3.12 Description of a glacial paleowater case study, Estonia

Title of Case Study	Dating of Glacial Palaeogroundwater and its Implications on Groundwater Management in Estonia, North-Eastern Europe.
Location (region, Country)	north-eastern Europe, Estonia
Other information	

Description of Case Study (background information on the region)
Estonian territory is located in the northern part of the Baltic Artesian Basin (BAB), which is a groundwater reservoir in north-eastern Europe. Here, groundwater recharged prior to the beginning of the Holocene has been observed in various depths and locations. In northern Estonia, groundwater originating from subglacial recharge during the Pleistocene glaciations has been preserved in the deep sandstone aquifers of Cambrian-Vendian (Ediacaran) and Ordovician-Cambrian aquifers (Vaikmäe et al., 2001; Raidla et al., 2009, 2012; Pärn et al., 2016, 2019). Their presence is revealed mainly by very light isotopic composition ($\delta^{18}O$ values from −16‰ to −23‰) that differs markedly from values found in modern precipitation and shallow groundwater in the study area (about −10‰ to −12‰; Raidla et al., 2016). More recently this groundwater has also been dated using ^{3}H, ^{14}C, ^{85}Kr, ^{81}Kr, ^{40}Ar and radiogenic ^{4}He as tracers (Raidla et al., 2012; Gerber et al., 2017; Pärn et al., 2019).

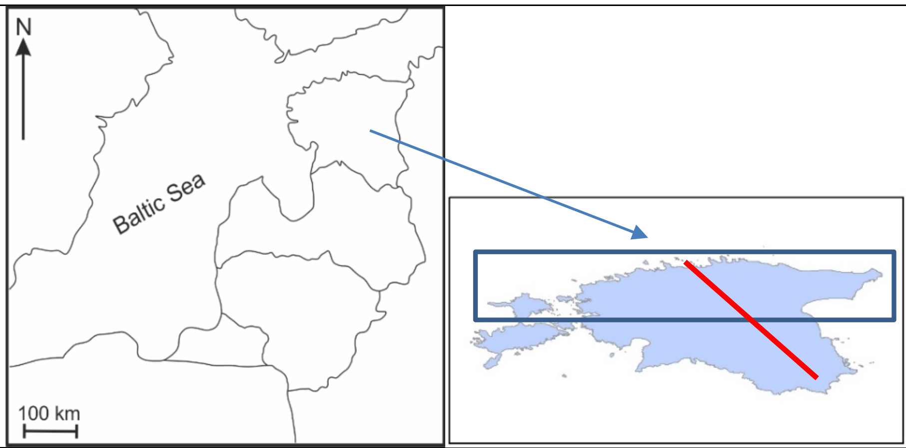
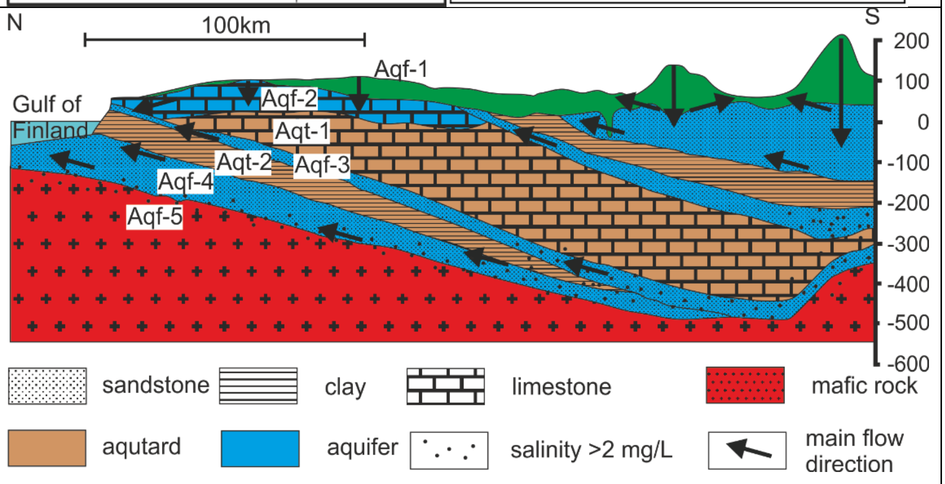
Description of problem (why is this location chosen for a Cases Study)
Groundwater in the Cambrian-Vendian and Ordovician-Cambrian aquifer system is a unique groundwater resource in Europe, where a large portion of water originating from the Pleistocene Ice Sheets has been preserved. The first step towards a responsible and sustainable management of such a resource would be the determination of its origin, age and renewal rates. Groundwater is the most important source of public water supply in Estonia making up ~60% of all consumed water from public water supply networks. Understanding the processes influencing recharge and geochemical evolution of groundwater is crucial for predicting the effects of groundwater abstraction on its composition and availability. Also, glacial palaeogroundwater offers possibilities to study the multi-faceted nature of information about pre-Holocene environmental conditions recorded in palaeogroundwater reservoirs. More specifically, they provide an example on how groundwater can serve as an important paleoenvironmental archive enabling the study of variations in climatic and environmental conditions during glacial-interglacial cycles in the Pleistocene (Raidla et al., 2019). Finally, the study of palaeogroundwater occurrence enables one to establish the depth of the zone where active exchange with modern infiltration takes place and renewable groundwater is formed. A weak connection of glacial palaeogroundwater reservoirs with modern groundwater recharge and isolation from potential anthropogenic contamination makes it a high-quality resource, which should be treated as a strategic reserve and used for specific purposes (e.g. for potable water).

Methods to be used in the Case Study (analytical and isotope techniques, modelling)
Glacial palaeogroundwater in Estonia has been studied using a multi-tracer approach involving the hydrochemical composition of groundwater, a suite of stable ($\delta^{2}H_{H2O}$, $\delta^{18}O_{H2O}$, $\delta^{13}C_{DIC}$, $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, $\delta^{13}C_{CH4}$, $\delta^{2}H_{CH4}$) and radioactive isotope tracers (^{3}H, ^{14}C, ^{85}Kr, ^{81}Kr, ^{40}Ar and radiogenic ^{4}He) and the study of dissolved gas compositions in groundwater (CH_4, CO_2, noble

gases). In addition, the geochemical evolution and groundwater age has been studied with geochemical modelling using the software programs GWB, PHREEQC and NETPATH.

Results from this Case Study
The spatial and vertical distribution of glacial palaeogroundwater in the northern part of the BAB is shown to be wider than previously thought (e.g. Pärn et al., 2016; Pärn, 2018). The corrected radiocarbon age of the Cambrian–Vendian groundwater suggests that infiltration occurred not earlier than 14,000–27,000 radiocarbon years ago, which is coeval with the advance and maximum extent of Scandinavian Ice Sheet during the LGM (Raidla et al., 2012). The dating of glacial palaeogroundwater in the O-Cm aquifer system allowed to identify groundwater originating from three different climatic periods: (1) the Holocene (0–10 ka BP); (2) the LGM (~10–22 ka BP) and (3) the pre-LGM period (>22 ka BP; Pärn et al., 2019). To the south the salinity and residence time of groundwater increases with brines found in the central parts of the BAB (Latvia and Lithuania) having ages >1.3 Ma years based on noble gas age tracers ^{81}Kr, ^{4}He and ^{40}Ar (Gerber et al., 2017). Glacial palaeogroundwater in the northern BAB has gone through a significant geochemical evolution after its infiltration. Its chemical composition has been altered through the dissolution of carbonate minerals, cation exchange reactions, oxidation of organic matter and mixing with groundwater originating from modern precipitation, saline formation water and the Baltic Sea. These processes have sometimes led to an increase in concentrations of F^-, NH_4^+, Ba^{2+}, ^{226}Ra and CH_4 which can affect the drinking water quality, but overall the glacial palaeogroundwater complies well with the drinking water quality standards (Marandi, 2007; Suursoo et al., 2017; Pärn et al., 2018; Raidla et al., 2019a, b). The results also suggest that the zone where active exchange with modern infiltration takes place and renewable groundwater is formed, does not reach as deep as previously thought (down to 250 m), but glacial palaeogroundwater weakly connected to the modern hydrologic cycle can already be found locally at shallow depths of 50 m, b.g.s. Finally, the study of the isotopic composition of CH_4 suggests that during the advance of continental ice sheets in Pleistocene, large volumes of this organic matter accumulated beneath it. Subsequently, both the organic matter and its oxidation products were carried into the subsurface by infiltrating glacial meltwater (Raidla et al., 2019).

Impact - how this Case Study contributes to the overall project aims
The results of the Case Study contribute to the enhancement of understanding of natural variability of groundwater quality and the risk of transfer of anthropogenic dissolved compounds to aquifers. More specifically the results contribute to quantifying groundwater age distributions and evaluating the efficiency of programme of measures, the design and assessment of monitoring programmes and the creation of EU-wide aquifer vulnerability maps.

Name of pilot area / aquifers / type: North Estonia / Quaternary, Ordovician, Cambrian and Ediacaran sand- and limestone aquifers / dual porosity	**Country:** Estonia **Region:** North-Estonia
Study level	Transboundary : ☐ Regional: x Local: ☐ Single well(s): ☐
Type of observations *(choose one of the options, create separate template if needed for each type if each type need specific information)*	☐ Short screened observation wells (not pumped) ☐ Long screened observation wells (not pumped) x Pumped wells, long screens in one aquifer ☐ Pumped wells, long screens over multiple aquifers ☐ Springs ☐ Other (eg. research wells; indicate type and information on pumping):
Approximate location of pilot:	
Geological cross section / conceptual model of the pilot area:	
Name of Shape- / Geopackage file defining the area: Eesti_wgs84.shp	**Projection to be used:** WGS84 (Epsg4326)

Hydrological parameters:	**Mean annual precipitation (mm or range in mm)**	**Mean annual groundwater recharge (mm or range in mm)**	**Mean annual groundwater recharge temperature (°C)**	**Thickness of unsaturated zone (range in m)**
	600-800	30-270	unknown	0-30
Pumped wells only		**Typical pump discharge of sampled individual well (m^3/day):**		**Typical pump discharge of complete well field (m^3/day):** *If relevant*
List of aquifers and aquitards in pilot area		**No. of confined or semiconfined aquifers in pilot area: 2**		**No. of unconfined aquifers in pilot area: 1**
Aquifer no. (aqf): 5 **Aquitard no. (aqt): 2** **Aquiclude no. (aqc): 0**	**Aquifer/aquitard type and/or name**	**Lithology *(Resource WP6 terminology)***	**Depth range (m)**	**GW age range (yr)**
Aqf-1: Q	Quaternary deposits	Fine sand to gravel	Mainly 0 – 50 (locally up to 100 m)	unknown
Porosity type	Porous: X	Fissured: ☐	Karst: ☐	Fissured and porous / dual porosity: ☐
Aqf-2: S-O	Silur-Ordovician	Limestones	0 – 200	unknown ($\delta^{18}O$=-11 to -16‰)
Porosity type	Porous: ☐	Fissured: ☐	Karst: ☐	Fissured and porous / dual porosity: X
Aqt-1: O		Clay, argillite		
Porosity type	Porous: X	Fissured: ☐	Fissured and porous / dual porosity: ☐	No hydraulically active porosity: ☐
Aqf-3: O-Cm	Ordovician-Cambrian	Sandstones	0 – 250	modern – >30,000
Porosity type	Porous: X	Fissured: ☐	Karst: ☐	Fissured and porous / dual porosity: ☐
Aqt-2: Cm		Clay		
Porosity type	Porous: ☐	Fissured: ☐	Fissured and porous / dual porosity: ☐	No hydraulically active porosity: X
Aqf-4: Cm-V	Cambrian-Vendian	Sandstone	60 – 300	14,000 – at least 180,000
Porosity type	Porous: X	Fissured: ☐	Karst: ☐	Fissured and porous / dual porosity: ☐
Aqf-5: PR_2	Crystalline	Mafic rocks	unknown	unknown
Porosity type	Porous: ☐	Fissured: ☐	Karst: ☐	Fissured and porous /

	dual porosity: X
Applied tracer age indicators (^{3}H, ^{3}H/^{3}He, ^{85}Kr, ^{39}Ar, ^{14}C, ^{36}Cl, ^{81}Kr, ^{4}He, CFCs, SF_6, etc.) **Applied recharge temperature indicators** (^{18}O, D, noble gases)	**Aquifer-1** ^{18}O, D
	Aquifer-2 ^{14}C, ^{18}O, D
	Aquifer-3 ^{3}H, ^{3}H/^{3}He, ^{14}C, ^{4}He, ^{18}O, D noble gases
	Aquifer-4 ^{14}C, ^{18}O, D noble gases
	Aquifer-5 ^{14}C, ^{18}O, D
Number of sites (wells/springs) with age indicators	**Aquifer-1** **1-5:** ☐ **5-10:** X **10-25:** ☐ **>25:** ☐
	Aquifer-2 **1-5:** ☐ **5-10:** ☐ **10-25:** ☐ **>25:** X
	Aquifer-3 **1-5:** ☐ **5-10:** ☐ **10-25:** ☐ **>25:** X
	Aquifer-4 **1-5:** ☐ **5-10:** ☐ **10-25:** ☐ **>25:** X
	Aquifer-5 **1-5:** X **5-10:** ☐ **10-25:** ☐ **>25:** ☐
GW age range (GAR) **GAR-1: Modern (< 60 yr)** **GAR-2: Old (> 60 yr and 10 kyr)** **GAR-3: Paleowaters (> 10 kyr)**	**Aquifer-1** **GAR-1: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** ☐ **>50%:** X **GAR-2: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** ☐ **>50%:** ☐ **GAR-3: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** ☐ **>50%:** ☐
	Aquifer-2 **GAR-1: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** ☐ **>50%:** X **GAR-2: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** X **>50%:** ☐ **GAR-3: 1-10%:** X **10-25%:** ☐ **25-50%:** ☐ **>50%:** ☐
	Aquifer-3 **GAR-1: 1-10%:** X **10-25%:** ☐ **25-50%:** ☐ **>50%:** ☐ **GAR-2: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** X **>50%:** ☐ **GAR-3: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** ☐ **>50%:** X
	Aquifer-4 **GAR-1: 1-10%:** X **10-25%:** ☐ **25-50%:** ☐ **>50%:** ☐ **GAR-2: 1-10%:** ☐ **10-25%:** X **25-50%:** ☐ **>50%:** ☐ **GAR-3: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** ☐ **>50%:** X
	Aquifer-5 **GAR-1: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** ☐ **>50%:** ☐ **GAR-2: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** X **>50%:** ☐ **GAR-3: 1-10%:** ☐ **10-25%:** ☐ **25-50%:** ☐ **>50%:** X
Groundwater age ranges (GAR) estimated by:	**Tracer based estimates** X **Flow and age model simulations** X **Combination of model and tracer estimates** X **Expert judgement:** X

Objective of age dating studies:

Basic research or General groundwater management	Assessment of pollutant history	Assessment of the efficiency of remediation and mitigation measures	Indication of vulnerability of aquifers and water supply wells
x			

Water Usage *(not relevant for observation wells)*	**Water supply**	**Irrigation**	**Industry**	**Other**
	x	x	x	

Geoenergy related activities *(not relevant for observation wells)*	**Shallow Geo-T**	**Deep Geo-T**	**Hydrocarbons**	**Nuclear waste disp.**	**CO_2 storage**
	x				

Mining activities *(not relevant for observation wells)*	**Construction materials**	**Minerals / metals**	**Coal**	**Other**
	x		x	

REFERENCES

OPEN Access reports and papers (PDF versions made available in EGDI repository making them downloadable via maps and keyword / free text searches):

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Remarks / other relevant information: The serious consequence of intensive groundwater use in Soviet era (1950 to 1990) include the formation of regional depressions of potentiometric level, which has caused cardinal changes in the direction and velocity of filtration flows in the lower aquifers (O-Cm and Cm-V). Nowadays use of groundwater could be little or missing in these urban (eg Tallinn) or former industrial areas, but the groundwater potentiometric level is still more than 10 m lower than the natural potentiometric level. Lateral flows conduce the transport of brackish water from the deeper Crystalline aquifer. Seawater intrusion into the groundwater intakes has not noted yet. In this light, the pumping rate of individual well (m^3/day) doesn't reflect the real situation and we don't give any number because they can be very misleading.