4th Annual Meeting of G@GPS

Palaeogroundwater from past and present glaciated areas

Estonia, 5-9 July 2015

Abstracts & Field Guide

Institute of Geology at Tallinn University of Technology

4th Annual Meeting of G@GPS IGCP 618 Project

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Edited by
Joonas Pärn, Valle Raidla, Rein Vaikmäe, Anto Raukas & Heikki Bauert

Tallinn, 2015

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Preface

The global G@GPS (Groundwater@Global Palaeoclimate Signals) project was formally started in 2012 with coordinating meeting in Niagara Falls, Canada. The G@GPS project is an inclusive group of scientists that involves around 70 participants from 32 countries and has held annual meetings and workshops with training courses in different continents and countries (2013 in Bobole, Mozambique and 2014 in Leizhou Peninsula, Guangdong Province, China).

The present volume was prepared for the 4th annual meeting "Palaeogroundwater from past and present glaciated areas" and mini-workshop on time-series and spectral methods in climate variability analysis as related to groundwater held in Tallinn, Estonia. The meeting was hosted by the Institute of Geology at Tallinn University of Technology (TUT) on 5–9 July 2015. Over 40 participants attended the meeting. The scientific sessions and the mini-workshop were held in the campus of the Tallinn University of Technology on 6th and 7th of July. The post-conference excursion was organised on 8th of July to visit the post-glacial landscape of the northern part of the Baltic Artesian Basin (BAB). A short demonstration of sampling for groundwater noble gas and total gas composition analyses was run by Werner Aeschbach-Hertig.

Talks of this meeting summarised recent advances in studies on the G@GPS flagbasins, modelling and age dating of palaeogroundwater together with other related topics. *The organizers thank all contributors and are particularly grateful to keynote speakers Victor Bense and Roland Purtschert; to Werner Aeschbach-Hertig for running the demonstration of groundwater sampling and to Jason Gurdak and Jesse Dickinson for running the mini-workshop. The Organizing Committee acknowledges the generous financial support from UNESCO IGCP and from INQUA. Finally, the logistic support from the TUT and the Institute of Geology at TUT is gratefully acknowledged.*

Rein Vaikmäe
On behalf of the Organising Committee

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Estimating the past from deep groundwaters in Finland

L. Ahonen, R. Kietäväinen and T. Ruskeeniemi

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Development of a concept for safe geological disposal of spent nuclear fuel from the Finnish power plants launched new lines of hydrogeological research, focusing on the origin and long-term evolution of groundwaters in the fractures of crystalline rock of the Fennoscandian Shield. The bedrock subjected to repeated glaciations may contain signs of glacial melt waters that can be used in constructing past courses of events as a scientific basis for future scenarios. Stable isotopes of water provide a most useful tool in unravelling environmental conditions, time scale and sources of water hosted by deep crystalline formations. On the other hand deep groundwaters in the Finnish bedrock are often saline and contain variable amounts of dissolved gases. A striking feature observed recently along with improved sampling methodologies is the relatively high concentration of dissolved helium in deep saline groundwaters.

Stable isotope composition of groundwaters in crystalline bedrock has been determined in numerous drill holes in Finland as a function of depth between about 50 – 2500 m. Most of the fresh and brackish water samples plot close to the GMW-line in a deuterium vs. O-18 diagram, having $\delta^{18}O$-values between about -15 – -11 per mil), but there are two groups of "outliers" in the data that have been of special interest: isotopical very light waters ($\delta^{18}O < -15$; $\delta^{2}H < -110$) and deep saline waters, which are relatively heavy and plot clearly above the GMWL.

Very light isotope compositions indicating an average precipitation clearly colder than present are interpreted to have been affected by the past glaciation(s) of the Fennoscandian Shield. Sites where this type of waters have been observed situate close to the Salpausselkä end formations, i.e., Palmottu Natural analogue site in Southern Finland, Outokumpu mining and exploration area in Eastern Finland, and a 600 m deep drill hole in Satakunta sandstone, Western Finland.

Deep saline waters in Finland (typically at depths >500 m) contain Ca, Na and Cl as the main dissolved salts at total concentrations (TDS) from some tens to more than 100 g/L. Dissolved gases are also abundant in these waters: methane concentration varies, but often it is the predominant component, whereas nitrogen and helium seem to be present constantly as the other main components. Distinct stable isotope composition of these waters can be explained by long-term water/rock interaction and evolution from warm-temperature rain water. Isotope studies also indicate that dissolved helium is derived from natural radioactive decay. Thus, time scale of evolution of these waters was estimated to be in the range of tens of millions of years.

Investigation of recharge and discharge mechanisms of a multi-aquifer system using environmental isotopes

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This study aims to determine the recharge, discharge and the mixing mechanisms of a complex aquifer system located above the Kazan trona ore field using the environmental isotopes of deuterium, oxygen-18, carbon-13 and carbon-14, chlorofluorocarbons (CFC-11, CFC-12) and the noble gas isotopes (He, Ne, Ar, Kr and Xe).

There are four basic rock sequences exposed in the study area which are, from bottom to top, Paleozoic Metamorphics, Eocene sequences (Mülk formation and Akpınar Limestone), Neogene Units and Plio-Quaternary deposits (Toprak and Rojay, 2000, 2001 and Rojay et al., 2002). The trona mineral, found in the Eocene deposits, is planned to be extracted by the solution mining. In order to assess the potential impacts of the mining activities on groundwater resources, detailed hydraulic and hydrogeochemical studies were carried out (Yazicigil et al., 2001; SRK, 2001 and 2004; Camur et al. 2008; Yazicigil et al. 2009). The groundwater system under investigation consists of three different aquifers named as shallow, middle and deep. The Akpınar formation lying between deep and middle systems acts as an aquitard (SRK, 2004).

$\delta^{18}O$ and $\delta^{2}H$ vary from -8.10‰ to -12.80‰ and from -60.89‰ to -92.60‰ VSMOW within the whole system. There is an isotopic contrast between the shallow and deeper aquifer systems and even between the unconfined and confined parts of the middle and deep aquifers. The average isotopic depletion between unconfined and confined parts of the system is -2.5‰ in $\delta^{18}O$ and -20‰ in $\delta^{2}H$. It is not possible to explain this depletion solely with the elevation effect (Arslan, 2008; Arslan et al., 2013, Arslan et al., 2015).

CFC concentrations indicate modern recharge to the shallow aquifer system, whereas the concentrations are close to the detection limits therefore CFC's were unable to date the middle and deep aquifer systems however proves the existence of modern recharge to this system (Arslan, 2008; Arslan et al., 2015).

The Noble Gas Temperatures (NGT) indicate the average yearly air temperatures in shallow aquifer system (14 °C) whereas the recharge temperatures are 4 to 8 °C lower than todays in deep groundwater system. This finding is also supported by the dissolved inorganic carbon's radiocarbon activities being close to the detection limits in the same system. These activities together with the stable isotope data reveal the evidence of recharge to the middle and deep aquifer systems under considerably cooler climatic conditions as compared to today during the late Pleistocene (Arslan, 2008; Arslan et al. 2013).

Mantle-He escape to shallow aquifer system is believed to be along a deep buried fault system located in downgradient areas (Arslan et al., 2015).

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Modelling of the groundwater isotopic composition using precipitation water isotope model as forcing

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The isotopic signal in the groundwater is derived from isotopic signal in precipitation with modulation introduced by local recharge conditions as well as underground mixing due to convection and diffusion. Here we aim to test, if it is possible to explain the observed $\delta^{18}O$ and $\delta^{2}H$ values in the groundwater using a regional hydrogeological flow model and modelled isotopic composition of precipitation as forcing.

We use the three-dimensional hydrogeological model of the Baltic Artesian Basin from Virbulis et al. (2013). The isotopic signal in precipitation from Terzer et al. (2013) is used as external forcing. For model validation we use a data set of almost two hundred $\delta^{18}O$ and $\delta^{2}H$ measurement values in the groundwater.

The mean $\delta^{18}O$ value in the groundwater is -11.1‰ with standard deviation 0.7‰, while the mean $\delta^{2}H$ value -79.9 ‰ with standard deviation of 5.1‰, respectively. The isotopic composition follows the global meteoric water line. The exception is few most enriched samples, where $\delta^{18}O$ is relatively more enriched than the $\delta^{2}H$ is, suggesting evaporative enrichment. In comparisons the modelled range in yearly average precipitation of $\delta^{18}O$ value is from -9.06‰ to -11.91‰ and from -64.3‰ to 88.9‰ in case of $\delta^{18}H$ (Terzer et al., 2013) in the area covered by the hydrogeological model. So, the isotopic values of groundwater largely are within the modelled range of precipitation.

The transitional flow model set-up treats the isotopic values as passive tracers introduced at the earth surface along with infiltration water. To honour the legacy of ice-age on the hydrogeological system in the region, the initial condition of the model is defined as having uniform, strongly depleted groundwater isotopic composition through the system.

We acknowledge that the current model setup involve a list of significant simplifications, for example, ignorance of changing isotopic signal in precipitation during the Holocene, or seasonality of groundwater recharge or dramatic simplification of geological structure in the hydrogeological model. Nevertheless the modelling experiment will give qualitative if not quantitative and certainly informative results.

Acknowledgments. This research is supported by NRP project EVIDENnT project "Groundwater and climate scenarios" subproject "Groundwater Research".

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Evaluating the impact of past glaciations on the present-day hydrogeology of sedimentary aquifer systems

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It has been well established that the occurrence of anomalous fresh groundwater deep in sedimentary aquifer systems is associated with hydrogeological conditions during Pleistocene glaciations, when groundwater recharge rates were often strongly elevated compared to present-day conditions. In addition, today's patterns of elevated and strongly reduced pore pressures have been recognised as being the result of the mechanical loading and unloading by the weight of the ice-sheet which has been waxing and waning over the land surface. These and other signatures of the current transient nature of the hydrogeology of these basins which have been studied in America (e.g. Williston and Michigan Basins), or in Eurasia (e.g., Baltic Basin), are the result of the long equilibration times of these systems to changes in boundary conditions, which significantly exceed the time-scale of Pleistocene glacial cycles. Effective, safe and sustainable execution of human activities such as the extraction of geothermal energy, the recovery of shale gas, the sequestration of carbon dioxide or the storage of nuclear waste, require a well-developed understanding of the hydrogeological conditions in which these activities take place. Both heuristic and site-specific numerical modelling has been carried out for the hydrogeological evolution of these systems forced by glacial cycles in order to better understand the present-day state of these basins. These modelling efforts have attempted to include the relevant transient hydrogeological processes, and sufficient detail on the geological make-up in order to interpret specific field data for these processes. However, in many cases it is unclear how hydrogeological boundary conditions in these models need to be assigned and what the relative importance of different processes is over the time scales of millennia. We will explore the state-of-the-art in the numerical modelling of these systems, and the design of modelling studies. We will discuss specific difficulties of data-model comparisons for these systems.

A snapshot of groundwater residence times and water stable isotope results across the Australian continent (2015 update)

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The G@GPS (Groundwater@Global Paleoclimatic Signals) was setup to explore links between paleogroundwater climate-derived observations (low resolution) and other palaeoclimate archives (higher resolution) e.g. speleothemes, palynological reconstructions, etc. Initially, an emphasis was placed in large aquifers (e.g. Baltic Aquifer Basin, etc) and intercontinental comparisons. However, the addition of smaller groundwater basins has improved paleoclimatic interpretations and allowed intracontinental interpretations. Several reasons contribute to this: 1) better geographic distribution; 2) smaller basins are more likely to contain groundwater with residence times between 0 to ~30 ka, the gap where $^{14}C_{DIC}$ can obtain best results and better matching to other paleoclimate proxy records; 3) shorter flow paths minimize intense water-interaction processes, maximising residence time estimations; and 4) small systems are more likely to record local conditions while bigger counterparts (e.g. Great Artesian Basin, Australia) represent mixtures of several regional recharge zones in some cases thousands of kilometres away from the recharge zone.

During the last 5 years several new datasets have been incorporated into our snapshot of Australia groundwater (Fig 1). The need to understand inter-aquifer connectivity, particularly within coal seam gas (CSG) exploitation zones, and regulatory assessments of aquifer sustainability, have driven most of the research in Australia. In the case of CSG studies, many groundwater samples are beyond ^{14}C capabilities and occasionally $^{36}Cl/Cl$ residence times have been suggested. In order to interpret the distribution of paleo-groundwater recharge across Australia, we have assembled a continent wide database comprising over 1300 groundwater samples. Information includes geographical, geological data as well as available geochemical information. Geochemical data include mostly $^{14}C_{DIC}$, $\delta^{13}C_{DIC}$ and

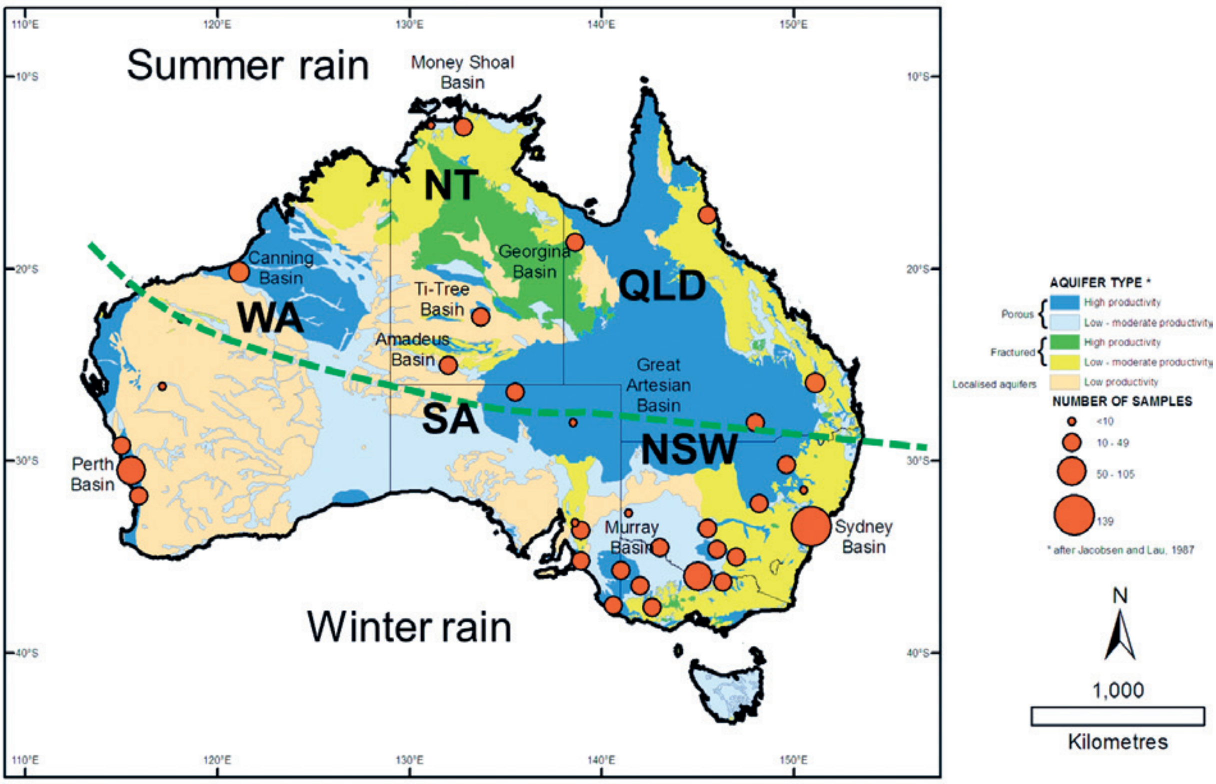

Figure 1. Hydrogeological map of Australia with groundwater localities used in the assessment.

water stable isotopes ($\delta^{18}O$, $\delta^{2}H$) with other complementary information such as ^{3}H activity or major ion composition available in some cases.

In general, $^{14}C_{DIC}$ shows a wide spread of values (0 – 140 pmC) with an average of ~51 pmC. Radiocarbon values have been filtered so all "bomb-pulse" affected samples are considered modern, prior to building a chronological framework. Due to the uncertainties associated with hydrogeochemical ^{14}C corrections and the difference of input data for each individual study, original corrections were maintained, if provided. Any other treatment was done on individual basis when data from neighbouring basins allowed better estimates for input parameters. Interestingly, there are observable patterns and distinctions in the frequency of pmC data over the last ~30 ka. The greatest frequency of observations occurred in the range of 0 – 10 pmC, which assuming no sampling bias, would suggest important late Pleistocene recharge. There also seems to be a slight 'dip' in pmC frequency during the period of 20–40 pmC. This may indicate a period of less recharge and/or an enhanced dryness with a diminished water cycle, roughly coinciding with the end of the last glacial.

Water stable isotopes show the meteoric origin of groundwater across the continent and reveal important evaporation processes during recharge for some basins, including: Otway Basin (SA), Murchinson River Basin (WA), West Canning Basin (WA), Murray Basin (Lake Cooper, VIC) and Murray-Darling Basin (NSW, QLD). In general groundwater isotopic trends are more depleted from the coast to the interior, particularly in northern areas where major rainfall is dominated by the Australasian monsoon. The increasing aridity in the Holocene in most of the continent suggests only large, rainfall/flooding events produced effective recharge. On a general temporal scale, modern groundwater generally appears to be more isotopically enriched.

Paleoclimatical signals from large aquifers: a case study in North China Plain

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Major aquifers worldwide, under favorable conditions, can retain low temporal resolution information on climatic conditions at the time of recharge. This generally geochemical information can be used to better constrain reaction of the aquifer to climatic changes or even to assess long term groundwater sustainability. Understanding whether major aquifers at similar latitude world-wide share similar climatic responses and records is one of the objectives of the G@GPS (Groundwater@Global Palaeoclimatic Signals) network. One emblematic aquifer in the North China Plain (NCP) was selected as case study. The NCP is located in the eastern China between 35º00'–40º30'N and 113º00'–119º30'E, bounded by the Taihang Mountains to the west, the Yanshan Mountains to the north, the Bohai Sea to the east, and the Yellow River to the south. The plain was formed through fault subsidence since the Cenozoic and deposition of Quaternary sediment 400–600 m thick by the Yellow River and other main rivers.

Deep aquifers of more than 100 m depth were found to be older than 10 ka using the ^{14}C method (Chen, 2010), some groundwater samples were found to be 770 ka BP by using $^{36}Cl/Cl$ though mixing of various sources was suspected (Dong et al., 2002). 4He was also tested to date groundwater ages in the NCP and relatively consistent results were obtained comparable to those from ^{14}C (Wei et al., 2011). As stable isotopic features are the mixture signal of both temperature and other factors, noble gases collected from groundwater were used to calculate the recharge temperature and thus differentiate the influences of temperature and monsoon intensity (Kreuzer et al., 2009). This could be compared to high resolution records obtained fromstalagmite calcite in two caves Dongge and Hulu, China (Wang et al., 2001; Dykoski et al., 2005).

The objectives of this paper are: 1 – reconstruction and analyses of paleoclimatic signal from groundwater of the NCP with additional information. 2 – Identification of possible recharge events with the frequency distribution of data series. 3 – Comparison of the paleoclimatic signal from the aquifer with that from stalagmite calcite records.

Paleoclimatic reconstitution from geochemical investigations of the recharge conditions of a deep confined aquifer in an arid region (case of the Continental Intercalaire in Southern Tunisia)

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The stable isotope contents in the Continental Intercalaire (CI) aquifer throughout the Southern Tunisia (30°10'–34°10' N; 7°30'–10°30' E) reflect differences in paleoclimatic conditions of the recharge scenario from the late Pleistocene to the present.

$\delta^{18}O$ and $\delta^{2}H$ signatures shown in the deeper groundwater of the CI aquifer (Nefzaoua area), typical of old water, have ranges of -8,6 to -7,3‰ vs V-SMOW for $\delta^{18}O$ and -67,01 to -50,5‰ vs V-SMOW for $\delta^{2}H$. These depleted $\delta^{18}O$ and $\delta^{2}H$ signatures are related to humid periods of the Late Pleistocene and Early Holocene. This water age is consistent with the negligible radiocarbon contents. However, the measured stable isotope contents in the shallower groundwater of the CI (Eastern piedmont of Dahar uplands) range from -7,7 to -4,8 ‰ vs V-SMOW for $\delta^{18}O$ and from -59.9 to -32.9 ‰ vs V-SMOW for $\delta^{2}H$. Compared with the current annual isotopic precipitation signatures of the nearest stations such as Sfax (-4.60 ‰ vs V-SMOW for $\delta^{18}O$ for the period 2012–2013) and Kairouan (-4.52 ‰ for $\delta^{18}O$ vs V-SMOW from 2008 to 2012), the most enriched samples of the aquifer system could present a process of recent recharge. Tritium activities of these samples showed values of more than 1 TU indicating therefore that the origin of this component comes from recent precipitations on the CI outcrops in the eastern piedmont of Dahar.

Also, results from chemical analysis support the evolution of the CI groundwaters from the piedmont of Dahar up to the Chott region. The temperature increases progressively with the deepening of the aquifer which highlights the thermal gradient in accordance to the SE-NW flow path of the aquifer. Groundwater well head temperatures range around 21°C in the Dahar area and 60°C in the Nefzaoua area. The total dissolved solids show values less than 1g/l in the piedmont of Dahar which reflects the infiltration of rain water in the CI outcrops. However, in the region of Nefzaoua they increase up to 5g/l which could be mainly explained by an interaction from the hosting rock enhanced by a long residence time of water in the reservoir.

Modelling palaeogroundwater in cold-climate regions

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Groundwater basins in cold-climate regions are probably among the least studied hydrogeological systems in the World. Foremost, this is because such systems are mainly situated in remote areas with harsh climatic conditions, where population densities are low. Moreover, where the permafrost is continuous over large areas, groundwater recharge is expected to be very limited and terrestrial discharge mainly takes place in some few springs. A study of sub-permafrost groundwater was carried out in Svalbard, the Arctic Archipelago north of Norway. Based on field observations and simulation models it was concluded that major discharge conduits only formed during extensive global glacial phases, beneath the parts of the ice-sheet were the ice was temperate. During most of the interglacial periods, when the glaciers retreat, the number of discharge springs will decrease gradually while continuous permafrost develops across the area. Presently, the amount of recharge and thereby discharge in each individual groundwater spring is highly dependent on short-time fluctuations in precipitation and air temperature. This situation may also be applicable in other areas with continuous permafrost where glaciers are abundant and parts of them are temperate. Such conditions occur in e.g. Greenland and on islands north of the North American mainland, as well as in parts of Antarctica.

However, we cannot invoke a scenario of glacial development and retreat in all cold-climate regions to explain the present-day existence of sub-permafrost groundwater flow systems. Sub-permafrost groundwater also exists in permafrost areas where few or no glaciers occur today and where the recharge has taken and takes place under e.g. larger lakes, rivers or snowfields.

In many areas the groundwater systems may be much older than assumed in Svalbard. Their cycles may relate to multiple glaciations or to true non-glacial periods in the past. The development and melting of thick continuous permafrost are slow processes and the dynamic of the related groundwater systems may be dependent on the alternation between cold and mild climate episodes lasting for many thousands of years. Hence, cold-climate groundwater systems have many of the same characteristics as the large groundwater basins in arid and semi-arid areas in warmer parts of the World in which recharge conditions are also governed by long term climate fluctuations.

We will present different conceptual models for polar groundwater occurrence and dynamics and discuss how to approach large-scale numerical modelling of such data-poor systems. We want to examine how to use palaeoclimate information to understand the changes of the recharge and discharge over long time spans.

Estimation of transit times in a Kart Aquifer system using environmental tracers: Application on the Jeita Aquifer system-Lebanon

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Estimating transit times in aquifer systems is very important to assess the vulnerability of an aquifer to contaminants. Transit time is site specific since it depends on recharge rates, temperatures, elevation, saturated and unsaturated zones, and on the aquifer media. Groundwater in karst aquifer is assumed to be relatively young due to fast preferential pathways, however these aquifers contain slow flow components resulting from stored water in the fissured matrix that are not renewed quickly. These differences create significant variation in the groundwater age as the water sampled will be a mix of different water that has been transported through different flow pathways (fissured matrix and conduits). Several methods can be applied to estimate water transit time of an aquifer. Groundwater age dating using different environmental tracers is being widely used. Groundwater residence time in the Jeita spring aquifer (Lebanon) was estimated using several environmental tracers such as Chlorofluorocarbons (CFCs), Sulfur Hexafluoride (SF_6), Helium-Tritium (^3H, ^3H- ^3He). Additional analysis such as Oxygen and Hydrogen stable isotopes ^{18}O, ^2H, and major ions was performed in groundwater samples for the characterization of the water types. Groundwater samples were collected from six different wells in the Jeita catchment area (Jurassic Kesrouane aquifer) as well as from the spring itself. Preliminary results are satisfactory and reproducible; however final results will be available end of May to be compared and contrasted, whereby processes playing a role in the variation of age within each system will be discussed.

In Lebanon this type of groundwater age dating was not applied previously. An analysis of CFCs, SF_6, Helium and Tritium in four springs from different catchment areas was done as part of the Jeita Project (Geyer and Doummar, 2013). The obtained results show that water is relatively young ranging between 1 – 10 years. But the collected samples didn't account for the atmosphere interaction with the spring water which resulted in this age variation, as spring water equilibrates with ambient air in the cave.

Therefore, the use of environmental tracers in karst systems in semi-arid environments is a new approach that will help characterize the transit time distribution in the Jeita catchment along with its mean transit time. Furthermore, this study is complemented with the analysis of a series of artificial tracer tests to assess fast transit times under various flow conditions in different compartment in the Jeita karst system (Doummar, 2012). Tracer experiments showed that transit times ranged between 3 and 292 hours. The shortest transit times were recorded in the Jeita subsurface conduit (3 to 19 hours under various flow conditions) while injections in sinkholes yielded fast to moderate transit times ranging between 25 and 90 hours, however the fissured matrix and fissured unsaturated zone resulted in a wider range of relatively long transit times (69 to 292 hours).

Thus, the results from different mentioned techniques; namely tracer experiments and environmental tracers are combined to assess the variation of transit times in the Jeita karst aquifer, considered one of the most important springs/ feature in Lebanon.

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A global compilation of paleowater isotope compositions

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Chemistries of paleowaters, represented by groundwater that recharged before the Holocene, have long been used to explore and better understand climate changes of the past. Shifts in $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios between the last ice age and the late-Holocene preserved in paleogroundwaters can be used to better understand impacts of the ~4°C warming (Annan and Hargreaves, 2013) of Earth's atmosphere that took place over the past 20,000 years. Understanding past, natural warming is important for anticipating impacts of current manmade climate warming on regional water resources. Here the isotope compositions of paleowaters derived from direct precipitation (Jasechko et al., 2015) and subglacial meltwaters (Ferguson and Jasechko, *in review*) are compiled from within the primary literature. While the temporal resolution of groundwater records is poor relative to speleothems and glacial ice, groundwater records of last glacial period to Holocene $\delta^{18}O$ and $\delta^{2}H$ shifts are twice as common as the combined total of speleothem and ice core records. Global patterns of $\delta^{18}O$ and $\delta^{2}H$ changes from 20−50 ka to ~0−5 ka are consistent with enhanced isotopic distillation of air masses during the last ice age, likely impacted by the larger glacial-interglacial temperature changes at high-latitudes relative to the equator (Annan and Hargreaves, 2013). Results from five isotope enabled general circulation model simulations of pre-industrial and last glacial maximum climates highlight that models capture glacial-interglacial shifts well across North America and Europe, while diverging from measurements in parts of the humid tropics. This compilation is incomplete as important records are likely dispersed within grey literature. Bolstering this first compilation could enable further interpretation of continental scale climate changes since the last ice age.

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Subglacial groundwater flow pattern and its influence on salt water intrusions in Southern Denmark – a numerical model approach

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Today, groundwater is the main source of water supply in Denmark. Aquifers in the low lying areas near the Wadden Sea in Southern Denmark are vulnerable to saltwater intrusion which is likely to intensify due to the relative rise of sea level. To understand the dynamics and development of this complex flow system, the initial conditions imposed by the last Scandinavian ice sheet (SIS) must be taken into account.

In the presented study we investigate the influence of SIS during the Weichselian glaciation (ca. 115.000 – 11.000 a BP) on the current groundwater flow pattern. Special focus is on the development of salt water intrusions in the coastal aquifers in Southern Denmark due to the postglacial sea level rise. During the Weichselian, the eastern part of Denmark was covered by few-hundred-meters-thick ice sheet while the sea coast was located west of the British Isles. Additional pressure of frozen water impacted the hydraulic conditions and the groundwater flow patterns both in the underlying aquifers and in the glacier foreland. Potentiometric surface in the vicinity of the ice surface amplified the hydraulic pressure and generated a high hydraulic gradient oriented from the ice sheet interior toward its margin forcing the groundwater deep into the bed, and towards and beyond the ice margin. It can be speculated that as a result of the increased hydraulic head, the Eemian marine salt water has been flushed out of the subglacial and foreland aquifers. Hence, at the end of the Weichselian the aquifers likely contained freshwater only. With the ice melting, the groundwater pressure decreased initiating again changes in the flow patterns. During the postglacial sea level rise the shore migrated to the east and salt water penetrated the coastal aquifers in southwest Denmark. It is likely that the groundwater-flow dynamics, driven by the postglacial hydraulic head drop and the relative sea level rise are not yet equilibrated and, enhanced by the potential future sea level rise due to climate change, contamination of fresh-water aquifers will continue.

The 620-km^2 - large study in the south-western part of Jutland was not overridden by the Weichselian ice sheet but lay in its immediate foreland. Geophysical and geological research shows salt water intrusions up to 20 km inland from the present coast. A densely discretized voxel model (100x100x5m) spans Miocene through Quaternary deposits to a depth of 500 m. A 3D large-scale finite-difference numerical groundwater flow and transport model, including density-driven flow is used in a first step to simulate the distribution of the current saltwater intrusion. Particle tracking and direct age simulations are performed to identify the recharge areas and constrain groundwater ages. In a second step a palaeo-geological model will be constructed as a basis for a groundwater flow model simulating the impact of ice sheet cover and the imposed pressures on groundwater flow patterns.

During a field campaign in February 2015, groundwater samples, both from Miocene and Quaternary aquifers, were collected for isotope age dating that later will be used to calibrate and validate the transport model. From the chemical and isotopic composition the origin of the groundwater will be determined. Where the collected data and simulations indicate groundwater recharged during the last glaciation analyses of heavy noble gases will be carried out in order to estimate recharge temperatures and evaluate the recharge mechanism (i.e. the possibility of subglacial recharge).

Groundwater dating and reconstruction of past climate recharge conditions

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In the past decade aquifers have increasingly become palaeoclimatic archives in their own right alongside ice cores, sediments and other proxy records. The main tool for this task has been the noble gas palaeo-thermometer in combination with quantitative groundwater dating using radionuclides. Noble gas radionuclides play a unique role as tracers in environmental studies due to their chemical inertness and low concentration making them ideal tracers. The same properties on the other hand make them difficult to measure on natural concentration levels. Therefore for decades low level counting (LLC) was the only method for detecting radioisotopes of argon and krypton at an atmospheric level. In recent times and with the increase of interest and potential applications the analytical efforts with novel detection methods have been intensified. In the talk noble gas groundwater dating techniques over times scales from decades to millions of years are discussed in relation to noble gas palaeorecords at different locations. Special attention is put on recharge conditions in glacial and arid environments.

Overview of groundwater studies in the Baltic Artesian Basin at Tallinn University of Technology

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1. INTRODUCTION

The hydrogeological research in the Baltic Artesian Basin (BAB) at Tallinn University of Technology (TUT) has been mainly focused on the palaeogroundwater of glacial origin in the northern part of the basin. Most of the studies have concentrated on groundwater in the deepest Cambrian–Vendian (Cm–V) aquifer system, which is characterized by the lightest isotope composition recorded in Europe ($\delta^{18}O$ values from –18.5‰ to –23‰) in its northern part. In recent years the focus of the groundwater studies has shifted to locating palaeogroundwater in the aquifer systems overlying the Cm–V, noble gas studies, groundwater dating using ^{81}Kr, and development of a groundwater flow model to explain the infiltration history of groundwater in the northern part of the BAB.

2. PREVIOUS RESEARCH

The current direction of groundwater studies at Institute of Geology at TUT was initiated by the discovery of fresh groundwater in the northern part of the Cm–V aquifer system with very light isotope composition and low radiocarbon activities (Juodkazis and Zuzevičius, 1977; Punning et al., 1987; Mokrik and Vaikmäe, 1988; Vaikmäe and Vallner, 1989). The origin of these waters was associated with recharge in glacial or periglacial conditions. More detailed studies on the aquifer system followed (e.g. Kivit et al., 1993; Savitskaja et al., 1994). Hypotheses were put forward on the formation of waters with negative isotope composition, such as origin from Baltic Ice Lake after the retreat of the continental ice sheet (Yezhova et al., 1996) and formation due to cryogenic metamorphism (Mokrik, 1997). The currently most widely accepted view on the origin of palaeogroundwater in the Cm–V aquifer system was put forward in the multi-proxy study ($\delta^{18}O$, $\delta^{13}C$, ^{3}H, ^{14}C, noble gases, total gas content and composition) by Vaikmäe et al. (2001). It was stated that these waters have originated from recharge of subglacial meltwater from the Scandinavian Ice Sheet (SIS) during the Late Weichselian glaciation. Subsequent studies have revealed that the groundwater in the Cm–V aquifer system is a mixture of three end-members (glacial meltwater, relict brine and recent meteoric water) (Marandi, 2007; Raidla et al., 2009) and that the glacial meltwater recharge was coeval with the advance and maximum extent of the SIS in the Late Weichselian (Raidla et al., 2012).

In parallel with the mentioned studies, a hydrogeological model for the northern BAB area (Estonia) was developed by Vallner (2003), which enables simulations of the three dimensional distributions of groundwater heads, flow directions, velocities, and flow rates as well as simulations of transport characteristics and calculations of basin-wide or local groundwater budgets. This work has been developed further in recent years.

3. RECENT FINDINGS AND FUTURE PERSPECTIVES

More recent studies have dealt with the influence of the origin and subsequent reduction of sulphate on the carbon mass balance in the Cm–V aquifer system (Raidla et al., 2014). Also, the investigations into groundwater residence times in the aquifer system have been complemented by the ^{81}Kr dating method in cooperation with the IAEA since 2013 with the first results due later this year.

Palaeogroundwater of glacial origin has also been found in the aquifer systems overlying the Cm–V, namely the Ordovician – Cambrian (O–Cm). Here groundwater with a wide variety in isotope composition ($\delta^{18}O$ and $\delta^{2}H$ values from –11.5‰ to –22.5‰ and from –82‰ to –169‰, respectively) has been found that has also formed due to mixing of waters from three end-members (glacial meltwater, brine and recent meteoric water) (Pärn et al., *submitted*). Noble gas studies at the north-western part of the Cm–V and O–Cm aquifer systems have shown that these waters are characterised by a high excess air amount indicative of recharge under glacial conditions (Weissbach, 2014). The observed depletion of neon with respect to other noble gases offers interesting perspectives for future interpretations of the noble gas data from waters originating from glacial meltwater recharge. The few isotope data available from the Silurian – Ordovician and Devonian aquifer systems indicate that the presence of palaeogroundwater of glacial origin in the northern part of the BAB extends even further to these upper aquifer systems.

In cooperation with the University of Bern, University of Heidelberg and Argonne National Laboratory, ^{81}Kr dating together with noble gas and isotope analysis has been carried out in the deep brines of the BAB. In brines from Kemeri (Latvia) and Genciai (Lithuania), ^{81}Kr concentrations are below the detection limit (R/Ra = 0.02) indicating water that is older than 1.3 Ma (Vaikmäe et al., 2015). These are the first samples for which a ^{81}Kr abundance below detection limit has been reported. ^{4}He and $^{40}Ar/^{36}Ar$ measurements confirm the generally very high residence time of these waters (Vaikmäe et al., 2015). A research article on the topic is currently being prepared.

Lastly, a HydroGeosphere model to explain the flow history and the influence of glacial meltwater recharge on groundwater flow in the BAB is being developed in cooperation with Jean-Michel Lemieux and Arnaud Sterckx from University of Laval.

The BAB is a unique groundwater basin that contains large volumes of palaeogroundwater originating from glacial meltwater recharge, pre-glacial meteoric freshwaters and brines. Although parts of it have been extensively studied using both hydrochemical, isotope and noble gas methods, in relatively large parts of the basin the origin and geochemical evolution of groundwater is still unknown. Future studies based on multi-proxy approaches (including isotopes previously unused in the BAB, e.g. $^{87}Sr/^{86}Sr$, $\delta^{37}Cl$, $\delta^{81}Br$) complemented with better understanding of past and present groundwater flow dynamics are needed to reconstruct the evolution of groundwater in the BAB. These studies are essential in providing the policy-makers with the knowledge needed for responsible management of these unique groundwater resources.

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Transient groundwater flow in the deep aquifer systems of the Baltic Basin

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The Baltic Basin (BB) is a multilayered intracratonic sedimentary basin composed of complex aquifer – aquitard system. The deepest Ediacaran – Cambrian aquifer system (CAS) in general in depths below – 2000 b.s.l. display abnormally high hydraulic pressures, which cannot be explained by steady state Darcy flow.

The present study attempts to simulate abnormal hydraulic pressures in the CAS as a function of changing forcing of the Ice sheet and non-glacial conditions. For simulations a 3D hydrogeological model of the BB was used. To simulate the cyclic events of the ice sheet advance a transient model setup was developed, simulating the subglacial conditions for 20 Kyr and non-glacial for 100 Kyr. The subglacial conditions were simulated as a constant head equivalent to the weight of the ice sheet, while the non-glacial conditions where simulated as a constant head equal to the topographical surface. The ice thickness distribution from the ICE 6G model 24 Kyr time slice (Peltier et al., 2013) for the BB area was used to simulate subglacial groundwater flow conditions.

In total 12 simulation scenarios were calculated comprising various settings for hydraulic conductivities and specific storage values for deep aquitard and aquifer systems.

The calculations suggest that observed abnormal pressures head (higher than 100 m above earth surface) could be explained as a result of ice sheet loading and unloading. Fluctuation of the hydraulic pressure in the CAS is a result of direct meltwater intrusion. The sensitivity analysis shows that abnormal pressures could be recreated in the case when glacier meltwater is directly recharged into the CAS is, suggesting that the presence and duration of the permafrost in the CAS outcropping is one of the main controlling mechanisms of the abnormal hydraulic pressure generation within the CAS.

These simulations also show that hydraulic pressures in deep aquifers of the BB in present are still adjusting to the present day (topography driven) groundwater flow, suggesting that in basin scale modeling of the groundwater flow in deep aquifer systems geological history of the groundwater flow evolution have to be taken into account.

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Correlation of climate and groundwater data from Greenland, Denmark, Syria and Egypt

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Comparison of climate history data from Greenland, Denmark, Syria and Egypt – representing polar, temperate, subtropical and tropical climate in the last 150.000 years facilitates the interpretation of the groundwater springs tufa deposits in Yabroud and Kharga.

This paper shows that the Yabroud cultures excavated in spring tufa can be correlated to the glacial Dansgaard/Oeschger events, and that the "Out of Africa" hypothesis can be supported by optically stimulated luminescence (OSL) dating of Paleolithic tools buried in the spring tufa indicating that Anatomical Modern Human (AMH) lived here 100–60.000 years ago (Schrøder et al., 2012).Also continued OSL work in the spring tufa of Kharga promises to give answers to how AMH was able to cross the Sahara in the last interglacial period, and give a better determination of the rainfall history, crucial for determining the sustainability of continued development of the groundwater irrigation in the area.

The comparison of post glacial climate data from Denmark and the Middle East shows an inverse development of rainfall; while some changes in the rainfall history clearly is correlated with sea-level change, the study also supports the theory that the stop of rainfall in Sahara 6000 years ago was provoked by the deforestation during the Neolithic Revolution (Schrøder et al., 2004; Schrøder, 2015). At the end of the Atlantic period in Denmark – at 6 ka, the hunter-fishing society made room for a new economy based on cattle, where grass was needed - so the wood had to be burned, and as a consequence we see decline in pollen from the native trees Elm and Lime, whereas scrubs (Hazel, Alder and Ash) as pioneer plants, conquered the burned land.

In all it seems that the changes of climate periods in Denmark (the Blytt-Sernander system), can also be found in the Levant. However the rainfall history of the Levant contrasts with the Danish, the North Atlantic Oscillation (NAO) being the decisive agent.

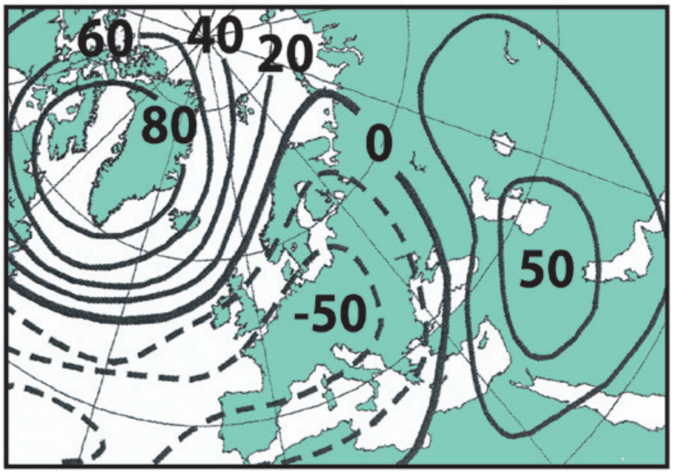

Figure 1. The Correlation map (correlation coefficients x 100) of atmospheric pressure variance in winter for the level of the 700 hPa shows clearly that NAO, is causing not only contrasting weather conditions in Denmark and Greenland, but also between Denmark and the and the Levant. So when there are wet winters in Denmark there are dry winters in the Levant – and visa versa (after Namias (1981)).

The changes in human occupation in the Levant and in Denmark both seems to correlate with the proxies of climate change: the chance from Boreal to Atlantic around 9 ka, the change from Atlantic to Subboreal around 6 ka and the change from Subboreal to Subatlantic around 2.6 ka.

The rainfall curve for the Levant is reconstructed from a record of lake level changes in the Dead Sea. This change in lake level reflects to a high degree the average rainfall in the Golan Heights. In the wet periods the lake level is rising or high and in the dry periods the lake level is falling or low. It has been debated if the environmental changes have been the effect of human activity, or whether the changing human activity has been the effect of climatic change.

While the cause of the transition from Subboreal to Subatlantic around 2.6 ka is not well understood, the chance from Boreal to Atlantic around 9 ka in NW Europe clearly seems to be an effect of the rising sea level making the climate change from continental to coastal, with subsequent changes in the dominant wind systems. However the change from Atlantic to Subboreal around 6 ka seems to be a consequence of human activity.

Between 7 – 6 ka the areas with temperate deciduous woods in central and northern Europe were the arena of the Neolithic revolution. Pollen research has shown that the Neolithic populations made extensive use of fire. Setting fire to forests and shrubs facilitates hunting and improves the conditions for pastoralism. Shifting from gathering wild plants to crop production increases the food supply. For hunters-gatherers having processed and consumed wild cereals only the sowing needs to be implemented. Paleolithic gatherers, who were using fire for preparation of food, must have seen that the plant they were eating proliferated if some seeds were left in the ashes. So if there was shortage of some plants they could sow gathered seeds in ashes of fire lit for providing grass for the cattle.

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The impact of glaciations on groundwater flow: a numerical investigation

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Numerical models are widely used to investigate the impact of glaciations on groundwater flow. However, a glaciation involves several glacial processes and we don't know if they are all relevant in terms of hydrogeology. In this context, modellers have to choose arbitrarily or to estimate which processes they need to account for. To overcome this problem, glacial processes have been numerically simulated to assess their specific impact on groundwater flow. The following processes have been simulated: meltwater infiltration beneath the ice-sheet, hydromechanical loading due to the weight of the ice, isostasy, the presence of pro- and post-glacial lakes, as well as permafrost. Simulations were run in 2D along a simple and theoretical geological cross-section, yet inspired from the Estonian Monocline. Solute transport was also simulated to track groundwater from subglacial origin. A single glacial cycle was represented, from 21 ky BP until now. To interpret the results, the scenario considering only subglacial infiltration was selected as a base case, with which the other simulations results were compared. The concentration of "glacial" water in the subsurface was also used. When comparing the results at the end of the simulations (i.e. at present-day), it appeared that none of the aforementioned glacial processes led to a significant difference in respect to the base case, be it in terms of meltwater distribution or concentration. Only the scenario considering the presence of proglacial lakes led to the significant conservation of meltwater beneath large water bodies. These results open interesting perspectives: they show that simulating glaciation doesn't imply to simulate all the associated glacial processes. If one misses field data to represent properly one of these processes (which is often the case in paleohydrogeology), in a context of time consuming models, it may be wiser to neglect it.

Isotope systematics δ^2H-$\delta^{18}O$, $^{234}U/^{238}U$ and other tracers for paleoreconstruction and modern processes diagnostic

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Introduction. Notoriously, that the stable isotopes δ^2H and $\delta^{18}O$ are the proxy tracers of climate and can be used for paleoreconstruction. Winter and annual temperature during groundwater and ice wedge origin could be calculated. Sometimes influence of freezing on the water isotope composition could be detected. But questions about presence of permafrost in the past and time of its thawing remain unresolved. Stable isotopes (^2H, ^{18}O, ^{13}C), noble gases (^3He, ^4He, ^{20}Ne) and $^{234}U/^{238}U$ ratio were studied in groundwater of several sites on north-western part of Russia, where influence of Eemian sea, Baltic ice sheet and permafrost of last glaciations' could be detected. These data, together with groundwater dating, gave possibility to identify water, which was descended from permafrost or paleo-sea intrusion or could be formed due to subglacial drainage processes.

Arkhangelsk. There is anomaly of iodine in groundwater in the North Dvina River valley near Arkhangelsk city. Abundance of iodine is up to 40 mg/L, salinity of water is up to 25 g/L and stable isotope composition varies from $\delta^{18}O$ = –5.2 ‰ and δ^2H = –38 ‰ to $\delta^{18}O$ = –7.9 ‰ and δ^2H = –64 ‰ in anomaly area. Isotope composition of water with low contents of iodine is from $\delta^{18}O$ = –13.2 ‰ and δ^2H = –96 ‰ to $\delta^{18}O$ = –14.9 ‰ and

δ^2H = –114 ‰, and salinity is less than 10–15 g/L. Modern groundwater is fresh and its stable isotope composition is from $\delta^{18}O$ = –15.0 ‰ and δ^2H = –115 ‰ to $\delta^{18}O$ = –17.4 ‰ and δ^2H = –135 ‰. Groundwater with low salinity and modern water have detectable concentration of tritium in contrast to iodine water, which has no tritium. Groundwaters have wide range of $^{234}U/^{238}U$ ratio, which varies from 1 (by activity) to 8. Very disequilibrium ratio could be explained by influence of water-bearing sediments freezing in last stadial (Tokarev et al., 2005).

Mikulian (Eemian) marine clay, which fills the North Dvina River valley and have very high contribution of buried organic material, is the source of iodine. But iodine anomaly is obtained in Vendian sandy-argillaceous sediments (analogue of Lomonosov aquifer in Baltic artesian basin), which are located below marine clay. It seems squeezing of iodine water from marine clay to Vendian sediments is result of permafrost occurrence here in last ice age. Function of $\delta^{18}O$ vs. salinity for modern White Sea is known, so $\delta^{18}O$ for estuarine of the paleo-Dvina River could be calculated from groundwater salinity as $\delta^{18}O$ = –4… –6 ‰. This estimation is not far from measured oxygen isotope composition. Thus, water with anomaly of iodine is likely lens of the relict Eemian Sea water, which is not disappeared due to low permeability of water-bearing sediments.

Petrozavodsk. From 1979 to 2014 the ferruterous mineral water near Petrozavodsk (Karelia) was studied by monitoring the isotope and chemical tracers. In 1979 – 1980 figurative points strongly shifted to right from the meteoric line on δ^2H vs. $\delta^{18}O$ diagram. It could be caused by secondary fractionation of deuterium and oxygen-18 due to cryogenic metamorphism of water in the last glacial period. Very negative $\delta^{13}C$ value, $^3He/^4He$ and $^{20}Ne/^4He$ ratios, slightly disequilibrium $^{234}U/^{238}U$ ratio and presence of ^3H show that the studied groundwater was formed by mixing "old" and "young" components.

The composition of all isotope proxy tracers has strongly changed for last 25 years due to overexploitation of mineral groundwater. Now δ^2H and $\delta^{18}O$ values fit on the local meteoric line and other isotope tracers become closer to the recharge water. So, now it is observed the rapid penetration of the atmospheric precipitation from Earth surface to discharge area and gradually disappearance of the "old" component in this hydrogeological system.

Leningrad district. The stable isotopes (δ^2H and $\delta^{18}O$), chemistry (major components and microelements) and in some cases tritium, helium, radium and radon were studied in groundwater near the north-east margin of the Baltic Artesian Basin in terrigenous and carbonate aquifers from a crystalline basement up to Earth surface. Monitoring of stable isotope in atmospheric precipitations were done.

It seems water of the Baltic Ice Lake is fixed for Cambrian aquifer in Tallinn water-intake (Estonia) due to high depletion in oxygen-18 and deuterium abundance (δ^2H = –160 ‰, $\delta^{18}O$ = –21 ‰) (Raidla et al., 2009). Cambrian aquifer is raised to Earth surface to the east from Tallinn. Following this raising the isotope composition of water is gradually enriched by oxygen-18 and deuterium and stable isotope composition is increased to δ^2H = –125 ‰, $\delta^{18}O$ = –17 ‰ near the boundary between Estonia and Russia, and up to δ^2H = –100 ‰, $\delta^{18}O$ = –13 ‰ (that is like to modern precipitation) near Sosnovy Bor (Leningrad district), where Cambrian aquifer is provided on surface.

The relict water (probably due to the Eemian sea intrusion) was opened in Vendian aquifer near town Sosnovy Bor and in Saint-Petersburg (south part of studied area). It is salty (M = 4 – 6 g/l) and isotopically fractionated water. This secondary fractionation of water look like as depletion of water by oxygen-18 and deuterium on one site and as enrichment on another site. Water, which has the enriched isotope composition actually is water, which was re-formed from thawed permafrost, then depleted water should be the residual water. Taking into account position of the enriched and depleted water in the geological section, it could be concluded, that in last ice age the lower edge of permafrost was on depth about 80 – 100 m from modern earth surface.

Conclusion. On the north-west margin of Eurasia the regional drainage basis of surface and groundwater repeatedly has been changed its elevation in last 120 Ka. Eemian sea have occupied aquatories of modern Baltic and White seas and part of theirs watersheds. In this time the sea water intrusions in the continental aquifers could be formed near palaeo-shoreline. During the last ice age the sea level was significantly lower than modern one, therefore part of the deep aquifers in periglacial area of the Scandinavian ice sheet could be discharge on surface and the regional level of groundwater was lower, than before and after. Together with the underglacial hydrology all these changes should be formed the complex image of the groundwater chemistry in Baltic region. This complex situation could be decrypted by the environmental isotope tracers, which are archive of the paleohydrology conditions, and by groundwater dating.

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Palaeoclimate information obtained from past-recharged groundwater. The "flag basin" in South America: the Guarani Aquifer System (GAS)

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The Guaraní Aquifer System (GAS) is one of the world's most important fresh groundwater reservoirs. Underlying a region of approximately 24000000 inhabitants, the GAS is shared by four South American countries: Argentina, Brazil, Paraguay and Uruguay, which use the resource for very different purposes at varying exploitation levels (Figure 1).

In Brazil, the GAS lies under the eight most developed states of the country. In São Paulo State, the most industrialized, the aquifer is increasingly exploited. Nowadays, it is used mainly for domestic and industrial water supply, irrigation, therapeutic baths and mineral water. In Argentina and Uruguay, the main uses are balneotherapy and recreation. In Uruguay, the GAS is also used for water supply and irrigation. In Paraguay, the main use of the aquifer is to supply water to rural villages located in the eastern part of the country.

This aquifer is situated in aeolian and fluvial sandstones of continental origin deposited in Triassic and Jurassic times. The sandstones are generally covered by Cretaceous basaltic formations that provide

Figure 1. Location of the Guarani Aquifer System.

different degrees of confinement. Covering approximately 60 – 65% of its extent, the basalt thickness ranges from 200 to more than 1000 m. Therefore, and depending on the places, the aquifer system is both confined and unconfined (Montaño et al., 2004).

Other distinctive characteristics of the GAS are: artesian pressures and high yields at many points (500 m3/h where the aquifer is thickest), good quality groundwater and temperatures ranging from 38°C to 60°C by geothermal gradient. Generally, the water in this aquifer system is of good quality, with an average salinity of 300 mg/l. The unconfined zones are characterized by water of a calcium-bicarbonate composition, whilst the confined ones produce water with a sodium-bicarbonate composition.

According to Fili and Tujchneider in Montaño et al. (1998), hydrochemistry and isotope hydrology have proved to be particularly useful for analyzing the system behaviour in the Argentina-Uruguay border. According to the concentrations of the major ions the groundwater extracted from the sandstones are divided into two main groups: fresh and salt groundwaters (Ca-HCO_3 type and Na-Cl type, respectively). Both groups were also detected by the $\delta^{2}H$-$\delta^{18}O$ and $\delta^{18}O$-TDS relationships. The isotope composition showed the meteoric origin of the groundwater which reached the aquifer under differential climatic conditions. These isotope compositions compared with both world and local (Buenos Aires) meteoric lines did not show evidences of thermal phenomena in a strict sense. Similarly, Montaño et al. (2004) defined two subsystems for the aquifer in Uruguay with almost the same characteristics.

According to Tujchneider et al. (2007) this aquifer system presents geological and structural discontinuities, as well as quality and age water variations. Based on published investigations in the four countries the age of the water lodges in this system range from recent waters (near water recharge areas) to waters with a residence time greater than 40,000 years. Isotopic data also show indirectly that an important part of the present recharge area of the sandstone outcrops of the Guarani Aquifer becomes part of the local flow systems that eventually feed the surface channels.

One of the limitations mentioned in the various sources consulted, was the representativeness of the wells that were used in the studies. The other limitation was the inadequate information on their stratigraphy.

It should be noticed that the first knowledge from this aquifer system was provided by the academics of the different countries which worked together to define what is nowadays called SAG.

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Simulation of ^{18}O concentration in the Estonian Artesian Basin

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Isotopic variations in nature are small and it is not convenient to express the original differences as isotopic abundances (mole fractions) typically with many leading zeros. Moreover, the absolute isotopic abundances often are less important than the changes in isotopic abundances that have occurred. Thus, it has been common agreement and practice for more than half a century to express the deviations in isotopic composition using a specialised notation, the isotope delta (δ) notation (Brand and Coplen, 2012). So the ^{18}O content in water is reported in units of parts per thousand (denoted as $\delta^{18}O$, ‰ or per mil) relative to the SMOW or VSMOW standard. Thereat, the ratios $\delta^{18}O$ are usually not considered as parameters continuously changing in the space-time, but as sole records determined for detached sampling points. The spatial distribution of $\delta^{18}O$ values are interpolated or even extrapolated by means of geometric formulas for the groundwater systems. Thus, the impact of hydrodynamic factors of the groundwater flow on the spatial distribution of the ^{18}O concentration cannot be functionally accounted. It constrains the possibilities to use the ^{18}O content as a tracer to interpret the events of the groundwater flow and transport.

To overcome the problem, the groundwater contained in pores and cracks of water-bearing layers should be considered as a solution where molecules of $H_2{}^{18}O$ represent a solute dissolved in a solvent composed by molecules of $H_2{}^{16}O$. In that case, the movement of $H_2{}^{18}O$ molecules and mixing them with $H_2{}^{16}O$ molecules in the solution (groundwater) saturating the porous medium can be treated as a process of the molecular diffusion. In low-permeability layers, the velocity of the groundwater movement is low and the diffusion is the dominant transport mechanism of $H_2{}^{18}O$ molecules. However, the advection influenced by mechanical dispersion is the dominant transport mechanism in layers of higher permeability. The $H_2{}^{18}O$ transport should be controlled by the spatial distribution of the hydraulic pressure and permeability parameters of the groundwater system. Consequently, the distribution of the ^{18}O content in a groundwater system can be described by a continuous concentration function C(x, y, z, t) having dimension [ML^{-3}] whereby x, y, and z are Cartesian space coordinates, and t is time.

The mass concentration C(x, y, z, t) in a water sample (denoted $C^{18}O$) can be calculated by following equation:

C_{18O} (in mg/L) = 2003.499 + 2.004 × $\delta^{18}O$.

The equation has following assumptions and simplifications: g/kg ≈ 1000 mg/L, the deuterium/ protium ratio is not taken into account, ^{17}O abundance is ignored, and the hydrogen molar mass is equalized to 1,00794 g/mol. Characteristics of ^{18}O concentration of some genetic types of natural waters calculated by equation are presented in the Table 1.

Table 1

Water type	$\delta^{18}O$, ‰	C_{18O}, mg/L
Dead Sea water	+6.6	2017
Red Sea water	+1.3	2006
VSMOW	0	2004
Basin brine	-5	1994
Meteoric water	-10	1983
do	-15	1973
Glacial water	-23	1957
do	-24	1955
do	-35	1933

Proceeding from above assumptions, the spatial time-dependent distribution of concentration C in a non-uniform, multi-layered, and heterogeneous groundwater system can be simulated by popular computer code Visual MODFLOW Classic coupled with the groundwater transport programme MT3DMS (Schlumberger 2015, Zheng 2010).

Based on this code a time-dependent groundwater flow and transport model of the Estonian Artesian

Table 2

Model	Timespan, ka BP		Paleogeographical situation
	Start	End	
1	22,0	20,0	Covering of the northwestern part of the EAB by ice sheet
2	20,0	18,0	Covering of whole EAB by ice sheet, Last Glacial Maximum
3	18,0	14,7	Thinning of the continental ice cover due to deglaciation
4	14,7	12,0	Freeing of EAB southern and central parts from the ice sheet
5	12,0	10,3	Perishing of the ice sheet and forming of the Baltic Ice Lake
6	10,3	5,0	Early evolution stages of the Baltic Sea
7	5,0	0,1	Forming of the contemporary topography

Basin (EAB) has been created (Vallner 2003; Vallner and Porman, *in press*). The EAB includes the territory of Estonia with the surrounding portions of Baltic Sea, Gulf of Finland, and Lake Peipsi. The regional hydrogeological model (RHM) involves all main aquifers, aquifer systems, and aquitards in the area of 88,000 km^2. They are represented by 22 model layers. The top boundary of the model coincides with the ground surface or bottom of the river network, lakes, and seas. A virtual surface lying at a depth of 100 m beneath the upper surface of the crystalline basement acts as a supposed impermeable bottom boundary of the model. The thickness of all water-bearing formation modelled varies from 100–150 m in northern area to 600–900 m along the southern boundary of the area. The RHM was profoundly calibrated against measured elevation of hydraulic heads, and rates of the base flow records of several years (1976, 1990,

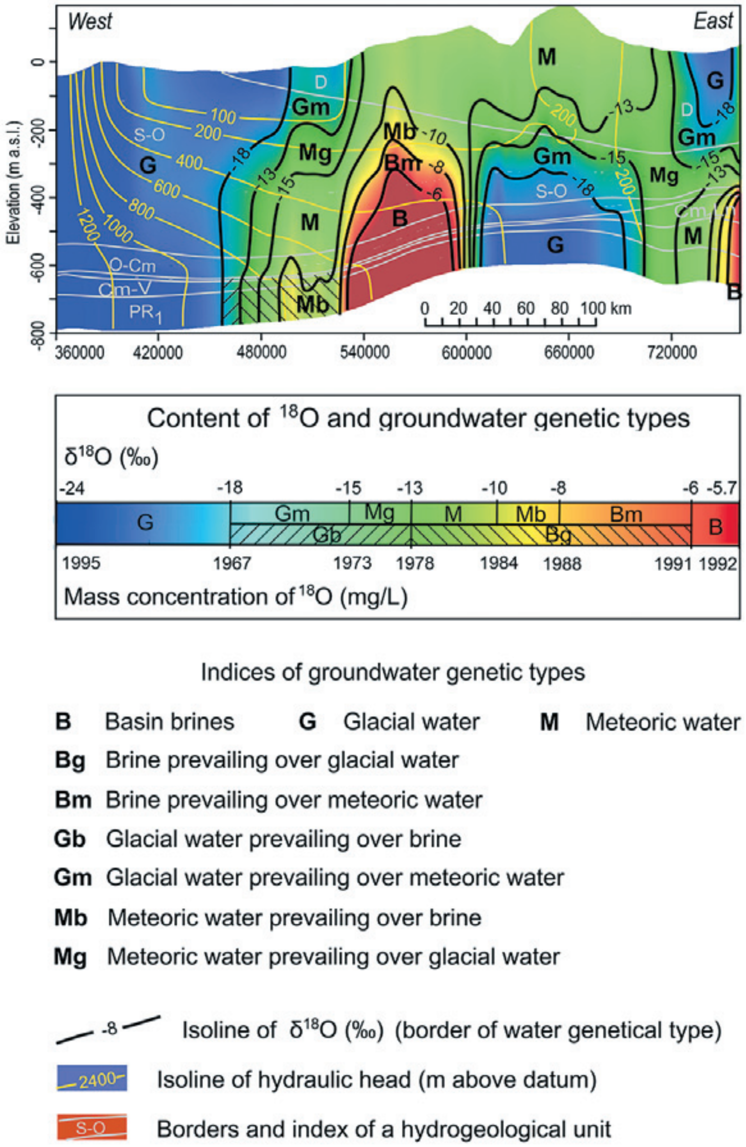

Figure 1. Simulated $\delta^{18}O$ values and groundwater genetic types in the cross-section of the EAB from west (Lümandu) to east (Mehikoorma) at 18 ka BP.

1998, 2006, and 2013). The model has been tested and used to investigate the groundwater resources and complicated problems of water contamination.

The transport simulations of ^{18}O as a conservative tracer were performed by RHM to reconstruct the main hydrogeological events induced by last glaciation and its retreating in the EAB in the time interval from 22 until 0.1 ka BP. The period was modelled by seven transport models functionally connected to each other (Table 2). Initial and boundary conditions of models expressing the changing thickness of the ice sheet, vertical movements of the Earth crust as well as the presumed values of ^{18}O mass concentrations of water's main genetic types were established accordingly to former geological and hydrological investigations. Previously collected ^{18}O data in present day aquifers of RHM were used to calibrate and verify the model simulations.

The modelling showed that the infiltration of meteoric water, with $\delta^{18}O$ of –10‰ was replaced by vertical intrusion of ice meltwater into subsoil during the transgression of the ice sheet in the period from 22 to 18 ka BP. The ice meltwater with $\delta^{18}O$ value of –23‰ came into being because of an upward heat transfer and due to frictional heating of the moving glacier at the base of the ice sheet. The discharge of basinal brines with the $\delta^{18}O$ value of –6‰, and meteoric water from the layers of the EAB into the depressions of the Baltic Sea and the Gulf of Finland was replaced with lateral encroachment of glacial meltwater into bedrock layers during this period. Deep groundwater, including basinal brines, partially raised upward being drained by network of subglacial currents. Starting 18 ka BP, deglaciation began and continental ice perished from the area of the EAB at 12 ka BP. After that, the ice lakes and the Baltic Sea flooded the western lowlands of the present-day Estonia until 2 ka BP. During deglaciation and flooding of the model area, the meteoric water began to reinfiltrate, intruding into layers filled earlier with glacial meltwater.

The spatial distribution of the ^{18}O concentration in the EAB expressing the complicated mixture of waters of different genetic types was simulated for the main stages of glaciation, deglaciation and and evolution of the Baltic Sea (Figure 1). The adequacy of the whole methodology of modelling were proved by the correlation coefficient equal to 0.86 between calculated and observed values of the 18O content determined for 185 monitoring points over the territory of the EAB.

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Noble gases of glacial origin in palaeogroundwater in the northern part of the Baltic Artesian Basin, Estonia

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Groundwater was sampled in the northern part of the BAB, out of the Cambrian – Vendian and Ordovician – Cambrian aquifer systems. A special characteristic of these aquifer systems is the stable isotope composition with $\delta^{18}O$ values as low as -22 ‰, which is unique in Europe (Vaikmäe et al., 2001). Former studies dated the groundwater by radiocarbon to approximately 19000 up to 22000 years BP (Raidla et al., 2012). These findings are clear indicators for a recharge during the late Weichselian glaciation. According to Vaikmäe et al. (2001), the recharge of the Cambrian – Vendian aquifer system probably occurred by subglacial drainage of the Fennoscandian ice sheet through tunnel valleys.

An extended noble gas survey was conducted to test this presumption. Dissolved noble gases contain information about past climate conditions, since the solubility of each noble gas in water is temperature dependent (Mazor, 1972). In contrast to surface water, groundwater is often equipped with a noble gas excess above the atmospheric equilibrium concentrations, the so called "excess air" (Heaton and Vogel, 1981). There are several models to describe the excess air amount and composition in groundwater, the most straightforward explanation is the unfractionated excess air or UA model. It assumes a complete dissolution of entrapped air bubbles in the soil and implies that the excess in groundwater has the same composition as the entrapped gas which is assumed to be atmospheric air (Heaton and Vogel, 1981). In groundwater infiltrated under normal conditions, the excess air is often fractionated with respect to air (Aeschbach-Hertig et al., 2000), because the relatively low hydrostatic pressure is insufficient to completely dissolve the trapped air. In contrast, for subglacial recharge it may be reasonable to assume that atmospheric air enclosed in the ice is completely forced into solution by the high pressure load of the ice cover. We therefore use the UA model as a reference to compare to the observed noble gas patterns in the BAB groundwater.

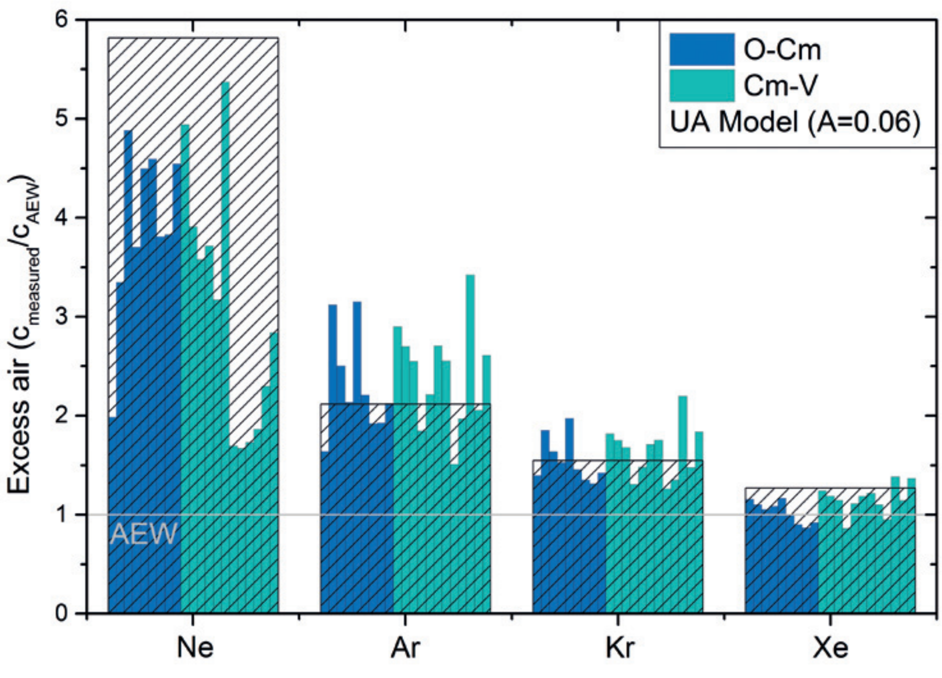

Figure 1. Noble gas pattern of the sampled wells, ordered by aquifers (indicated by different colours). The measured concentrations are normalised to the concentrations calculated for air-equilibrated water (AEW) at 0°C. The shaded areas illustrate the composition of an ideal sample with an excess air component according to the UA model and A = 0.06, also normalised to AEW. O–Cm: Ordovician – Cambrian aquifer system; Cm–V: Cambrian – Vendian aquifer system.

First results show that the BAB groundwaters exhibit enormous excess air amounts, which could be caused by trapped air in glacial ice that was forced into solution during recharge beneath an ice sheet. Furthermore, the noble gas composition of the Estonian wells clearly shows a depletion of Ne compared to equilibrated water plus atmospheric air, which is not completely understood yet. A small proportion of the depletion could be due to a loss of Ne by diffusion through the ice, but a depletion in the range of 30% up to 70% (see Figure 1) seems unlikely to be due to the diffusion through the ice matrix. Partitioning of noble gases between water, ice, and gas phase beneath the ice sheet may play a role, yet no conclusive scenario for the formation of the highly unusual noble gas signature is currently available.

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Counting ^{81}Kr atoms in groundwater

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Because of the chemical inertness and unique physical properties, noble-gas radioisotopes have relatively simple mechanism during the transportation and mixing process, therefore they are ideal tracers for environmental samples, such as air, groundwater and ices (Collon et al., 2004). Long-lived rare noble-gas radioisotopes, ^{85}Kr ($t_{1/2}$=10.76 yr, I.A. =2.5E-11), ^{39}Ar ($t_{1/2}$=269 yr, I.A.=8.1E-16), and ^{81}Kr ($t_{1/2}$=229,000 yr, I.A.=5.2E-13), are particularly interested, which dating range covers from modern to one million years before present. While the extremely low abundances limit their applications. Atom Trap Trace Analysis (ATTA) (Chen et al., 1999) is a new laser based method, determining the abundance of particular rare isotope by counting the atoms in a magneto-optic trap (MOT) with micro-liters (STP) gas. Only atoms resonating with the laser frequency will be trapped and counted, without influence from other atoms or molecules.

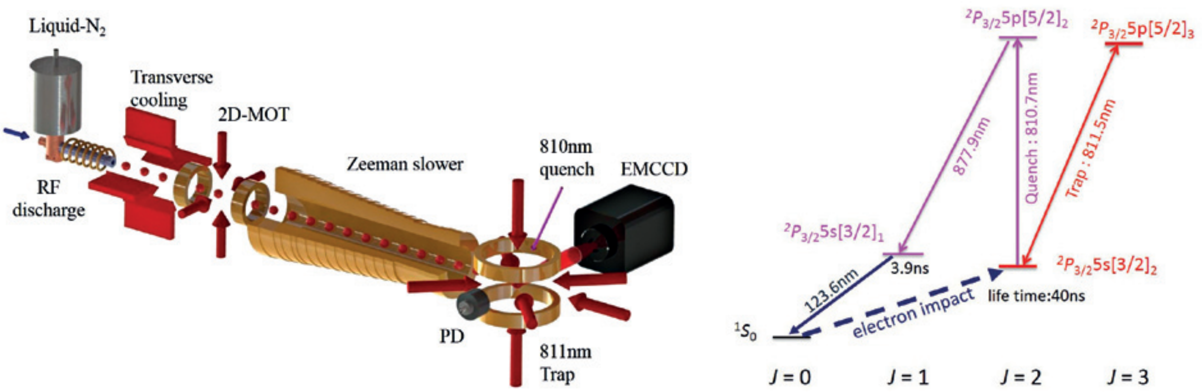

Figure 1. Schematic diagram of the ATTA instrument.

The schematic diagram of an ATTA instrument is shown in Fig.1. Krypton atoms are first excited through a RF discharge inside a ceramic tube pre-cooled by liquid-N_2 to a metastable state ($5s[3/2]_2$, life time 40s), where the $5s[3/2]_2 \rightarrow 5p[5/2]_3$ cycling transition can be applied for manipulation. Atomic beam is transversely compressed, focused, slowed in a Zeeman slower, and finally trapped in the MOT. Due to the extremely low abundances of ^{85}Kr and ^{81}Kr, only individual atoms will be trapped at a time. Fluorescence emitted from trapped atoms is imaged by an electron-multiplying charge-coupled device (EMCCD), as presented in Fig.2. The single atom counting rate, being proportional to the isotopic abundance in the sample, may drift slowly due to the change in experimental conditions. As a reference to calibrate the counting efficiency, loading rate of stable isotope ^{83}Kr (^{83}Kr/Kr = 11.5%) is determined through a "quench and capture" method (Cheng et al., 2013). The quantitative reliability and capability of ATTA is verified by an inter-comparison, using 12 samples with ^{85}Kr/Kr ratios in the range of 10–13 to 10–10, with independent measurements carried out in three laboratories (Yang et al., 2013): a low-level counting laboratory in Bern (Switzerland), and two ATTA laboratories, one in Hefei (China) and the other in Argonne (USA).

A sampling apparatus for sampling groundwater in the field, and a purification system to extract krypton and argon samples in the laboratory, have been built in Hefei (Tu et al., 2014). Typically, 5L STP dissolved air will be extracted in the field from about 100L groundwater within 2 hours. Over 10 groundwater samples in North China Plain were sampled and measured, shows that the deep groundwater has a Kr-81 age up to 1 million years old. The Kr-85 and Kr-81 ages of some other groundwater samples obtained in urban Zhanjiang city (south China), Xinjiang (northwest China) have also been determined.

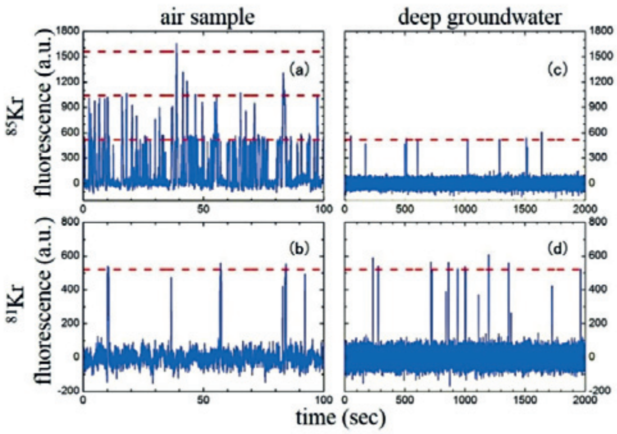

Figure 2. Atom counting. (a) and (b) are the signals of ^{85}Kr and ^{81}Kr, respectively, from an air sample; (c) and (d) those from a deep groundwater sample.

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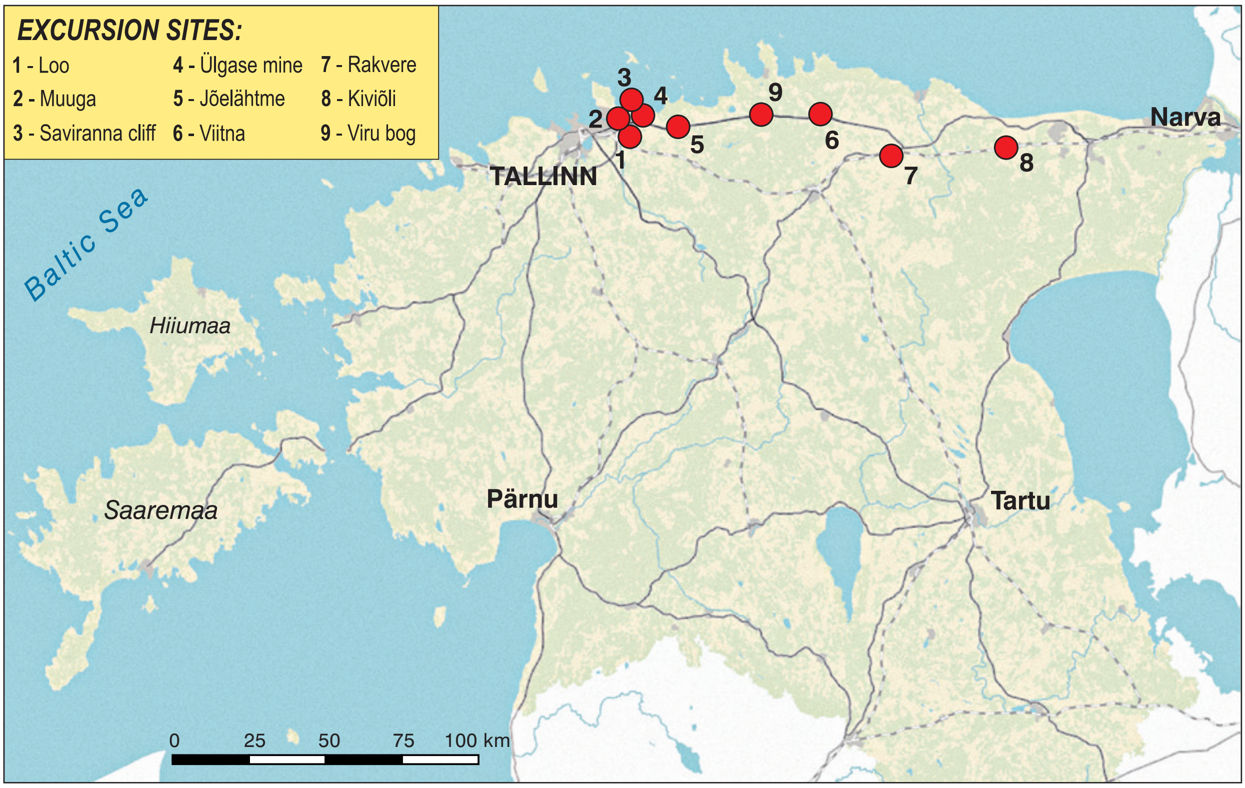

EXCURSION SITES:
1 - Loo
2 - Muuga
3 - Saviranna cliff
4 - Ülgase mine
5 - Jõelähtme
6 - Viitna
7 - Rakvere
8 - Kiviõli
9 - Viru bog
TALLINN
Narva
Tartu
Pärnu
Baltic Sea
Hiiumaa
Saaremaa
0 25 50 75 100 km

Institute of Geology at Tallinn University of Technology

4th Annual Meeting of G@GPS IGCP 618 Project

Palaeogroundwater from past and present glaciated areas

Estonia, 5-9 July 2015

Field Guide

Edited by
Joonas Pärn, Valle Raidla, Rein Vaikmäe, Anto Raukas & Heikki Bauert

Tallinn, 2015

1. General background

1.1. Geological and hydrogeological description of the northern part of the BAB

Joonas Pärn and Valle Raidla

The Baltic Artesian Basin (BAB) is situated in the north-western part of the East European Craton (EEC). It is the hydrogeological equivalent of the marginal Phanerozoic sedimentary basin called the Baltic sedimentary basin. BAB is one of the largest groundwater basins in Europe, covering an area of ~460,000 km^2 i.e. the territories of Estonia, Latvia and Lithuania together with parts of Russia, Poland and Belarus (Fig. 1). Approximately half of the BAB is covered by the Baltic Sea. The sedimentary cover consists of Neoproterozoic, Palaeozoic, Mesozoic and Cenozoic sedimentary rocks and reaches a thickness of 5000 meters in the south-western part of the basin. The crystalline basement reaches the surface at the northern and south-eastern parts of the BAB.

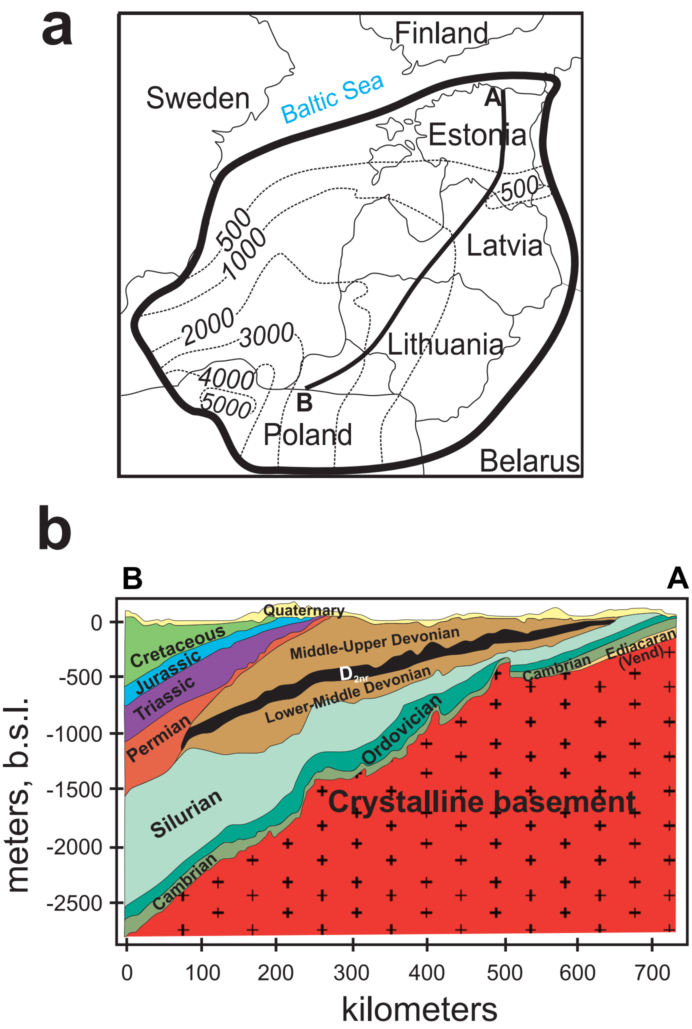
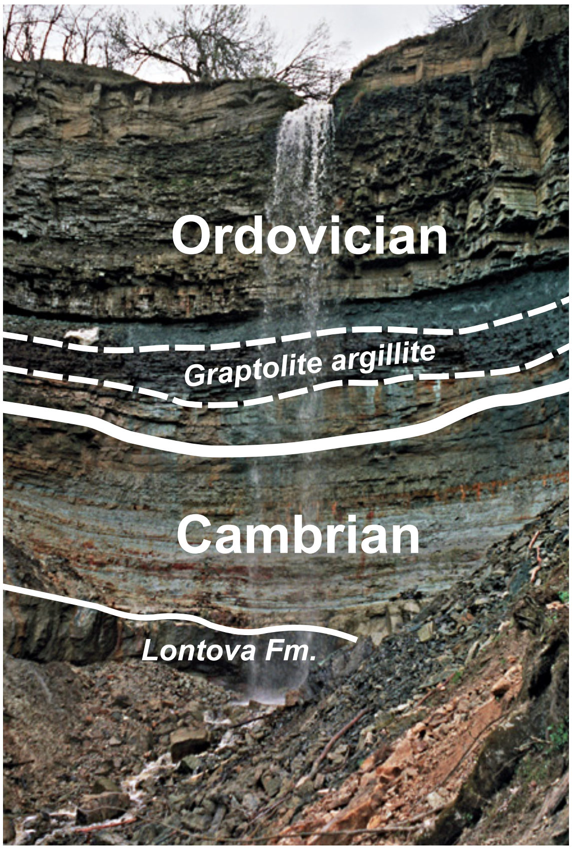


Figure 1. (a) The location and boundaries of the BAB together with iso-lines characterising the depth of the crystalline basement in meters, b.s.l., (b) the geologic cross-section of the BAB along the line A–B on figure a; D_{2nr} – Narva regional aquitard. (*modified from:* Juodkazis, 1980; Virbulis et al., 2013).

In the northern part of the BAB are distributed sedimentary rocks from Ediacaran to Devonian Eras. They are overlain by Quaternary deposits of variable thickness. The thickness of the Quaternary cover increases from north to south and the majority of it consists of glacial, glaciolacustrine and glaciofluvial deposits. The sedimentary bedrock is of questa-like character and is generally dipping about 2–4.5 m/km to the south. The Quaternary deposits are underlain by Devonian sand- and siltstones from central Estonia southwards and by Silurian and Ordovician carbonates (limestones and dolostones) in the northern part of the country (Fig. 2, 3). The basal Ordovician strata are comprised of relatively thin section of clastic sediments – sandstones, argillites and clays. The underlying Cambrian Series consists mainly of clastic sediments (sand- and siltstones) with the basal part formed by Lower-Cambrian clays and siltstones of the Lontova Formation. Under this formation are distributed Ediacaran clastic sediments of sandstones, siltstones and clays. They lie directly on the Paleoproterozoic crystalline basement.

The lithological characteristics of the different sedimentary sequences result in different hydraulic characteristics of these deposits and in the formation of several aquifer systems and aquitards. The groundwater system in the northern part of the BAB (Estonia) can be divided into three principal hydrogeologic units (Perens and Vallner, 1997):

- **Quaternary deposits**, where a lot of water either circulates by the agency of capillary force or evaporates, in addition to the filtration flow;



- **Bedrock**, which consists of terrigeneous and carbonate sedimentary rocks that form porous, fissured and karstified, mostly confined aquifers, which are isolated from each other by aquitards of different isolation capacity;

- Groundwater in the fissures of igneous and metamorphic rocks of the **crystalline basement** that is almost stagnant in natural conditions. The lower portion of the crystalline basement can be viewed as an aquiclude for the whole overlying water-bearing formation.

The most important groundwater resources in the northern part of the BAB are associated with sedimentary sequences of the bedrock. There the main water yielding aquifer systems can be found that are separated from each other by several regional aquitards (Fig. 3).

Excursion sites related to this chapter:
Site 1, Site 3, Site 4, and Site 5.

Figure 2. A geological cross-section of the northernmost part of the BAB in the north Estonian coast, Valaste. (Photo: A. Miidel).

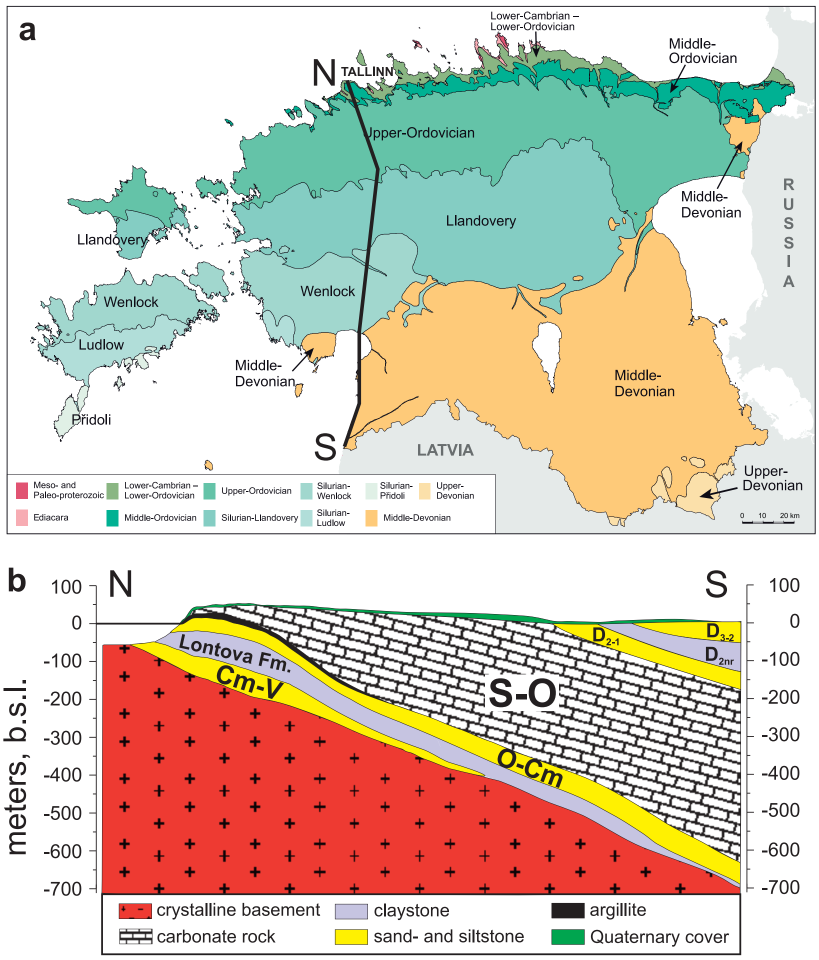


Figure 3. (a) A geological map of Estonia; (b) the north-south cross-section of the northern part of the BAB together with the major aquifer systems and regional aquitards. Abbreviations: Cm-V – Cambrian-Vendian aquifer system; Lontova Fm. – Lükati-Lontova regional aquitard; O-Cm – Ordovician-Cambrian aquifer system; S-O – Silurian-Ordovician aquifer system; D_{2-1} – Middle-Lower Devonian aquifer system; D_{2nr} – Narva regional aquitard; D_{3-2} – Upper-Middle Devonian aquifer system.

1.2. Groundwater in the northern part of the BAB

Joonas Pärn and Valle Raidla

1.2.1. A general description of the groundwater system in the BAB

The vertical sequence of groundwater bearing formations in the BAB can be divided into three main hydrodynamic zones (Vallner, 1997; Mokrik, 2003). The active water exchange zone where infiltration of recent meteoric water predominates can reach down to the depths of up to 400 meters. The zone of delayed (moderate) groundwater exchange is located at depths from 400 to 1800 meters. Below depths of 1800 meters, one can find the stagnant Ca-Cl type brines (Mokrik, 2003). The Baltic Sea is one of the main discharge areas for the deep artesian groundwater associated with moderate water exchange zone. The general flow direction of the deep groundwater in the BAB is directed from the deeper south-western part of the basin towards the periphery monoclines.

The distribution of different hydrodynamic zones is illustrated by the changes in isotopic composition of groundwater in the vertical direction (Fig. 4). In the shallower depths, one can find fresh groundwater with isotopic composition in line with the intra-annual variability of modern precipitation. In deeper aquifer systems, the saline waters and brines are characterised by an isotopic composition enriched with respect to modern precipitation. These waters plot below the global meteoric water line (GMWL). The situation is different in the northern part of the BAB where one can find waters with depleted isotopic composition relative to modern precipitation. Vaikmäe et al. (2001) suggested that these freshwaters

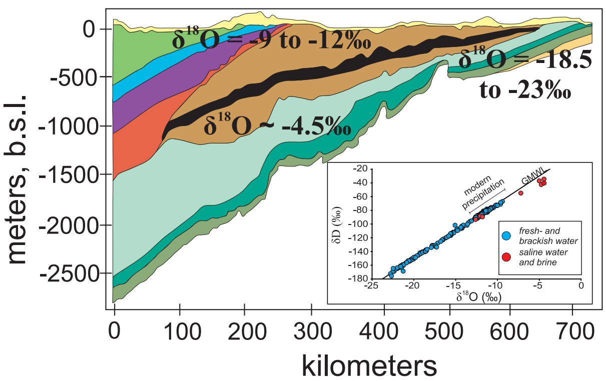


Figure 4. The geological cross-section of the BAB together with the characteristic isotopic composition of waters at different depths. A δD-δ^{18}O covariance for different waters in the BAB is given as a reference (*source: Institute of Geology at Tallinn University of Technology database*).

in shallow aquifer systems (burial depths <200 m) have originated from subglacial meltwater from the Scandinavian Ice Sheet (SIS) of the Weichselian Glaciation. The glacial origin of these waters is further confirmed by their position on GMWL, suggesting a meteoric origin.

1.2.2. The influence of Pleistocene glaciations on the geochemical evolution of groundwater in the BAB

The whole territory of the BAB was significantly affected by several glaciations during the Quaternary. Taking into account all the lithostratigraphical, biostratigraphical and geochronological information available, the existence of three Pleistocene glaciations – Elsterian (480–420 kyr BP), Saalian (300–130 kyr BP) and Weichselian (110–11.7 kyr BP) – separated by two interglacial periods – Holsteinian (420–300 kyr BP) and Eemian (130–110 kyr BP) – have been determined in the northern part of the BAB (Kalm et al., 2011).

Sedimentary records from Early Pleistocene or older glaciations have not been preserved in Estonia (Kalm et al., 2011). Strong erosion by subsequent glaciations has destroyed all the evidence. On the basis of present knowledge, deposits of Lower Pleistocene and older Quaternary ages are absent from Estonia and even the Middle Pleistocene sequence is rather incomplete (Raukas et al., 2004). During the Late Pleistocene, Estonia was ice-free at least between 115–68 and 44–27 kyr ago which leaves in theory 24 kyr (68–44 kyr) for a possible early Middle Weichselian glaciation (Kalm et al., 2011) (Fig. 5). The beginning of the Late Weichselian glaciation in Estonia has not been directly dated, but the

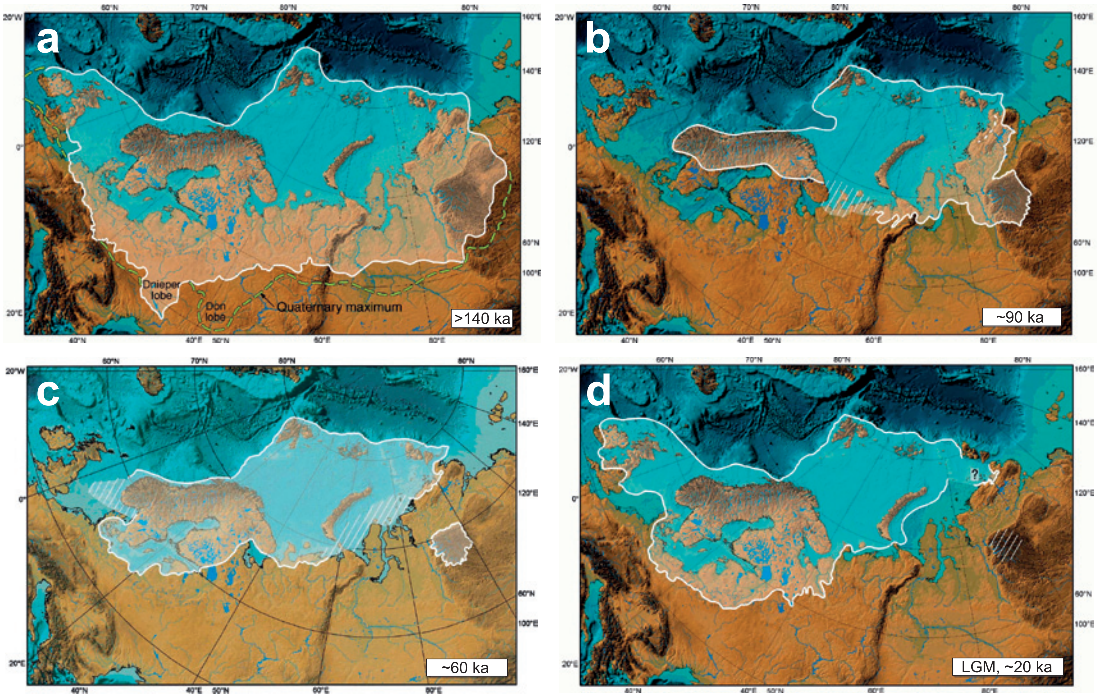


Figure 5. The extent of the Scandinavian Ice Sheet in the BAB area and in its vicinity in (a) Late Saalian, (b) Early Weichselian, (c) Middle Weichselian, (d) Last Glacial Maximum (LGM) in Late Weichselian. (*modified from:* Svendsen et al., 2004).

available data from areas located more centrally in relation to the Scandinavian Ice Sheet (e.g. Finland) suggest that the onset may have occurred around 22 kyr ago. Configuration of glacier bedforms and end moraines in south-eastern Lithuania, northern Belarus and on the Valdai Heights in north-western Russia indicate that the earliest advance to the most accepted Last Glacial Maximum (LGM) position was predominantly from the north-west. The maximum thickness of the Scandinavian Ice Sheet during the Late Weichselian ice age over northern BAB (i.e. Estonian and Latvian territory) reached ~2000 meters (Siegert and Dowdeswell, 2004).

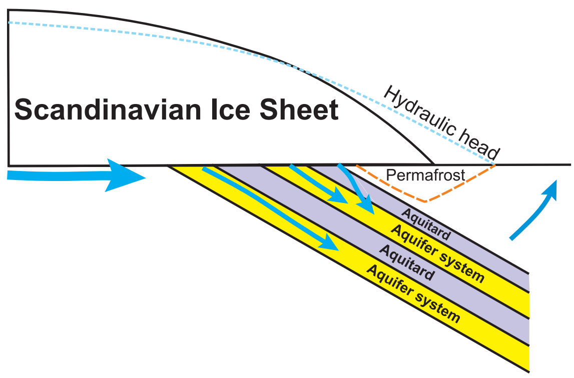


Figure 6. A schematic section illustrating a possible mechanism for glacial meltwater recharge in the northern part of the BAB.

The recharge of glacial meltwater to the proglacial sedimentary aquifer systems in the northern part of the BAB was made possible by the changes in the distribution of regional hydraulic heads during the advances of the continental ice sheet. During the Late Weichselian, Scandinavian ice sheet increased hydraulic pressure at the base of the glacier. The hydraulic gradient was at least 0.003 (Jõeleht, 1998), which is about one order of magnitude more than today that reversed the regional groundwater flow. This led to a recharge of isotopically light glacial meltwater in Northern Estonia where the aquifers crop out (Fig. 6).

1.2.3. Origin and geochemical evolution of groundwater in the northern part of the BAB

The groundwater in the northern part of the BAB has originated from three main end members: fresh glacial meltwater, relict saline water and brine, and meteoric water. Locally the intrusion of the Baltic Sea water has also played an important role. The geochemical evolution, the origin of groundwater and the mixing processes between different water types can be illustrated by using the co-variance of conservative geochemical tracers $\delta^{18}O$ and Cl^- (Fig. 7a-f).

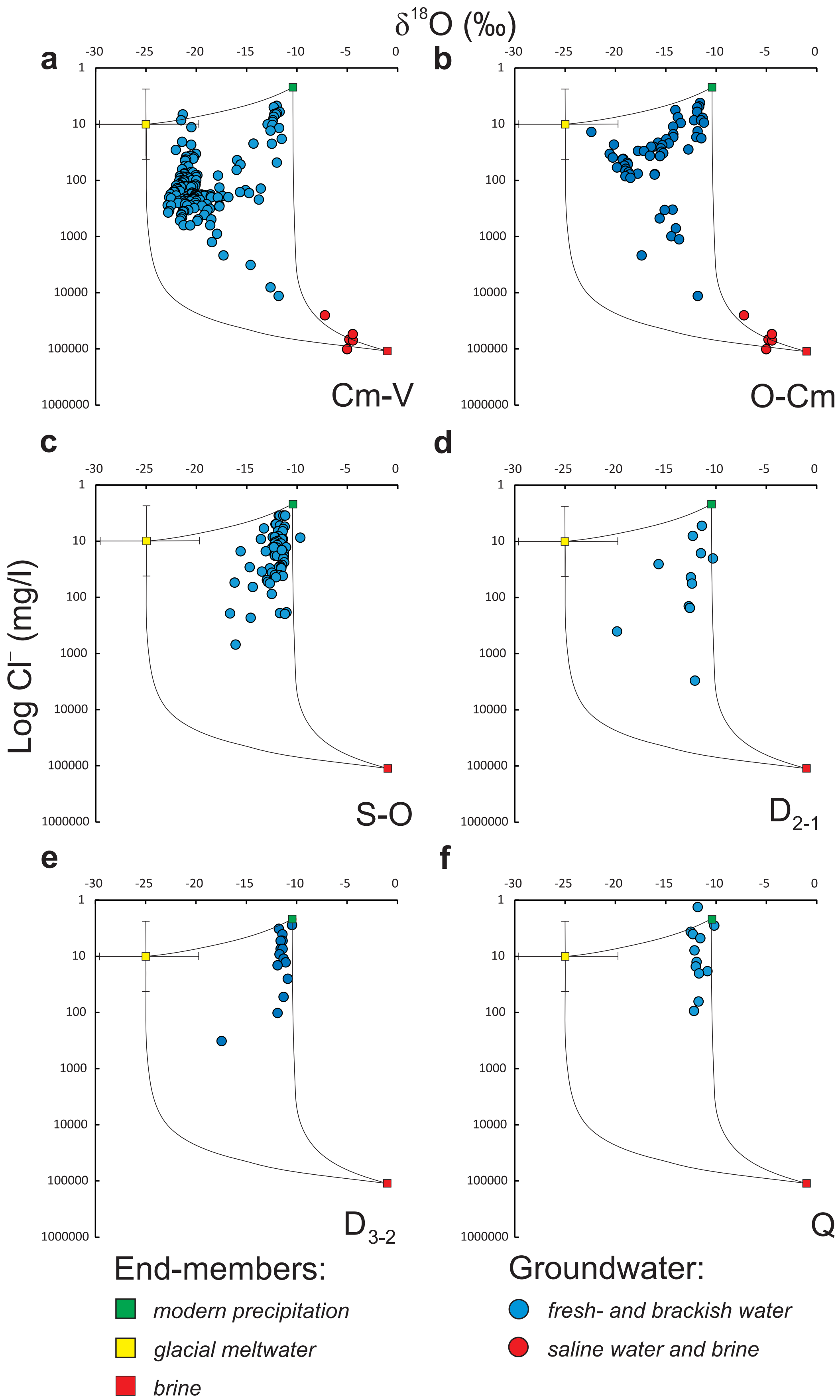


Figure 7. The geochemical evolution of groundwater in the northern part of the BAB as illustrated by the mixing relationships using conservative tracers $\delta^{18}O$ and chloride. The abbreviations of different aquifer systems are given in figure 3. (*source: database of Institute of Geology at Tallinn University of Technology*).

Groundwater in the Quaternary cover and Devonian aquifer systems

The Quaternary cover is represented by a variety of sediments with different lithological composition, distribution and origin. Thus, many local aquifers and aquitards are formed. The isotopic composition of water in these local aquifers corresponds mainly to the isotopic composition of modern precipitation (Fig. 7a).

Groundwater in Devonian sedimentary rocks underlying the Quaternary cover in southern Estonia (see Fig. 3) can be divided into two main aquifer systems which are divided by the Narva regional aquitard.

The Upper–Middle Devonian aquifer system ($D_{3\text{-}2}$) is hosted by karstified and fissured dolomites and dolomitized limestone of the Upper Devonian Series together with the sandstones, siltstones and interlayers that belong to the upper Middle-Devonian Series (Givetian Stage). The groundwater in the aquifer system is mainly freshwater of Ca-Mg-HCO_3 type with TDS concentrations of 200–600 mg/l (Perens et al., 2001). The isotopic composition of groundwater is mainly similar to modern precipitation while some waters with more negative isotopic composition have been observed in the basal layers of the aquifer system that may refer to the influence of glacial meltwater recharge (Fig. 7b).

The Upper–Middle Devonian aquifer system is underlain by the Narva regional aquitard (D_{2nr}). It consists of siltstone, dolomite, marl and clay of the Middle Devonian Eifelian Stage with a total thickness of up to 90 meters (Perens and Vallner, 1997). In southern Estonia and Latvia this sequence can be viewed as an uppermost effective bedrock aquitard.

The Middle–Lower Devonian aquifer system ($D_{2\text{-}1}$) consists of the water-bearing layers of Middle and Lower Devonian rocks (Lochovian, Pragian and Emsian Stages) underlying the Narva regional aquitard. It consists of fine-grained weakly cemented sand- and siltstones with interlayers of clay and dolomitized sandstone (Perens and Vallner, 1997). The dominant water type of the aquifer system is the Ca-Mg-HCO_3 type which changes gradually to Mg-Ca-HCO_3 and Na-Ca-HCO_3 types in the southern areas with the TDS concentrations varying from 300 to 500 mg/l (Perens et al., 2001). In southernmost Estonia the TDS concentrations of water in the aquifer system increase to over 1000 mg/l (Perens et al., 2001). A majority of waters from the aquifer system seem to originate from modern precipitation (Fig. 7c). However, waters with $\delta^{18}O$ values ranging from −14‰ to −20‰ have been found in south-western Estonia. This suggests that palaeogroundwaters of glacial origin have been preserved in this part of the aquifer system.

Silurian–Ordovician aquifer system (S–O)

The Silurian–Ordovician aquifer system consist of a variety of limestones and dolostones with clayey interlayers of Silurian and Ordovician Systems. These rocks underlie the Quaternary sediments in northern and central Estonia. The total thickness of the water-bearing rocks can reach up to 400 m. The upper 30 m of the rock matrix is karstified and is extremely cavernous, with numerous cracks and fissures (Perens and Vallner, 1997). In deeper parts of the rock matrix, the cracks and fissures are rare and the aquitard system gradually turns into an aquitard (Perens and Vallner, 1997). The whole Silurian-Ordovician sequence can be viewed as a regional aquitard at increasing depths.

In Northern Estonia (where the overlying Quaternary cover is thin or non-existent) the water in the aquifer system is mostly of Ca-Mg-HCO_3 or Mg-Ca-HCO_3 type with the TDS concentrations varying between 300 and 500 mg/l (Perens et al., 2001). In Western Estonia, the water in the aquifer system is characterised by higher concentrations of Na^+ and Cl^- coinciding with higher TDS concentrations (up to 2000 mg/l) as a result of the influence of the Baltic Sea (Perens et al., 2001). Concentrations of Na^+ and Cl^- are also increase with depth in the aquifer system.

Similarly to the Lower–Middle Devonian aquifer system, the majority of waters in the Silurian-Ordovician aquifer system have isotopic composition similar to modern precipitation in the area (Fig. 7d). However, under numerous aquitards of local distribution, palaeogroundwaters with isotopic composition depleted with respect to modern precipitation ($\delta^{18}O$ values from −13‰ −17‰) have been preserved locally. The most negative values have been observed in western Estonia.

Ordovician-Cambrian aquifer system (O–Cm)

The Ordovician–Cambrian aquifer system underlies the Silurian–Ordovician regional aquitard. The aquifer strata consist of fine-grained sandstones and siltstones of the Early Ordovician and Cambrian age (Perens and Vallner, 1997). The chemical composition of water in the aquifer system is diverse. In northern Estonia, water is predominantly of Ca-Mg-HCO_3 and Na-HCO_3 type with the TDS concentrations of 200–600 mg/l (Perens et al., 2001; Pärn et al., *submitted*). In southern and south-western Estonia the chemical type of groundwater changes to more saline Na-HCO_3-Cl and Na-Cl types with the increasing depths. The TDS concentrations of these waters can rise up to 2000 mg/l and more (Perens et al., 2001).

From the Ordovician–Cambrian aquifer system, $\delta^{18}O$ values as negative as −22.4‰ have been reported (Pärn et al., *submitted*). They are similar to most negative values found in the Cambrian–Vendian aquifer system. Groundwater in the Ordovician–Cambrian aquifer system has also been influenced by three-component mixing between fresh glacial meltwater, brine and recent meteoric water end-members similar to the Cm–V aquifer system (Fig. 7e).

Cambrian-Vendian aquifer system (Cm–V)

The Cambrian–Vendian aquifer system is the most extensively studied aquifer system in the northern part of the BAB. The aquifer system has been studied with various isotopic and geochemical tools (^{3}H, ^{14}C, $\delta^{18}O$, $\delta^{13}C$, ^{39}Ar, ^{4}He, $^{40}Ar/^{36}Ar$, noble gas (Ne, Ar, Kr, Xe) content, amount and composition of extracted gases), and the results of these studies have been published in a number of research papers (e.g. Vaikmäe et al., 2001, 2008; Karro et al., 2004; Marandi, 2007; Raidla et al., 2009, 2012, 2014).

The Cm–V aquifer system underlies the Lontova–Lükati regional aquitard (C_{1lk}–C_{1ln}) which is represented by siltstones and clays belonging to Lower Cambrian Series with the transversal conductivity of 10^{-7}–10^{-5} m/d (Perens and Vallner, 1997). The Cm–V aquifer system consists mostly of Ediacaran (Vendian) sand- and siltstones with interlayers of clay that lie directly on the Paleo-proterozoic crystalline basement. The thickness of the aquifer system decreases from 80–90 m in its north-eastern part to only a few metres in its north-western part (Perens and Vallner, 1997).

As the figure 7f illustrates, the groundwater in the Cm–V aquifer system has evolved through the mixing of waters originating from three end-members: fresh glacial meltwater, brine and modern precipitation. The age of the glacial meltwater intrusion to the aquifer system is at least coeval with the advance and maximum extent of the Late Weichselian Glaciation in the area with infiltration of the water occurring not later than 19000 to 27000 radiocarbon years ago (Raidla et al., 2012).

The Cm–V groundwater in the northern part of the aquifer system is characterised by fresh Na-Ca-Cl-HCO_3 and Ca–Na-Cl-HCO_3 waters with TDS content between 0.4 and 1.0 g/l (Savitskaja and Viigand, 1994). Groundwater in the northern part of the aquifer system has the lightest isotopic composition recorded in Europe ($\delta^{18}O$ values from −18.5‰ to −23‰) (Vaikmäe et al., 2001; Raidla et al., 2009). In southern and central Estonia, the aquifer system contains relict saline groundwater with TDS values of up to 22 g/l. In this zone Cl^- and Na^+ predominate over all other ions (Karise, 1997).

Excursion sites related to this chapter: *Sites 1–7*.

2. Field excursion

2.1. Site 1: Loo

Joonas Pärn

The municipal water supply wells in Loo village yield water from two different aquifer systems in the northern part of the BAB: Cm–V and O–Cm (Fig. 8).

The deeper of the two wells (no. 14114) yields water from the Cm–V aquifer system underlying the Cambrian clays of Lontovo Formation that serves as a strong regional aquitard in whole of the BAB. The isotopic composition of water ($\delta^{18}O = -22.3‰$) is depleted with respect to the range of values found in modern precipitation of the area (Fig 3.1). The negative $\delta^{18}O$ values from −18.5‰ to −23‰ found in waters all over the northern part of Cm–V aquifer system have been associated with recharge of subglacial meltwater from the Scandinavian Ice Sheet in Pleistocene (Vaikmäe et al., 2001). The water from the well is also characterised by higher chloride content compared to groundwater in shallower aquifer systems. One of the characteristics common to groundwater originating from glacial meltwater recharge is a high total gas content which is also visible during sampling (Fig. 9).

The shallower well (no. 4650) which yields water from the Ordovician–Cambrian aquifer system overlying the regional aquitard of Cambrian clays is characterised by a more positive isotopic composition ($\delta^{18}O = -12.8‰$) that is more similar to modern precipitation in the area ($\delta^{18}O = -10.4‰$; Punning et al., 1987). It is also characterised by lower chloride concentrations compared to the deeper well. These characteristics suggest that a majority of the sampled water originates from recent meteoric recharge.

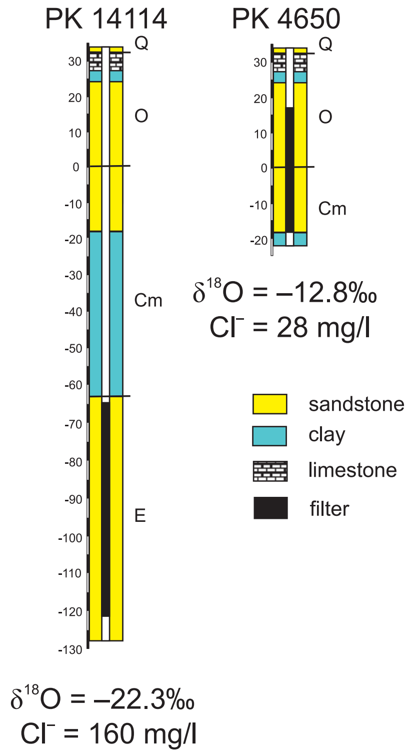


Figure 8. A cross-section of the sampled wells in Loo. Characteristic $\delta^{18}O$ values and chloride concentrations are shown for reference. Abbreviations: E – Ediacaran; Cm – Cambrian; O – Ordovician; Q – Quaternary.

Figure 9. A picture of groundwater originating from glacial meltwater in Loo well no. 14114 with a characteristic high gas content. (Photo: V. Raidla).

2.2. Site 2: Muuga

Joonas Pärn

The influence of Quaternary glaciations is not only observed in groundwater but also in the landscape. Owing to the closeness of the Fennoscandian Shield the Estonian territory is scattered with numerous huge granite blocks of great height, and with thousands of erratic boulders. These have been transported by the Scandinavian Ice Sheet as a glacial drift (Raukas, 1997). In the last century gigantic boulders gave scientists the idea of a continental glaciation. This served as the main evidence for motivating the corresponding theory. There are approximately 2150 large boulders registered in Estonia. Around 1900 of them have a length of more than 3 meters (Raukas, 1997). One of the most remarkable examples of its kind is the Muuga Chapel Stone near Tallinn (Fig. 10). It's one of the largest glacial erratic boulders in northern Europe being 6.4 meters high and having a circumference of 58 meters. The boulder consists of rapakivi granite.

Figure 10. The Muuga Chapel Stone. (Photo: H. Bauert).

2.3. Site 3: The Saviranna cliff

Joonas Pärn

The Saviranna cliff (Fig. 11) is part of the Baltic Klint near the town of Maardu. The Baltic Klint is an approximately 1200-km-long system of erosional escarpments in the Lower Palaeozoic (Cambrian to Ordovician) sedimentary rocks between the Öland Island in Sweden and Lake Ladoga in Russia. It coincides more or less with the boundary between the Fennoscandian Shield and the East European Platform. In the Saviranna cliff are exposed sedimentary rocks of Early Cambrian age. The main part of the cliff is formed by clays of the Lükati Formation that is a part of the Lükati–Lontova regional aquitard which separates the Cm–V and O–Cm aquifer systems. The clays are overlain by the siltstones of the same formation that are separated from the clays by drying cracks representative of a sedimentary hiatus. Despite being more than 500 million years old the clay has retained a natural plasticity together with a high water content/porosity. The underlying Lontova clays are used as raw material for the cement and brick industry.

Figure 11. The Saviranna cliff. (Photo: O. Hints).

2.4. Site 4: The Ülgase mine

Anto Raukas

The biggest resources of phosphorite in the European Union are in Estonia. It can be found as shell detritus of phosphatic brachiopods in Lower Ordovician sandstones. According to the estimations the Rakvere Deposit consist of approximately 700 million tonnes of P_2O_5. The phosphorite layer is 2 – 12 meters thick and lies at a depth of 42 – 210 meters over an area of 1000 km^2.The first recorded attempts to use phosphate rocks in Estonia were published in the 19th century. The sites most suitable for excavating were found west and northeast from Maardu, near Tallinn and in Ülgase near the coast of the Gulf of Finland (Fig. 12). In 1920, Estonian agricultural activists founded the joint-stock company "Eesti

Figure 12. A phosphorite mine from 1920s in Ülgase near the town of Maardu. (Photo: M. Isakar).

Wosworiit" (Estonian Phosphorite) with the aim to mine phosphate rock. A mine In the Soviet times, a powerful chemical plant named "Estonfosforit" was established. From this plant, millions of tonnes of phosphate ore was mined and 15 different goods produced. As a result air and water pollution worsened and the soils were overturned. After Estonia regained its independence, the green movements started protesting against damaging emissions into the atmosphere, and the plant was closed in 1991.

Lower Ordovician graptolite argillite overlying the phosphorite layer is rich in uranium and other microelements (e.g. Mo, V, Th). It was deposited in waste dumps during mining. The oxidation of shale is connected to a large-scale leaching of several components by water filtrating through the heaps as well as to their dispersion. The leaching from the heap is not directly dependant on the amount of water flowing through the heap, but rather on the intensiveness of the oxidisation process of the rocks. It is worth noting that the Lower Ordovician graptolite argillite acts as an important local aquitard. It protects the underlying O–Cm aquifer system from recharge of recent meteoric water. This has enabled the waters originating from glacial meltwater to be preserved in the aquifer system.

2.5. Site 5: Jõelähtme

Anto Raukas

Alvars are areas on carbonate rocks where Quaternary cover is missing or very thin (less than 20–30 cm). The area of alvars in northern Estonia is the oldest agricultural region in the area, where the first primitive slash-and-burn clearing of woods took place as early as 2500 years ago. The region is rich in archaeological findings, remains of ancient cult stones in the fields and stone graves. One can find a special type of burial mounds here – stone-schist barrows dating from the end of the first millennium B.C. and the first century A.D. A barrow consists of a limestone schist surrounded by stones which are arranged in a circle to imitate a yard. Nearby, one will find the 2.9x0.5 km Kostivere karst field (Fig. 13). The karst phenomena is related to tectonic joints. The underground river of Jõelähtme passes through the karst area.

Figure 13. Karstic features in the Kostivere karst field near Jõelähtme village. (Photo: H. Bauert).

2.6. Site 6: Viitna

Joonas Pärn, Valle Raidla and Anto Raukas

The influence of advancing-retreating ice sheets is characterised by various glacial and interglacial deposits in Estonia. Estonia belongs to a zone of glacial erosion and of moderate accumulation as the thickness of glacial deposits increases generally from north to south. About 95% of the Pleistocene cover is formed of glacial, glaciolacustrine and glaciofluvial deposits (Raukas and Kajak, 1997; Kalm et al., 2011).

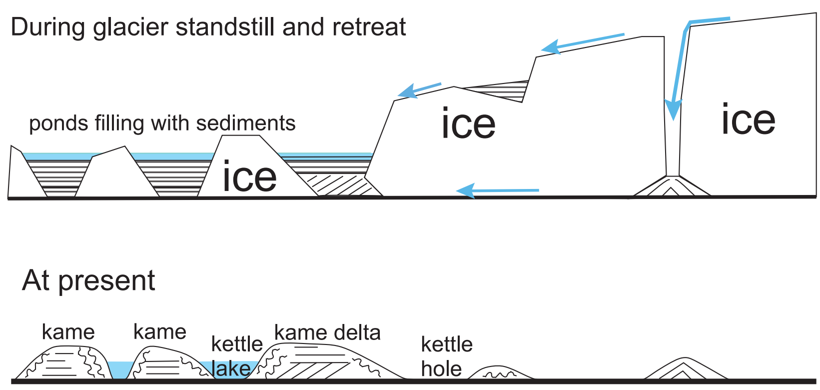


Figure 14. The formation of kames.

The Quaternary deposits are thickest in Haanja and Otepää heights in southern Estonia and in the deep buried valleys (Raukas and Kajak, 1997). The former are so-called "accumulative insular heights" characterized by a hummoky topography and by a considerable thickness of Quaternary deposits (of up to several hundred metres). The heights have formed between large ice lobes as a result of frequent redeposition of older deposits, accounting for the mosaic pattern of sediments (Raukas and Kajak, 1997). The deep buried valleys are erosional valleys filled with Quaternary sediments that cut through the bedrock strata.

Thick Quaternary deposits are also encountered on lee-sides of heights and elevations (e.g. the Saadjärve Drumlin Field in the "shadow" of the Pandivere Upland) and in front of escarpments oriented against the movement of glaciers which favoured the accumulation of a considerable amount of sediments.

Kames are positive relief forms, hills and short ridges, resulting from the accumulation of aqueoglacial deposits in cracks and cavities of passive or dead ice or between isolated blocks of dead ice (Fig. 14). They consist mainly of sand and gravel. Morphologically, kames are represented by hills, knolls, cupolas, crests, ridges, ramparts and plateaus. They form kame fields and kame groups often with lakes in between.

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The Viitna kame field is located on the northern slope of the Pandivere Upland (Fig. 15). The Viitna – Ohepalu esker ridge runs through the radial kame field about 3 km^2 in area. This area has a lot of glaciokarstic hollows, some of which are occupied by lakes and filled with peat. Forests cover 90% of the territory.

Figure 15. View at the Viitna Pikkjärv in the Viitna kame field. (Photo: H. Bauert).

2.7. Site 7: Rakvere

Joonas Pärn, Valle Raidla and Anto Raukas

Five major ice-marginal zones (in order of decreasing age: Haanja, Otepää, Sakala, Pandivere and Palivere) are usually distinguished in Estonia (Kalm et al., 2011) (Fig. 16). They were formed either as a result of stillstands of the ice margin or in some cases, as a result of re-advances. At a larger scale, the ice-marginal zones in Estonia are sinuous compared to the next, more northerly, relatively linear Salpausselkä end moraines in southern Finland. This suggests a gentler slope of the ice sheet during the deglaciation of Estonia when large ice-stream complexes drained the ice sheet (Kalm et al., 2011).

The deglaciation of the Estonian territory from the Haanja ice-marginal zone to the recession of ice from the Palivere zone took place approximately 2000 years from 15 kyr and 13 kyr BP (Kalm, 2006; Veski et al., 2012). In contrast to the older oscillatory phases (Haanja, Otepää, Sakala, Pandivere), the Palivere ice-marginal zone is clearly of a re-advance character, as reflected by the distribution of push moraines and by the fact that the older glaciolacustrine sediments are overlain by glaciofluvial material.

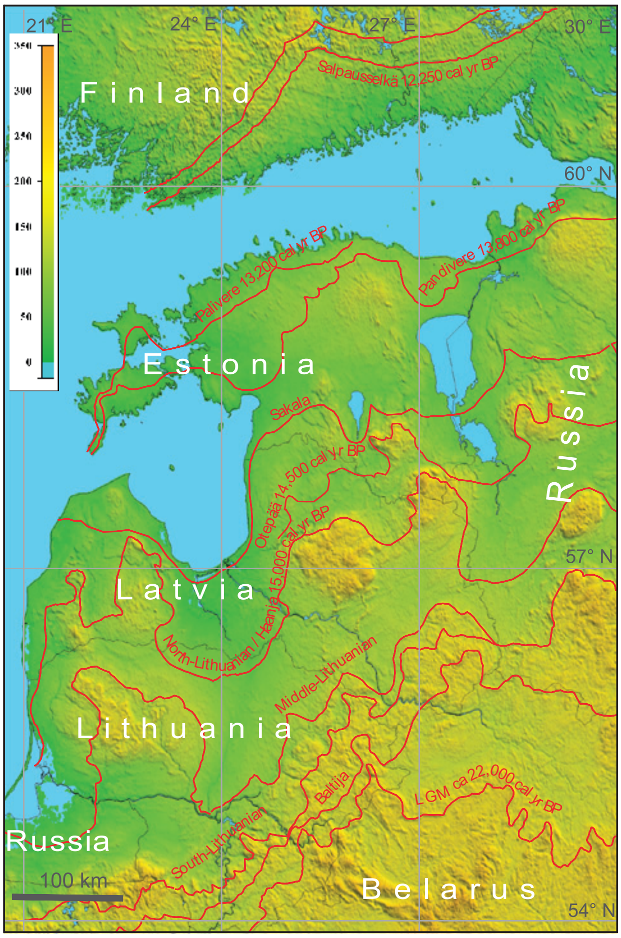

Figure 16. The main Late-glacial ice marginal positions in the BAB area with ages in cal. yr. BP. (*modified from*: Veski et al., 2012).

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Eskers are steep-sided, sinuous ridges of stratified sand and gravel, which can be followed over several tens of kilometres. They consist of streambeds, originally laid down within large crevasses of the glacier or deposited by meltwater moving through or beneath the ice. Radial eskers mark the direction of the continental ice sheet flow, while marginal eskers have formed in front of the retreating ice sheet. Eskers consist mostly of sorted sand and gravel layers as well as of rounded stones. Especially picturesque eskers are found in Lääne-Viru County, one of them is the Rakvere esker. On the top of it are the ruins of an old castle from the 13th century (Fig. 17).

Figure 17. Rakvere castle from the 13th centrury on top of the Rakvere esker. (Photo: H. Bauert).

2.8. Site 8: Kiviõli

Anto Raukas

The Estonian Oil Shale Basin is situated in the north-eastern part of Estonia and extends eastwards into Russia. To distinguish Estonian oil shale from the other kinds of oil shale in the world it is called kukersite (from the word Kuckers, the German name for Kukruse manor, where the rock was first described) (Fig. 18). The Estonian oil shale deposit is the largest explored and commercially exploited oil shale deposit in the world; its total resources exceed 7 billion tonnes. The mineable seam in the Estonia deposit consists of seven kukersite layers and of four to six limestone interlayers at a depth of 0–100 meters with a thickness of 1.4–3.2 meters in an area of 2884 km^2. Oil shale is currently used for electricity generation in power plants, for shale oil production and in small amounts also for producing cement and chemical products. The production of oil shale and its use as a raw material in the oil and chemical industry and power engineering may cause some temporary environmental problems. Oil shale mining is accompanied by the lowering the water level for the time of mining activities (mainly influencing the Silurian–Ordovician aquifer system) and by a discharge of mine water into bodies of surface water. The total amount of drained water is formed from precipitation water, surface water, subsurface water (free surface groundwater) and from pressurized groundwater. The components of the balance of water pumped out from open-casts and underground mines differ significantly.

Figure 18. Oil shale mining in the Põhja-Kiviõli open-cast pit, Ida-Viru County. (Photo: H. Bauert).

Calculations of the components of the inflow balance of open-cast mine fields showed that pressurized groundwater makes up 10% of the total inflow, the proportion of free surface groundwater in different open-cast mine fields accounts for 6–34% and precipitation water makes up 66–84% in the depleted area. In closed mines, the inflow of groundwater makes up 60% of the total pumped out water.

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The Kiviõli hill consists of semicoke – a substance formed from the fuel oil production from the oil shale in vertical retorts with low thermal internal heating. It appears as a blackish, coarse gravel sand of high intergranular porosity. It is classified in Estonian and European Union waste lists as hazardous waste since it contains tarry and bituminous substances. The large depositions of semicoke or semicoke hills are dangerous to the surrounding environment because of a high concentration of hydrocarbons, phenols and ketones. The semicoke hill at Kiviõli is over 90 m high and is now an attraction for tourists (Fig. 19). One can admire a good view on the oil-shale basin from the top of the hill. A popular winter sports centre has been opened here.

Figure 19. A ski resort founded on a former semi-coke hill in Kiviõli. (Photo: M. Kämärä)

2.9. Site 9: The Viru bog

Joonas Pärn

The occasionally rather thick Holocene deposits occur practically everywhere above the Pleistocene deposits in Estonia (Raukas and Kajak, 1997). The various deposits include ancient shore line deposits of different stages of the Baltic Sea, peat and lacustrine (e.g. gyttja, lake marl, travertine), alluvial and aeolian deposits. All in all, there are 9836 peat bogs and about 1150 lakes bigger than 1 ha on the Estonian territory (Raukas, 1997).

One of the most remarkable forms of Holocene deposits in Estonia are bogs. A bog is a mire that accumulates peat. In the majority of cases, it is formed by the undecayed remains of *Sphagnum* mosses. Bogs are common in cold and temperate climates in places where water run-off has been hindered by underlying sediments or adjacent landforms. The water accumulating in the bog is almost entirely derived from precipitation, creating an acidic environment low in nutrients. The water flowing out of the bog is characterised by brown colour due to dissolved organic species. The bogs act as a sink of carbon in the carbon cycle and are characterised by distinctive assemblages of plant and animal species.

The accumulation of water in bogs causes the formation of various water bodies inside the bog. A bog hollow is a wet depression that periodically fills with water and consists of wet peat. The larger water bodies in bogs are called bog pools. The formation of these water bodies is a sign of the old age of the bog. Bog water is acidic, containing plenty of organic matter while the TDS concentrations are very low.

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The Viru bog (Fig. 20, 21) in northern Estonia is located in a former lake basin, which formed after the continental ice melted and glacial lakes receded. Lake sediments can still be found among the bottom sediments of the bog. The overgrowing of the lake took place about 5000 years ago and as a result bog started to develop. Its expansion has been limited by the surrounding dune walls. Maximum thickness of the peat layer in the Viru bog varies between 6–8 meters.

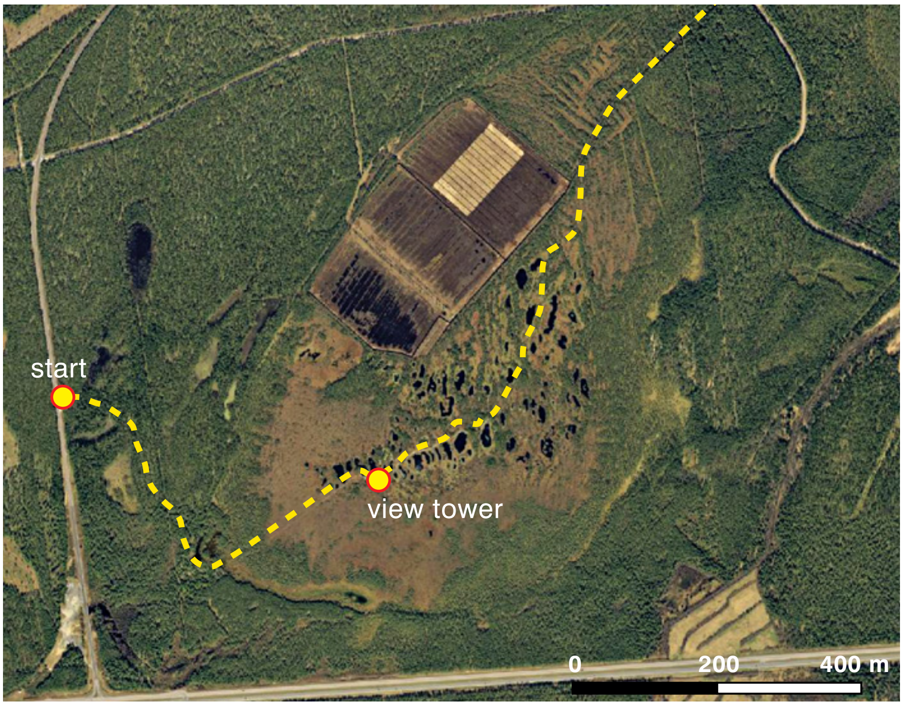

Figure 20. An aero photo of the Viru Bog together with the excursion route. (Photo: Estonian Land Board, 2015).

Figure 21. A view over the Viru bog. (Photo: M. Isakar).

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