Conceptualizing transboundary aquifer systems using geochemical signatures of springs – an attempt to bring clarity to one big mess

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European Regional Development Fund
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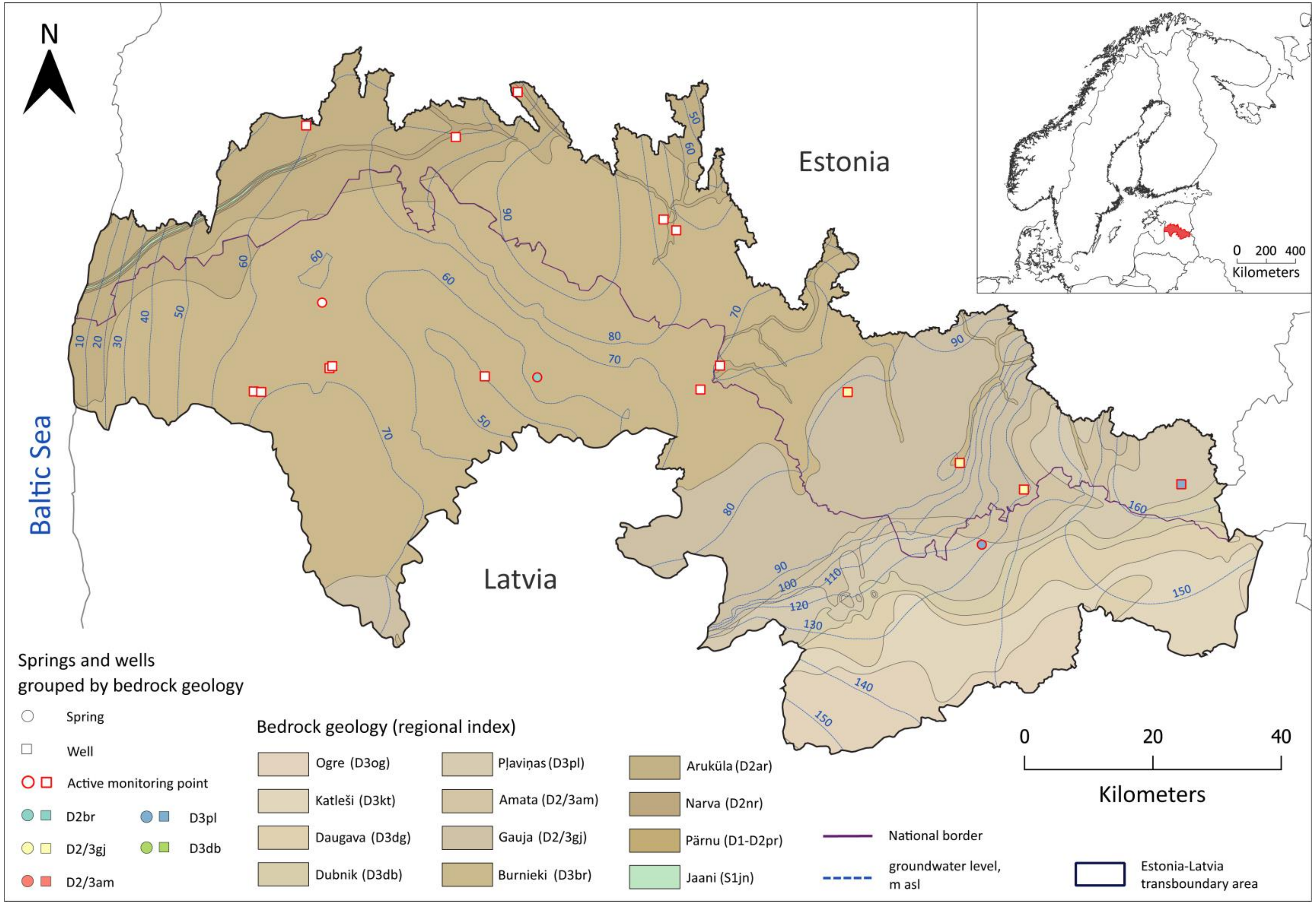
WaterAct
Joint actions for more efficient management
of common groundwater resources

13-14th of September 2022

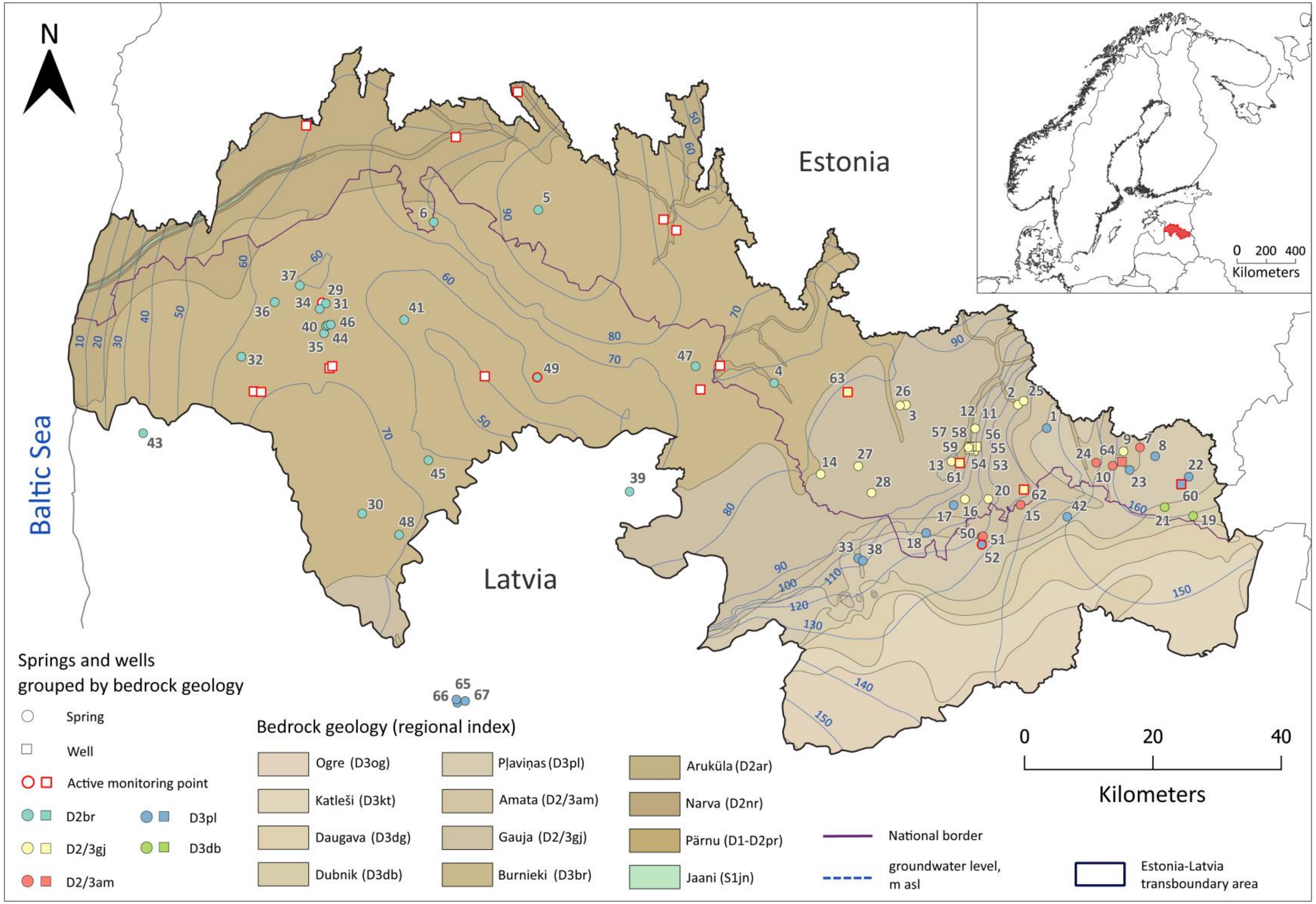
Shared groundwater resources

- Groundwater does not follow country borders
- Need for joint assessment and management of transboundary groundwater resources
- Scarce monitoring network in the peripheral areas



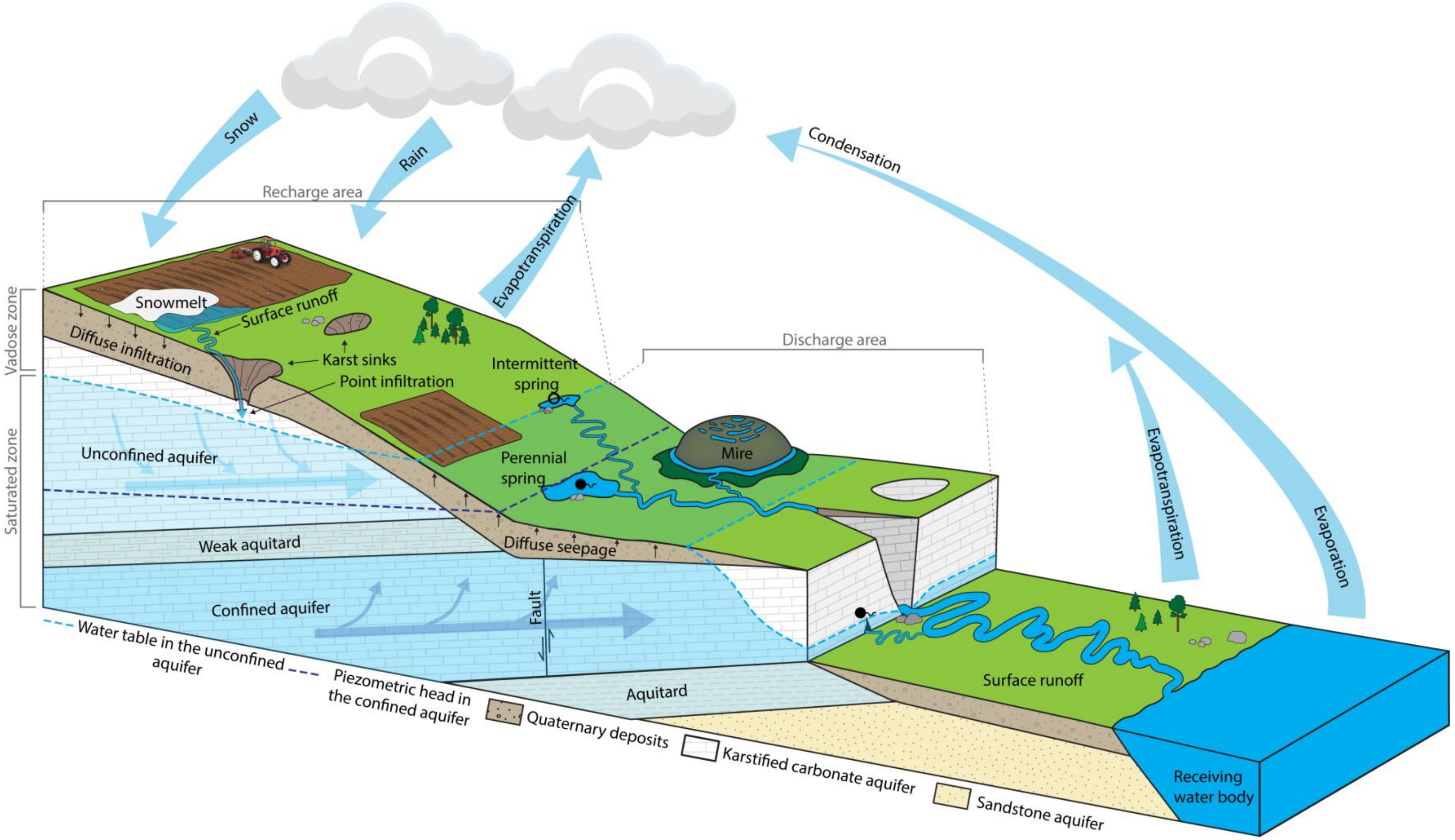
Shared groundwater resources

- Groundwater does not follow country borders
- Need for joint assessment and management of transboundary groundwater resources
- Scarce monitoring network in the peripheral areas
- **Springs could fill the gaps!?**



Springs

- Springs are usually the convergence points of groundwater flow systems
- Cost effective
- But where does the water come from?



Objective of the study

- Propose representative springs for the monitoring network of transboundary groundwater bodies (GWB) of Estonia and Latvia

Approach

- Map and sample the springs in the transboundary area
- Gather all the available data about the GWBs from both countries
- Sample some wells to define aquifer end-members
- Multivariate statistics and machine learning to identify the links between the springs and aquifer systems

Sampling campaigns

- Three sampling campaigns
  - April 2021
  - August 2021
  - March 2022
- 89 water samples were collected from 64 locations
  - EE – 55 samples
  - LV – 34 samples


Solinst
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Multiparameter


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250 mL

Sampling

- Solinst 410 peristaltic pump or a syringe and in-line 0,45 um RC filter.
- Bottles and preservation:
  - Cations (15 ml HDPE) – HNO_3
  - Anions (15 ml HDPE)
  - Trace elements (15 ml HDPE) – HNO_3
  - $^{18}O/^{2}H$ (15 ml HDPE)
  - DOC/N_{tot} (60 ml HDPE)
  - P_{tot} (175 ml HDPE) – H_2SO_4
- *In-situ* field parameters and hardness and HCO_3^- titration.

Analysis (58 parameters)

- *In-situ* field parameters (pH, SEC, ORP, temp., DO) and alkalinity
- Tallinn University lab:
  - **Major ions** (Na+; NH4+; K+; Mg2+;Ca2+; F-; Cl-; NO2-; Br-; NO3-; PO43-; SO42-) – *HPLC - SHIMADZU® RID-10A või CDD-10A; Shodex IC YS-50 ja Shodex IC SI-50.*
  - **Nutrients** (DOC; IC; TC; N_{tot}; P_{tot}; PO4-P; OP) – *Analytik Jena multi N/C 3100 TOC/TNb analyzer and spectrophotometry*
- University of Latvia lab:
  - **Trace elements** (Al; As; B; B; Ba; Be; Ca; Cd; Co; Cr; Cu; Fe; K; Li; Mg; Mn; Mo; Na; Ni; P; Pb; S; Sb; Se; Si; Sr; Ti; Tl; V; Zn) – *Thermo Scientific Inc. iCAP7000 ICP-OES*
  - **Stable isotopes** (^{18}O; ^{2}H) - *Picarro Isotopic Water Analyzer L2130-I (Cavity Ring-Down Spectroscopy)*

Dataset

- A hydrochemical dataset was assembled consisting of 409 groundwater observations from:
    - WaterAct (89 samples)
        - EE – 55 samples
        - LV – 34 samples
    - GroundEco (Koit et al., 2021; Kalvans et al., 2021)
    - KESE
    - EELIS
    - VEKA
    - LEGMC

Koit O, Tarros S, Pärn J, et al (2021) Contribution of local factors to the status of a groundwater dependent terrestrial ecosystem in the transboundary Gauja-Koiva River basin, North-Eastern Europe. J Hydrol 600:126656. https://doi.org/10.1016/j.jhydrol.2021.126656

Kalvāns A, Koit O, Bikše J et al (2021) Groundwater and surface water quantity and quality measurement results for groundwater dependent ecosystem in Kazu leja, Latvia in 2019 and 2020 (1.0). Zenodo. https:// doi. org/ 10. 5281/ zenodo. 51411 13

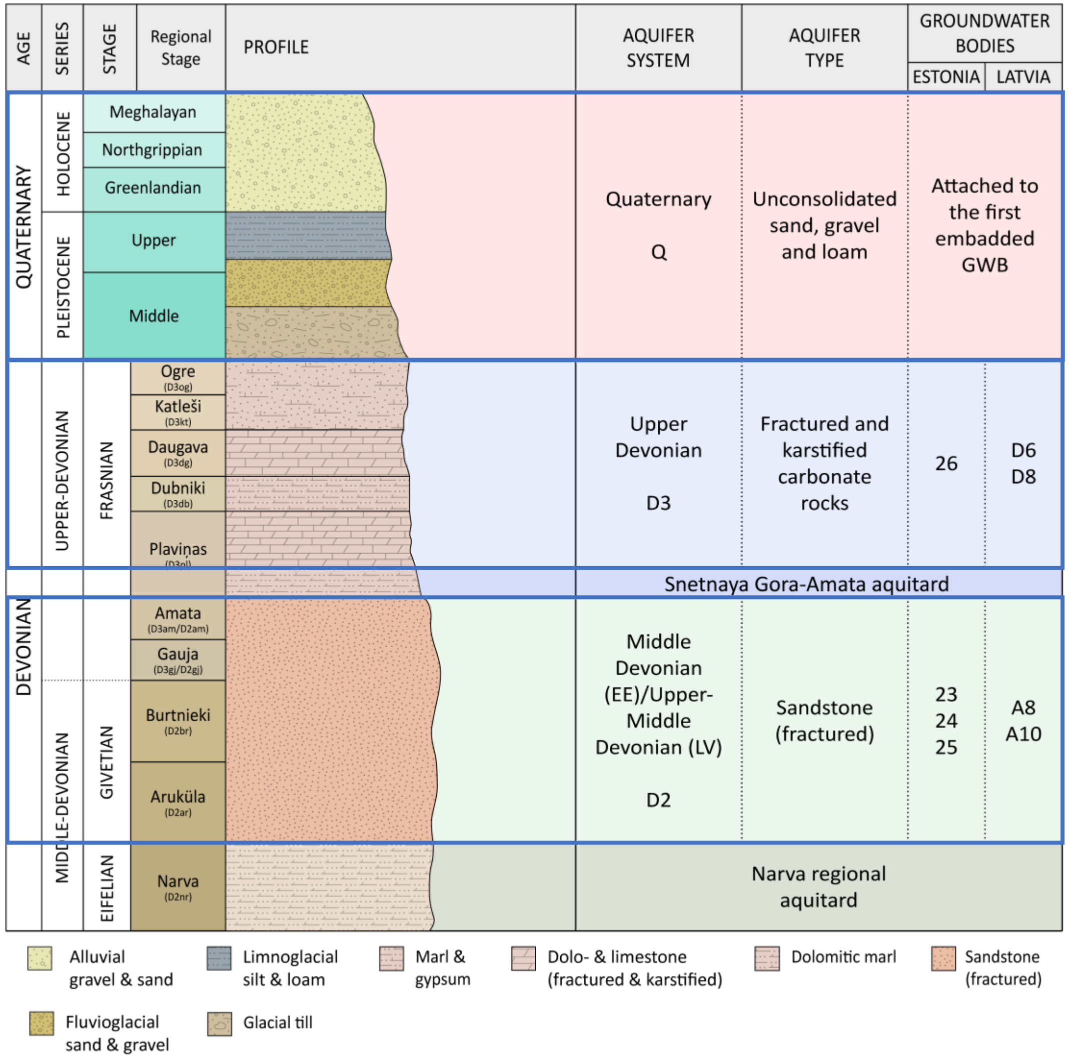
Preliminary grouping of springs

- The springs (n=58) were assigned to presumed aquifer systems proposed by Perens & Vallner (1997); Retike (2021).
  - Geology
  - Discharge characteristics
  - Expert judgment

You shall be D3!

Aquifer system	Aquifer type	Number		Elevation	Quaternary thickness	Discharge	Specific conductance (SEC)
				mean±SD (m asl)	mean±SD (m)	mean±SD (l/s)	mean±SD (µS/cm)
Q	Sand, gravel and loam	Springs	32	100.2±68.1	44±29.6**	0.6±0.9**	378±168**
		Wells	4	120.8±41.7	41.9±17.6		414±125
D3	Fractured and karstified carbonate rocks	Springs	9	97.1±36.3*	20.9±8.6**	3.2±3.9**	578±88**
		Wells	13	198.5±13.3*	52.9±18.1		480±94
D2	Sandstone (fractured)	Springs	18	62.8±10.6*	18.5±6.4**	1±0.8**	546±164**
		Wells	15	85.5±47.3*	43.1±24.8		509±95

Significant differences between classes according to Kruskal-Wallis test (at α=0.05): *D2 vs. D3; **Q vs. D2/D3



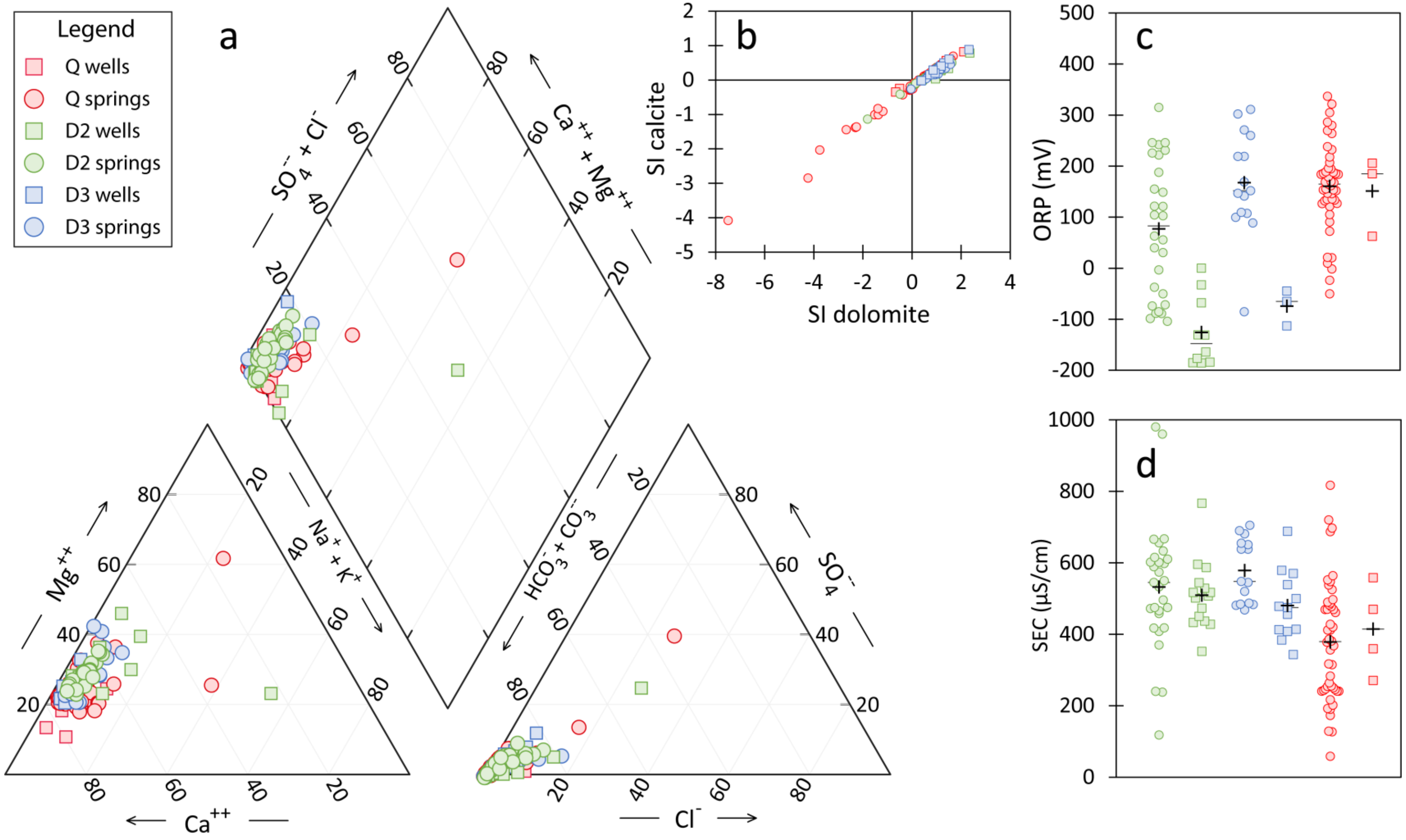
AGE	SERIES	STAGE	Regional Stage	PROFILE	AQUIFER SYSTEM	AQUIFER TYPE	GROUNDWATER BODIES ESTONIA	GROUNDWATER BODIES LATVIA
QUATERNARY	HOLOCENE		Meghalayan		Quaternary Q	Unconsolidated sand, gravel and loam	Attached to the first embadded GWB	
			Northgrippian					
			Greenlandian					
	PLEISTOCENE		Upper					
			Middle					
DEVONIAN	UPPER-DEVONIAN	FRASNIAN	Ogre (D3og)		Upper Devonian D3	Fractured and karstified carbonate rocks	26	D6 D8
			Katleši (D3kt)					
			Daugava (D3dg)					
			Dubniki (D3db)					
			Plaviņas (D3pl)					
					Snetnaya Gora-Amata aquitard			
			Amata (D3am/D2am)		Middle Devonian (EE)/Upper-Middle Devonian (LV) D2	Sandstone (fractured)	23 24 25	A8 A10
			Gauja (D3gj/D2gj)					
	MIDDLE-DEVONIAN	GIVETIAN	Burtnieki (D2br)					
			Aruküla (D2ar)					
		EIFELIAN	Narva (D2nr)		Narva regional aquitard			

Alluvial gravel & sand
Limnoglacial silt & loam
Marl & gypsum
Dolo- & limestone (fractured & karstified)
Dolomitic marl
Sandstone (fractured)
Fluvioglacial sand & gravel
Glacial till

Perens, R., Vallner, L., 1997. Water-bearing formation. In: Raukas, A., Teedumäe, A. (Eds.), Geology and Mineral Resources of Estonia. Estonian Academy Publishers, Tallinn.
Retike, I., Männik, M., Marandi, M., Borozdins, D., Demidko, J., Bikše, J., Dēliņa, A., Popovs, K., Kukela, A. 2021. Conceptual Model Development for the Assessment of Transboundary Groundwater Resources in Cross-border Area (Estonia- Latvia). Conference: Conference: ISARM2021, 2nd International Conference Transboundary Aquifers Challenges and the way forward, 06 – 09 December 2021At: UNESCO, ParisAt: Paris, France ; https://isarm2021.org/

General ion chemistry

- Homogeneous ion chemistry, as also stated earlier (Levins & Gosk, 2008; Koit et al., 2021)
- Predominantly Ca-HCO$_3$ type
- Carbonate minerals are everywhere!



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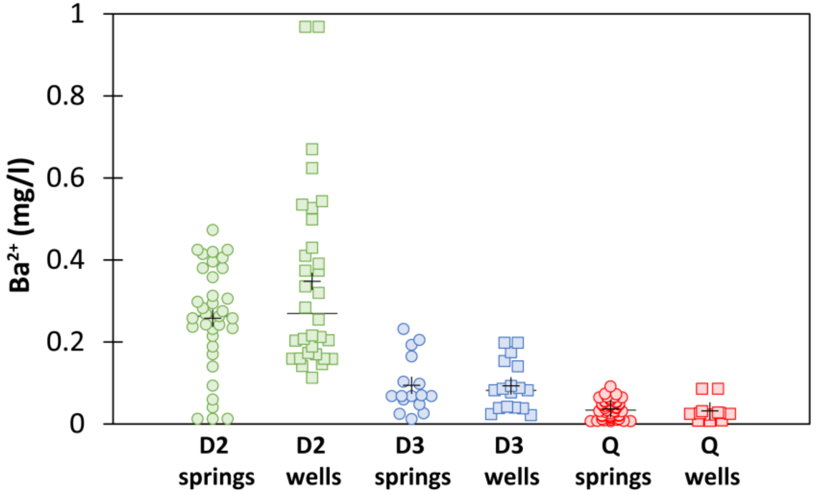
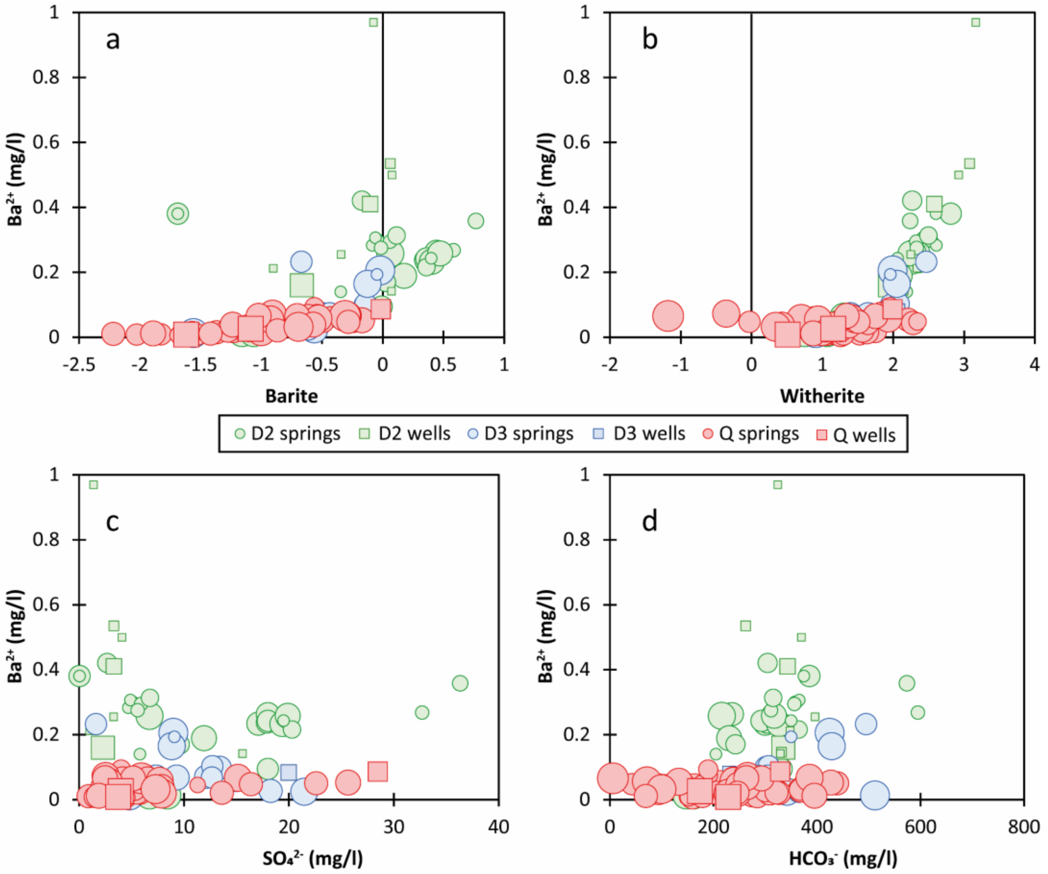
Levins I, Gosk E (2008) Trace elements in groundwater as indicators of anthropogenic impact. Environ Geol 55:285–290. https://doi.org/10.1007/s00254-007-1003-4

Barium

- **Ba^{2+} median concentrations significantly different in all three aquifer systems**
- Koit et al. (2021) used Ba^{2+} in a previous study to distinguish between D2 and Q groundwater
- Abundant in Devonian aquifers, but little studied (Edumnds & Shand, 2009; Levins & Gosk, 2008)
- Possibly originating from barite ($BaSO_4$) dissolution (Marandi et al. 2004; Mokrik et al. 2009)

Variable	K (Observed value)	K (Critical value)	df	p (Two-tailed)*	n (D2)	n (D3)	n (Q)	Significant differences between the sample groups*		
								D2 vs. D3	Q vs. D3	Q vs. D2
Ba (mg/l)	50.079	5.991	2	**< 0.0001**	34	18	52	**0.0211**	**0.0014**	**< 0.0001**
rBa/Ca (mmol/mol)	36.445			**< 0.0001**	34	18	52	**0.0011**	0.1759	**< 0.0001**
rBa/Sr (mol)	34.152			**< 0.0001**	31	18	52	**0.0040**	0.0835	**< 0.0001**
Fe (mg/l)	27.534			**< 0.0001**	41	30	54	**0.0484**	**0.0080**	**< 0.0001**
SO42- (mg/l)	13.288			**0.0013**	41	30	54	**0.0191**	**0.0003**	0.1989





Edmunds WM, Shand P (2008) Natural Groundwater Quality. Blackwell Publishing, Ltd, Oxford, UK

Testing the pre-assigned spring classifications

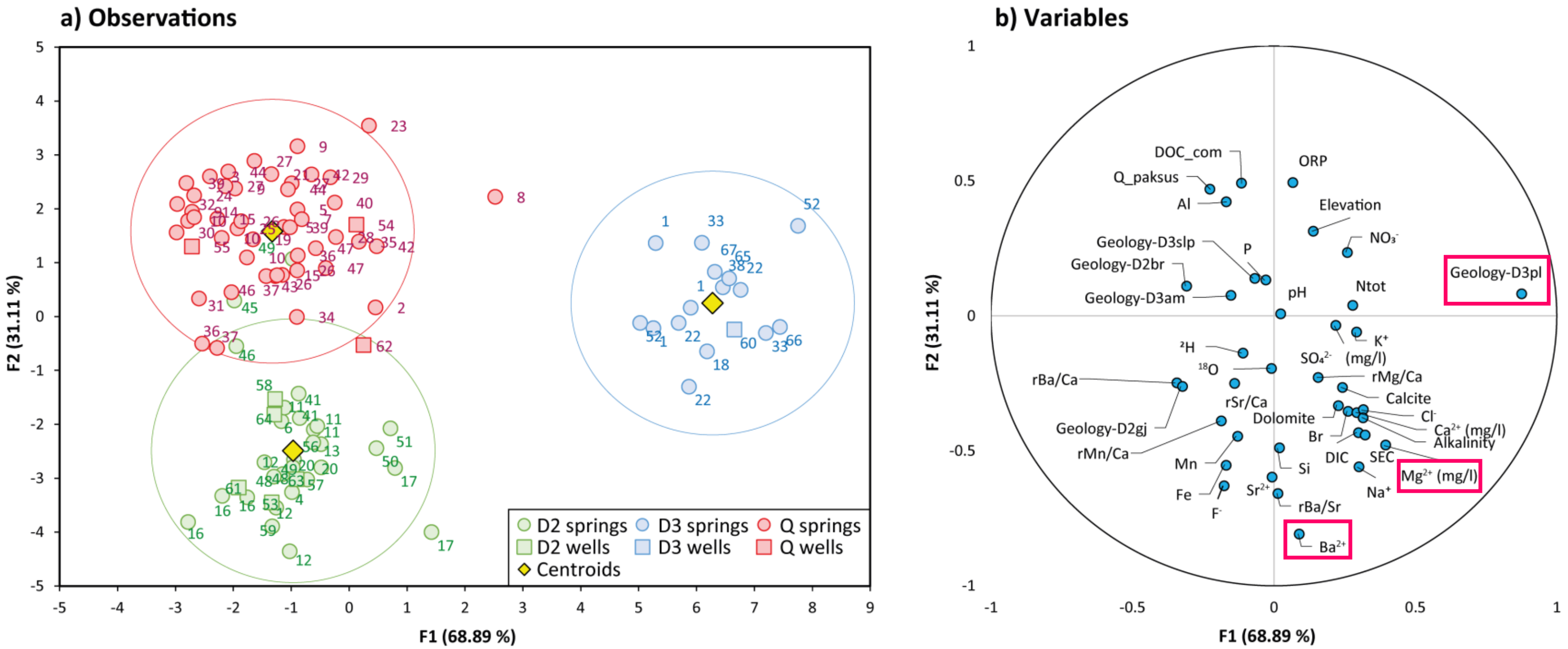
- **Discriminant analysis (DA) and random forests (RF) were used to test the classifications**
- Important role of Ba^{2+}, Mg^{2+} and bedrock geology in the classification of observations

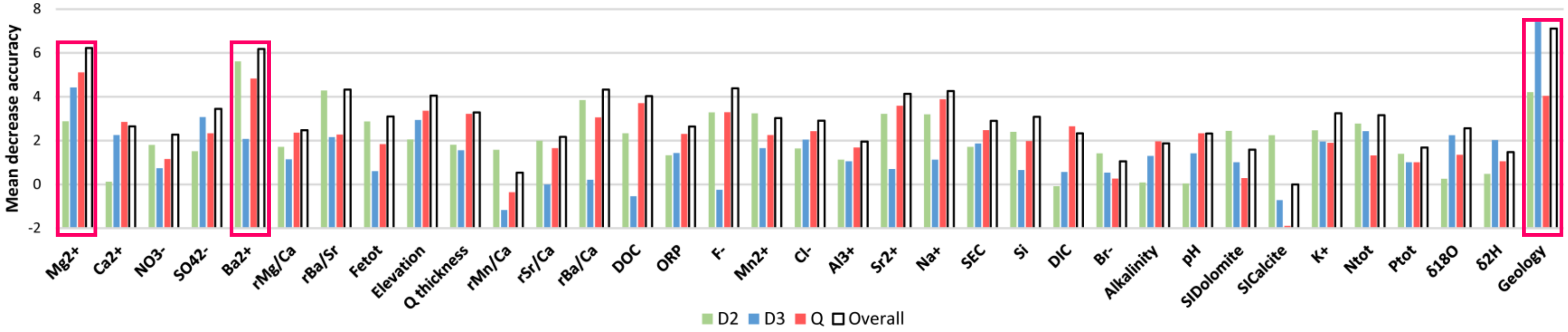
a) Confusion matrix for the training sample of DA

from \ to	D2	D3	Q	Total	% correct
D2	31	0	3	34	91.18%
D3	0	16	0	16	100.00%
Q	1	0	50	51	98.04%
Total	32	16	53	101	96.04%

b) Confusion matrix for the RF (OOB sample)

from \ to	D2	D3	Q	Total	% correct
D2	28	2	3	33	84.848
D3	0	12	1	13	92.308
Q	6	2	47	55	85.455
Total	34	16	51	101	86.139



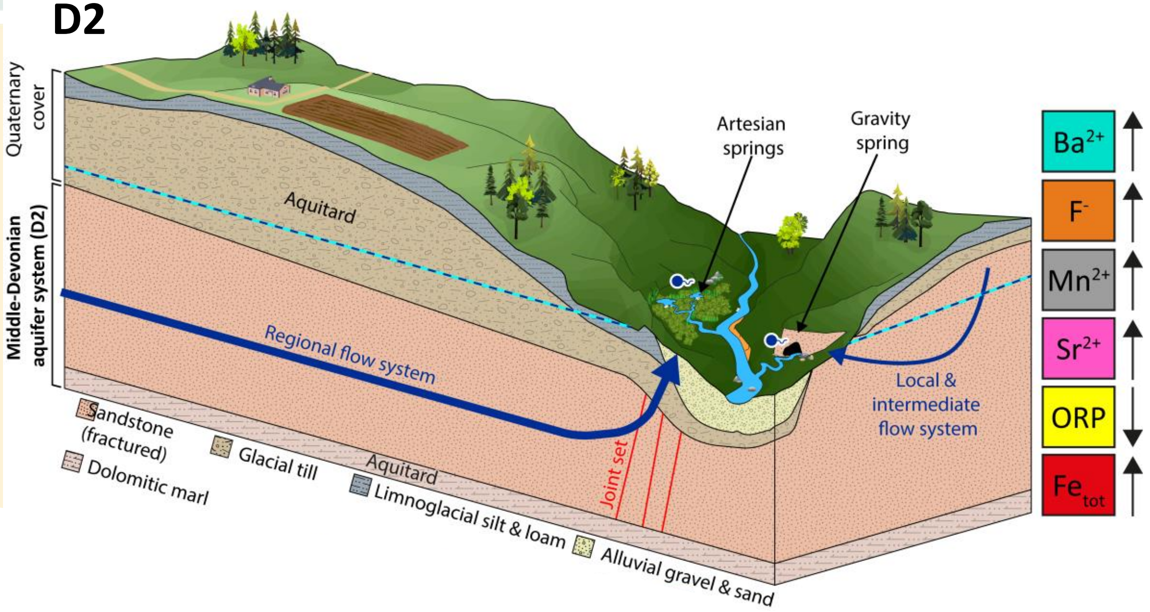


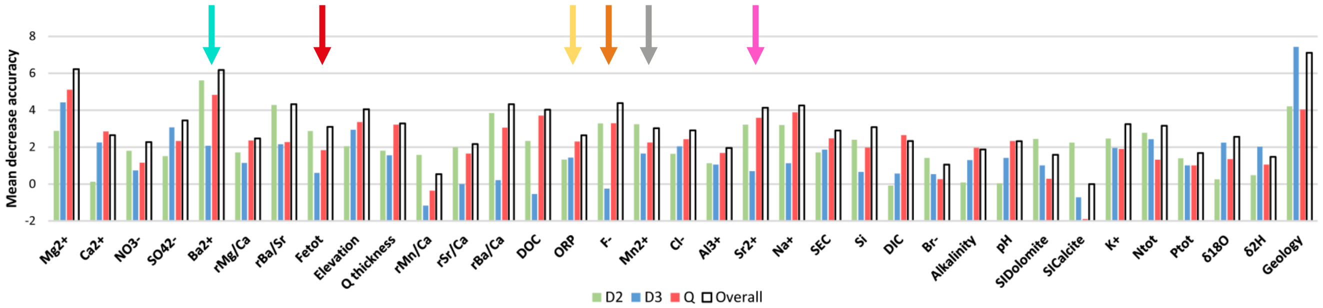
Marandi A, Karro E, Puura E (2004) Barium anomaly in the Cambrian-Vendian aquifer system in North Estonia. Environmental Geology 47:132–139. https://doi.org/10.1007/s00254-004-1140-y

Mokrik R, Karro E, Savitskaja L, Drevaliene G (2009) The origin of barium in the Cambrian-Vendian aquifer system, North Estonia. Estonian Journal of Earth Sciences 58:193–208. https://doi.org/10.3176/earth.2009.3.04

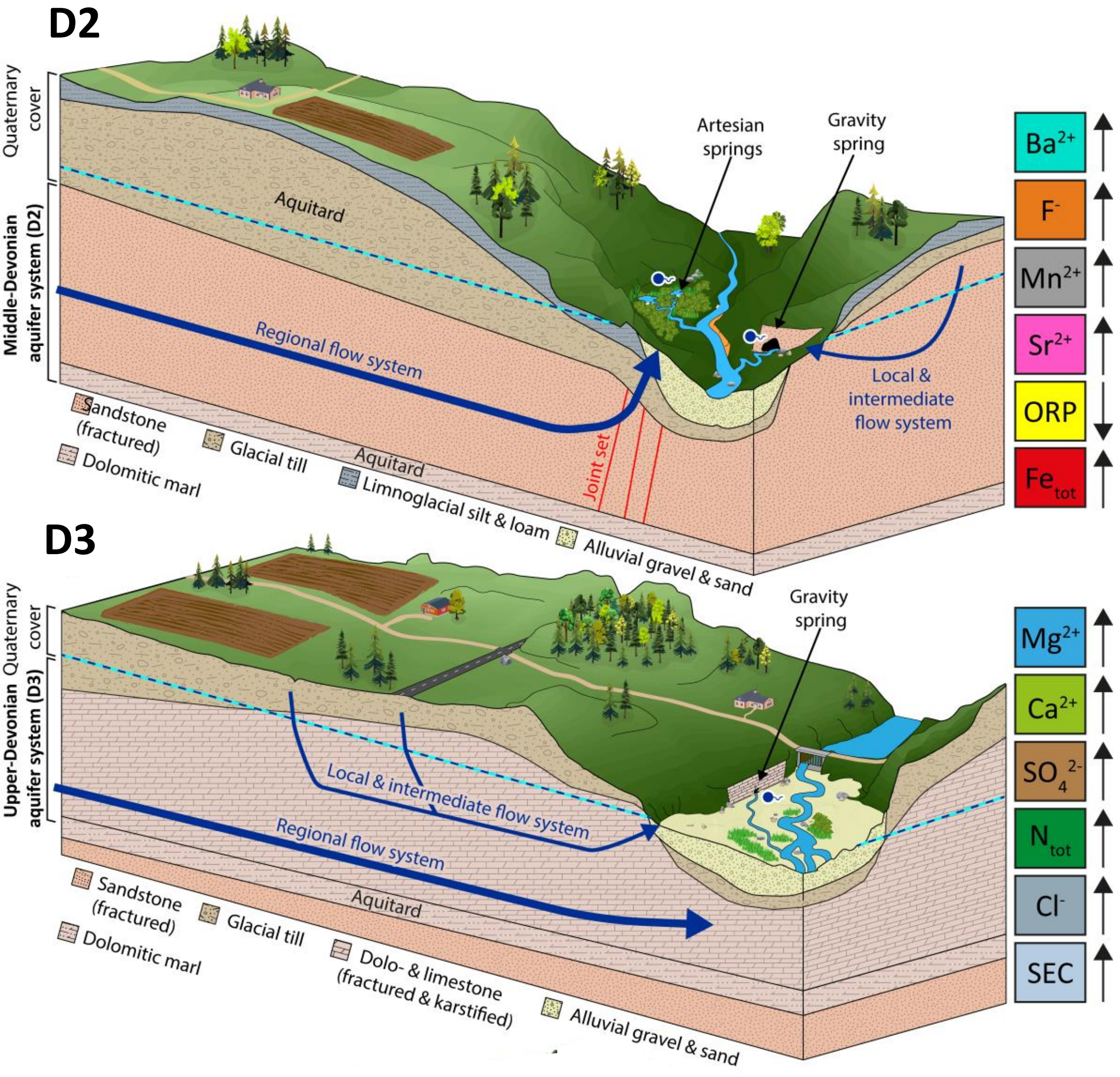
Conceptual models

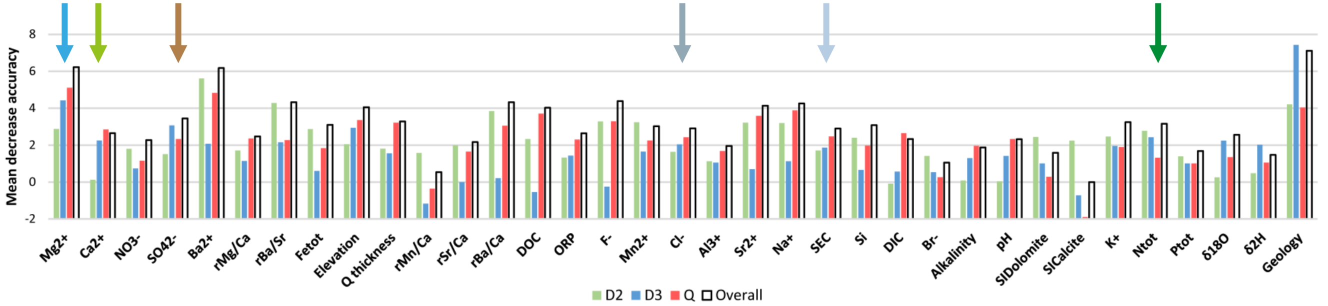
D2



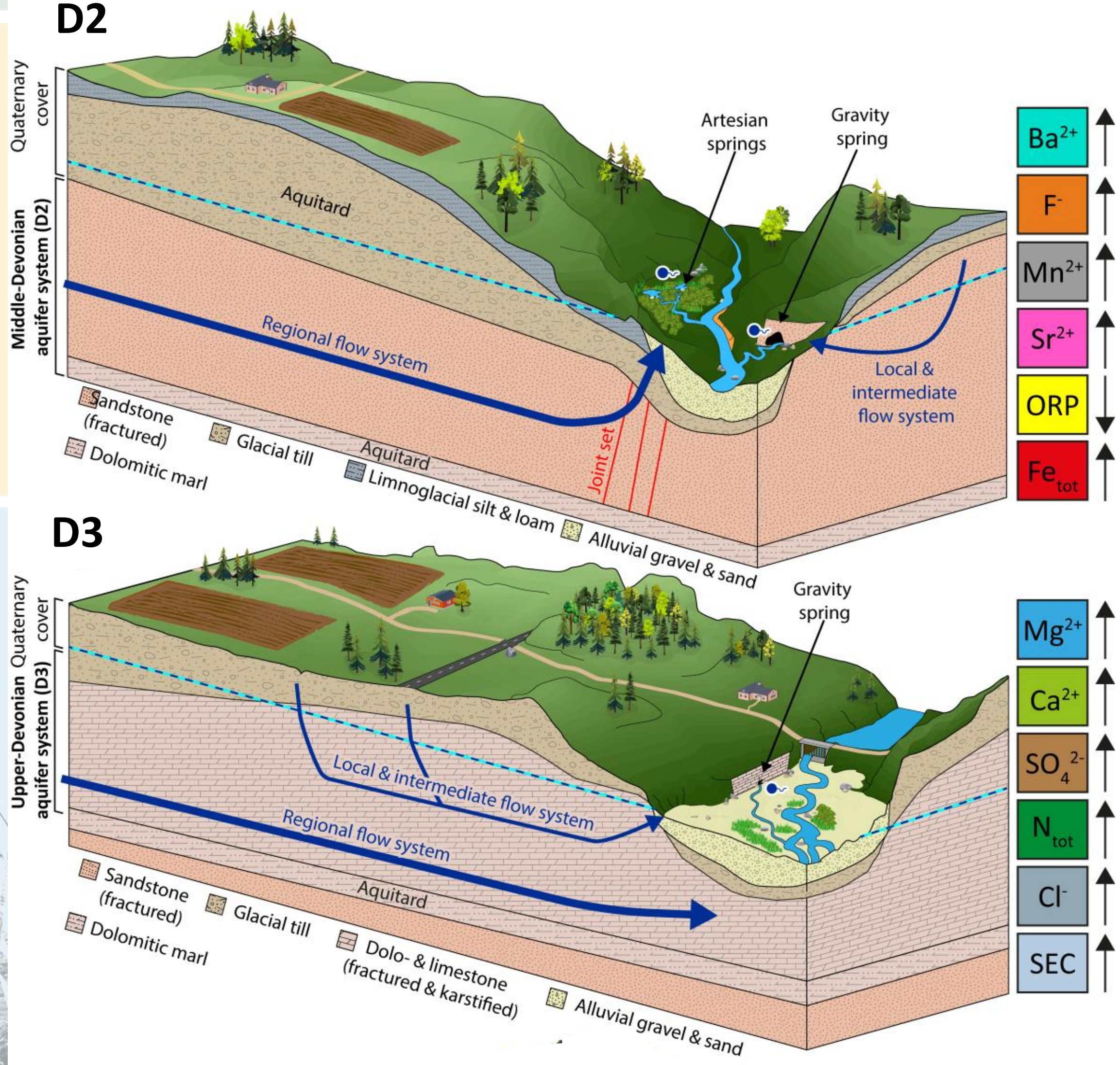


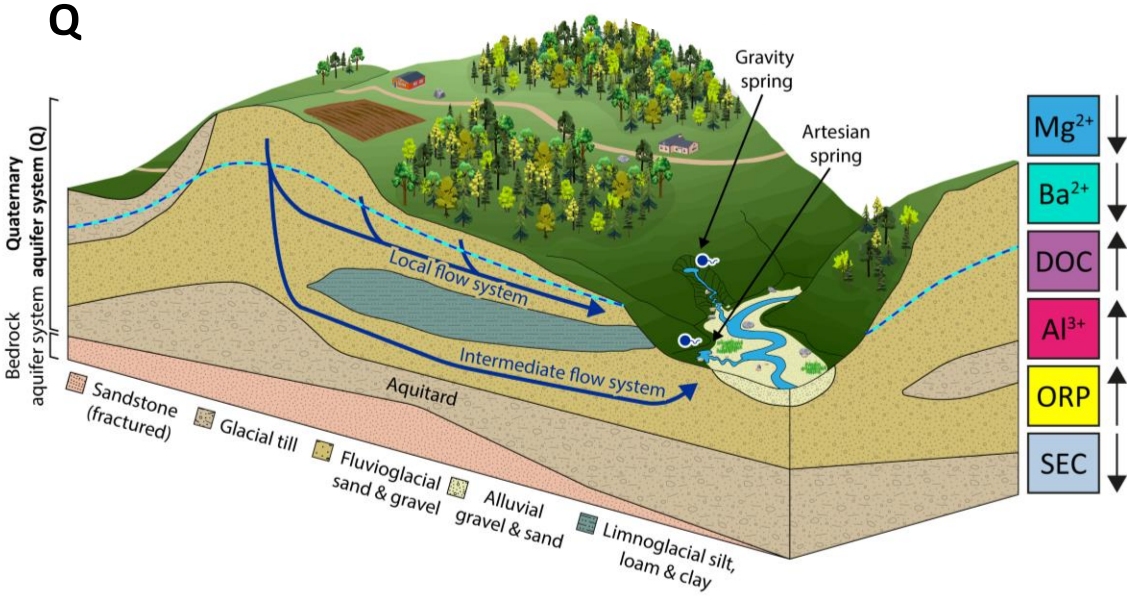
Conceptual models

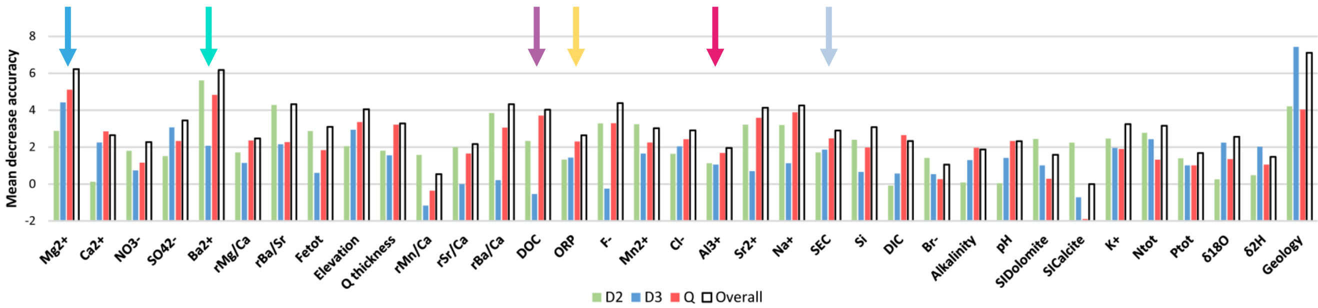




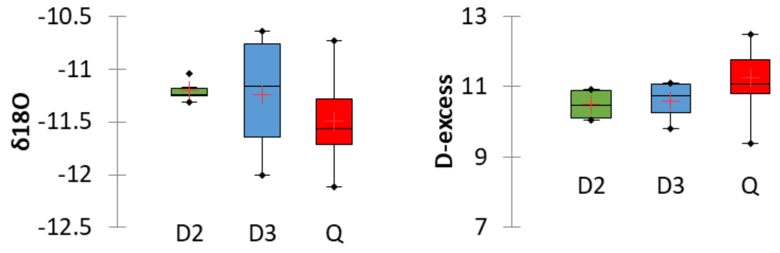
Conceptual models



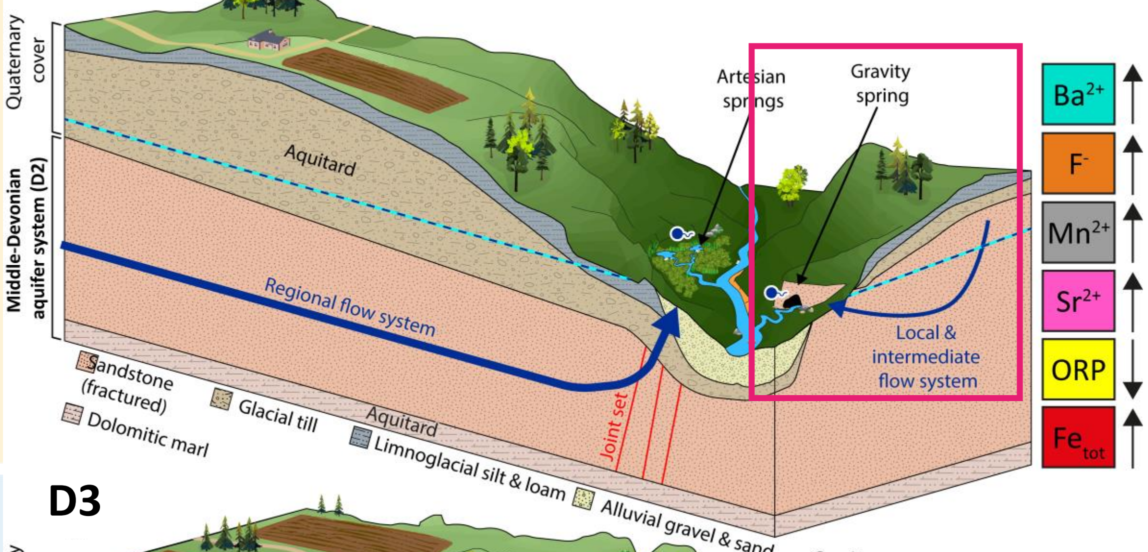




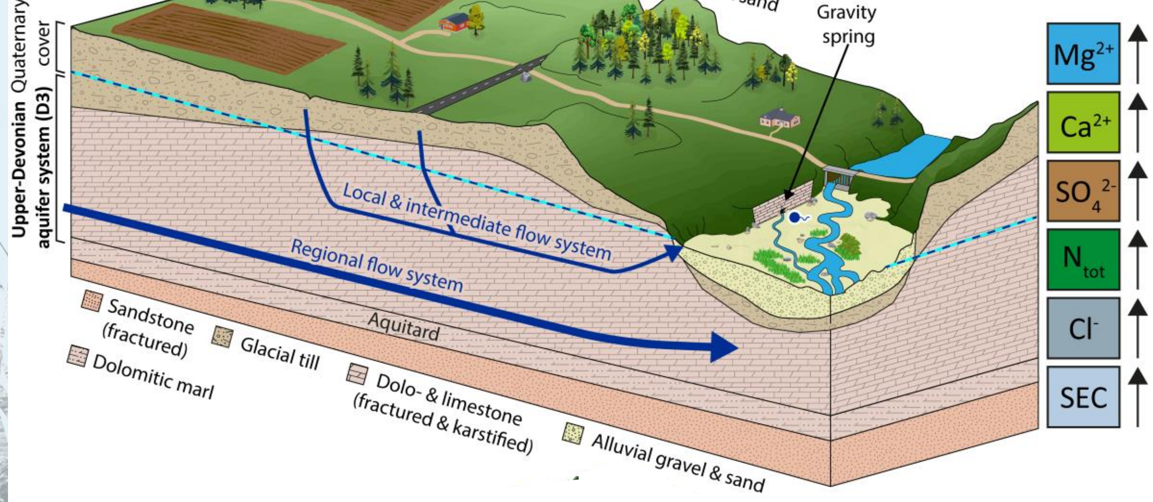
Conceptual models



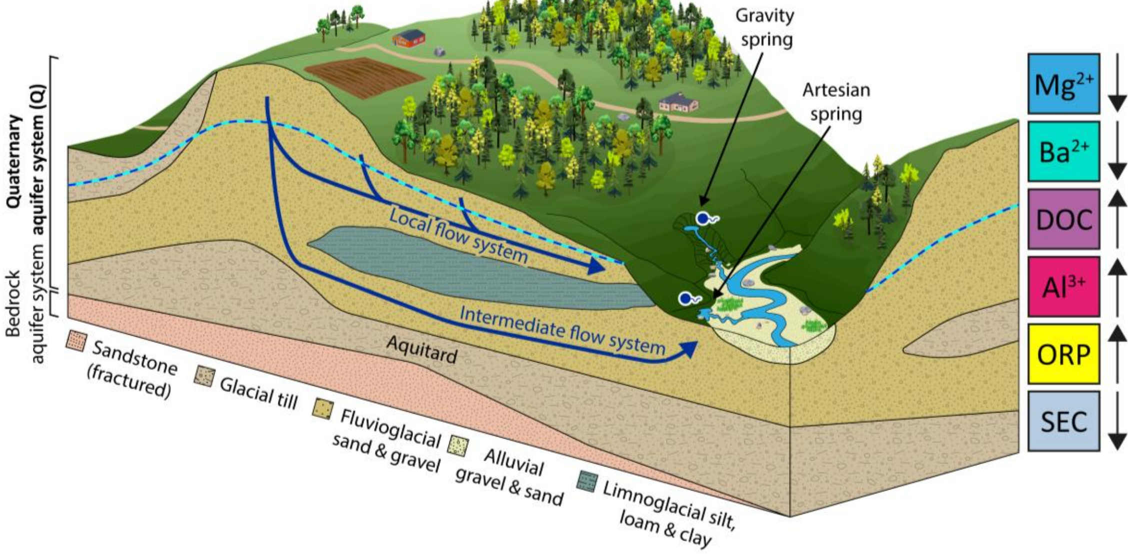
D2

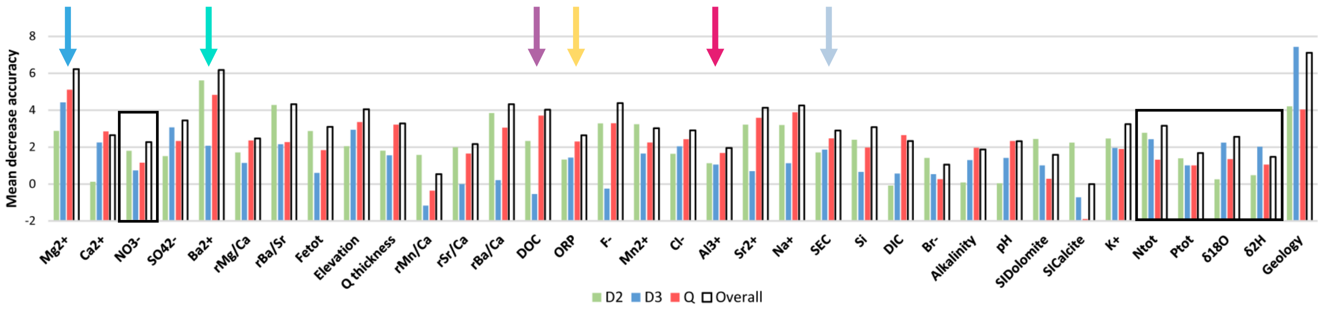


D3



Q



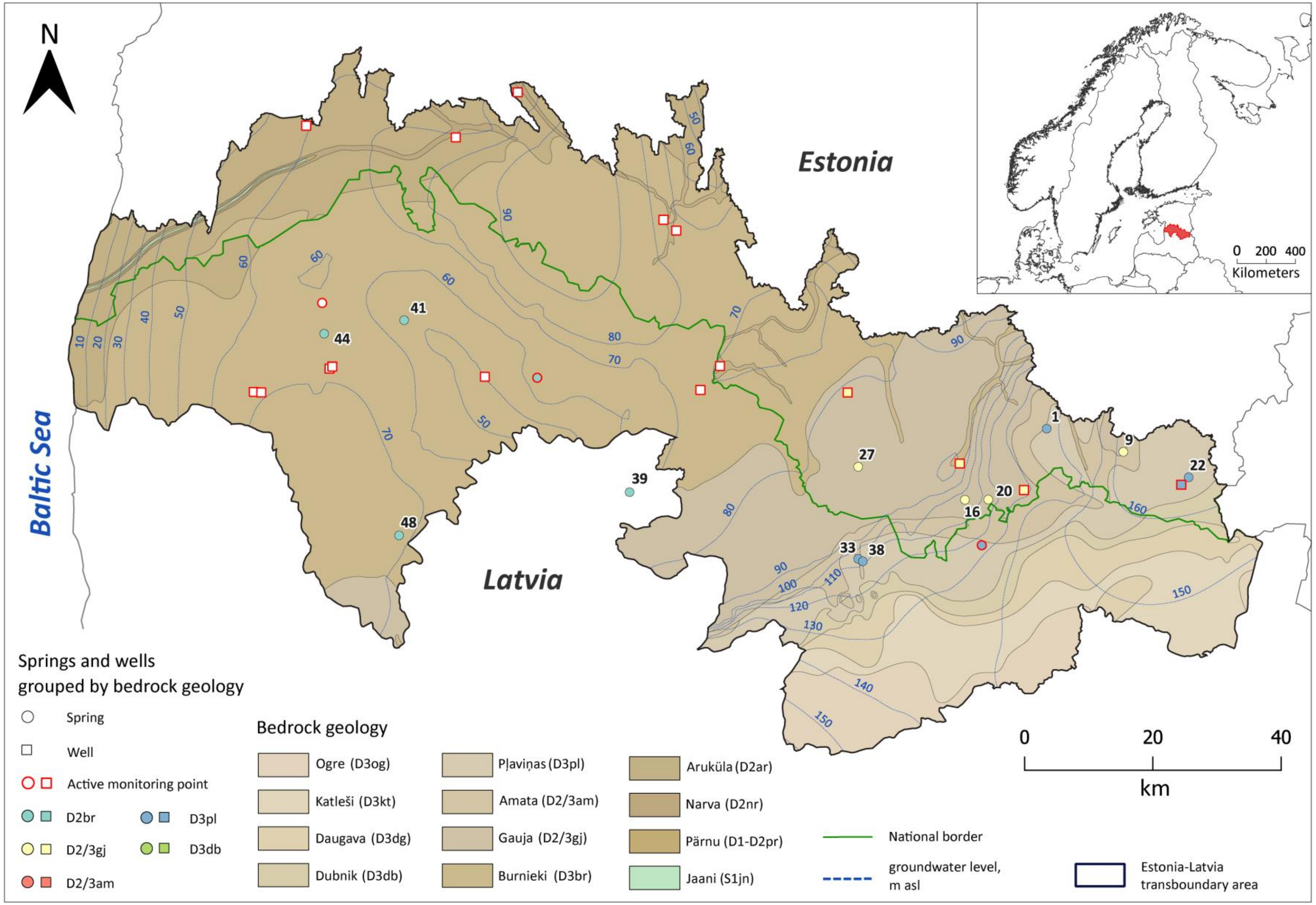


Selection of representative monitoring springs

- What could be the specific purpose of adding a spring in the GWB monitoring plan?
  - Local pollution survey?
  - Long-term background monitoring?
  - Drinking water quality in the popular “sacred” springs?

Aquifer system	Spring name	B	L	Elevation (m asl)	Quaternary cover thickness (m)	Bedrock index	Pre-assigned aquifer system	DA predicted aquifer system	Topography-derived watershed area (m2)	Bedrock watershed area (m2)	Specific conductance (µS/cm @ 25° C)
Q	Roodsi-Mõtsakunna spring	57.64576	26.39533	79.3	57.5	D2gj	Q	Q	15905	4161244	241
	Vorstimäe spring	57.65146	27.08879	237.1	111.4	D2gj	Q	Q	18299	1039958	490
	Velnakmens spring	57.86216	25.01626	42.1	19.5	D2br	Q	Q	45332	440313	190
	Oliņu spring	57.62026	25.79675	42.4	29.5	D2br	Q	Q	184930	4625614	127
D3	Viinavabriku springs	57.61156	27.25587	177.8	27.6	D3pl	D3	D3	21897	2519696	545
	Veskiläte spring	57.68862	26.89132	129.2	27.5	D3pl	D3	D3	16601	1080074	481
	Lauvas mutes spring	57.51329	26.39856	71.5	16.5	D3pl	D3	D3	10103	39745605	681
	Gaujienas spring	57.51695	26.38675	69.4	19	D3pl	D3	D3	11403	9202939	655
D2	Laurimäe spring	57.59401	26.67028	73.5	12.7	D2gj	D2	D2	12202	960161	533
	Tuurimäe spring	57.59298	26.73124	79	15.5	D2gj	D2	D2	11902	10481264	472
	Pantenes spring	57.86807	25.21666	46	19.2	D2br	D2	D2	12608	43990764	667
	Zilaiskalns spring	57.56691	25.19345	53.2	22.4	D2br	D2	D2		4803322	610

Selection of representative monitoring springs



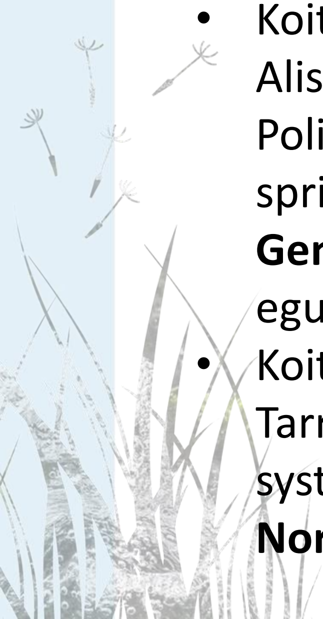
Concluding remarks

- Challenging to distinguish spring-aquifer links in multi-aquifer systems
- Specific tracers can help but need verification and confirmation
- Qualitative parameters could help to limit the uncertainty and ambiguity
- The used approach resulted in a satisfactory conceptual framework for further refinement

Research paper

- In parallel with the project, a scientific article has also been written.
- This presentation, as well as the general summary in the final report, are based on the analyzes and results of this article being written.

Scientific communication



- Koit, Oliver; Retike, Inga; Terasmaa, Jaanus; Bikše, Jānis; Lode, Elve; Vainu, Marko; Popovs, Konrāds; Babre, Alise; Abreldaal, Pamela; Sisask, Karin; Tarros, Siim; Marandi, Andres; Hunt, Marlen; Männik, Magdaleena; Polikarpus, Maile (2022). What we can learn about transboundary aquifers from geochemical signatures of springs. What we can learn about transboundary aquifers from geochemical signatures of springs: **EGU General Assembly 2022, Vienna, Austria, 23–27 May 2022**. Copernicus GmbH. DOI: 10.5194/egusphere-egu22-5008.
- Koit, O.; Retike, I.; Terasmaa, J.; Bikše, J.; Lode, E.; Vainu, M.; Popovs, K.; Babre, A.; Abreldaal, P.; Sisask, K.; Tarros, S.; Marandi, A.; Hunt, M.; Männik, M.; Polikarpus, M. (2022). Conceptualizing transboundary aquifer systems using geochemical signatures of springs. In: NHC2022: **Hydrology and Water-related Ecosystems. The Nordic Hydrological Conference (NHC2022)**, Tallinn, 15.08-18.08.2022.

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