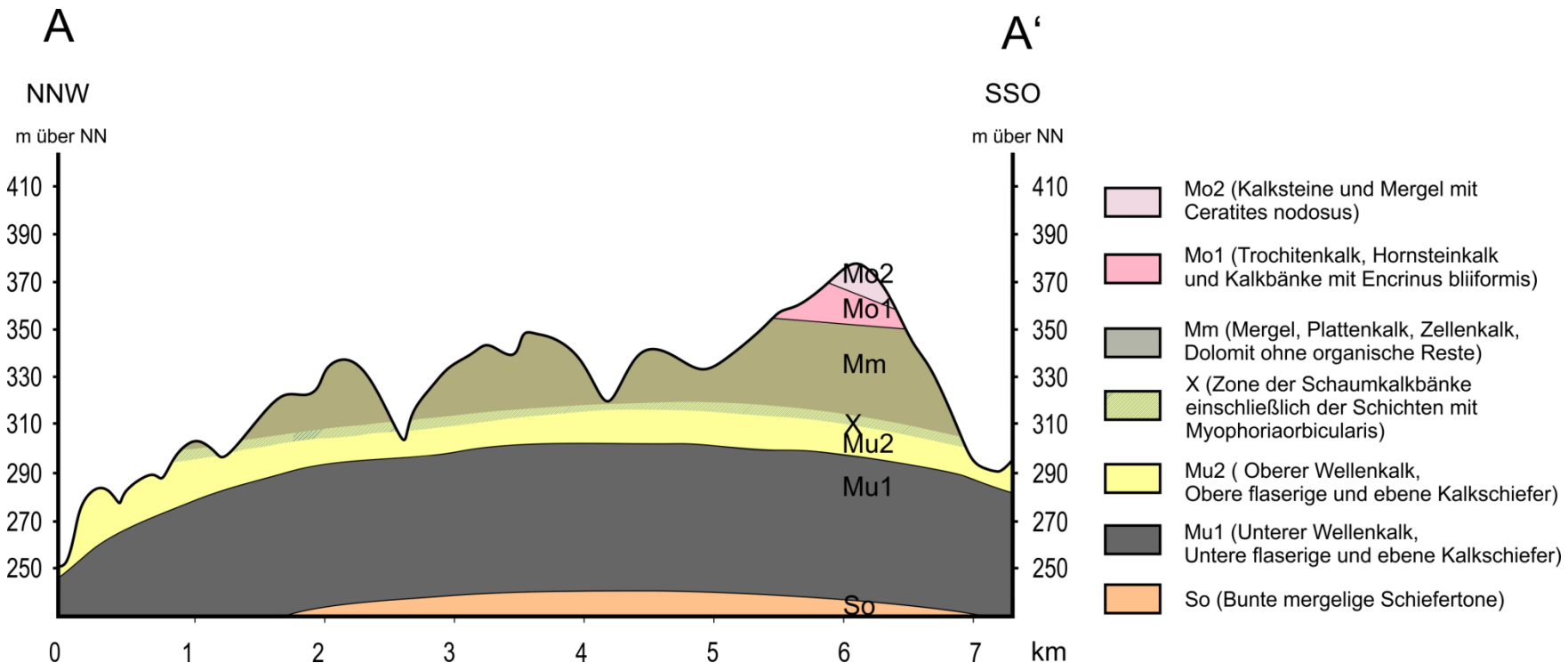
5) Literature

- Walter, T., Beer, A., Brose, D., Budziak, D., Clos, P., Dreher, T., Fritsche, H.-G., Hübschmann, M., Marczinek, S., Peters, A., Poeser, H., Schuster, H., Wagner, B., Wagner, F., Wirsing, G., Wolter, R. (2012): Determining natural background values with probability plots. *In: Groundwater Quality Sustainability*, p. 331-341.

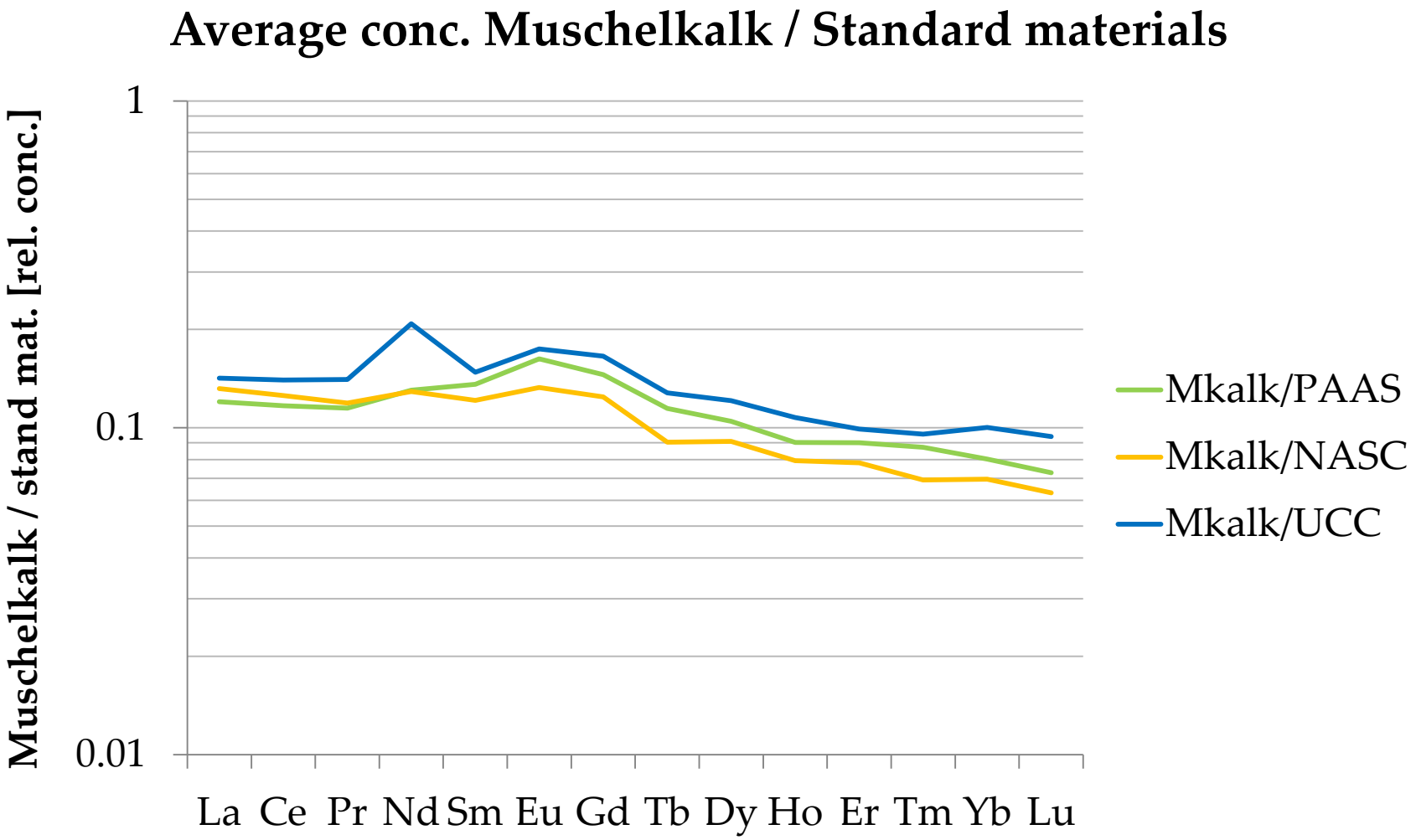
2) Project Outline



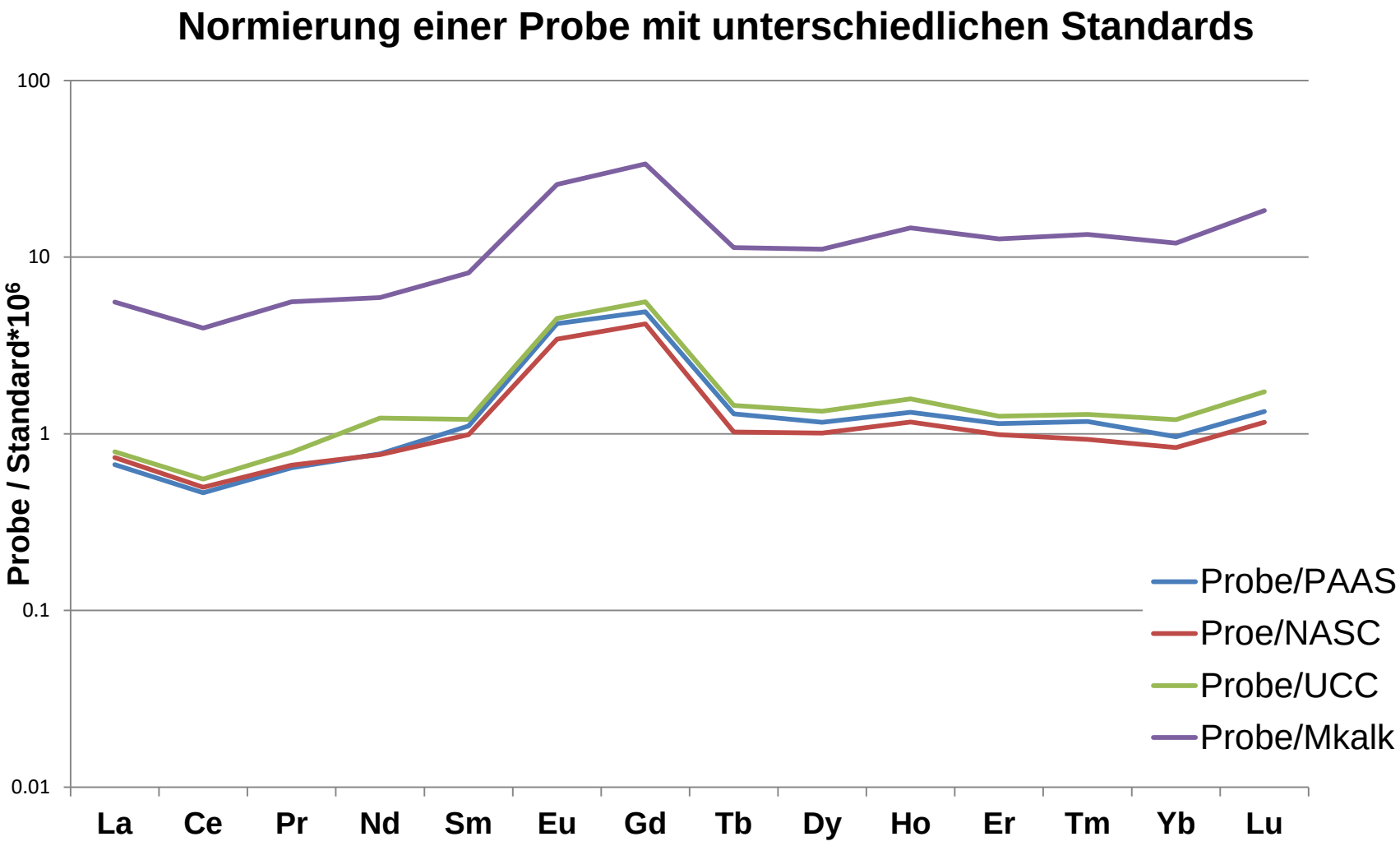
2.1) Geological profile



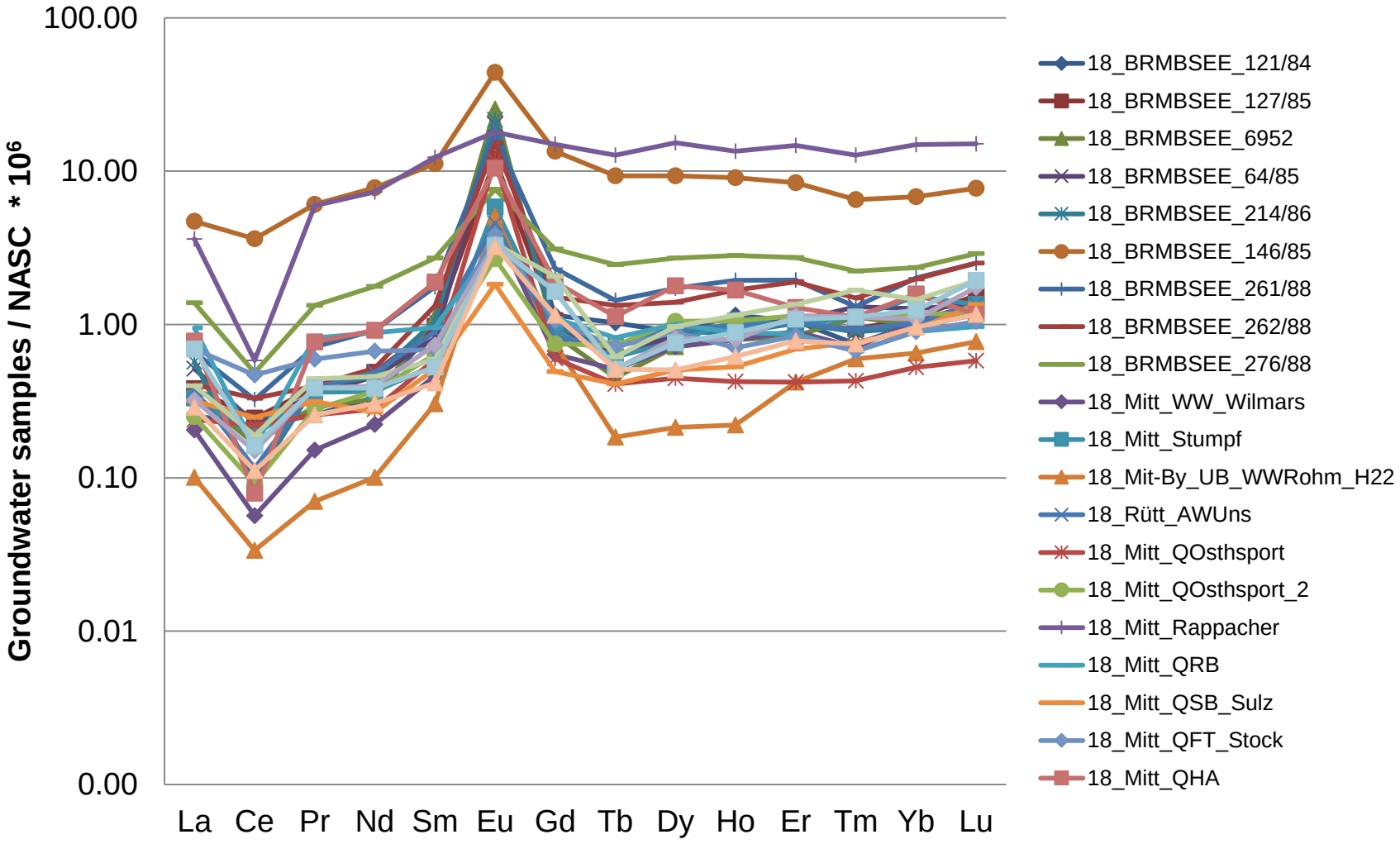
Normed element patterns



Comparison of standard materials



SEE-Pattern in groundwater samples (preselected)



3.1) SEE-pattern in surface water samples